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ANALYTICAL APPLICATIONS OF ARSENAZO III—II*

DETERMINATION OF THORIUM, URANIUM, PROTACTINIUM, NEPTUNIUM, HAFNIUM AND SCANDIUM

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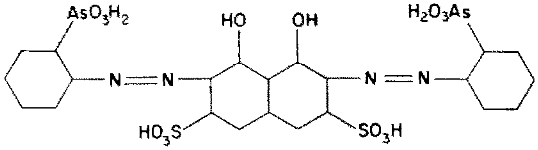
Summary—The particular analytical utility of arsenazo III is its capacity for forming especially stable complexes with certain elements. This permits determinations to be carried out in strongly acid media (for quinquevalent and quadrivalent elements—Pa, Np^{IV}, Th, Zr, Hf, U^{IV}—up to 10MHCl or H_2SO_4), which ensures good reproducibility, ease of working, and little interference by anions. The high sensitivity (0·1–0·01 μg/ml, molar absorption coefficient 50–150 × 10^3) is a result of the good contrast effect of the reaction (pink → emerald-green, displacement of the absorption maximum 125 mμ), the nature of the spectrum, and the possibility of reaching extreme dilutions without dissociation of the complex.

THE reagent arsenazo III, produced[1] in 1959, is widely used at the present time for determining thorium,[1–10] uranium,[1,2,11–13] zirconium,[2,14–16] hafnium,[17] protactinium,[18] scandium,[19,20] neptunium,[21,22] and the rare earth elements.[19] Some of the papers mentioned,[3,4,6,8,13,14] having been considered in a previous review[2] are not discussed in the present paper.



PROPERTIES OF ARSENAZO III

Arsenazo III is a dark red powder, moderately soluble in water to give a pink solution. The solutions are stable for an unlimited time in air. Arsenazo III gives colour reactions (violet, blue, and green) in the range from pH 4 to 10M HCl or H_2SO_4 with more than 20 elements.[2] The main distinguishing characteristic of the reagent is its capacity for forming particularly stable metal chelate complexes, their stability exceeding that of the corresponding arsenazo I complexes by more than two or three orders of magnitude.[23]

The high stability of the complexes permits the elements to be determined in strongly acid media at high dilution and in the presence of complex-forming anions—phosphates, sulphates, fluorides, complexone III, and the like. All this permits the analysis to be considerably simplified, making it more reliable and selective. In many cases, it is not necessary to isolate in the pure state the element to be determined; the determination is carried out directly on a solution obtained by dissolving in acids the sample to be analysed.

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* Part I—see ref. 2.

The sensitivity of the colour reactions is of the order of 0·1–0·01 μg/ml of the element. The molar absorption coefficient for multiply charged elements is of the order of 50–150 × 10^3. Methods for ensuring the necessary selectivity of the reactions have been discussed previously.[2]

METHODS FOR DETERMINING THE ELEMENTS

Thorium

Methods have been previously been described for determining micro-amounts down to 0·01 μg of thorium,[3] thorium in zircons,[4] in rocks (down to 0·0001% of Th),[6] and in Nb-containing products, *etc.*[8]

In the determination of thorium in the presence of zirconium, oxalic acid is added to bind the latter[1]; the determination is carried out in 2·5–3*M* HCl. In the absence of zirconium, the determination is carried out in 1:1 HCl (~6*M* HCl) and no oxalic acid is added. The maximum sensitivity is found in 8*M* HCl. In view of the high acidity, the presence of oxidising agents, for example, nitric acid or chlorine, which are sometimes present in technical acids, is inadmissible (decomposition of the reagent). It is best to use distilled hydrochloric acid. Sometimes powerful reducing agents (for example, Ti^{III}) which also decompose the reagent, may be formed in the process of decomposing and treating the material to be analysed. In this case these must be oxidised by adding, for example, a small crystal of $KMnO_4$ followed by ascorbic acid to decolorise the solution.

In recent papers a method has been described for determining thorium in silicate rocks with a high content of Zr, Ti, rare-earth elements, and the like. The method is based on the separation of Zr, Ti, and the rare-earth elements by ion exchange on KU-2 cation-exchange resin in the H form. Titanium is not sorbed from 1*M* HCl; the rare-earth elements are eluted by 2*M* HCl, and Zr by a 0·5% solution of oxalic acid. The thorium is then eluted quantitatively by means of a saturated solution of ammonium oxalate, and is determined photometrically with arsenazo III in 5*M* HCl without separation of the oxalates. The sensitivity of the method is 10^{-3}–10^{-4}%, and the relative error is ±4%; 6–8 parallel determinations can be completed in 10 hours.[7]

A method has been reported for determining thorium in metallic tungsten, and in natural and other materials.[9] The concentration and photometric determination of thorium in natural waters in which it is present in ultra-high dilution has been described.[5] The thorium is co-precipitated with methyl violet tannate, and the precipitate is filtered off and decomposed by wet ashing. The residue is dissolved in 6*M* HCl, and phenylarsonic acid is added to precipitate the zirconium. The thorium is determined photometrically in hydrochloric acid solution containing lithium chloride (to bind UO_2^{2+}) and oxalic acid. The smallest amount of thorium which can be determined in 5–20 litres of river water is 0·5–1 μg.

Uranium

Uranium may be determined after its preliminary reduction[11] to U^{IV}. An extraction-photometric method consisting of the extraction with butanol of the diphenylguanidinium salt of the complex of UO_2^{2+} with arsenazo III, from a solution containing complexone III, has been described.[13] A method has been developed for determining uranium in rocks, minerals, and solutions of complex composition. UO_2^{2+} is extracted with a 20% solution of tributyl phosphate in carbon tetrachloride from a solution containing ammonium nitrate and Complexone-III; the uranium is re-extracted with a solution of arsenazo III and is determined photometrically. The method permits the determination of uranium when its concentration in the solution to be analysed is 0·002 μg/ml and above.[12]

UO_2^{2+} is determined photometrically at pH 1·5–3·5 and U^{IV} in 6–9*M* HCl.[1,2]

Zirconium

Zirconium is determined under approximately the same conditions as thorium—in 6–9*M* HCl.[2] If a high sensitivity is not required, the determination of Zr can be carried out at a lower acidity, for example, in 2*M* HCl. Various methods of determining it in ores, in concentrates, and in Al, Cu, Mg, Ti, Nb, and Fe alloys have been described.[14–16]

Hafnium

Hafnium is determined under approximately the same conditions and with the same selectivity as zirconium.[2] When Zr and Hf are present simultaneously, a two-pH method is possible.[2,24]

The method of determining Zr in metallic Hf is as follows: 10–20 g of metallic hafnium are dissolved in HF. The solution is fumed off with H_2SO_4. The residue is dissolved in 4*M* HCl and is transferred to a 500-ml measuring flask. An aliquot is taken containing not more than 50 μg of Hf, the solution is heated and, after cooling, 2 ml of a 0·05% solution of arsenazo III is added. The solution is made up to 50 ml with 4*M* HCl and is subjected to photometry. The content of zirconium is found from a calibration curve. Th, U^{IV}, and Ti^{IV} interfere with the determination. The accuracy of the method is ±20% at a Zr content of 0·5% and ±10% at a Zr content of 1%.[17]

Scandium

The determination of scandium is carried out in a fairly acid medium—pH 1–2—, *i.e.*, under conditions where no formation of polynuclear scandium cations takes place. This is of particularly great importance for Sc—almost as much as for Zr—to ensure reproduceability of the results and the reliability of the determinations.[19]

A method has been described for the photometric and complexonometric determination of Sc with arsenazo III as metal indicator.[20] The possibility of working in an acid medium ensures that the reaction takes place rapidly and, at the same time, that the selectivity is greater.

Lanthanum and the lanthanides

In weakly acid solutions with a pH of the order of 1·5–3·5, Y, La, and the lanthanides form an intense blue-green coloration with arsenazo III. The sensitivity is 0·01 μg/ml of the element. A method for determining the individual rare-earth elements has been described by Savvin and Muk.[19]

Protactinium

Arsenazo III gives a colour reaction with Pa^V over a wide range of acidities—from slight acidity up to 5*M* H_2SO_4, 10*M* HCl or more. The complex is green, and it is stable for more than 1 day. The reaction may also be carried out by an extraction-photometric method: the complex of Pa with arsenazo III is extracted almost completely by an equal volume of isoamyl alcohol from sulphuric acid solutions with concentrations of the acid greater than 2*M*. In order to increase the selectivity of the determination of the protoactinium, the organic phase is used for the photometric measurements.[18]

The molar absorption coefficient of the Pa–arsenazo III complex is 22 × 10^3 at $\lambda = 660$ mμ; in the range of concentrations investigated (0·3–3·1 μg/ml of Pa), Beer's law is applicable. The accuracy of the determination is ±3·5%. With a slight excess of reagent, the composition of the complex is 1:1.

The possibility of extracting the Pa–arsenazo III complex from strongly acid media ensures that the determination of protactinium is highly selective. Other elements reacting with arsenazo III either do not pass into the extract at all (Fe, Ti, La, and the like) or are extracted to only a slight extent (Th, U, Zr). The effect of Th, U, and Zr is eliminated by washing the extract with a solution of oxalic acid in 3·5M H_2SO_4. The oxalic acid does not affect the formation and extraction of the complex of Pa with arsenazo III. Mention must be made of the favourable action of sulphuric acid itself, which binds many elements in the form of stable complexes, and, consequently, increases the selectivity of the determination of protactinium.

The chemical analogue of protactinium—niobium—does not react with arsenazo III under these conditions. There is therefore a possibility of determining protactinium in the presence of elements (Nb, Zr, *etc.*) which are always present in uranium ore, and which accompany protactinium when it is isolated.

The procedure is as follows:[18] 0·2–1 ml of the initial sulphuric acid solution containing 1–10 μg of Pa is placed in a 5-ml tube with a ground-in stopper and is treated with 0·8 ml of a $10^{-4}M$ aqueous solution of arsenazo III and concentrated H_2SO_4 in such an amount that the final acidity is 3·5–4M with respect to H_2SO_4. Extraction is carried out with 2 ml of isoamyl alcohol previously saturated with 3·5M H_2SO_4.

After separation of the layers, the extract is transferred into a centrifuge tube and the aqueous phase is extracted with a further 1 ml of isoamyl alcohol. The extracts are combined and centrifuged in order to achieve complete separation of the phases. After centrifuging, the extract is transferred to a 10-mm cuvette and is examined photometrically at 660 mμ against an extract of the reagent alone obtained under the same conditions as the extract of the material to be analysed. The content of protactinium is found from a calibration curve (Fig. 1).

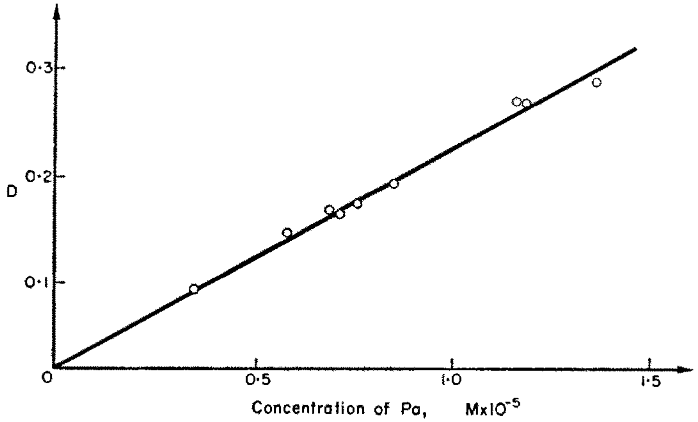

FIG. 1.—Calibration curve for the determination of protactinium. (Concentration of arsenazo III, 2·3 × $10^{-5}M$.)

When Pa is determined in the presence of Th, U^{IV}, and Zr, the extract is washed before centrifuging with one or two 1-ml portions of a 0·5M solution of oxalic acid in 3·5M H_2SO_4. The amount of reagent is increased by a factor of 1·5–2.

Neptunium

A method has been described for determining quadrivalent neptunium with arsenazo III.[21] Np^{IV} with arsenazo III in 1–5*M* HNO_3 forms a green complex, an excess of reagent causing the colour to change to violet. At a concentration of nitric acid of more than 5*M* the coloration of the complex is pale blue and in 8*M* acid it is dark blue. Colorations are formed instantaneously, and are stable for at least some hours. In the presence of iron sulphamate no decomposition of the reagent in concentrated nitric acid solutions takes place. Over the range 4–6*M* HNO_3 the intensity of the coloration changes little with a change in the acidity. The molar absorption coefficient at 665 mμ is approximately 100,000.

Since other quadrivalent elements—U^{IV}, Pu^{IV}, Th, Zr—also form coloured compounds in strongly acid media, these must be removed. This is achieved by extracting the elements with appropriate organic solvents, the NpO_2^+ ions, which are not readily extracted, remaining in the aqueous phase. The neptunium is then reduced to Np^{IV} and is determined with arsenazo III.

For the extraction of U, Pu and Th, Chudinov and Yarkoplev[21] have used a 0·25*M* solution of di-2-ethylhexyl orthophosphate in carbon tetrachloride, which extracts these elements from 0·5*M* nitric acid with a partition coefficient of the order of 100–1000. When quinquevalent neptunium stabilised with sodium nitrite is extracted under the same conditions, only about 2% of the original amount of Np passes into the organic phase. At a ratio of Np to interfering elements of about 1:2000, extraction must be carried out three times to eliminate the latter completely. About 10% of the original amount of Np is lost during the extraction process.

The stabilisation of Np^V is carried out by oxidising it to NpO_2^{2+} with potassium permanganate, and subsequently reducing it to NpO_2^+ with sodium nitrite. Oxidising agents (for example, potassium dichromate) and large amounts of reducing agents interfere with this operation, and they must therefore be removed beforehand.

The following cause no interference in the determination of 1–10 μg of Np: 4 mg of Pu, 3 mg of U, 0·5 mg of La, 2 mg of Th, 1 mg of Zr, 0·2 mg of Cr, and up to 5 mg of Mg, Al, Ca, Co, and other elements. The lower limit for the determination of Np is 0·04 μg/ml ($D = 0{\cdot}02$ at $l = 20$ mm, photoelectric colorimeter, red filter). The accuracy of the determination is between 1% and 7% relative.

In the reaction of Np^V with arsenazo III a green coloration[22] is produced over the pH range 4·4–7·4. The complex has a 1:1 composition, and its molar absorption coefficient is 70,800. Complex-forming substances weaken the coloration. Since the coloration of the complex vanishes on acidification to pH 3, it may be concluded[22] that no change in the valency of the Np compound takes place during complex formation.

Zusammenfassung—Der besondere analytische Nutzen von Arsenazo-III besteht in seiner Fähigkeit, mit bestimmten Elementen besonders stabile Komplexe zu bilden. Das erlaubt Bestimmungen in stark sauren Medien (bei fünf- und vierwertigen Elementen—Pa, Np(IV), Th, Zr, Hf, U(IV)—bis 10 m HCl oder H_2SO_4), was gute Reproduzierbarkeit, leichtes Arbeiten und geringe Störung durch Anionen garantiert. Die hohe Empfindlichkeit (0,1–0,01 μg/ml, molarer Extinktionskoeffizient 50–150 . 10^3) rührt vom guten Kontrasteffekt der Reaktion (rosa–smaragdgrün, Verschiebung des Absorptionsmaximums um 125 mμ), der Natur des Spektrums und der Möglichkeit, extreme Verdünnungen zu erreichen, ohne daß die Komplexe dissoziieren.

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ANALYTICAL APPLICATIONS OF ARSENAZO III—III*

THE MECHANISM OF COMPLEX FORMATION BETWEEN ARSENAZO III AND CERTAIN ELEMENTS

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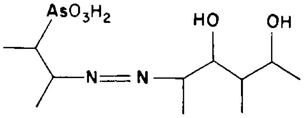
Summary—The two functional-analytical groups of the molecule of arsenazo III are present in two almost isolated conjugated systems. Complex formation with the elements takes place through only one of these: this leads to the appearance of two absorption bands in the visible region of the spectrum. The composition of the complexes for Me^{II} and Me^{III} correspond to MeR; and for Me^{IV} to MeR or MeR_2 (according to the acidity and the concentrations of the components.) Elements whose ionic radii are less than 0·7–0·8 Å give no colour reaction with arsenazo III. The stabilities of the complexes formed by reagents of the type of arsenazo III (bis-azo derivatives of chromotropic acid) with elements depend on the nature of the Me—N bond, and are determined by the extent of the system of conjugated bonds of the molecule of the reagent and the nature of the substituent.

IN recent years the attention of investigators has been attracted to analytical reagents forming particularly stable complexes with elementary cations. Among these are reagents such as complexone III (EDTA) and its analogues, forming colourless complexes and reagents giving coloured complexes—arsenazo III and its analogues, bis-azo derivatives of chromotropic acid containing various salt-forming groups.[1,2] The theory of the analytical action of reagents of the type of complexone III has been studied in relatively great detail, but that of reagents of the type of arsenazo III quite inadequately. Some preliminary observations on the mechanism of complex formation between arsenazo III and various elements have been made by the present author.[3]

The functional-analytical group responsible for the formation of complexes between arsenazo III and elements (as with the other reagents of the arsenazo class, *i.e.*, those containing arsenic and an azo group) is the following:



I

Two such groups are present in the reagent arsenazo III.

Now that further experimental material is available, the mechanism of the formation of complexes of the elements with the functional group is fairly clear.[4–18] Analogies can be drawn with similar reactions between simple inorganic compounds and other organic compounds having the same grouping.[4,13,14] Elements such as UO_2^{2+}, Th, U^{IV}, Zr, Hf, TR form a direct covalent bond with an AsO_3H_2 group and an OH group. For Al, Ti, and some other elements, chromotropic acid is also

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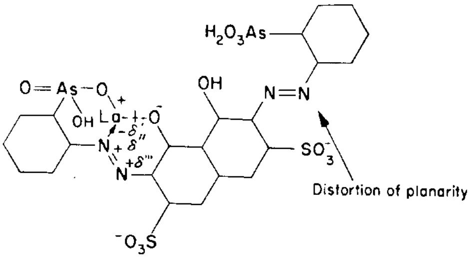
* Part II—see ref. 2

specific and for Zr even one azo group together with a labile hydrogen atom. Depending on the nature of the reagent and, for a given reagent depending on the conditions, complex formation may take place at different groups. Earlier, for example, by analogy with the corresponding complexes of arsenazo I and thoron I[6,11–13] the following structure was proposed for the complex between La and arsenazo III:



II

A special role is played by the Me—N co-ordinate link. Besides the considerable increase in stability resulting from the formation of two six-membered rings possessing almost aromatic properties, complex formation leads to the transfer to the chromophoric centre of the molecule—the azo group—of some charge, resulting in a marked deepening of the colour of the complex. The same effect is favoured by the transfer of some negative charge to the residue of the hydroxyl group of the naphthalene ring of the reagent.[4,5] The dipole arising at the ends of the system of conjugated bonds, including the chromophoric centre—the azo group—(the magnitude of which depends to some extent on the nature of the metal and the conditions) causes a marked change in the colour of the reagent, *i.e.*, the corresponding colour reaction. A metal cation therefore here plays the role of a peculiar extremely powerful positive auxochrome. This is in complete agreement with modern views, developed, in particular, for azo dyes,[9,15,16] on the theory of the colour of organic compounds.

In the case of arsenazo III, this scheme, which is generally accepted in the literature, is again but only one of the two functional groups is capable of reaction.

Coloration of the reagent and coplanarity

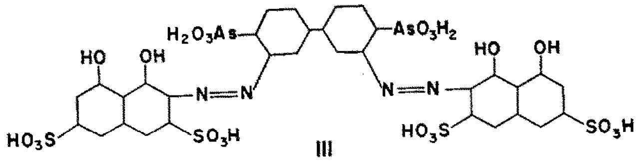
The bis-azo derivatives of chromotropic acid, in contrast to its mono derivatives, and as a result of the conjugation of the two parts of the molecule and the associated planar structure, usually possess deep colours—violet and dark blue. These compounds are unsuitable as photometric reagents. The pink coloration of arsenazo III in acid solutions is the result of a disturbance of the planar structure and the conjugation (consequent on the presence in the *o*-position to the azo group of such voluminous substituents as AsO_3H_2 groups.) The same colour effect is found in the case of certain other substituents: —NO_2 and —SO_4H.

The steric hindrance due to the arsono group is also shown by the considerable difficulty in synthesizing arsenazo III if this is carried out by the methods usually used for azo-coupling reactions.

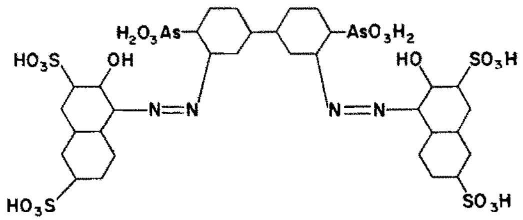
The coloration of arsenazo III in alkalis (dark blue) and in concentrated H_2SO_4 (green) is connected, in the first place, with the ionisation of the hydroxyl groups of the naphthalene nucleus and, in the second place, with the protonisation of the azo groups; this agrees well with views given in the literature.[4–6]

Absorption spectra of the reagent and the complexes

In acid solutions the absorption maximum of arsenazo III in the visible region is located at 540 mμ. The absorption spectra of complexes of arsenazo III with the elements have two maxima in the visible region—$\lambda_1 = 665$ mμ and $\lambda_2 = 610$ mμ (Figs. 1 and 2). The latter circumstance is quite unexpected: with the overwhelming majority of photometric reagents and with all reagents of the arsenazo-thoron group, including the bifunctional reagents arsenazo II and thoron II [Reagents (III) and (IV)], only one absorption band is found in the visible region. It is an essential feature that the characteristic shape of the spectra of the complexes of arsenazo III is retained for all the elements investigated over wide ranges of pH and ratios of the concentrations of the metal and the reagent (Fig. 2). Hence this cannot be a consequence of the simultaneous presence in the solution of two different complexes of dissimilar composition or structure. The two maxima can only be connected with the presence of two weakly interacting (dissociated) chromophoric systems in a single molecule of the reagent, different in magnitude or present in different ionic states. Similar phenomena—*i.e.*, the presence of two absorption bands in the visible region—are known for certain complex cyanine dyes having two dissociated chromophoric systems.[17]



III



IV

In the case of a molecule of arsenazo III not bound in a complex, which is obviously symmetrical, both chromophoric systems, consisting in the present case of functional-analytical groups, are identical, and their absorption spectra coincide, giving a single maximum. Complex formation at *one* group disturbs the symmetry of the molecule and if the system (molecule) does not consist of a single optical unit, *two* absorption maxima appear. The maximum corresponding to the greater depth of colour, $\lambda_1 = 665$ mμ, we ascribe to the functional-analytical group directly linked with the metal and the second maximum at $\lambda_2 = 610$ mμ to the chromophoric centre (conjugated system) not directly connected with the element but, owing to a definite and, apparently, considerable, influence of the first functional-analytical group passing into a different ionic state. To be precise, we assume the transfer of some positive charge to the azo group, more in the first case and less in the second.

It is interesting that the absorption spectrum of the reagent in concentrated

H_2SO_4, where protonisation of the azo group takes place, has a single maximum at the same wavelength as in the case of a complex—665 mμ. In dilute H_2SO_4, protonisation is apparently possible at only one azo group; the symmetry is disturbed and two maxima appear, the first remaining at the same wavelength, 665 mμ. Both for the reagent and for a complex, the first maximum is considerably higher than the second. In alkaline solutions where no protonisation of the azo group takes place, the depth of the coloration is less, the absorption maximum being between 580 and 610 mμ.

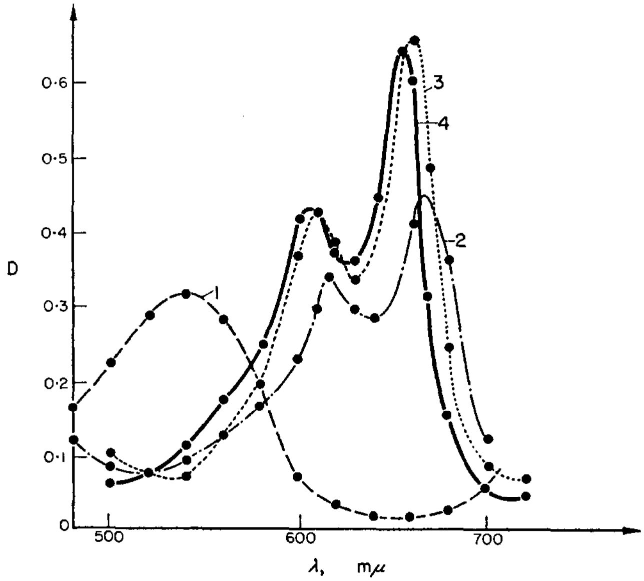


FIG. 1.—Absorption spectra.

(1) Arsenazo-III, 0·5 × $10^{-5}M$;
(2) Zirconium–arsenazo III complex in 9*M* HCl;
(3) Uranyl–arsenazo III complex, pH 1·5;
(4) Lanthanum–arsenazo III complex, pH 3
(SF-4 spectrometer: 10-mm cell: recorded against water)

There is, of course, also the possibility that the extremely large bathochromic effect on complex formation (from pink to green, displacement of the maximum by 125 mμ) is also connected in part with some divergence of the molecule from the non-coplanar state because of the "drawing together", as it were, of the benzene and naphthalene nuclei by the forces of the chemical bond between the metal and the complexing agent; and especially through the quite strongly expressed aromatic character of the two six-membered rings formed with the participation of the metal.

Composition of the complexes

With elements forming doubly charged cations (UO_2^{2+}, Cu, Pb, *etc.*) arsenazo III forms only complexes with a 1:1 composition. This is confirmed by data on the spectrophotometric titration of an element and the reagent, by curves of isomolar series (graphs not given here), and also by the non-dependence, in practice, of the nature of the spectrum of the complex (two absorption bands) on the Me:R ratio in the reaction medium. For example, for molar ratios UO_2^{2+}:R of 1:1 and 10^5:1 the nature of the spectrum remains unchanged; even a 10^5-fold excess of the metal does not give rise to the formation of a complex of the composition Me_2R which, because of its symmetry, would have one absorption maximum. The two absorption maxima are retained at any acidity at which the existence of a given complex is possible.

With elements forming triply charged cations, arsenazo III again forms complexes with a 1:1 composition. This is confirmed by the same methods. With elements forming a quadruply charged cation arsenazo III forms complexes both of the composition MeR and MeR_2. A greater ratio of R to Me is impossible, not so much because valency saturation has been reached, but because of steric considerations which do not permit the co-ordination about Me^{IV} of more than two molecules of so large a ligand. However, Nemodruk and Kochetkova[18] have discussed the possibility of the formation of more highly saturated complexes.

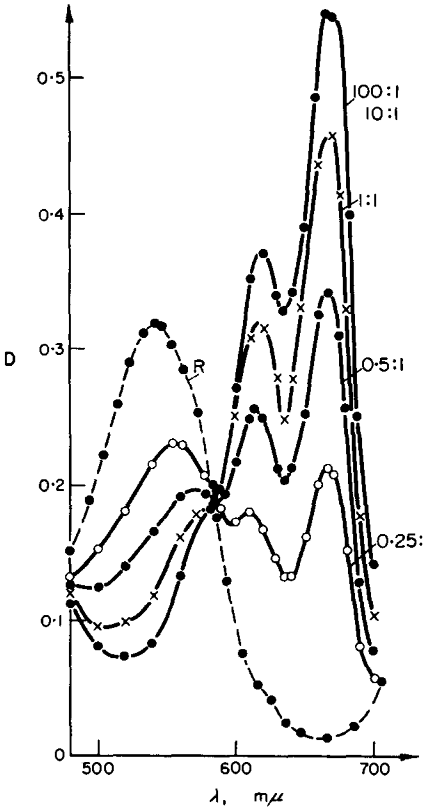


FIG. 2.—Absorption spectrum of thorium–arsenazo III complex at various M:Re ratios ($8M$ HCl: concentration of reagent 0·9 × $10^{-5}M$)

In the spectrophotometric titration of elements forming quadruply charged cations, the point of inflection corresponding to the 1:1 and 1:2 (and, even more, the 1:3 and 1:4) compositions are not clearly expressed; the results obtained by this method are difficult to interpret. It is possible, however, to use the method of determining the absorption of the saturated complexes. It can be seen from Fig. 3 that at a 100–1000-fold excess of thorium (composition known to be 1:1) D = 0·520. The same number of moles of thorium with a 10–20-fold excess of reagent give D = 1·15, *i.e.*, approximately twice as great. In the second case, the formation of a complex ThR_2, having a molar absorption coefficient approximately twice that of ThR may be assumed. This follows from the fact that at a high acidity, when the Th^{4+} ion has appeared quite strongly, the ionic state determining the coloration of the two co-ordinated molecules of arsenazo III is similar, and corresponds to the ionic state of the residue of the arsenazo III molecule in the 1:1 complex.

The same state of affairs is found for zirconium. At an arsenazo III concentration of $0{\cdot}9 \times 10^{-5}M$ and an excess of zirconium in 9*M* HCl, D = 0·5. At a zirconium concentration of $0{\cdot}9 \times 10^{-5}M$ and an excess of reagent in 9*M* HCl, the extinction is approximately twice as high, at D = 1·1.

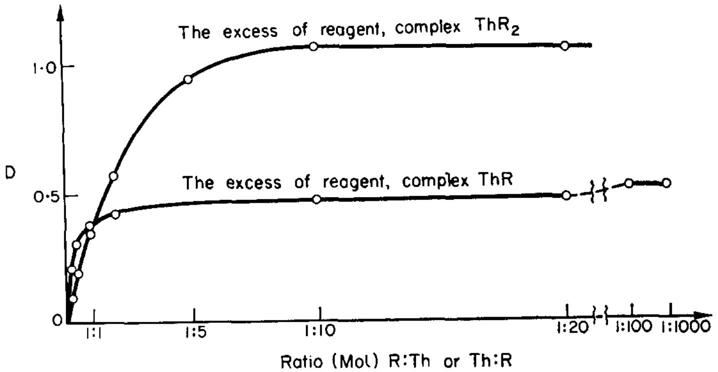


FIG. 3.—Spectrophotometric titration producing saturated complexes for the thorium–arsenazo III system
(Concentrations of MeR and MeR_2, $2{\cdot}2 \times 10^{-7}M$: recorded against reagent)

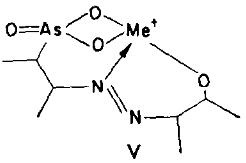
*Influence of the p*H

For arsenazo III and a number of elements (Th, Zr, Hf, U^{IV}, UO_2^{2+}, La, Sc, Cu) curves of isomolar series have been constructed at various values of pH. For triply and doubly charged cations, over the whole range of pH values, the composition corresponds to 1:1. For Th in 0·1*M* HCl, without an excess of reagent there is a 1:1 composition. In 1*M* HCl and at other values of pH, with an excess of reagent the composition is ThR_2, *i.e.*, the more stable form is apparently the ThR_2 complex.

The same thing is found in the case of zirconium. In 0·25*M* HCl and 0·84*M* HCl the composition determined by the Ostromyslenskii—Job method is close to 1:1; but when the acidity is increased (in 2·0 and 5·0*M* $HClO_4$) the composition is close to 1:2.

For Zr and Hf at comparable ratios of Me to R, as the acidity is increased a marked deepening of the coloration is found (violet → dark blue → green). This is apparently connected with a gradual conversion of the Zr ions from a partially hydrolysed to a purely ionic state, which leads to a marked enhancement of the positive auxochromic action of the cation. The same increase in the absorption intensity (at $\lambda = 665$ mμ), but considerably less marked, is found for Th, U^{IV}, and UO_2^{2+}—in the case of UO_2^{2+} right down to those values of the pH (~1) at which the complex begins to decompose.

On the basis of the determination of the compositions of the Me^{II}, Me^{III}, and Me^{IV} complexes and the literature data on the structure of complexes of the elements with reagents of the arsenazo group cited above, two possible structures of the complexes of arsenazo III with the elements may be assumed, fragments of which, for Me^{IV}, are illustrated in (V) and (VI):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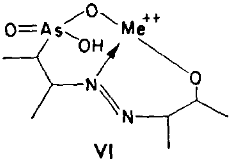

VI

Structure of the complex in limits of the functional-analytical nucleus

M. P. Volynets and the author[35] have carried out experiments with Th and La to determine the number of protons liberated in the reaction with arsenazo III at various ratios of Me to R. The method of high-frequency titration was used, which permits inflections on the titration curves of the metal and addend to be determined more accurately.[19] The experiments were carried out on the VU-2A apparatus of GEOKhI AN SSSR[20] with a cell in the form of a thin-walled beaker (capacity 30 ml, diameter 23 mm), coated on the inside. The results of the titration were converted into graphs of microammeter reading versus ratio of the components in the solution (the curves are not given here). The use of this apparatus involved some limitations on the conditions of carrying out the experiment: the apparatus is sufficiently sensitive only for the titration of 10^{-2}–$10^{-4}M$ solutions. At such a concentration, and at high acidity, the separation of precipitates is possible; consequently, complex formation was studied at pH 3. Two preparations of arsenazo III were used—in the form of the Na salt and in the form of the acid. In the latter case the reagent, in the form of a mixture of the free acid and the salt, was passed through a column of KU-2 cation exchanger in the H-form. The concentration of the solution to be titrated was generally $0{\cdot}001M$, and the concentration of the titrating agent was 10 times greater.

The results obtained are given in Table I.

TABLE I.—DETERMINATION OF THE NUMBER OF PROTONS LIBERATED WHEN THORIUM AND LANTHANUM FORM COMPLEXES WITH ARSENAZO III

Ratio, *Me:R*, of components	KOH, *equivalents*			
	Th		La	
	Arsenazo III Acid	Arsenazo III Na salt	Arsenazo III Acid	Arsenazo III Na salt
1:1	3·1	2·95; 3·1	2·0	2·1; 1·9
1:2	3·85	4·2; 4·2	—	—

The results in Table I show that three protons are liberated in the formation of a 1:1 thorium complex and 4 protons in the case of a 1:2 complex. In the formation of a lanthanum complex, two protons are liberated.

Thus, the thorium complex of composition ThR has structure (V) (with one positive charge) and the ThR_2 complex has structure (VI), the remaining two valencies being compensated by a second molecule of arsenazo III. The complex of La with arsenazo III has structure (VI). Elements forming doubly charged cations apparently also form complexes of type (VI).

Results for complexes extracted in the form of their diphenylguanidinium salt confirm the conclusions drawn. The ThR_2 (excess of reagent) and UO_2R complexes are extracted considerably more readily than the LaR and ThR complexes. In the latter case, to compensate for the positive charge of the complex, heavy hydrophobic anions must be added to the solution.[21]

Selectivity

It is possible to distinguish selectivity determined by the chemical properties of the element and selectivity determined by the nature of the reagent. In the first case, for reagents of the type R—OH the selectivity is based on the different tendencies of the ions of the elements to hydrolyse. In strongly acid media, a colour reaction is given by elements the ions of which have a considerable tendency to hydrolyse: Zr, Hf, U^{IV}, Th, Np^{IV}; in moderately acid media by UO_2^{2+}, rare earths, Bi, Fe^{III}; and in the weakly acid media by Pb, Cu, Ba, Ca, and NpO_2^+. Thus, in the determination of Me^{IV} a high selectivity is attained. The same case includes the possibility of increasing the selectivity by using masking complex-forming substances, extraction-photometric methods, and the like.[21]

The selectivity of a reagent, as is well known, is determined by the nature of the functional-analytical group. The more simple its structure, the higher its selectivity. To explain the different selectivities of reagents utilising one particular functional-analytical group, supplementary conceptions must be brought in.

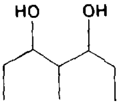
Arsenazo III gives colour reactions with a smaller number of elements than arsenazo I or arsenazo II. It is found that no colour reactions are observed for elements the cations of which have a radius less than 0·7–0·8 Å. In Table II the first column gives the element, the second the ionic radius[22] in Å, and the third the molar absorption coefficient at $\lambda = 665$ mμ.

TABLE II.—RELATION BETWEEN IONIC RADIUS AND MOLAR ABSORPTION COEFFICIENT

E^{II}	r, Å	K	E^{III}	r, Å	K	E^{IV}	r, Å	K
Be	0·314	~ 0	Al	0·55	~ 0	Ge	0·55	~ 0
Zn	0·566	~ 0	Ga	0·65	~ 0	Ti	0·60	~ 0
Pb	1·28	10×10^3	In	0·95	~ 0	Sn	0·65	~ 0
Ca	1·051	10×10^3	Sc	0·81	19×10^3	Hf	0·77	95×10^3
Sr	1·175	10×10^3	Y	0·93	55×10^3	Zr	0·80	120×10^3
Ba	1·395	10×10^3	Ce	1·18	47×10^3	U^{IV}	1·02	100×10^3
UO_2^{2+}	—	53×10^3	La	1·14	45×10^3	Th	1·10	130×20^3

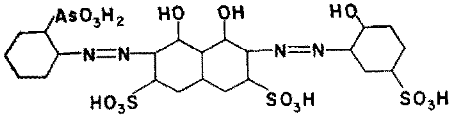
The figures suggest that apparently no ring-closure takes place when the radius of the metal ion forming the complex is relatively small. The values of K in Table II are approximate.

For some elements, complex formation may not take place through the functional-analytical group comprising the AsO_3H_2 group. For example, with Al and Ti the chromotropic acid grouping may form the complex:



VII

In the case of arsenazo I, arsenazo II, and unsymmetrical analogues of arsenazo III [reagents (VIII)–(XIV)], or even of reagents not containing salt-forming groups in the *o*-position to the azo group [(XV), (XVI)] this leads to the formation, within the framework of the conjugated system, of a molecule with some dipole character; and with this is associated a deepening of the colour. In the case of symmetrical reagents—arsenazo III and reagent (XVII)—no dipole is formed and no visible

VIII


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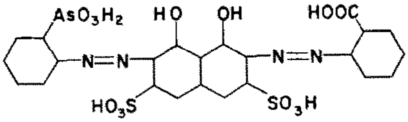
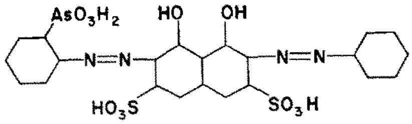
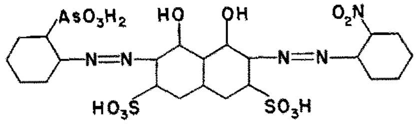
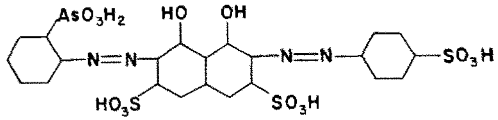


X


XI


XII


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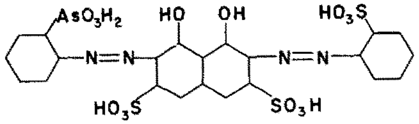
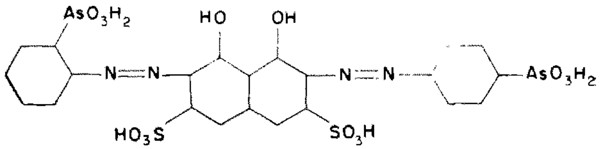
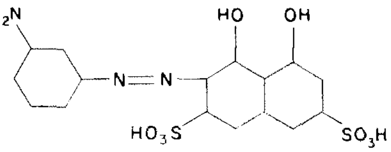
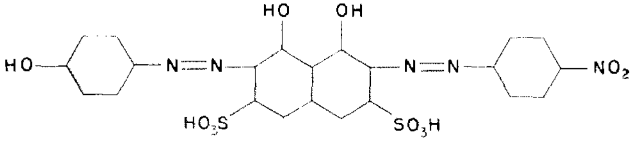


XIV


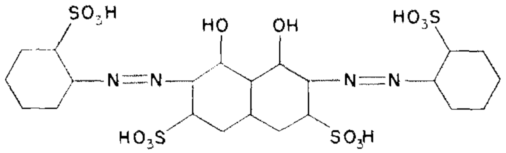
XV



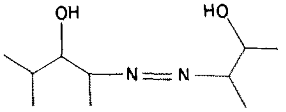
XVI



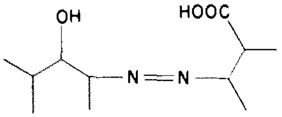
XVII



effects are found. With reagents (VIII) and (IX) complex formation may also take place through the second functional-analytical grouping:



XVIIIa

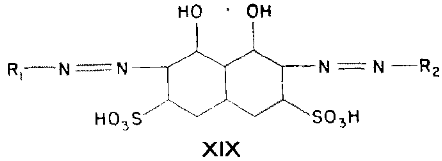


XVIIIb

which also leads to the appearance of a colour reaction.

Analogues of arsenazo III

In order to study the formation of complex formation by arsenazo III, more than 100 bis-azo derivatives of chromotropic acid and various amines of the type of



XIX

have been synthesized, no full list of them being given here. Many of the compounds obtained proved to be extremely interesting analytical reagents in themselves, and may be of interest in the determination of Nb, Zr, Hf, Th, Be, Pb, Cu, and some other elements.

Previously, results have been given (masking coefficients or specific instability indices[23]) showing that all the bis-azo derivatives of chromotropic acid containing even one *o,o'*-azo-hydroxyarsono group form considerably more stable complexes with elements than, for example, arsenazo I.[24,25] This is also found where the second benzene ring completely lacks a salt-forming group [reagents (X), (XI)]; or the group is not specific for thorium (XIII); or it is not located in the *o*-position to the azo group (XII, XIV). This shows that the marked rise in the stability of the complexes observed with arsenazo III and other bis-azo derivatives of chromotropic acid cannot be caused by the simultaneous participation in complex formation of two functional-analytical groups and by the formation of closed rings, as is the case with EDTA.

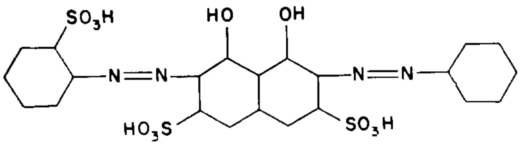
An indirect influence of the second substituent (possibly by enhancement of the tendency to protonisation of the azo group of the functional-analytical nucleus, and the marked stabilisation of the Me—N bond connected with this) is more probable. In addition, a definite effect is also attributed to the repeated occurrence in the reagent molecule of a grouping specific for a given element—if this does not lead to a marked deepening of the colour (through an enlargement of the system of conjugated bonds), to diminished solubility, and other undesirable features.

Somewhat unexpected is the extremely pronounced reduction in the reactivity of the second functional-analytical group when the first takes part in complex formation. It may be assumed that a certain mutual influence of the two conjugated systems leads, when the first group takes part in complex formation, to the transfer of some positive charge to the second azo group, thus lessening the possibility of the formation of a second Me^{n+}—N bond. The lengthening of the conjugated chain in arsenazo III as compared with arsenazo I, and the associated possibility of the distribution of a positive charge transferred to the first azo group, is possibly one of the causes of the increased tendency to protonisation of one of the azo groups and, in the end, leads to a stabilisation of the Me^{n+}—N bond and of the whole complex.

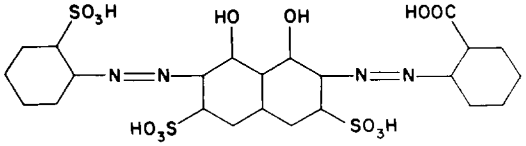
The other bifunctional reagents—arsenazo II and thoron II [reagents (III) and (IV)] have almost completely isolated conjugated systems. These reagents can form with Me^{II} a complex of the composition Me_2R having only one absorption band in the visible region, and having a considerably lower stability than the arsenazo III complexes, although higher than those of arsenazo I. The latter apparently indicates some slight interaction between the systems.

Marked stabilisation of the complexes is also found with the analogues of arsenazo III—bis-azo derivatives of chromotropic acid—containing other salt-forming substituents in place of AsO_3H_2: $-PO_3H_2$, $-SO_3H$, —COOH, —OH. The mechanism of complex formation for these compounds does not apparently differ in principle from the mechanism of the formation of arsenazo III complexes, with the essential limitation that the nature of the salt-forming substituent determines the selectivity of the action of the reagents.

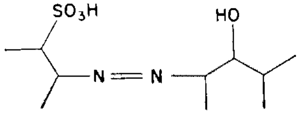
A reagent[26] containing two—PO_3H_2 groups—chlorophosphonazo III—gives a colour reaction in acid solutions with U^{VI},[27] with Pa,[28,29] and with Th, Sc, Ti, and Zr.[30,31] Reagents containing —COOH and —OH groups are specific for Al, Ti, Cu, Nb, and Ta; reagents containing $-AsO_3H_2$, —COOH, and $-SO_3H$ groups have been proposed as metal indicators for the barium ion in the determination of sulphates.[32,33] Examples are reagents (IX) and (XIII). The following reagents are also promising as metal indicators:[33]



XX



They all contain as the complex-forming group of atoms:



XXI

Reagents with two of these groupings [(XVII), *etc.*[33]] form particularly stable complexes with Ba and Sr. The stability of the complex formed by reagent (XVII) with barium can be judged by the simple fact that an intensely coloured complex is formed even in acid media—down to pH 1—which is completely non-specific for barium and is not decomposed by sulphates. The sensitivity is 0·1–0·5 μg/ml of the element.[33]

SYNTHESIS OF ARSENAZO III

In the synthesis of arsenazo III, the method of increasing the activity of chromotropic acid, by treating it in the form of its cyclic salts,[4,34] is used.

Synthesis

Dissolve 60 g (0·276 mole) of *o*-aminophenylarsonic acid in 100–200 ml of water and 60 ml of concentrated hydrochloric acid. Treat the solution with 100–200 g of ice and add slowly, with vigorous stirring, a solution of 20 g of sodium nitrite (0·29 mole) in 50–100 ml of water. Destroy the excess if nitrous acid by the addition of *o*-aminophenylarsonic acid.

Dissolve 26 g (0·0717 mole) of chromotropic acid (mono- or disodium salt) in 200–300 ml of water, and add a mixture of 40 g of calcium oxide and 200–400 ml of water. Treat the mixture with 300–400 g of ice, and add the solution of diazotised *o*-aminophenylarsonic acid with stirring. Allow the mixture to stand for some hours at room temperature.

Then add 4–5 litres of water and 0·5 litre of concentrated HCl, stir the mixture carefully, and set it aside. Then filter, wash the product on the filter with 1:5 hydrochloric acid, water, and ethyl alcohol, recrystallise 2–3 times. Check the purity of the product by the quantitative reaction with thorium salts. Yield of arsenazo III 53–56 g.

Zusammenfassung—Die zwei analytisch wesentlichen funktionellen Gruppen des Arsenazo-III-Moleküls liegen in zwei fast voneinander isolierten konjugierten Systemen. Die Komplexbildung findet nur an einem davon statt; dies führt zu zwei Banden im sichtbaren Spektralbereich. Die Zusammensetzung der Komplexe für Me(II) und Me(III) entspricht MeR, bei Me(IV) MeR oder MeR_2 (je nach Acidität und Konzentration der Komponenten). Elemente mit einem Ionenradius unter 0,7–0,8 Å geben keine Farbreaktion mit Arsenazo-III. Die Stabilität der mit Reagentien vom Typ des Arsenazo-III (Bisazoderivate der Chromotropsäure) gebildeten Komplexe hängt von der Natur der Me-N-Bindung ab und wird durch die Größe des konjugierten Systems im Reagens und der Natur des Substituenten bestimmt.

Résumé—Les groupes à deux fonctions analytiques de la molécule d'Arsenazo-III sont présents dans deux systèmes conjugués presque isolés. La formation de complexe avec les éléments n'intervient que dans le cas d'un d'entre eux. Ceci donne l'apparence de deux bandes d'absorption dans la région visible du spectre. La composition des complexes pour Me^{II} et Me^{III} correspond à MeR et pour Me^{IV} à MeR ou MeR_2 (selon l'acidité et les concentrations des composants). Les éléments à rayon ionique plus petit que 0,7–0,8 Å ne donnent pas de réaction colorée avec l'Arsenazo-III. La stabilité des complexes formés par les réactifs du type Arsenazo-III (dérivés bis-azo de l'acide chromotropique) avec des éléments dépend de la nature de la liaison Me-N et est déterminée pat la proportion de liaisons conjuguées dans la molécule du réactif et par la nature du substituant.

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A SYSTEMATIC SCHEME FOR THE IDENTIFICATION OF POLYATOMIC ANIONS BY INFRARED SPECTROSCOPY

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Summary—Using infrared absorption spectroscopy, a systematic scheme has been established for the identification of the following 16 anions: ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate, salicylate, benzoate, bromate, iodate, silicate, oxalate, tartrate, phosphate, arsenate, chromate and sulphate.

INFRARED spectrophotometry has been established for some time as a popular—indeed well nigh indispensible—method for the identification and determination of organic compounds. Although it has also been used for the investigation of inorganic anions, only one application to systematic qualitative analysis has been attempted.[1]

In the present work infrared spectroscopy has been applied to the systematic identification of the following polyatomic anions: ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate, bromate, silicate, iodate, salicylate, benzoate, oxalate, tartrate, phosphate, arsenate, chromate and sulphate. The above anions are separated into five groups according to the M.A.Q.A. Scheme of semi-micro qualitative inorganic analysis.[2-4] A few mg of each group of anions, after being separated by its selective group precipitant, are washed with a suitable reagent, and dried; the precipitate is mixed with KBr, and a suitable disc is made. The infrared spectrum obtained permits the identification of the anions present.

EXPERIMENTAL

Apparatus and reagents

The infrared spectra were recorded on a Perkin-Elmer "Infracord" spectrophotometer, model 137. The KBr discs were prepared with a Perkin-Elmer die using an "Apex" hydraulic press with a 10-ton capacity on a ram of 2⅛ inch diameter. Before use, the KBr, which was Analytical Reagent grade, was dried at 150° for at least 24 hr. All other chemicals used in the work were AnalaR.

Procedure

The procedure, technique, and equipment have already been described elsewhere.[1,2]

RESULTS

Characteristic absorption of the various anions

Slight differences were found when the characteristic frequencies of the various anions, determined using the KBr disc technique, were compared with those obtained as mulls. These shifts can, in general, be attributed to the short range crystal forces operating on the anions when pressed into the KBr lattice, thus perturbing the vibrational levels. These effects do not occur in the mull, where the material under investigation preserves its own crystal structure and is merely dispersed in an inert medium.

Among the compounds studied here by the KBr disc technique, were some originally investigated by the mull technique,[5] such as silica gel, silver bromate, calcium orthoarsenate, calcium phosphate (dibasic), and barium chromate.

The characteristic absorptions observed were as follows:

(1) Silver ferrocyanide: very strong, sharp absorption at 4·9 μ with two other intense bands at 6·12 μ and 6·2 μ. A deep shoulder is noted at 4·95 μ on the 4·9 μ peak.

(2) Silver ferricyanide: a very strong, sharp band at 4·73 μ, (m. and sp. with sh.)* band at 4·90 μ, and two intense bands at 6·12 μ and 6·2 μ. The main and characteristic absorption band for ferricyanide is that at 4·73 μ; some of the others probably arise from ferrocyanide, produced on grinding the precipitate of silver ferricyanide with KBr. The fading of the orange colour of silver ferricyanide in the grinding process is evidence of this reduction.

(3) *Silver thiocyanate*: a very strong, sharp band at 4·77 μ, with a shoulder at 4·82 μ.

(4) *Silver arsenite*: strong bands at 6·92 μ and 13·5 μ, with two (s, b) bands at 12·5 μ and 14·5 μ. A deep shoulder is observed at 11·3 μ and a weak band at 6·1 μ.

(5) *Silver periodate*: a strong band at 6·92 μ, two (b, s) bands having maxima at 13·65 μ, 14·45 μ.

(6) *Benzoate* (as benzoic acid): (vs. sp) 14·05 μ, 5·92 μ; (s, sp) 7·55 μ, 7·75 μ; (m, sp) 6·9, 7·04 μ, 14·9 μ; (m) 10·66 μ; (w. sp) 14·55 μ, 9·74 μ, 9·32 μ, 8·86 μ, 6·34 μ; (w) 12·3 μ, 8·46 μ; (v, w) 10·0 μ, 9·1 μ, 6·7 μ, 6·18 μ, 6·25 μ, 6·12 μ, 5·6 μ, 5·22 μ, 4·8 μ, 3·9 μ, 3·74 μ, 3·54 μ, 3·35 μ, 3·1 μ.

(7) *Salicylate* (as salicylic acid): (vs, sp) 14·25 μ, 13·1 μ, 8·65 μ, 8·26 μ, 8·02 μ, 7·75 μ, 6·95 μ, 6·85 μ, 6·75 μ, 6·05 μ; (m) 11·15 μ; (m, sp) 12·68 μ, 11·68 μ, 9·7 μ, 8·42 μ, 7·58 μ, 6·22 μ; (w) 11·48 μ, 10·35 μ, 9·2 μ, 7·25 μ, 6·35 μ, 3·85 μ, 3·5 μ, 3·35 μ, 3·1 μ; (v, w) 12·35 μ, 10·05 μ, 7·15 μ, 6·58 μ, 5·72 μ, 5·48 μ, 5·22 μ, 5·15 μ, 5·06 μ, 4·82 μ, 4·62 μ.

(8) *Silicate* (as silica gel, $SiO_2 \cdot xH_2O$): a very strong band at 9·2 μ and a weak band at 10·4 μ.

(9) *Silver bromate*: a very strong band at 12·55 μ with a shoulder at 12·75 μ.

(10) *Silver iodate*: a very broad, strong band, having maxima at 13·0 μ, 13·75 μ and 13·3 μ. Medium shoulders at 12·5 μ, 14·0 μ and 14·2 μ are also observed.

(11) *Calcium oxalate*: (vs) 6·18 μ; (s, sp) 7·25 μ; (s, sp) 7·6 μ; (s, sp) 12·72 μ.

(12) *Calcium tartrate*: (m) 3·86 μ; (vs) 6·3; (vw) 6·75; (s, sp) 7·24, (sh) 7·0, (sh) 7·15, (m, sp) 7·52, (m, sp) 7·82; (w, sp) 8·1, (vs, sp) 8·72, (vs, sp) 9·42, (m, sp) 9·9, (m) 10·4, (vw) 10·82, (vw) 11·28, (vw) 11·76, (m, sp) 12·2, (m) 14·0.

(13) *Calcium orthoarsenate*: a (vs, vb) band at 11·9 μ with a shoulder at 11·3 μ.

(14) *Calcium phosphate* (*dibasic*): a very broad, strong band, having maxima at 9·7 μ, 9·35 μ and 8·9 μ.

(15) *Barium chromate*: (s) 10·60 μ, (vs) 11·10 μ, (vs) 11·45 μ, (vs) 11·60 μ.

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* m = medium sp = sharp sh = shoulder s = strong b = broad w = weak v = very.

(16) *Barium sulphate*: (vs) 8·48 μ, (vs) 8·95 μ, (vs) 9·25 μ, (m, sp) 10·15 μ.

Note: Absorption bands caused by reagents used in the course of analysis, such as the bands at 6·1 μ, 6·2 μ and 7·25 μ, are neglected.

Qualitative studies on mixtures of anions in groups

It would appear from the foregoing results that the infra-red absorption spectra of the anions under study could provide a useful method for their identification either alone or in mixtures:

Group 1: *Ferrocyanide, ferricyanide, thiocyanate, arsenite, periodate*: In a mixture containing all of these anions, identification of either arsenite or periodate was found impossible; however, if only one of these two is present alone [Fig. (1)] identification is possible. Ferrocyanide, characterised by its 4·9 μ absorption band, is always found wherever ferricyanide is present in the mixture. This band shows itself either as a shoulder on the thiocyanate peak, or separate, when present in higher ratio.

Ferricyanide, characterised by its 4·73 μ absorption band, may give a separate band or a shoulder on the thiocyanate peak, depending on the ratio of ferricyanide to thiocyanate.

Thiocyanate is identified either by its 4·77 μ absorption band; by the twin bands with ferrocyanide; or by the shoulder at 4·82 μ which at increased concentration develops into a new peak. This depends on the ratio of thiocyanate to the complex cyanide in the mixture and on the increase of the transmittancy of the disc.

Group 2: *Salicylate, benzoate*: For a mixture of salicylic and benzoic acids, the spectrum shows the characteristic absorption bands of the individual anions (Fig. 2), particularly at 7·04 μ, 10·66 μ, 12·3 μ, 14·55 μ, for benzoic acid; 13·1 μ, 12·68 μ, 11·68 μ, 11·15 μ, 8·65 μ, 8·26 μ, 8·02 μ, 6·75 μ for salicylic acid.

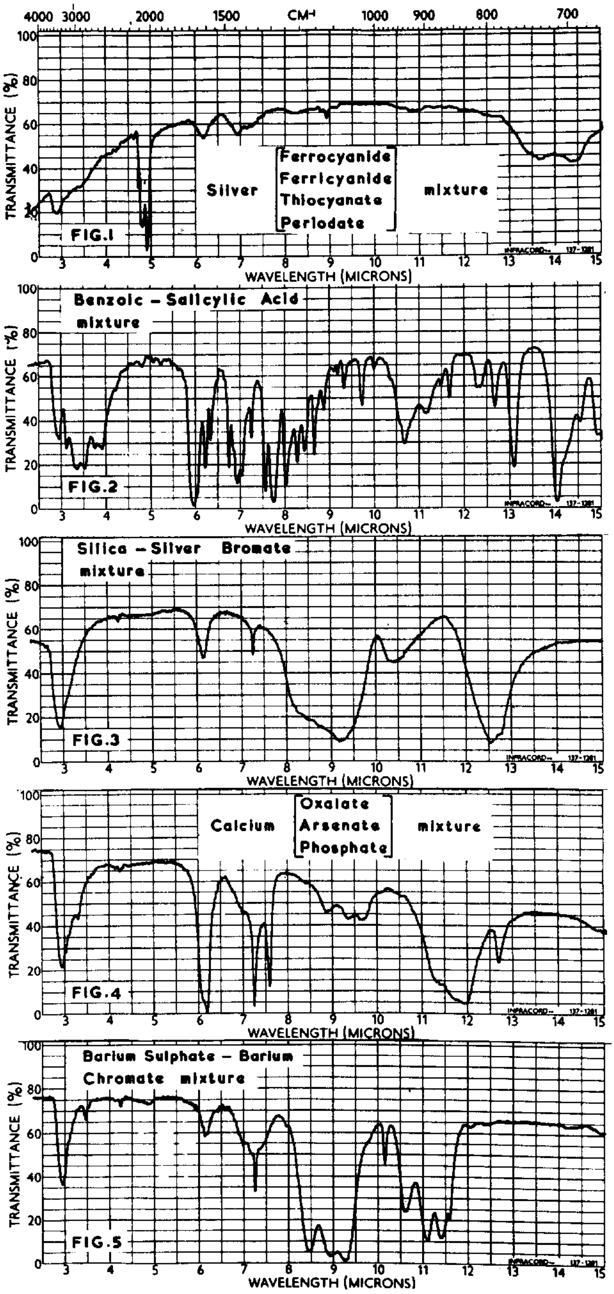
Group 3: *Bromate, silicate, iodate*: In a spectrum of a mixture of these three anions, only the presence of silicate and iodate can be detected, because the bromate peak is masked by the broad iodate band. When the bromate-iodate ratio in the mixture is increased, a change in the shape of the iodate band is observed which may be taken as evidence of the presence of bromate. Fig. 3 shows a spectrum of a mixture of silicate and bromate.

Group 4: *Oxalate, tartrate, phosphate, arsenate*: In a spectrum of a mixture of oxalate, phosphate and arsenate, the three anions can be identified (Fig. 4) from their characteristic absorption bands. Although a spectrum of all four anions of this group showed overlap of some bands, identification of the four individual anions is, however, possible by the following: oxalate by the 12·72 μ band; tartrate from the 14·0 μ band; phosphate and arsenate from their characteristic absorption bands (which may undergo slight modification in mixtures.)

Group 5: *Chromate, sulphate*: A spectrum of these two anions exhibits (Fig. 5) the characteristic absorption bands of the individual anions. No overlapping of the bands is observed.

DISCUSSION

Although attempts were made to use other existing schemes for the separation of anions[6–8] as the basis for this study, none of them proved satisfactory. This was caused by the accumulation of the spectral bands of many anions when precipitated in one


4000 3000 2000 1500 CM⁻¹ 1000 900 800 700
TRANSMITTANCE (%)
0 20 40 60 80 100
3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)
INFRACORD 137-1281
FIG.1
Silver
Ferrocyanide
Ferricyanide
Thiocyanate
Periodate
mixture
FIG.2
Benzoic – Salicylic Acid
mixture
FIG.3
Silica – Silver Bromate
mixture
FIG.4
Calcium
Oxalate
Arsenate
Phosphate
mixture
FIG.5
Barium Sulphate – Barium
Chromate mixture

FIGS. 1–5

group, and the impossibility of identifying the individual anions in the resulting spectrum. The effect of the reagents added during the course of analysis is very limited and the bands associated with them produce no interferences. Because of the decomposition at 100° of the silver salts (especially of Group 1) and the consequent accumulation of silver oxide, which tended to produce deformed spectra with poor transmittance, an alternative drying process, therefore performed in a vacuum desiccator, is recommended for this Group. Drying of Group 2 salts was done under a funnel attached to a water pump. Other groups may either be dried in an oven at 100°, or under vacuum. For oxalate and tartrate, vacuum drying is preferable. Under the above drying conditions, calcium dibasic phosphate, and calcium orthoarsenate are produced.

Washing is necessary for the elimination of strong absorptions by adsorbed reagent. Water is used for washing Group 1 precipitates; $0{\cdot}04M$ HNO_3 for Group 3 precipitates; $0{\cdot}04M$ ammonia for Group 4 and 5 precipitates. Washing is carried out by stirring the precipitate with the wash liquid, using a glass rod, discarding the washings after centrifuging.

The transmittances of the KBr discs of the compounds studied, were better than 80%, except for those made from silver arsenite and periodate; reasonable transmittance for these is only obtained when they are present in lower concentration in KBr. The decomposition of these two compounds, with the production of silver oxide, was also observed when their discs were subjected to infrared radiation, the discs being blackened at the end of each experiment. It is unlikely that the decomposition is brought about either by the grinding of the material with potassium bromide, or in the actual disc preparation, because clear discs could be made and stored successfully. The blackening of the disc during the duration of the experiment might be ascribed to either or both of thermal decomposition because of temperature rise of the disc, or photochemical decomposition of the material, since the disc is exposed to a wide range of wavelengths of light. The minimum wavelength given out by the source is of the order of 1000 Å, and these wavelengths could result in the partial decomposition observed.

Halides and sulphides are, of course, unsatisfactory for spectroscopic investigation, being transparent to infrared radiation. One possible further application, however, is the identification of those anions which, when treated with acid, evolve gases: a multiple-path cell could be used to achieve enhanced sensitivity. Such anions include sulphite, carbonate, hypochlorite, hypobromite.

Zusammenfassung—Mit Hilfe der IR-Absorptionsspektroskopie wurde ein systematisches Schema zur Identifizierung folgender 16 Anionen aufgestellt: Hexacyanoferrat(II) und -(III), SCN^-, AsO_3^{3-}, IO_4^-, Salicylat, Benzoat, BrO_3^-, IO_3^-, Silicat, Oxalat, Tartrat, PO_4^{3-}, AsO_4^{3-}, CrO_4^{2-} und SO_4^{2-}. Die Methode ist einfacher, schneller und empfindlicher als die orthodoxen Identifizierungsmethoden.

Résumé—L'emploi de la spectroscopie d'absorption infra-rouge permet d'établir un tableau systématique d'identification des 16 anions suivants: ferrocyanure – ferricyanure – thiocyanate – arsenite – périodate – salicylate – benzoate – bromate – iodate – silicate – oxalate – tartrate – phosphate – arseniate – chromate et sulfate. Cette méthode est supérieure aux méthodes d'identification habituelles car elle est simple, rapide et sensible.

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RE-ACTIVATION ANALYSIS OF VANADIUM

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Summary—Re-activation analysis is applied to the determination of vanadium. After the addition of vanadium carrier to the irradiated sample, vanadium-52 is separated radiochemically pure by extraction with benzene as vanadium oxinate. The γ-ray spectrum of the vanadium-52 is recorded; the height of the photopeak at 1·44 MeV is measured and compared with that of a vanadium standard. The chemical yield of the purification step is decided by re-irradiation of the separated vanadium oxinate solution and comparing the activity of the vanadium-52 with that of a further vanadium standard. The vanadium content of the sample is determined from the activity of the vanadium-52 induced by the first irradiation and corrected for the chemical yield from the second irradiation.

IN previous papers[1,2] the authors reported on the method of re-activation analysis and its application to the determination of aluminium. This method has the advantage of determining precisely the chemical yield after counting without loss of the sample.

In a normal destructive activation analysis using short life nuclides, the chemical yield is determined by weighing a suitable precipitate of the element being analysed after counting its activity. For the precise determination of chemical yield it is not desirable to treat the irradiated sample after being counted.

On the other hand, when the element to be determined does not have a suitable precipitate for weighing, the chemical yield is determined using a radio-isotope tracer. This method has the disadvantage of producing an error from the difference of chemical yield in each separation.

In re-activation analysis, the chemical yield is easily corrected by re-activation of the counted sample and thus the source of error mentioned above can be eliminated.

The re-activation technique consists of several typical steps, *viz.* the first irradiation of the sample, addition of a carrier, radiochemical separation, counting of the induced activity from the first irradiation, sealing the counted sample in a polyethylene tube, cooling, a second irradiation and counting the induced activity from the second irradiation. The element is determined by measuring the induced activity from the first irradiation, which is corrected for the chemical yield calculated from the induced activity from the second irradiation.

In other words, the technique of non-destructive activation analysis is applied to determine the yield of radiochemical separation in normal destructive activation analysis. This method has now been satisfactorily applied to the determination of vanadium.

THEORETICAL

Solvent extraction was adopted for the radiochemical separation of vanadium because of its rapidity. In this method, the carrier to be added is limited to a rather small amount. Therefore, the amount of the element to be determined in the sample cannot be neglected in the calculation of the chemical yield. From these considerations an equation for determining an element in the sample from the induced activities from the first and second irradiations has been derived:[2]

$$W = \frac{A_{sam} \cdot W_c \cdot W_{st}}{\dfrac{A_{st} \cdot A'_{sam} \cdot W'_{st}}{A'_{st}} - A_{sam} \cdot W_{st}} \qquad (1)$$

where W = weight of vanadium in the unknown sample (g),

A_{st} = induced activity of vanadium-52 in the standard sample from the first irradiation,

W_{st} = weight of the standard sample for the first irradiation (g),

A_{sam} = induced activity of vanadium-52 isolated from the unknown sample after the first irradiation,

W_c = weight of vanadium carrier added to the irradiated unknown sample (g),

A'_{sam} = induced activity of vanadium-52 from the unknown sample after the second irradiation,

A'_{st} = induced activity of vanadium-52 in the standard sample from the second irradiation,

and W'_{st} = weight of the standard sample for the second irradiation (g).

The calibration curves of vanadium for the first and second irradiations (Figs. 2 and 3) were not linear and therefore the amount of vanadium could not be determined from equation (1).[2] However, if the calibration curves are used to find the weights of vanadium corresponding to A_{sam} and A'_{sam}, then A_{sam} and A'_{sam} become equal to A_{st} and A'_{st}, respectively, and equation (1) can be simplified to:

$$W = \frac{W_c(W_{st})_{obs}}{(W'_{st})_{obs} - (W_{st})_{obs}} \qquad (2)$$

where $(W_{st})_{obs}$ = weight of vanadium corresponding to A_{sam} as observed from the calibration curve for the first irradiation (Fig. 2),

and $(W'_{st})_{obs}$ = weight of vanadium corresponding to A'_{sam} as observed from the calibration curve for the second irradiation (Fig. 3).

EXPERIMENTAL

Standard samples

224·5 mg of ammonium vanadate (G.R.) were dissolved in 100 ml of water. This solution was further diluted to give vanadium solutions of several different concentrations. 1 ml of each standard solution was sealed in a polyethylene tube and placed in the centre of a capsule by packing with soft paper.

Samples

Samples containing different amounts of vanadium, manganese, sodium and potassium were prepared in the same way as the vanadium standard samples.

Apparatus

The JRR-1 reactor was used as a neutron source and the RCL-256 channel pulse height analyser with a 1·75 × 2 inch NaI (Tl) crystal (well-type) used as a counter.

Neutron irradiation

All irradiations were made in the No. 16 experimental hole (pneumatic tube) at a neutron flux of about 3×10^{11} neutrons.cm^{-2}.sec^{-1}. The first irradiation was continued for 3 min and the second irradiation for 10 sec.

Procedure

After irradiation in the reactor for 3 min, the unknown sample solution was transferred to a separating funnel. 1 ml of vanadium carrier solution (48·889 μg of vanadium) was added, followed by 50 ml of 0·1M ammonium tartrate solution (pH 4·6). Vanadium was then extracted with 5 ml of a 1 % w/v solution of oxine in benzene. The benzene phase was transferred to a polyethylene tube, which was mounted in the NaI (Tl) crystal 5 min after the end of irradiation, counted for 2 min and the resultant γ-ray spectrum plotted. The polyethylene tube containing the benzene phase was sealed and allowed to cool sufficiently for the vanadium-52 activity to decay to a negligible amount. It was then irradiated for 10 sec, cooled for 110 sec, counted for 1 min and the resultant γ-ray spectrum plotted. The γ-ray spectra of the irradiated standard samples for the first and second irradiations were recorded under the same conditions as for the unknown sample. Vanadium carrier solution was not added to either standard sample nor was the solvent extraction carried out. In each of the resultant γ-ray spectra, the height of the photopeak at 1·44 MeV from the vanadium-52 was measured.

Calibration curves were prepared for the first and second irradiations using the data of standard samples. $(W_{st})_{obs}$ and $(W'_{st})_{obs}$ were determined from these curves as the weights of vanadium producing the same activities as A_{sam} and A'_{sam}, respectively. The amount of vanadium in the unknown sample was then calculated by equation (2).

RESULTS AND DISCUSSION

γ-Ray spectrum

An example of the γ-ray spectrum of vanadium-52 measured after the extraction with oxine-benzene solution is shown in Fig. 1.

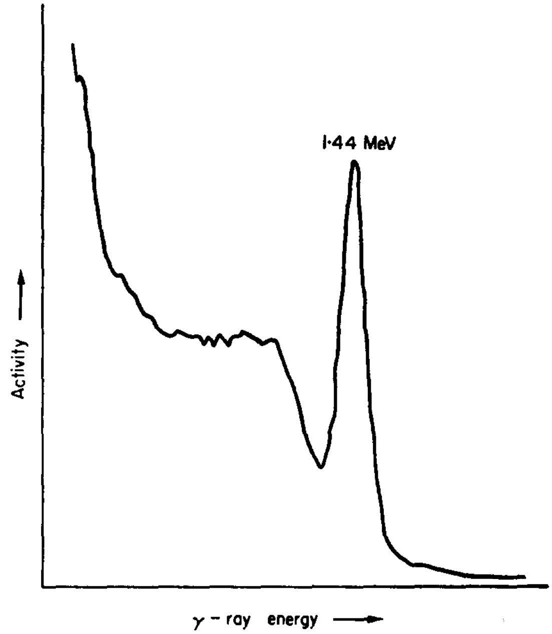

FIG. 1.—γ-Ray spectrum of vanadium.

Calibration curves

The calibration curves of vanadium for the first and second irradiations are shown in Figs. 2 and 3, respectively

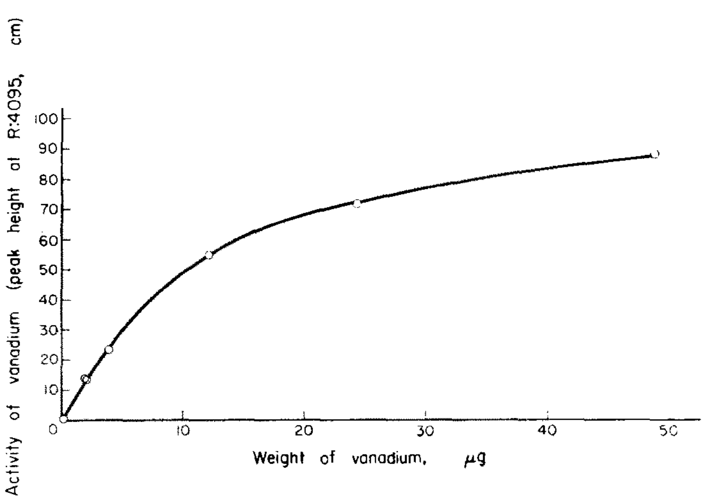

FIG. 2.—Calibration curve of vanadium for the first irradiation.

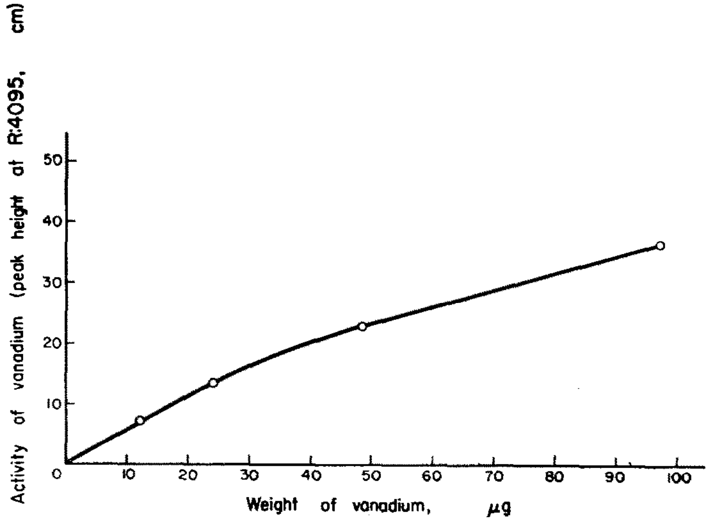

FIG. 3.—Calibration curve of vanadium for the second irradiation.

Results

Some results of analyses by this method are shown in Table I. The upper and lower limits of determination of vanadium are 25 μg and about 0·05 μg, respectively. The coefficient of variation of analysis for 3·91 μg of vanadium is 3·81% (6 results).

Interferences

γ-Rays which may be confused with the 1·44 MeV γ-ray of vanadium-52 are the 1·368 MeV of sodium-24, 1·37 MeV of holmium-166, 1·479 MeV of molybdenum-93m, 1·49 MeV of nickel-65 and 1·53 MeV of potassium-42. Also, the 1·81 MeV γ-ray of manganese-56 would affect measurement of the height of the 1·44 MeV vanadium-52

TABLE I.—ANALYSES OF VANADIUM BY RE-ACTIVATION ANALYSIS

Sample no.	Sample		V found, μg
	V taken, μg	Other elements taken, *mg*	
1	0·20	0	0·20
2	0·39	0	0·29
3	1·96	0	2·07
4	3·91	0	3·68
5	3·91	0	4·00
6	3·91	0	4·01
7	3·91	0	4·12
8	3·91	0	3·78
9	3·91	0	3·90
10	12·22	0	11·8
11	24·44	0	27·2
12	3·91	Na 0·1	3·78
13	3·91	Na 1	3·90
14	3·91	K 0·1	3·90
15	3·91	K 1	3·91
16	3·91	Mn 0·1	4·61

peak. The interference from manganese-56, sodium-24 and holmium-166 must be taken into account because of their high activation cross sections and saturation factors.[3]

Because sodium and potassium are not extracted with oxine-benzene solution, these elements do not affect the determination of vanadium by the present method. Manganese should not affect it either, because of its non-extractability with oxine-benzene solution, but some interference was found. Some precipitation of manganese hydroxide takes place at the pH of the sample solution at the extraction stage and part of this precipitate is presumably carried into the benzene phase. No method of overcoming the interference from manganese was found.

Zusammenfassung—Die zweistufige Aktivierungsanalyse wird auf die Bestimmung von Vanadin angewandt. Nach Zugabe von Vanadinträger zur bestrahlten Probe wird ^{52}V radiochemisch rein als Oxinat durch Extraktion mit Benzol abgetrennt. Das Gammastrahlenspektrum des ^{52}V wird registriert; die Höhe der Linie bei 1,44 MeV wird gemessen und mit der eines Vanadiumstandards verglichen. Die chemische Ausbeute des Abtrennungsschrittes wird durch erneute Bestrahlung der Vanadiumoxinatlösung bestimmt; deren ^{52}V-Aktivität wird mit der eines weiteren Vanadiumstandards verglichen. Der Vanadingehalt der Probe wird aus der durch die erste Bestrahlung hervorgerufenen ^{52}V-Aktivität berechnet und für die auf Grund der zweiten Bestrahlung bestimmte chemische Ausbeute korrigiert.

Résumé—L'analyse par réactivation est appliquée à la détermination du vanadium. Après addition d'un porteur de vanadium à l'échantillon irradié, le vanadium-52 est séparé sans impureté radiochimique par extraction au benzène sous forme d'oxinate de vanadium. On enregistre le spectre de rayon γ du vanadium-52; la hauteur du pic à 1,44 MeV est mesurée et comparée à celle d'un spectre étalon de vanadium. On détermine le rendement chimique de la purification en irradiant à nouveau la solution séparée d'oxinate de vanadium et en comparant l'activité du vanadium-52 à celle d'un autre étalon de vanadium. On détermine la quantité de vanadium contenue dans l'échantillon à partir de l'activité de vanadium-52 provenant de la première irradiation et la correction due au rendement chimique est calculée à partir de la deuxième irradiation.

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SEPARATION OF THE OLIGOPHOSPHATES

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Summary—Mixtures consisting of orthophosphate, its linear polymers up to and including tridecaphosphate, and three cyclic polymers have been separated by ion-exchange chromatography. One of the cyclic polymers (found in polyphosphate glasses of $\bar{n} \simeq 10$) is probably pentametaphosphate. Its cyclic nature has been demonstrated by end-group titrations and by paper chromatography, but attempts to determine the number of phosphorus atoms in the ring failed because of the very small amount of the compound available. Evidence is presented in support of the common assumption that the linear phosphates above the tetramer are eluted in the sequence of their increasing degree of polymerisation.

INTRODUCTION

THE oligophosphates consist of two homologous series of reasonably stable compounds. The linear polymers can be represented by the general formula $Na_{n+2}P_nO_{3n+1}$, while the cyclic polymers have the general formula $Na_nP_nO_{3n}$.[1] In the latter case, the trimer and tetramer are commercially available. Evidence for the existence of the higher cyclic phosphates in partially degraded Graham salt (long-chain linear polymers) has been obtained by paper chromatography,[2] but these compounds have been isolated only in trace quantities.

In dilute aqueous solution, all of the oligomers undergo slow degradation to orthophosphate. However, at room temperature and at pH levels near 7, the degradation is slow enough to permit the analysis and the study of the properties of the individual polymeric species.

The properties of adjacent members of the polymeric series are so similar that the analysis of mixtures of these polymers is a difficult task. Classical, wet chemical methods are not able to distinguish between oligomers greater than the trimer.[3] Two-dimensional paper chromatography has isolated "spots" for both the linear and cyclic polymers through the tetramers and has partially resolved spots for higher compounds of both types.[4] Quantitative applications of this technique are subject to relative errors of several per cent because of the small samples and the relatively harsh elution conditions. Ion-exchange chromatography has been utilised for the separation and determination of each constituent in mixtures of phosphates.[5–9] The fundamental theory of this approach, applied to the phosphates, was published in 1954,[6] and succeeding papers have extended the original separation to higher oligomeric species. A description of a device for the automatic recording of the elution graph in the analysis of phosphate mixtures has been published.[10]

Matsuhashi[8] extended the range of the ion-exchange method as far as the dodecaphosphate. However, his separation of the linear polymers above the trimer was not quantitative and the cyclic polymers would have overlapped the linear in any single elution. Jameson[9] achieved a quantitative separation of the linear polymers through the dodecaphosphate by gradient elution, but he did not separate the cyclic polymers from the linears.

RESULTS AND DISCUSSION

Anion-exchange chromatography

Previous work in this laboratory[5,7] had indicated that moderately crosslinked polystyrene resins with the ionic group $-CH_2N^+(CH_3)_3$ are best for the separation of the condensed phosphates. Amberlite XE–119 (analogous to IRA–400 but with a mesh range of 400 to 600) was selected.

In the previous work,[5] the pH of the eluent had been chosen with the aid of equations (19) and (20) of reference 6 (or similar equations) so as to give maximum separations between neighbouring members of the polymeric series.

A difficulty was experienced in the present work in applying these equations because the values of the ionisation constants and the selectivity coefficients are not known for the polymers above the tetramers. Therefore, the following semi-empirical method was used to predict the elution behaviour of the higher linear polymers at pH 5.[11]

From the data of Irani and Callis,[12] it seems likely that for any oligophosphoric acid, $H_{n+2}P_nO_{3n+1}$, the last three ionisation constants will have the values: $K_{Z-2} \cong 10^{-2}$, $K_{Z-1} \cong 10^{-6}$, $K_Z \cong 10^{-8}$ $(Z = n + 2)$. It can then be calculated that at pH 5·0, almost 91% of the polymer is present as H_2A^{-Z+2}, 9% as HA^{-Z+1} and negligible amounts as other species. By neglect of all species except the predominant H_2A^{-Z+2} it can be proved[6,11] that at pH 5·0

$$C = \frac{WQ}{V} \cdot \frac{E_{Z-2}}{[Cl^-]^{Z-2}} \tag{1}$$

W is the dry weight of the resin in the column (g); Q is the exchange capacity of the resin (mequiv/g); V is the interstitial volume of the column (ml); E_{Z-2}, the selectivity coefficient, is the classical equilibrium constant of the exchange reaction between the ions $H_2A^{-(Z+2)}$ and Cl^-. For any given ion-exchange column, WQ/V is constant over a range of eluent concentrations. Then equation (1) indicates that each linear phosphate in Fig. 1 should have a slope of $-(Z - 2) = -n$. The actual slopes from $n = 1$ to $n = 3$ are about 10% steeper than the predicted values. The data for these species were taken from the work of Lindenbaum and coworkers.[5,6] Furthermore, E_{Z-2} for these linear phosphates did not vary much over the range of eluent concentrations used nor from one polymer to another.[11] Therefore the graphs for the species larger than the trimer were drawn with slopes of $-1{\cdot}10\,n$ and with $E_{Z-2} = 6 \times 10^{-2}$ in all cases.

Because all ionisation constants of the cyclic phosphates are very large, their elution behaviour is not affected by the pH of the eluent. Their C values vary with the concentration of the eluent[6] approximately according to the equation

$$C = \frac{WQ}{V} \cdot \frac{E_Z}{[Cl^-]^n} \tag{2}$$

For cyclic phosphates, $Z = n$.

The position of any peak in an elution graph with only one concentration of eluent is given by the equation

$$U^* = CV + V \tag{3}$$

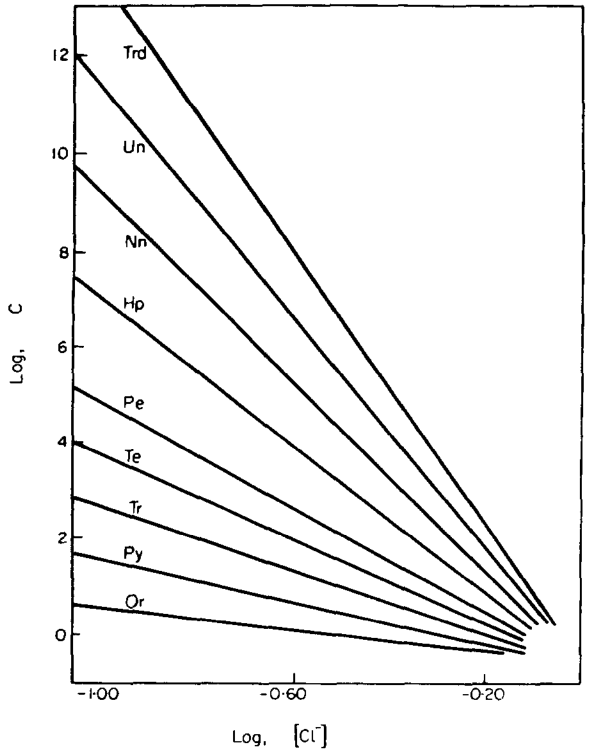

FIG. 1.—Values of log C for various linear phosphates eluted by potassium chloride at pH 5·0:

Trd—tridecaphosphate,
Un—undecaphosphate,
Nn—nonaphosphate,
Hp—heptaphosphate,
Pe—pentaphosphate,
Te—tetraphosphate,
Tr—triphosphate,
Py—pyrophosphate,
Or—orthophosphate.

Log C is plotted against the logarithm of the eluent concentration. The curves for ortho- through triphosphate were determined experimentally,[5,6] while those for tetra- through tridecaphosphate were determined as described in the text.

where U^* is the volume of effluent at the peak. The separation factor for any two adjacent polymers is the ratio of their C values, C_2/C_1. Thus the facility with which any two phosphates may be separated is given by $\Delta \log C = \log C_2 - \log C_1$, *i.e.*, the vertical distance between the appropriate graphs in Fig. 1. Obviously, the separation is very difficult (requiring very long columns) at large concentrations of eluent and much easier at small concentrations. On the other hand, small concentrations of chloride cause large values of C and U^* and hence lengthy elutions. In order to obtain a satisfactory elution, it is necessary to use an eluent less than 0·30M until several of the lower polymers are eluted, then to increase the concentration in several steps (or gradiently) to about 0·40M.

Several preliminary elutions were performed in which unsatisfactory separations were obtained. In each elution, the concentration or the volume of one or more of the eluents was changed to improve the separation according to the principles discussed above. Minor changes in pH of some of the eluents were also made in order to improve the separation of overlapping pairs consisting of one cyclic and one linear polymer. The elution shown in Fig. 2 was finally obtained. This shows a nearly perfect separation of the linear polymers as far as trideca and three cyclic compounds. The peaks of the compounds with four or less phosphorus atoms per molecule were identified by running elutions with known compounds under the same conditions. The identity of the other peaks, especially the "unknown cyclic phosphate" is discussed in the next section.

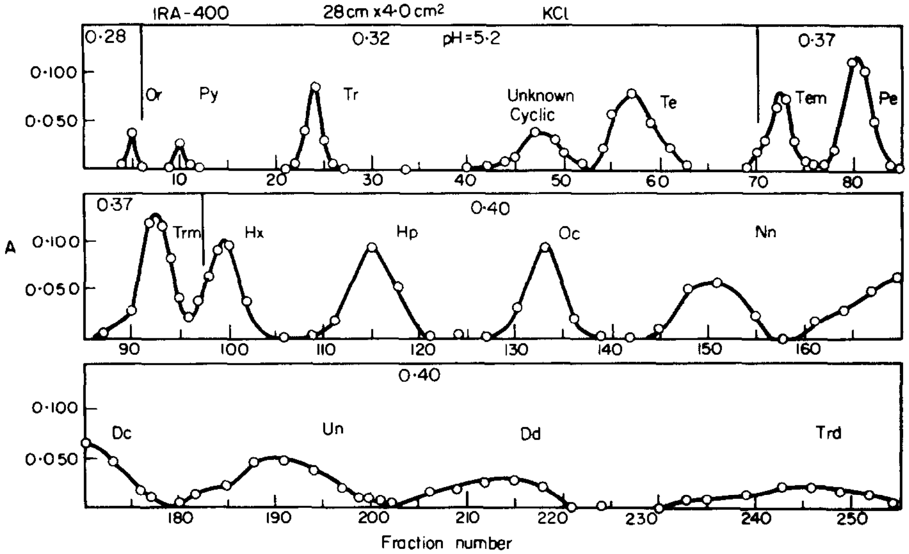

FIG. 2.—Separation of the oligophosphates by anion-exchange chromatography. Absorbance, A, at 400 mμ plotted against fraction number. Each fraction equals 26 ml. A flow rate of 0·42 cm/min was maintained. The sample contained 62 mg of a polyphosphate glass with $\bar{n} \simeq 8$. Trm and Tem denote trimetaphosphate and tetrametaphosphate, respectively.

"Unknown cyclic phosphate"

In several preliminary elutions, a "shoulder" appeared on the left side of the peak of tetraphosphate, indicating that another compound was being eluted at this point. As indicated in Fig. 2, conditions were found that gave a very good separation of these two compounds.

In attempting to identify the compound causing the new peak, the fraction of eluate containing it was collected and freed of the acetate buffer used in the eluent to control the pH. The solution of the unknown compound was then adjusted to a pH of about 4 and subjected to a potentiometric micro titration with sodium hydroxide solution. Under these conditions, linear phosphates above the tetramer give two jumps at pH values about 5 and 8; the base used between the jumps corresponds to the two weakly ionised hydrogens on the end groups. This titration in conjunction with a determination of total phosphorus furnishes the data needed to calculate the degree of polymerisation of the linear compound[1]

$$n = \frac{2G}{\theta} \tag{4}$$

where θ is the number of mequiv of weakly ionised hydrogen and G is the number of mg atoms of phosphorus present as linear polymer. The titration graph of the unknown compound showed only one jump[11] (Table I), indicating that it has no weakly ionised hydrogens and is therefore cyclic.

Further confirmation of the cyclic nature of the unknown compound was obtained by two-dimensional paper chromatography. Because the ratio of potassium chloride to phosphate in the eluate was too great for satisfactory paper chromatography, the major part of the potassium chloride was removed as described subsequently.

TABLE 1.—END-GROUP TITRATION OF THE UNKNOWN CYCLIC PHOSPHATE

Burette reading, *ml*	pH	ΔpH
0·0300	4·09	
		0·10
0·0340	4·19	
		0·16
0·0380	4·35	
		0·22
0·0420	4·57	
		0·42
0·0460	4·99	
		2·10
0·0500	7·09	
		1·44
0·0540	8·53	
		0·38
0·0580	8·91	
		0·27
0·0620	9·18	
		0·14
0·0660	9·32	

Total phosphorus = 14·8 μmole

Under conditions very similar to those recommended by Karl-Kroupa,[4] the unknown cyclic gave a spot in the region where pentametaphosphate would be expected. It was moved very little by the acidic solvent; in the basic solvent, its R_f value was 0·35 compared with 0·39 for tetrametaphosphate. These facts indicate that the unknown compound was probably pentametaphosphate. However, positive identification by chromatography, either on paper or through ion-exchange columns, requires the use of known cyclic polymers above the tetramer, which are not available.

Hydrolysis of cyclic phosphates by base results in large quantities of the corresponding linear phosphates.[13] Several attempts were made to apply this technique to determinations of the unknown cyclic phosphate.

Reasonably large quantities of this compound were isolated by successive elutions and subsequent removal of acetate ion. The samples were hydrolysed with various concentrations of sodium hydroxide solution. The temperature and time for the hydrolysis were also varied. After hydrolysis, cations were removed by the technique for the removal of potassium chloride. The neutralised solution was then subjected to anion-exchange chromatography under conditions similar to those of Fig. 2 in order to identify and determine the products of degradation. Large quantities of tetraphosphate were isolated along with smaller quantities of ortho-, pyro-, tri- and the unknown cyclic phosphate. Although pentaphosphate was not found in the hydrolysate, it is possible that this compound was formed during the hydrolysis, then was itself degraded. The small amounts of unknown cyclic compound present in these samples did not allow a detailed investigation of its properties. Because this sort of hydrolysis data is generally indicative rather than conclusive, this approach was not pursued further.

The compound is certainly cyclic as is evidenced by both its titration behaviour and its behaviour in paper chromatography. It is impossible to state, at the present time, the number of phosphorus atoms per ion. For this reason the compound has been designated "unknown cyclic phosphate".

Identification of peaks in the elution graph

The oligophosphates through the tetramer are easily prepared or obtained commercially. The peaks corresponding to these compounds have been identified by eluting the known compounds. Higher oligomers through the octamer have been identified by paper-chromatographic analysis of their degradation products.[14] In this laboratory, peaks corresponding to linear oligomers were identified by end-group titration, on the micro scale, of the appropriate fraction of eluate.

A titration of the phosphate contained in fractions 78 to 85, obtained from two successive elutions similar to that in Fig. 2, is summarised in Table II. Several of these micro end-group titrations are summarised in Table III. The phosphate had been degraded somewhat between the time of elution and the titration. The procedure for

TABLE II.—END-GROUP TITRATION OF FRACTIONS 78 TO 85

Burette reading, *ml*	pH	ΔpH	Δ^2pH
0·0600	4·99		
		0·33	
0·0640	5·32		+0·12
		0·45	
0·0680	5·77		−0·09
		0·36	
0·0720	6·13		
0·0800	6·90		
		0·44	
0·0840	7·34		+0·19
		0·63	
0·0880	7·97		−0·10
		0·53	
0·0920	8·50		

0·0866 − 0·0663 = 0·0203 ml = 2·40 μmole of end group

Volume = 26 ml (after acetate removal); NaOH = 0·118*M*; total phosphorus = 5·7 μmole

TABLE III

Fraction numbers	Titrant, μmole	Total P, μmole	Cyclic P, μmole	*n*, Experimental	Compound
78–85	2·4	5·7	0	4·8	penta
78–85	10·8	33·1	4·9	5·2	penta
103–113	8·2	34·2	6·6	6·7	hepta

acetate removal also removes oligomers smaller than the trimer; thus a major source of error in the titration was the presence of trimetaphosphate which resulted from the degradation.[14] This was corrected by precipitation of the linear phosphates by barium ion and the quantitative determination of the soluble trimetaphosphate.[15] The procedure differed in that the volume of the solution before precipitation was adjusted to 40 ml and 10 ml of $1{\cdot}5M$ barium chloride were added. The solution volumes were about one-fifth of those used in the other study.[15]

EXPERIMENTAL

Reagents

Reagent-grade chemicals and de-ionised water were used throughout this work.

Preparation of phosphate glasses: Samples of glassy sodium polyphosphate were prepared by mixing sodium pyrophosphate decahydrate with sodium dihydrogen phosphate monohydrate. The quantities of the two compounds were adjusted so that phosphorus was present in a 15% excess of the desired sodium to phosphorus ratio in order to compensate for the hydrogen that is not expelled by the fusion.[16] The mixture was placed in a platinum boat and inserted in an electric oven where it was kept at 600° for 17 hr. The mixture was removed and cooled rapidly between steel plates. The glassy buttons were broken and dissolved in water. The solution was filtered into a 100-ml volumetric flask, diluted to the mark and stored in a refrigerator at about 5°. A new sample of glass was prepared every month because of the degradation of the polymer.

Eluents: Preparation of the buffered eluents has been described previously.[7]

Procedure for ion-exchange chromatography

Preliminary treatment of resin. The resin was slurried with an excess of water and allowed to settle. The fines were removed by decantation. This process was repeated until the resin settled homogeneously. Supernatant water was poured off and the resin was slurried with $0{\cdot}1M$ hydrochloric acid. The slurry was then poured into a Pyrex tube with a fritted-glass plug at the bottom. A short piece of Tygon tubing was attached to the bottom of this tube and a Hoffman screw clamp was used to regulate the flow of liquid through the tubing. The resin was allowed to settle and was then washed with 1 litre of $0{\cdot}1M$ hydrochloric acid. This was followed by a washing with water until the acid was completely removed from the column.

The resin, in the chloride form, was converted to the hydroxide form by elution with $0{\cdot}1M$ sodium hydroxide solution until the eluate gave a negative test for chloride. Interstitial base was removed by washing with water and the resin was reconverted to the chloride form by the addition of $3M$ hydrochloric acid. After 12 hr the exchanger was washed with 1 more litre of acid.

The resin was then equilibrated with the first eluent. Experience in this field has shown that the first elution with a "prepared resin" is seldom satisfactory. In order to avoid this, a "pseudo elution" was performed, *i.e.*, an elution was carried out with a sample of phosphate glass, but the fractions, instead of being analysed, were discarded. The column was washed with $3M$ hydrochloric acid, allowed to stand overnight, and again eluted with the acid.

The purpose of these washings is to remove impurities which are trapped by the resin during the synthetic process. The forgoing eluents should remove iron$^{\mathrm{III}}$ ion, soaps, any phosphates originally present as well as most other materials.

Chromatography. The eluent was drained to within 1 mm of the resin bed. A 1- to 5-ml sample, was delivered to the top of the bed by means of a pipette. The solution was once again drained to the bed. Collection of fractions was started after this step. The wall of the tube was washed twice with 5-ml portions of the first eluent and drained to the bed between washings. Delivery of eluent was started at this point. The flow rate was maintained at 0·42 cm/min by means of a chromatographic "Minipump"(Milton Roy Company, Chestnut Hill, Pennsylvania, U.S.A.). The pump was connected to Tygon delivery tubes by means of "Vari-grip" fittings made of Teflon (Beckman Instruments, Inc., Mountainside, New Jersey, U.S.A.). The fraction-collecting assembly has been previously[6] described.

Upon completion of an elution, the pump was disconnected and the resin was equilibrated with $3M$ hydrochloric acid delivered with the aid of hydrostatic pressure. The resin was allowed to stand overnight in contact with the acid, then eluted with 1 litre of the $3M$ acid. High polymeric phosphates are removed by this procedure.

End-group titrations

Removal of acetate buffer. Fractions containing the desired phosphates were obtained by elutions similar to that in Fig. 2. The fractions were combined and diluted with water to give a solution

0·25*M* in potassium chloride. This was adjusted to pH 7·0 ± 0·3 by the addition of 0·1*M* sodium hydroxide solution. The entire solution was passed through a column of the resin in the chloride form which measured 6·0 cm × 3·8 cm^2. Potassium chloride (0·25*M*, pH 7·0 ± 0·3) which was free from acetate was passed through the column at a flow rate of 0·6 cm/min until the effluent gave a negative test for acetate. After removal of the acetate, the elution was continued with 0·70*M* potassium chloride which was at pH 7·0 ± 0·3. The desired phosphate was contained in the first one or two 26-ml fractions of this eluent.

These elutions condensed the volume of phosphate-containing solution from about 170 to 26 ml. The amount of potassium chloride present was decreased from about 42 to 18 mmoles.

Test for acetate. A 2·0-ml sample of 1·0 × 10^{-3}*M* hydrochloric acid was added to a 26-ml fraction of effluent and the pH was compared to that of a solution prepared from 26 ml of eluent and the acid. Identity of pH after the removal of carbon dioxide with nitrogen indicated the absence of acetate.

Titration procedure. After removal of the acetate buffer, the phosphate-containing samples were titrated with the aid of a Gilmont micro burette (Manostat Corporation, New York, U.S.A.) The sample was contained in a polyethylene bottle. A glass electrode and a fibre-type calomel electrode were inserted through a hole in the shoulder of the vessel. They were connected to a Beckman pH meter, model G. A thin Pyrex tube which was connected to a tank of nitrogen was introduced, through the plastic wall, into the solution. The microburette was similarly introduced into the liquid. The pH of the solution was adjusted to less than 4·0 by addition of 1*M* hydrochloric acid. The bottle was stoppered with a one-hole rubber stopper through which a short piece of glass tubing was inserted for the escape of gas. Nitrogen was bubbled through the solution for 15 min, expelling any dissolved carbon dioxide. The bubbling was maintained throughout the titration to afford mixing.

Sodium hydroxide titrant. The base was prepared from an aliquot of 18*M* reagent-grade sodium hydroxide and was diluted with freshly prepared de-ionised water. The solution was stored in a polyethylene bottle and protected against carbon dioxide by Ascarite. The solution was standardised against potassium hydrogen phthalate and potassium dihydrogen phosphate.

Determination of total phosphate in a fraction. Standard solutions of the phosphate were used to prepare a "Beer's-Law curve." Total phosphorus was determined after titration and separation by the use of this spectrophotometric technique.[5,6]

Paper chromatography

Elimination of potassium chloride eluent. A 26-ml sample of 0·70*M* potassium chloride, which contained a particular phosphate, was prepared by the procedure for the removal of acetate. A column of Dowex 50-X4, 200–400 mesh, which measured 6 cm × 3·8 cm^2 was converted to the hydrogen form with 3*M* hydrochloric acid. It was washed with water to remove the interstitial acid. The solution was passed through the column, the wall was washed with cold water and additional water was used as an eluent. The first 50-ml portion contained the desired oligophosphoric acid, some hydrochloric acid and no cations other than hydrogen ion. This procedure was carried out in the refrigerator to minimise degradation of the polymer.

The 50 ml of effluent were evaporated to about 2 ml *in vacuo*. A trap with a Dry Ice-acetone mixture was placed in the line. The rapid evaporation maintained the temperature of the solution at 5 to 10° and prevented serious degradation. The small aqueous residue in the flask was treated with a slight excess of 0·1*M* sodium hydroxide solution so that the resultant solution was basic.

The procedure was performed as soon as possible after the isolation of the phosphate by anion-exchange chromatography. As a result, only small amounts of its degradation products along with sodium chloride and hydroxide were also present. The quantities of these contaminants are probably not great enough to interfere seriously in the later experiments.

Paper-chromatographic procedure. This technique has been previously described.[2,4] Twenty μl of the phosphate solution, from which the potassium chloride had been removed, were applied to the paper in increments of 3 μl or less. Samples of tetraphosphate and tetrametaphosphate were similarly applied to the paper at some distance from the origin to serve as standards.

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Zusammenfassung—Mischungen aus Orthophosphat, seinen linearen Polymeren bis einschließlich Tridekaphosphat und drei cyclischen Polymeren wurden durch Ionenaustauschchromatographie getrennt. Eines der cyclischen Polymeren (das sich in Polyphosphatgläsern mit $\bar{n} \simeq 10$ findet), ist wahrscheinlich Pentametaphosphat. Seine cyclische

Natur wurde durch Endgruppentitrationen und durch Papierchromatographie bewiesen, aber Versuche zur Bestimmung der Anzahl der Phosphoratome im Ring schlugen fehl, da nur eine sehr geringe Menge der Verbindung zugänglich war. Es wird über Ergebnisse berichtet, die die übliche Annahme stützen, daß die linearen Phosphate oberhalb dem Tetrameren in der Reihenfolge ihres Polymerisationsgrades eluiert werden.

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DETERMINATION OF TRIMETAPHOSPHATE ION IN THE PRESENCE OF LINEAR PHOSPHATES

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Summary—A method for the determination of trimetaphosphate in the presence of linear oligophosphates above the trimer has been developed. It has been demonstrated that ortho-, pyro- and triphosphate are incompletely precipitated by barium ion, while higher oligomeric linear phosphates are precipitated quantitatively. The latter species have been isolated from phosphate mixtures by anion-exchange chromatography, mixed with known quantities of cyclic phosphate, and precipitated with barium ion. A mean error of +0·8 and a standard deviation of ±3 μmole of phosphorus as the cyclic ion have been found for mixtures containing from 0 to 203 μmole of phosphorus as trimetaphosphate in the presence of 0 to 81 μmole of phosphorus as the linear polymers.

A NUMBER of cases has been found in which there was a need for a rapid method for the determination of trimetaphosphate in the presence of linear phosphates.[1,2]

It is well known that the barium salts of linear phosphates are sparingly soluble while those of the cyclics are much more soluble. There was doubt, however, that a quantitative separation of these species was possible by precipitation. Jones[3] attempted to precipitate the degradation products of trimetaphosphate at pH 9 using barium chloride, while Healey and Kilpatrick[4] reported that the precipitation of orthophosphate was incomplete under these conditions. The determination of trimetaphosphate, by this technique, in the presence of ortho-, pyro- and triphosphate has been shown to be erratic.[5]

The following study was made to find out whether trimetaphosphate can be determined in phosphate mixtures by precipitation of the linear polymers by barium ion.

RESULTS AND DISCUSSION

All attempts to precipitate quantitatively the phosphates from solutions of phosphate glasses failed when the average degree of polymerisation ($\bar{n}$) was about 4. In these cases, the method described in the next section left 10 to 15 μmole of phosphorus in solution. Varying the pH from 5 to 9, precipitating from the solutions at 5° and "gathering" with sulphate did not improve the results appreciably.

On the other hand, the precipitation was nearly quantitative with samples of phosphate glasses with $\bar{n} \simeq 6$. The slightly low results were probably because of the presence of small amounts of cyclic compounds in these glasses.[6] It was, therefore, postulated that the method of precipitation is not quantitative with linear phosphates of $\bar{n} \leq 3$. In order to test this hypothesis, two samples of sodium triphosphate were treated with barium chloride, one in the presence and one in the absence of a phosphate glass of $\bar{n} \simeq 8$. In both cases, the same amount of phosphorus remained in solution.

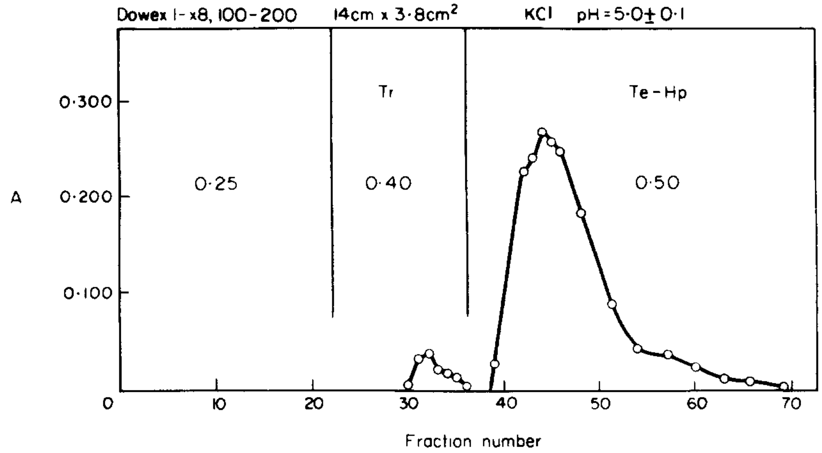

FIG. 1.—Elution of a phosphate glass by potassium chloride eluents at pH 5·0:
Tr—triphosphate,
Te—tetraphosphate,
Hp—heptaphosphate.

Absorbance, A, at 400 mμ plotted versus fraction number. The total number of μ mole of phosphorus in a fraction is equal to 39·0 A. Each fraction equals 10·8 ml. The concentrations of the potassium chloride eluents are indicated on the graph. Fourteen mg of a phosphate glass, with an $\bar{n}$ of about 4, were utilised.

TABLE I.—SUMMARY OF PRECIPITATIONS OF LINEAR PHOSPHATES BY BARIUM ION

Sample no.	P taken, *μmole*		P found, *μmole*		Error, *μmole*	
	Linear	Cyclic	Linear	Cyclic	Linear	Cyclic
1	65	0	61	4	−4	+4
2	66	26	61	31	−5	+5
3	68	71	67	72	−1	+1
4[a]	70	117	54	133	−16	+16
5	73	180	70	183	−3	+3
6	72	0	72	0	0	0
7	73	34	72	35	−1	+1
8	75	68	74	69	−1	+1
9	78	136	84	130	+6	−6
10	81	203	85	200	+4	−3
11	0	0	0	0	0	0
12	0·5	13	0	14	−1	+1
13	3·3	75	4·8	73	+2	−2
14	4·9	112	6·0	111	+1	−1
15	8·2	188	0	196	−8	+8
16	29	0	28	0	−1	0
17	29	0	30	0	+1	0
18	60	0	60	1	0	+1
			Mean		−0·7	+0·8
			Standard deviation		±3	±3

[a] Omitted in the calculation of the mean and the standard deviation.

As a further test of this hypothesis, linear phosphates below the tetramer were removed from phosphate glasses by anion-exchange chromatography. A typical elution is shown in Fig. 1. The fraction containing the polymers from the tetramer to about the heptamer was isolated and immediately used as a source of linear polymers. A known amount of trimetaphosphate was added to this fraction or an aliquot thereof. The resultant mixture was subjected to the precipitation procedure described below.

The results are given in Table I. The second column is the quantity of phosphorus in the glass plus the small amount of non-cyclic phosphorus present as an impurity in the recrystallised sodium trimetaphosphate (see next section). The third column is the corrected quantity of trimetaphosphate present. The fifth column is the quantity of phosphorus found in the filtrate after the precipitation. The fourth column is the total quantity of phosphorus less that in the fifth column. Except for one sample, the results are satisfactory.

EXPERIMENTAL

Reagents

De-ionised water and reagent-grade chemicals, except for sodium trimetaphosphate, were used. Commercial sodium trimetaphosphate (Victor Chemical Works) was recrystallised[7] and analysed by the method of Peters.[8] The analysis indicated that 96·0, 1·2, 1·4 and 1·6% of the total phosphorus were present as trimeta-, ortho-, pyro- and triphosphate, respectively.

Preparation of phosphate glasses. This has been described in a previous paper.[1]

Apparatus

All pH measurements were made with a Beckman pH meter, model G, to which a glass electrode and a fibre-type calomel electrode were attached.

Precipitation procedure

Low linear polymers were removed from solutions of fresh phosphate glasses by anion-exchange chromatography. The phosphate glasses had degrees of polymerisation of about 4. The fraction containing the linear phosphates from the tetramer to about the heptamer was isolated and diluted with water so that the resulting concentration of potassium chloride was 0·4*M*. Two-hundred ml of the solution were delivered into a 250-ml volumetric flask. A known quantity of a solution of sodium trimetaphosphate was added. The solution was diluted to the mark and a 25-ml aliquot was taken. Total phosphorus in the solution was determined from this aliquot. A 200-ml aliquot was removed, its pH was adjusted to 7·0 ± 0·1 with 0·1*M* sodium hydroxide solution, and the solution was transferred to another 250-ml volumetric flask. The phosphates were precipitated by a slow addition of 40 ml of 1·5*M* barium chloride which was at a pH of 7·0 ± 0·1. The solution was diluted to the mark and allowed to digest for 15 min. It was filtered through a fritted-glass funnel of fine porosity, and a 25-ml aliquot was taken for the determination of unprecipitated (cyclic) phosphate.

Phosphate determination

Total and unprecipitated phosphorus were determined by a spectrophotometric method.[7] Ten ml of 0·4*M* potassium chloride were added to the unprecipitated fractions before they were heated. The inside surface of the vessels, which are heated during the colour-development, should be extremely clean and smooth, otherwise a precipitate is noted during this step.

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Zusammenfassung—Eine Methode zur Bestimmung von Trimetaphosphat in Gegenwart linearer Oligophosphate oberhalb des Trimeren wurde entwickelt. Es wird gezeigt, daß Ortho-, Pyro- und Triphosphat durch Barium unvollständig gelfällt werden, wogegen höhere oligomere lineare Phosphate quantitativ gelfällt werden. Diese wurden aus Phosphatmischungen durch Anionenaustauschchromatographie isoliert, mit bekannten Mengen cyclischem Phosphate gemischt und mit

Barium gefällt. Ein mittlerer Fehler von +0,8 und eine Standardabweichung von ±3 Mikromol Phosphor als cyclisches Ion wurden für Mischungen mit 0 bis 203 Mikromol Phosphor als Trimetaphosphat neben 0 bis 81 Mikromol Phosphor als lineare Polymere gefunden.

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TITRIMETRIC DETERMINATION OF QUINOL

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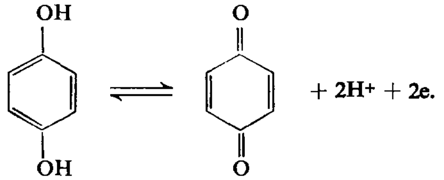
Summary—A critical review is presented of the literature on the titrimetric determination of quinol. For the standardisation of pure quinol solutions the cerimetric titration procedure can be recommended, but in the presence of various organic contaminants vanadate, hexacyanoferrate(III) plus zinc and dichromate are the best titrants.

INTRODUCTION

IN the literature many publications have appeared concerning the titrimetric determination of quinol (hydroquinone). The principle of these methods lies in the possibility to oxidise quinol quantitatively to quinone according to the equation:



The reason for the many different oxidimetric determinations is undoubtedly the fact that many of the impurities which can be present in quinol, *e.g.*, phenolic compounds, are oxidised partly or quantitatively by most of the common oxidimetric titrants. Accurate results for the analysis of low purity mixtures of quinol are therefore *a priori* impossible. It must be stated, moreover, that many of the titration procedures recorded in the literature are not very easy to carry out.

The use of quinol as a reductimetric titrant has increased of late, especially since the work of Zýka and coworkers[1,2]. Advantages connected with the use of quinol are that it can easily be obtained analytically pure, it is relatively inexpensive and, especially, its solutions in a weakly acidic medium (*ca.* 0·01 *N* sulphuric acid) show a constant titre for periods of up to 8 weeks; in contrast with the solutions of nearly all other reductimetric titrants, solutions of quinol are hardly subject to air oxidation.[3]

In view of these facts it seems useful to present a critical literature survey of the titrimetric determination of quinol. The survey has been arranged according to the various titrants which have been used.

Iodine[4,5]

The oldest known titrimetric determination of quinol originates from Valeur[6] and has been adopted in a sometimes more or less altered form by many authors;[4,5,7–9] independently, Gardner and Hodgson[10] reported an analogous method.

The great difficulty of the iodometric determination lies in correctly adjusting the pH of the solution to be titrated. In order to obtain quantitative reaction the pH must be at least 6;[4] at pH 8–9 (bicarbonate), however, one must take into account the air oxidation of quinol, the velocity of this oxidation being proportional to the square of the hydroxyl ion concentration in the solution.[11,12] Moreover, quinone may undergo disproportionation reactions in an alkaline medium, giving rise to the formation of coloured products and therefore a less sharp end-point; an extra consumption of iodine may also occur.[12,13]

The procedure which involves back-titration of excess iodine has the disadvantage of possible oxidation of thiosulphate to sulphate because of the excess iodine present in the alkaline solution:

$$I_2 + 2OH^- \rightleftharpoons OI^- + I^- + H_2O.$$

It is therefore recommended to use only a small excess of iodine and to use arsenite instead of the more usual thiosulphate.

When carrying out a direct titration it is not possible to use carbon tetrachloride or chloroform as indicator, because the quinone formed during the titration dissolves in the organic layer and forms a compound with iodine. According to Kolthoff[4] a direct titration is possible using a potentiometric end-point.

A serious drawback of the iodometric determination of quinol lies in the fact that many organic compounds are partly or wholly oxidised under the same conditions.

Potassium dichromate

The use of potassium dichromate for quinol determination has been recommended by Kolthoff,[4] who employed a redox indicator (diphenylamine) as well as potentiometric end-point detection. According to Kolthoff it is not possible to carry out the titration at room temperature. The solution must be warmed to 40–60° and even then the titration must be carried out slowly towards the end or over-titration will occur. This statement of Kolthoff has been corroborated by other investigators,[14] but it does not correspond with the conclusions of Casolari,[9] who carried out the titration at room temperature long before Kolthoff. In this connection it is remarkable that the Czech investigators,[3] who use quinol as a reductimetric titrant, standardise it according to Kolthoff, although it must be concluded from the procedures given that they work at room temperature! From experiments carried out by Brinkman and Snelders,[15] it follows that warming the solution has not much influence on the velocity with which the titration can be carried out and that, moreover, the results are practically the same.

According to Kolthoff the quinone formed during the titration poisons the platinum electrode in the potentiometric determination. In more recent investigations on cerimetric titrations in non-aqueous solvents (see below) Prabhakar Rao and Murthy[16] have had somewhat analogous experiences, but on the other hand, Furman and Wallace[8] contradict Kolthoff's statements for cerimetric titrations. In our potentiometric determinations[15] no indication of quinone poisoning was ever found. Instead of diphenylamine, *N*-phenylanthranilic acid has been recommended as an indicator for the direct titration with dichromate,[17] as well as the chemiluminescence indicator siloxene.[18]

Although the titration mentioned above is time-consuming and tedious (50°, slow titration), the use of dichromate is advantageous because it is an easily obtainable high-quality primary standard. A recent investigator[14] has, therefore, proposed an indirect titration in which an excess of ammonium iron^{III} sulphate is added to the solution in a weakly acidic medium; after reduction of iron^{III} to iron^{II} the equivalent amount of iron^{II} formed is titrated with dichromate using barium diphenylamines sulphonate as indicator. In this titration, of course, iron^{III} is the real oxidant, but for the sake of simplicity the method has been included under the heading of potassium dichromate.

As regards the dichromate titrations it can be stated that phenol and cresols do not interfere, whereas they do interfere in the iodometric titrations. Compounds like oxalic acid, citric acid, lactic acid and glycerol, which are normally not attacked by dichromate are, however, partly oxidised in the presence of quinol as inductor.[17]

Bromine water

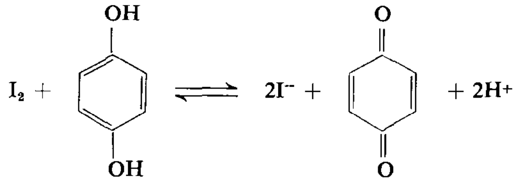
Rosenthaler[19,20] has recommended the use of an aqueous bromine solution for quinol titration; the hydrobromic acid liberated in the reaction can be titrated with a base using methyl red as indicator. The oxidation of quinol occurs immediately: the excess bromine can be blown out of the solution after some minutes, then the hydrobromic acid can be titrated. In the presence of much quinol, which consequently means the presence of much quinone in the neighbourhood of the end-point, the colour change in the acid-base titration is not very sharp.

Freshly prepared solutions of bromine water do not contain any free hydrobromic acid; nevertheless, it is necessary to correct the values found by the amount of alkali consumed by an equivalent amount of bromine water freed from bromine by blowing air through it. This corresponds with *ca.* 0·2 ml of 0·1M hydroxyl ion/100 ml of bromine water. For titration procedures in non-aqueous solvents, see reference 21.

Potassium bromate

Bromination with bromate-bromide mixtures in an acid medium yields titration procedures for many derivatives of benzene. Depending on the *o*- *p*- or *m*-directing influence of the substituents, in many instances di- or tribromo-substitution products are formed. In some instances, however, the reaction proceeds in a different way. With dihydroxy- and diaminobenzenes the *m*-compounds are brominated in the normal way yielding a tribromo product, but the *o*- and *p*-isomers do not take up any bromine. The two strongly *o*-*p*-directing groups present in the quinol molecule do not allow *m*-substitution.

Using the procedure given by Francis and Hill,[22] in which an excess of bromate-bromide is added to the acidified solution, after which potassium iodide is added, whereupon the iodine liberated is titrated with thiosulphate, no difficulties arise because of the temporary oxidation of quinol to quinone. Although this oxidation occurs initially, after the addition of potassium iodide the reaction:



proceeds quantitatively to the left.

Kolthoff,[4] who titrated quinol with bromate-bromide using a direct potentiometric procedure so that quinol was really oxidised to quinone, found in contradiction with the authors mentioned above, that at the equivalence-point free bromine reacts with the quinone present to form an addition or substitution product, so that sharp end-points were not possible.

Brinkman and Snelders[15] have found that in a titration of quinol with bromate-bromide at room temperature some bromination does indeed occur. This not only means a direct titration is difficult to carry out, but also that a titration of other benzene derivatives in the presence of quinol is subject to significant errors. When the titration is carried out, however, at about 0° there is very little bromination; although the results are not very accurate, they give a good indication of the ratio quinol/impurity, especially when this ratio is not too extreme.

Cerium^{IV} sulphate

Extensive investigations concerning the cerimetric titration of quinol have been carried out by Furman and Wallace.[8] According to these authors, the rapid and direct cerimetric titration that can be carried out in about 1*N* sulphuric acid is in many respects superior to the titrations with iodine or dichromate. In potentiometric determinations there is not the slightest indication of quinone poisoning of the platinum electrodes. Methyl red is not a very suitable indicator, but the use of ferroïn, diphenylamine or diphenylamine sulphonic acid is completely satisfactory. Recently, the iron^{II}-2,2′-dipyridyl complex[23] has been used as an indicator in a cerimetric titration. Other indicators mentioned in the literature are *e.g.*, brucine,[24,25] siloxene,[18] copper phthalocyanine tetrasulphonic acid[26] and such triphenylmethane dyes as erioglaucine A, eriogreen B and xylene cyanol FF.[27] Resorcinol and catechol are oxidised by cerium^{IV} farther than the quinone stage, although oxalic acid is not oxidised at all. Attention is called to the fact that both Gopala Rao and coworkers[28] and Brinkman and Snelders[15] have found results 0·3–0·5% too low in cerimetric determinations of pure quinol solutions.

Cerimetric titrations have also been carried out in non-aqueous solvents,[16] using ammonium nitratocerate(IV) as oxidant and acetonitrile as solvent. To obtain a reproducible and fast adjustment of the potential it is necessary to add glacial acetic acid to the solvent. The potentiometric determinations[8,29] can only be carried out when cerium^{IV} is titrated with quinol. In the reverse case quinol exhibits a curious behaviour in contact with the platinum indicator electrode; the results are much too low and, moreover, not reproducible. There is no satisfactory explanation of this fact.

The titrations in non-aqueous solvents can also be carried out with visual end-point determination, using ferroïn, diphenylamine, Janus Green or methyl red as indicator. Ferroïn and diphenylamine are reversible redox indicators under the conditions; with diphenylamine and methyl red the results are about 0·7% high.

An indirect titration of quinol with cerium^{IV} sulphate has been described by Singh and Singh,[30,31] who back-titrate the excess cerium^{IV} sulphate with the iron^{II}-EDTA complex using ferroïn as indicator.

Potassium permanganate

As far as has been investigated, potassium permanganate is the only oxidant that oxidises quinol further than quinone, the end-products in this case being carbon dioxide and water. Under the most favourable circumstances, *viz.* an alkaline medium and excess of permanganate, the time-consuming oxidation takes place almost quantitatively,[32] but many phenolic and other organic compounds are over 90%

oxidised under the same conditions. This very unselective titration can therefore hardly be recommended.

Hypobromite

Generally speaking, titrations with hypobromite are not very suitable because this titrant is not very stable for any length of time; moreover, the results are nearly always high because of the conversion of hypobromite into bromate. A procedure recommended by Kolthoff and Stenger[33] consists in the use of a calcium hypochlorite solution in a weakly alkaline medium, which is added to the solution to be titrated after the addition of potassium bromide. The oxidant hypobromite is generated *in situ*. In most instances, however, not only oxidation but also bromination occurs, *e.g.*, with phenol, oxine and aniline. This hypobromite titration is therefore only suitable in isolated cases, one of these being with quinol.[34] Under favourable conditions (passing of carbon dioxide) the results are not more than 0·2% high. Without carbon dioxide the error increases to about 1%. Most probably this oxidation is brought about by a partial bromination of quinone. It has been proved that the error is not caused by air oxidation.

Sodium metavanadate

Cerium^{IV} sulphate oxidises phenol, cresols and analogous compounds to coloured substances insoluble in concentrated sulphuric acid. Therefore Gopala Rao and coworkers[28] have investigated the use of vanadate as an oxidant for quinol. It appears that vanadate does not oxidise the above-mentioned phenols nor catechol, although it does attack resorcinol.

According to Gopala Rao the quinol concentration of the solution to be titrated must be below 0·01 M (0·02N) and the total acid concentration must be at least 1·0N in order to ensure a sharp end-point. A large quantity of oxalic acid is necessary as a catalyst. The results of the titration are 0·2–0·3% low. Diphenylbenzidine and *N*-phenylanthranilic acid are used as indicators.[28,35]

Hexacyanoferrate(III)

In the literature a potentiometric titration of hexacyanoferrate(III) with quinol in 50% sulphuric acid has been described, which can also be carried out with visual end-point detection.[36] Brinkman and Snelders[15] found that this titration can be carried out in the reverse direction, giving good results for quinol itself and for quinol in mixtures with oxalic acid. In the presence of, for example, phenol, catechol or resorcinol, the colour of the acid solution darkens considerably, however, thereby making titration impossible. Good results are obtained according to these authors,[15,37] when a large excess of hexacyanoferrate(III) is added to an acid quinol solution, whereupon the hexacyanoferrate(II) formed is titrated with a standard solution of zinc using diphenylamine as indicator. The titration can also be carried out potentiometrically, giving results that are about 0·5% high, but it can be used in the presence of oxalic acid, phenol, citric acid and tartaric acid; resorcinol and catechol must be absent, however.

Miscellaneous

In the literature titration procedures are also recorded for quinol with chloramine-B in a weakly acid medium,[38–40] chloramine-T,[41] *N*-bromosuccinimide,[42] manganese^{III}

pyrophosphate,[43] potassium copper^{III} periodate,[44] iron^{III} chloride,[45] potassium periodate[46-48] and iodine monochloride.[49,50] Beranová and Hudeček[51] describe a titration of quinol with barytes using a differential potentiometric titration technique. Tomiček and coworkers[21,52] have carried out titrations with various oxidants, *e.g.*, bromine, chromic acid, sodium permanganate and lead tetra-acetate in glacial acetic acid. They all give good results and the titration with lead tetra-acetate is even used for the standardisation of this substance.

Zusammenfassung—Es wird einen kritischen Überblick gegeben von den in der Literatur beschriebenen Methoden für Quinol Bestimmung. Für die Bestimmung von reinen Quinol Lösungen wird die cerimetrische Titration empfohlen, aber bei Anwesenheit von organischen Verunreinigungen sind Vanadat, Ferrizyanid mit Zink und Dichromat am besten geeignet.

Résumé—On présente un résumé critique de la littérature concernant les méthodes titrimétriques pour détermination d'hydroquinone. Pour le dosage des solutions pures d'hydroquinone, le titrage cérimétrique est recommandé; en cas de présence d'impuretés organiques au contraire, vanadate, ferricyanure avec zinc et dichromate sont les meilleurs titrants.

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SHORT COMMUNICATIONS

The determination of thiourea using chloramine-T

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METHODS are available for the determination of thiourea by oxidation with hypoiodite[1] and hypobromite[2] reagents. Eight equivalents of the oxidant are utilised for each mole of thiourea. In the present study, chloramine-T and sodium hypochlorite were examined as oxidants and a procedure evolved for the determination of thiourea using chloramine-T, which takes less time than the other hypohalite methods. Earlier work on the oxidation of thiourea with chloramine-T relates to acid media, in which the authors[3-5] have claimed quantitative results. However, our results indicate that the oxidation in acid medium is unreliable and unsuited for quantitative work.

EXPERIMENTAL

Reagents

Thiourea solutions of desired molarity (*M*/50–*M*/80) were prepared from dried, recrystallised solid and the strengths were checked by the hypoiodite method.

Chloramine-T was purified, dissolved in water (approx. 0·1*N* solution) and the solution was standardised by the method of Bishop and Jennings.[6]

Sodium hypochlorite solution (approx. 0·1*N*) was prepared from chlorine and sodium hydroxide,[7] and its strength was determined iodometrically.

The other chemicals used were of standard purity.

The extent of reaction between thiourea and chloramine-T, thiourea and sodium hypochlorite, ammonia and chloramine-T, and urea and chloramine-T was studied under different conditions and order of addition of reagents. The mixtures of known amounts of reagents were set aside for the

TABLE I.—OXIDATION OF THIOUREA(T) BY CHLORAMINE-T(CAT)
Total volume = 100 ml

Order of mixing reagents	T taken, *mM* (I)	CAT taken, *mequiv*	Duration of keeping reagent mixt., *min*	CAT used up, *mequiv* (III)	III/I
T–CAT	0·1250	2.520	2	0·9987	7·989
	0·1250	2·520	15	0·9994	7·997
	0·1875	2·520	2	1·504	8·021
	0·2750	2·520	2	2·201	8·005
	0·2750	2·520	15	2·204	8·015
T–NaOH–CAT*	0·1250	2·520	2	1·002	8·015
	0·1250	2·520	15	0·9984	7·987
	0·2750	2·520	2	2·198	7·993
T–HCl–CAT**	0·1250	3·124	15	0·8634	6·906
	0·1250	3·124	60	1·063	8·504
	0·2500	2·520	15	1·557	6·229
	0·2500	2·520	30	1·706	6·824
	0·2500	2·520	60	1·872	7·488
T–HCl–CAT–NaOH***	0·2500	2·520	15	1·943	7·772
	0·2500	2·520	30	1·940	7·760
	0·2500	2·520	60	1·941	7·764

* NaOH = 10 ml of 1*M* soln.

** HCl = 10 ml of 1*M* soln.

*** HCl = 10 ml of 1*M* soln., and 20 ml of 1*M* NaOH were added immediately after addition of CAT.

requisite periods of time, potassium iodide was added (and only then was added sufficient excess of acid if the main reaction was being carried out in neutral or alkaline medium) and the liberated iodine was determined with thiosulphate. The difference between the amount of chloramine-T or hypochlorite taken and the remaining excess, found iodometrically, gave the amount of oxidant used up in the main reaction.

In Table I are recorded typical results obtained for the thiourea-chloramine-T (T-CAT) system. The results indicate that exactly 8 equivalents of oxidant are consumed by 1 mole of thiourea when neutral or alkaline conditions prevail during the addition of chloramine-T to thiourea. The reaction is completed, in contrast with the other hypohalite methods, almost immediately after the reagents are mixed. The presence of free acid during the reaction, however, causes erratic results, the number of equivalents of chloramine-T used up being less than 8 when it is taken in small excess and more than 8 when it is taken in considerable excess over the thiourea. The titre of chloramine-T becomes less with time in acid medium, and corrections were made accordingly, using blank experiments run under identical conditions. Later addition of excess alkali to a T-HCl-CAT system does not yield good results. Invariably, a slight amount of the oxidant seems to be lost by side reactions in acid medium.

The oxidation of thiourea by chloramine-T in neutral or alkaline medium may proceed as follows:

$$NH_2CSNH_2 + 6H_2O \rightarrow 2NH_4^+ + CO_2 + SO_4^{2-} + 8H^+ + 8e \qquad (1)$$

(NH_3, HCO_3, CO_3^{2-} may also be present depending on the pH of solution); *or*

$$NH_2CSNH_2 + 10OH^- \rightarrow NH_2CONH_2 + SO_4^{2-} + 5H_2O + 8e \qquad (2)$$

The oxidation of ammonium chloride and of urea with chloramine-T was studied in order to ascertain the particular course of oxidation of thiourea. The results are recorded in Table II. This indicates that oxidation of NH_4^+ occurs rapidly in neutral medium and sluggishly in acid medium. At pH 10 and above, the ammonia (and NH_4^+) is not oxidised by chloramine-T. Urea is not oxidised in either alkaline or neutral medium; the NH_4^+ produced on very slow hydrolysis of urea in acid medium during 30 min consumes a low amount of chloramine-T. However, it was observed that hydrolysis of urea under similar conditions, for a keeping period of 10 min or less, was negligible, and no loss in the titre of chloramine-T occurred. The results indicate that thiourea is oxidised by chloramine-T according to the reaction (2), and that for the quantitative evaluation of thiourea in the presence of ammonium salts it is imperative that the oxidation be carried out in alkaline medium.

TABLE II.—EXTENT OF REACTION OF CHLORAMINE-T(CAT) WITH UREA(U) AND NH_4Cl(A)
Total volume = 100 ml

Order of mixing reagents	U taken, *mM*	A taken, *mM*	CAT taken, *mequiv*	Duration of keeping the mixt., *min*	Unreacted excess of CAT found, *mequiv*
U–CAT	0·5000		2·520	30	2·520
	20·00		2·520	30	2·518
U–NaOH–CAT*	0·5000		2·520	30	2·518
	20·00		2·520	30	2·523
U–HCl–CAT†	0·5000		2·520	30	2·504
	20·00		2·520	30	2·507
A–CAT		0·5000	2·520	1	2·498
		0·5000	2·520	60	0·463
		20·00	3·870	60	0·686
A–$NaHCO_3$–CAT (1 g.)		0·5000	2·520	60	2·514
A–NaOH–CAT*		0·5000	2·520	60	2·517
		20·00	2·520	1	2·519
		20·00	2·520	60	2·517
A–HCl–CAT†		0·5000	2·520	60	2·423
		20·00	2·520	2	2·442
		20·00	2·520	60	1·802

* NaOH added = 30 ml of 1*M* soln.
† HCl added = 10 ml of 1*M* soln.

Attempts to utilise the reaction between ammonium ion and chorlamine-T for the determination of ammonium did not yield promising results.

The oxidation of thiourea by hypochlorite was found to be very rapid and to proceed even beyond the stage of 8 equivalents in neutral and alkaline media. The presence of excess of potassium bromide slowed down the reaction appreciably, as expected, since the hypochlorite is converted to the hypobromite, but the reaction was of little analytical interest.

Procedure for determination of thiourea

To a solution containing 0·1–0·3 mmole of thiourea, add sufficient alkali to raise the pH to about 10. Add a known excess (*a* ml) of chloramine-T solution. After about 2 min, add 15 ml of 20% potassium iodide solution, acidify the solution with dilute hydrochloric acid, and titrate the liberated iodine with zN thiosulphate (V ml.) Carry out a blank with *a* ml of chloramine-T ($\equiv V_1$ ml of thiosulphate). The amount of thiourea in the sample is equal to $(V_1 - V).z/8$ mmole. Urea does not interfere, and large amounts of ammonium salts are tolerated.

Acknowledgment—The authors wish to express their grateful thanks to Prof. M. V. C. Sastri for his interest in the work.

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Summary—Chloramine-T oxidises thiourea quantitatively to urea and sulphate ion in neutral and alkaline media. The oxidation is completed within 2 min, even with a very small excess of the oxidant. Urea and ammonium ion do not interfere if the oxidation is carried out in an alkaline medium.

Zusammenfassung—Chloramin-T oxydiert Thioharnstoff in neutralen und alkalischen Medien quantitative zu Harnstoff und Sulfat. Die Oxydation ist in 2 Minuten beendet, selbst bei sehr geringem Überschuß von Oxydationsmittel. Harnstoff und Ammoniumionen stören nicht, wenn die Oxydation in alkalischem Medium ausgeführt wird.

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Titration of anthranilic acid with electrolytically generated bromine: Application to coulometric determination of copper

(*Received* 23 *September* 1963. *Accepted* 23 *October* 1963)

Although the coulometric titration of inorganic substances has been rather extensively investigated in recent years,[1,2] the application of coulometric titrimetry to the determination of organic substances has been somewhat limited. A discussion of the application of coulometric titrimetry to organic substances has been given by Lingane,[3] DeFord[4] and Bard.[5] The use of electrolytically generated bromine to oxidise thiodiglycol to thiodiglycol sulphoxide[6] and isonicotinic acid hydrazide to isonicotinic acid[7] are illustrations of oxididative reactions involving this reagent. Substitution bromination reactions for olefins[8] and 8-quinolinol[9] have been investigated. Aniline has been brominated by a back-titration technique in which the excess electrolytically generated bromine was titrated with electrolytically generated copper^I.[10] A study of the feasibility of titrating fifteen organic compounds of possible analytical significance by electrolytically generated bromine was undertaken

Attempts to utilise the reaction between ammonium ion and chorlamine-T for the determination of ammonium did not yield promising results.

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EXPERIMENTAL

Reagents

Double-distilled water was used throughout the investigation.

Electrolyte solution. Dissolve 11·9 g of reagent-grade potassium bromide in 370 ml of distilled water and dilute to 500 ml with 95% ethanol. This solution is 0·2*M* in potassium bromide and 25% by volume ethanol.

Anthranilic acid. Anthranilic acid (Eastman, technical grade) was recrystallised three times from ethanol-water solutions. Only the first crop of crystals was used in each successive recrystallisation. The melting point was 145–145·5° (uncorrected).

Standard anthranilic acid solution. Dissolve 10 mg of the recrystallised material in 27 ml of 95% ethanol and dilute with distilled water to 100 ml in a volumetric flask. One ml of this solution contains 0·1 mg of anthranilic acid.

Precipitant solution. Dissolve 1·0 g of recrystallised anthranilic acid in 50 ml of water containing 0·3 g of sodium hydroxide. Adjust the pH of this solution to 5–6 with dilute hydrochloric acid and dilute to 100 ml with distilled water.

Standard copper^{II} solution. Dissolve 0·5 g of reagent-grade copper sulphate pentahydrate in 1 litre of distilled water. Standardise gravimetrically by precipitating copper anthranilate.

Apparatus

A Leeds and Northrup coulometric analyser was used as the constant current source and timing mechanism. Constant current outputs of 64·3, 6·43 or 0·643 mA are available with this apparatus. The cell contained a platinum generating anode and a platinum counter electrode which was protected from the solution by a glass sleeve which made electrical contact through a fritted disc. A Beckman micro calomel electrode served as the reference electrode while a rotating platinum electrode was used as the indicator electrode. The micro electrode was driven at 1800 rpm by a Sargent synchronous stirrer. A Sargent Ampot was used for the amperometric measurements.

General procedures

The platinum micro electrode and generator electrodes were pretreated by the procedure described by Kolthoff and Tanaka.[12] The electrodes were immersed in concentrated nitric acid for 10–15 sec, washed with distilled water, immersed in a solution of 0·01*M* iron^{II} sulphate and 0·05*M* sulphuric acid for 5 min, then again rinsed with distilled water. The sleeve containing the cathode was filled with 0·2*M* potassium bromide solution.

The desired volume of sample or standard solution was pipetted into the cell and the electrolyte solution, which had been adjusted to the desired pH, added. The electrodes were inserted and the magnetic stirrer and synchronous stirrer motor for rotating the platinum micro electrode was started. A potential of 250 mV *vs.* S.C.E. was applied to the micro electrode. After 10–15 min the indicator current reached a constant value and the titration was started using a generating current of 6·43 mA. The generating current was interrupted periodically in order to obtain current readings of the indicator electrode. Several readings were taken before and after the equivalence point, the exact equivalence point being determined graphically.

In determining copper the following procedure was followed: Transfer the desired volume of copper^{II} solution to a 100-ml beaker and adjust to pH 4. Heat the solution to boiling and add 1% anthranilic acid reagent until a ten-fold excess is present. Maintain the solution just below boiling point for 5 min, then allow to cool for 5–10 min. Collect the precipitate on a filter stick, rinse repeatedly with small volumes of 0·005% anthranilic acid solution and finally twice with a few ml of distilled water. Dissolve the precipitate in 4 ml of 2*M* hydrochloric acid, drain through the filter stick into the suction flask and transfer to a 25-ml volumetric flask. Dilute to volume with distilled water and mix thoroughly. Transfer 5 ml of this solution to the coulometric cell for bromination and follow the previously described procedure.

RESULTS

Preliminary investigation showed that anthranilic acid reacted fairly rapidly with bromine to give tribromoaniline.[13] Ultraviolet absorption spectra confirmed the absence of a carboxylic group in the product. The effect of acidity on the rate and extent of bromination was investigated. The rate becomes slow in both very acidic and basic solutions. Quantitative bromination takes place in the pH range 1 to 6 with the optimum rate occurring at a pH of about 4.

When titrations were performed in strictly aqueous solution the results were found to be about 1% low, possibly because of some incompletely brominated product precipitating. When a 25–40% ethanolic solution was used, however, the stoichiometry was in accord with the calculated values.

When a generator current of 64·3 mA was used, the bromine was generated much faster than it was consumed by the anthranilic acid. A lower rate of 0·643 mA was also tried and found to be acceptable although a much longer time was required for the titration. Using the 6·43-mA current output, 0·1–2·0 mg of anthranilic acid can be titrated within 25 min. The coulometric method is sensitive to about 0·1 mg of anthranilic acid.

Some results of determining copper by precipitating copper anthranilate, dissolving the precipitate and titrating the liberated anthranilic acid with electrolytically generated bromine are given in Table I.

TABLE I. ESTIMATE OF ACCURACY AND PRECISION IN DETERMINATION OF COPPER

Copper taken, *mg*	No. of determinations	Copper found, *mg*	Relative standard dev., %	Relative error, %
0·099	3	0·019	11	−81
0·494	4	0·487	1·9	−1·4
0·988	3	0·994	0·26	+0·6
1·976	12	1·998	0·65	+1·1

When less than 0·5 mg of copper^{II} is present in about 50 ml of solution the solubility losses are too significant for quantitative results. The determination of larger amounts of copper (>2 mg) is not practical because of the time required for the bromination process. Other metals whose ions form precipitates with anthranilic acid should be determinable by this proposed coulometric titration method.[14]

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Summary—Anthranilic acid when brominated by electrolytically generated bromine requires 3 moles of bromine per mole. Amperometric detection of the equivalence point is utilised. Small amounts of copper (0·5–2 mg) can be determined by precipitating copper anthranilate, dissolving the precipitate and titrating the liberated anthranilic acid with electrolytically generated bromine.

Zusammenfassung—Bromiert man Anthranilsäure mit elektrolytisch erzeugtem Brom, so verbraucht sie 3 Mole Brom pro Mol, was durch amperometrische Äquivalenzpunktsbestimmung festgestellt wurde. Kleine Mengen Kupfer (0,5–2 mg) können durch Fällung als Kupferanthranilat, Lösen des Niederschlags und Titration der Anthranilsäure mit elektrolytisch erzeugtem Brom bestimmt werden.

Résumé—La bromuration de l'acide anthranilique par le brome généré électrolytiquement nécessite 3 moles de brome par mole. On a utilisé la détection ampérométrique du point d'équivalence. De petites quantités de cuivre (0,5–2 mg) peuvent être dosées par précipitation à l'état d'anthranilate de cuivre, dissolution du précipité, et titrage de l'équivalent d'acide anthranilique au moyen de brome généré électrolytiquement.

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A simple separation of large quantities of 8-hydroxyquinoline from trace gallium

(*Received* 11 *October* 1963. *Accepted* 23 *October* 1963)

DURING an investigation of the precipitation of gallium with 8-acetoxyquinoline, a method was required for the determination of the unprecipitated gallium ($<0{\cdot}2$ mg) in each filtrate (*ca.* 300 ml). The presence of the very large excess of 8-hydroxyquinoline (*ca.* 0·9 g) seriously interfered with the three methods attempted, *viz.* polarography, or extraction of the gallium 8-hydroxyquinolate followed by a spectrophotometric or fluorimetric measurement.

It was therefore necessary to remove almost completely the 8-hydroxyquinoline without loss of gallium. Because of the volatility of gallium compounds, evaporation to dryness and subsequent ignition of the residue was considered unsuitable. Wet ashing of 8-hydroxyquinoline with a perchloric-nitric acid mixture[1] resulted in "... rapid clearing at end of period; beaker caught fire with hissing noise." Berg[2] has sublimed ammonium 8-hydroxyquinolate.

The simplest procedure seemed to be steam volatilisation.[3] Although Wegner[4] has used this technique to separate 8-hydroxyquinoline from other organic materials, it has not previously been used to separate the compound from aqueous metal-ion solutions.

When a filtrate (pH *ca.* 4·0) was slowly evaporated in a 400-ml beaker on a steam bath, most of the 8-hydroxyquinoline was removed, except occasionally some colourless needles crystallised on the upper parts of the vessel. Two repetitions with 30–50 ml of water completely eliminated the compound, as was evidenced by the absence of its characteristic spectral peak[5] at 3,180 Å in a chloroform extract of the residue in the beaker.

Furthermore, in four experiments with 0·1–0·8 mg of gallium in the presence of 0·9 g of 8-hydroxyquinoline, a gallium recovery of $>97\%$ was experienced. It was also established that most of the gallium in the residue was in the form of its water-insoluble 8-hydroxyquinolate.

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Summary—A simple method for the removal of large amounts of 8-hydroxyquinoline from aqueous solutions containing traces of gallium has been devised. It involves steam volatilisation of the organic compound, and gives $>97\%$ recovery of gallium as a non-volatile residue.

Zusammenfassung—Eine einfache Methode zur Entfernung großer Mengen 8-Hydroxychinolin aus wäßrigen Lösungen mit Spuren Gallium wurde entwickelt. Es handelt sich um Dampfdestillation der organischen Verbindung, wobei mehr als 97% Gallium als nichtflüchtiger Rückstand gewonnen werden.

Résumé—On a trouvé une méthode simple pour éliminer de grandes quantités de 8-hydroxyquinoléine de solutions aqueuses contenant des traces de gallium. Elle comprend un entraînement à la vapeur du composé organique, et permet de récupérer plus de 97% du gallium à l'état de résidu non volatil.

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LETTER TO THE EDITOR

The reaction of copper^{II} and copper^{I} with 8-mercaptoquinoline

SIR,

Mercapto compounds are usually considered sufficiently strong reductants to reduce Cu^{II} to Cu^{I}. The assumption that this is true with all mercapto compounds can lead to erroneous conclusions. For example, Bankovskis and coworkers[1,2] found that the reaction of both Cu^{II} and Cu^{I} with 8-mercapto-quinoline led to the formation of the same dark brown complex having a ligand:metal ratio of 2:1. They proposed the following reaction scheme:

$$6C_9H_6N{-}SH + 2Cu^{II} \rightarrow C_9H_6NS{-}SNH_6C_9 + 2Cu^{I}(C_9H_6NS)(C_9H_7NS) + 4H^{+} \qquad (1)$$

and concluded that the complex involves 4-co-ordinate Cu^{I} in which one ligand is bonded in the anionic form and the other ligand as the neutral thione tautomer. This reaction scheme correctly describes the stoichiometry of the copper complex as well as the number of protons released per metal ion on complex formation.

In the course of an investigation of the metal chelate stabilities of 8-mercaptoquinoline[3] we have carried out potentiometric titrations of 8-mercaptoquinoline both in the absence and presence of Cu^{II} and have found that the amount of base consumed at the end-point corresponding to the neutralisation of the mercapto group is unchanged by the presence of Cu^{II}. Because equation (1) predicts that only ⅔ of a mole of protons is released for every mole of reagent involved in the reaction, the amount of base consumed in the titration must vary with the amount of Cu^{II} present. Thus, unless the postulated copper complex loses protons in exactly the same pH region as the free reagent, the above reaction scheme is incorrect.

In order to investigate the alternative possibility that the complex obtained from the reactions of Cu^{II} and Cu^{I} with 8-mercaptoquinoline is $Cu^{II}(C_9H_6NS)_2$, the electron spin resonance spectrum of a chloroform solution of the complex was examined. The signal obtained was characteristic of a Cu^{II} complex, and it was possible to account quantitatively for the copper content of the complex as Cu^{II}.

Therefore a mercapto containing ligand is capable of reacting with a metal in a higher oxidation state without reducing it. This probably results from the greater stability of the complex of the metal in the higher oxidation state.

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21 October 1963

ALFIO CORSINI
QUINTUS FERNANDO
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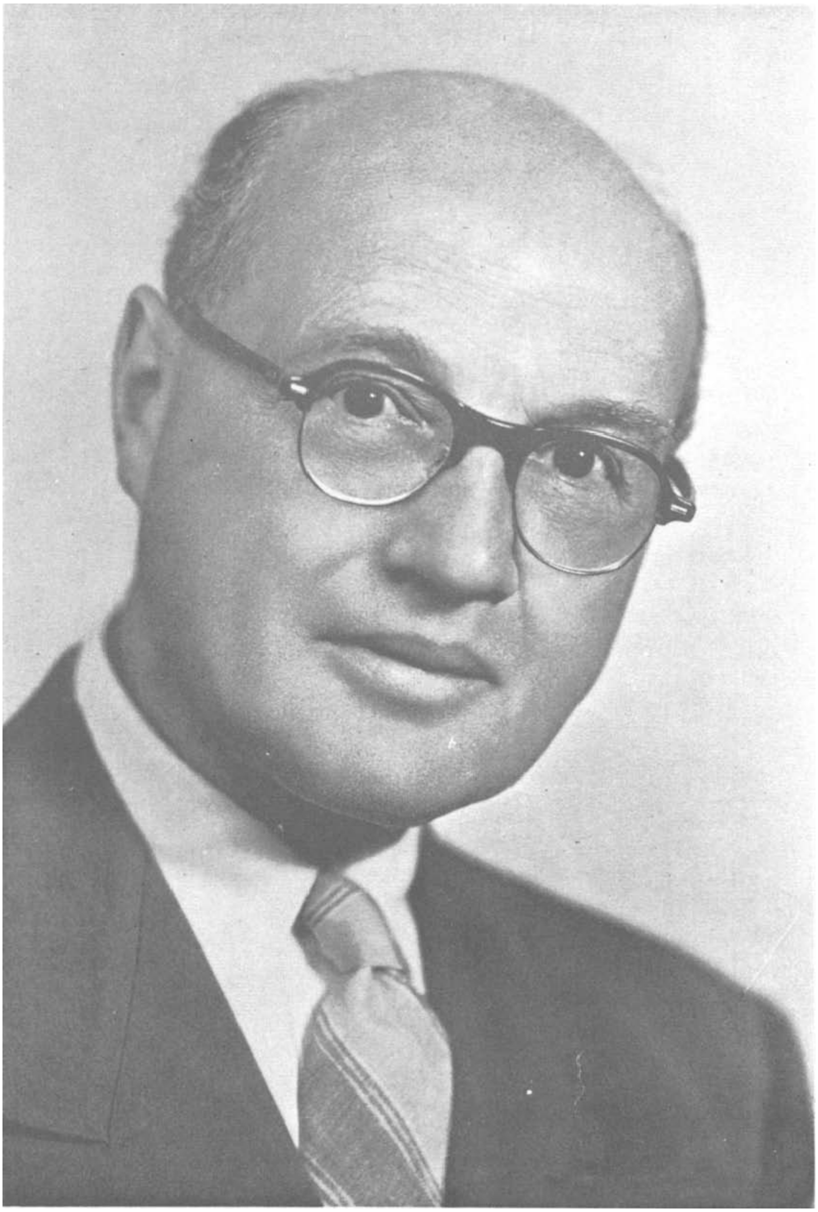
EDITOR'S FOREWORD

THE Editorial Board and Publishers of TALANTA take pleasure in honouring the seventieth year of

IZAAK MAURITS KOLTHOFF

by presenting this special issue, which is comprised entirely of invited contributions from his former students and associates.



Izaak Maurits Kolthoff

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IZAAK MAURITS KOLTHOFF

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IZAAK MAURITS KOLTHOFF, son of Moses and Rosetta (Wysenbeck) Kolthoff, was born on February 11, 1894, in Almelo, Holland.

In 1911, after graduation from Hoogereburger School, young Kolthoff's interest in chemistry already had been aroused, and the next logical step would have been graduate study of chemistry in a university. However, although he was fluent in English, French and German, in addition to his native Dutch, Kolthoff was barred from academic work in the "pure" physical sciences because he lacked the knowledge of Latin and Greek which at that time was a pre-requisite. As an alternative he enrolled in the chemical engineering curriculum at the University of Delft, but only a fortnight's stay convinced him that his real interest was elsewhere. Accordingly, he transferred to the school of pharmacy at the University of Utrecht. Here he came under the tutelage of Professor Nicholas Schoorl who guided him into his true vocation in analytical chemistry.

In retrospect, it might be said that one of the most important circumstances that has shaped the development of analytical chemistry over the past fifty years was Kolthoff's failure to acquire a knowledge of Latin and Greek during his high school days! If he had done so he probably would have gone on in the usual way to a university course in the "pure" physical sciences, he would not have come under the influence of Professor Schoorl, and, more than likely, analytical chemistry of our time would have been deprived of one of its most influential architects.

Kolthoff's first diploma at Utrecht was that of "Pharmacist", but the six-year curriculum on which it was based actually provided an education in chemistry as good as any available at that time. Indeed, the education in analytical chemistry offered by Professor Schoorl would have been hard to match anywhere, because Schoorl employed the approach (then rare) of emphasising the fundamental science underlying analytical chemistry and also had the gift of being able to inculcate in his students an appreciation for the equally important factual aspects of the subject. Schoorl's motto "Theory guides; experiment decides." has been the cardinal guiding principle of Kolthoff's scientific life.

In 1918, following an enlightened change in Dutch academic laws pertaining to the role of the classical languages in science education, Kolthoff was awarded the Ph.D. degree in chemistry from Utrecht for a thesis entitled *Fundamentals of Iodimetry*. This was not his first piece of original scientific investigation; actually, he had published his first research paper in 1915, and by 1918 it had been joined by 32 more papers all on subjects different from his Ph.D. thesis. His Ph.D. thesis itself certainly was not "thin", when one considers the series of nineteen papers on iodometric methods based on it which he published during 1919 and 1920. All this by the age of 26!

Dr. Kolthoff served as Conservator of the Pharmaceutical Institute at the University of Utrecht from 1917 to 1927, and concurrently as *privat docent* in applied electrochemistry from 1924 to 1927. Apparently a *privat docent* at that time was one who worked very hard in a university as teacher and investigator without being distracted by a salary! That this arrangement was well suited to Kolthoff's love of original investigation is evident from the fact that during this brief ten-year period he published 270 more research papers and wrote three books.

By 1927 not merely the amazing volume of his publications, but rather their high degree of originality and importance in analytical chemistry, had earned for Dr. Kolthoff an international reputation and he was invited on a lecture tour to Canada and the United States. Following this tour he accepted the position of Professor and Chief of the Division of Analytical Chemistry at the University of Minnesota. During the next 35 years, under his influence, the University of Minnesota became renowned as a leading research centre in analytical chemistry. In June 1962 Professor Kolthoff "retired", but for him this word is meaningless and his contributions to analytical chemistry continue unabated.

Kolthoff began his scientific life at the time when analytical chemistry was just emerging from its age of empiricism, and when applications of the principles of physical chemistry to analytical problems were appreciated only vaguely, and even vaguely by only a few. When he took his first course in quantitative analysis in 1913, S. P. L. Sörensen's definition of pH was only four years old, and even Arrhenius' theory of electrolytic dissociation was still a novel idea. Kolthoff began to demonstrate how these then new principles of solution physical chemistry could be applied to interpret, rationalise, and improve titrimetric analytical methods.

His earliest studies were in the field of acid-base titrimetry, and, beginning about 1914, he instituted a series of investigations of the dissociation equilibria of various weak acids and bases, the functional mechanism and characteristics of acid-base indicators, the use of indicators and indicator test-papers for pH measurement, and the properties of standard buffer solutions. He not only carried out studies in this field which were truly fundamental, but he also applied the knowledge thus gained to the development of many practical procedures. This combination of fundamental theory and practical application has been a characteristic of all his work ever since. These studies led to the publication in 1922 of his first monograph *Der Gebrauch von Farbenindicatoren*. That this book satisfied a real need is shown by the fact that it went through four editions between 1922 and 1932, and was translated into English by N. Howell Furman in 1926. In 1932 in collaboration with Harry Fischgold it was revised as *Säure-Basen Indicatoren*, and in 1937, with the assistance of Charles Rosenblum, it was again revised as *Acid-Base Indicators*.

Electrometric methods of analysis owe much of their development to Kolthoff, who appreciated their potentialities and began to exploit them when they were still virtually unknown to most analytical chemists. Starting about 1918 he carried out many studies of the application of electrolytic conductance to end-point detection in titrations, and these culminated in the appearance of his second monograph, *Konduktometrische Titrationen*, in 1923. This book was one of the first to systematise the theory and applications of the conductometric method. It also illustrates another of Kolthoff's characteristic traits, namely, that whenever he devotes himself to a particular subject a good monograph soon appears!

Another subject pioneered by Kolthoff was the field of potentiometric measurements and titrations. In connection with his investigations of protolytic equilibria and pH measurements he published many papers on the hydrogen, quinhydrone, antimony and other pH electrodes. Characteristically, these were particularly valuable because they emphasised the limitations and sources of error of the then relatively new potentiometric method of pH measurement. Kolthoff's approach to analytical problems *via* fundamental theory proved especially fruitful in his many studies of potentiometric equivalence-point detection in precipitation, complexation and redox titrations. In 1926, in collaboration with N. Howell Furman, Kolthoff published *Potentiometric Titrations*, the first monograph on this subject published in the United States. A second revised edition appeared in 1931, and even after 30 years it is still a most useful source of information on the practical performance of potentiometric titrations and on actual procedures.

The studies cited above, which engaged Kolthoff's attention during the period from 1915 to about 1926, would have been more than sufficient to satiate the scholarly impulses of any ordinary scientist. But during this same decade he had also found time to cultivate many other aspects of classical titrimetric analysis, and he recognised the need for a treatise on titrimetric analysis which would provide a comprehensive treatment of the theory of the subject and a critical evaluation and description of its manifold specific applications. Accordingly in 1927, with H. Menzel, he published the first volume of his famous *Massanalyse* (*Die theoretischen Grundlagen der Massanalyse*), and a year later this was followed by the second volume *Die Praxis der Massanalyse*. In 1928 the first American edition under the title *Volumetric Analysis* was made available with the translational assistance of N. Howell Furman. Kolthoff did not merely edit this book; he created it by personally testing nearly every procedure which it contained. During the period from 1942 to 1957 a revised edition was published in three volumes with the co-authorship of Vernon A. Stenger, George Matsuyama and R. Belcher, and it stands today as the most authoritative monograph on its subject.

Influenced by the great Dutch chemist H. R. Kruyt, Kolthoff had early acquired an interest in colloidal phenomena and surface chemistry. When he came to Minnesota in 1927 he intensified the investigations on coprecipitation and adsorption by precipitates which he had begun in Holland. He directed these studies to such analytically important precipitates as those of the Hydrogen Sulphide and Ammonia Groups, calcium oxalate, barium sulphate and the silver halides. The results obtained have done much to rationalise the practice of gravimetric analysis, and have added very significantly to knowledge of the mechanisms involved in the formation of micro-crystalline precipitates, and to the behavioural mechanism of adsorption indicators. In these studies Kolthoff, in collaboration with Charles Rosenblum, was among the pioneers in the use of radioactive indicators (Th B for Pb). At that time (1930) only the natural radioactive isotopes were available, and the activity was measured with a gold leaf electroscope.

During the fall of 1934 Kolthoff's interest was again attracted to electometric analysis, this time to polarographic analysis with the dropping mercury electrode. Polarography had been invented about a decade previously by Jaroslav Heyrovský at the Charles University in Prague, and the reader will recall that this discovery was rewarded recently by the award of the Nobel Prize in Chemistry to Professor Heyrovský. Although European analytical chemists had been quick to realise its potentialities, polarography was still unknown in the United States in the middle

1930's. Approaching this subject in characteristic fashion, Kolthoff's first concern was the theoretical basis of the method, and he carried out important studies of the various factors which influence the diffusion current, polarographic maxima, and the current-potential inter-relationship. At this same time, in collaboration with Herbert A. Laitinen, he instituted a series of studies on polarographic (voltammetric) analysis with stationary and rotated platinum microelectrodes. He was quick to recognise the potential utility of amperometric titration, and he played a major role in bringing this method to its present well-developed state. It was quite in character that he was not content merely to contribute to polarographic analysis by his own investigations. Realising the need for correlation and systematisation he published in 1941, with this writer's assistance, the monograph *Polarography*. This was the first comprehensive and critical treatment of the subject in the English language and it was a potent factor in the accelerated development of polarographic analysis which began in the early 1940's. A second, much enlarged edition of *Polarography* in two volumes appeared in 1952, and Professor Kolthoff currently is busy with the preparation of a third edition.

With the advent of the war in 1942, Kolthoff forsook his academic interests to direct a research project for the Office of Rubber Reserve. From pure analytical chemistry to synthetic rubber did not entail as drastic a change in Kolthoff's activities as might be supposed. The acquisition of detailed knowledge of the kinetics of polymerisation reactions in solution was an essential part of this programme, and, because the experimental study of such kinetics depends primarily on analysis, Kolthoff was eminently qualified for this task.

After the war Kolthoff again picked up the many irons which he had had to let cool by the fire's edge, although several years passed before the odour of styrene finally disappeared from the atmosphere of his laboratory. (As recently as 1957 he was still publishing results of his studies of the emulsion polymerisation of styrene.) He returned to his studies of polarography and amperometric titrations, and a steady stream of communications from his laboratory continues to enrich this field.

A complete list of Kolthoff's research publications up to about the end of 1963 is appended (p. 351). This list is restricted to original research papers, and it does not include routine writings such as book reviews, *etc.* No attempt will be made here to analyse in detail the amazing volume and variety of these contributions. The reader will appreciate that to do so adequately would require a book-length discussion, and I leave this task to some future historian of analytical chemistry. It is quite evident that analytical chemistry has never been served by a more original mind, nor a more prolific pen, than Kolthoff's.

Quite recently Professor Kolthoff was able to implement a long-held urge to provide practicing analytical chemists with a comprehensive, multi-volume reference monograph covering all phases of analytical chemistry. In partnership with Philip J. Elving, and with the collaboration of Ernest B. Sandell, several volumes of this *Treatise on Analytical Chemistry* have already appeared.

It is not uncommon for a gifted research scholar to be indifferent to educational aspects of his field, but here again Professor Kolthoff has been exceptional. Although his chief preoccupation has always been the education (not "training") of graduate students, and during all the years at Minnesota he never taught the elementary analytical course, he has not neglected undergraduate instruction in analytical chemistry. His elementary *Textbook of Quantitative Inorganic Analysis*, co-authored with Ernest B. Sandell, originally published in 1936 and since revised twice, is the comparison standard among American texts on this subject. Kolthoff's classroom teaching has been confined to seminars and to an advanced course devoted chiefly to electrometric methods of analysis. For use in the latter course he published in 1931 a textbook, *The Colorimetric and Potentiometric Determination of pH. Outline of Electrometric Titrations*, and a German translation was prepared the following year with the assistance of Oskar Schmitt. In 1941, in collaboration with Herbert A. Laitinen, a second revised edition appeared under the title *pH and Electro Titrations.*

Kolthoff has been outstanding as a teacher of graduate students; a list of those who earned Master's and Doctor's degrees under his guidance is appended. The analytical chemistry faculties of a surprisingly large number of American universities and colleges (as well as several in other countries) are composed of his former students, by their students in turn, and even by a third generation. His laboratory has also been a Mecca for many foreign post-doctoral fellows, which has further extended his influence in the educational sphere, because most of them returned to academic posts in their own countries.

Professor Kolthoff's deep-rooted concern for freedom of thought and expression, and his abhorrence of dogma in any guise, have always underlaid his relationships with his students. Each student was made to feel that he was a partner, not just a useful pair of hands, and he was given every opportunity to learn to behave as an intellectual equal. Kolthoff kept in close contact with each student's progress by daily, informal conferences. On occasion, these sessions with the "Chief" could be embarrassing, because nothing that the student had (or had not!) done ever escaped his incisive scrutiny. But a knife cannot be sharpened on butter, and the whetting of the younger against the experienced mind was education in its finest sense. Kolthoff never exerted the authority of his experience to "silence" a student, but rather the spirit of these discussions was always "Not *who* is right, but *what* is right". Small wonder that Kolthoff's students became and remain his enduring friends.

The intensity with which Kolthoff concentrates on scientific problems, and on his other intellectual pursuits, demands periodic release in physical activity, and for many years tennis was a favourite means of "letting off steam". Although his highly individualistic style, including ambidextrous use of the racket, may have been more baffling than "polished", it kept his opponent very busy. He enjoys swimming, whether in the bucolic surroundings of a pasture pond on a Minnesota farm, or in the North Sea off a Netherlands beach. Horseback riding has been a lifelong hobby, and his disdain of anything "lukewarm" applies to his choice of mount. On one occasion some years ago the horse won the bout, and the resulting fall produced a crippling spinal injury. However, even before he was able to discard crutches, he was back in the saddle.

Kolthoff's extra-professional contributions to analytical chemistry include service for many years on the editorial boards of Analytical Chemistry and the Journal of the American Chemical Society. He was active in the creation of the Section on Analytical Chemistry of the International Union of Pure and Applied Chemistry, and he has served as President of that section as well as Vice-President of the Union.

In addition to ordinary membership in the American Chemical Society, the Dutch Chemical Society and the Dutch Pharmaceutical Society, Kolthoff is an honorary member of a number of other scientific societies, including the American Pharmaceutical Association, the Society for Analytical Chemistry, Phi Lambda Upsilon, the Spanish Chemical Society, the Finnish Chemical Society, the Peruvian Chemical Society, the Czechoslovak Chemical Society and the Israeli Chemical Society. He is a Fellow of the American Academy of Arts and Sciences, and he has the distinction of being one of the few analytical chemists to achieve election to the United States National Academy of Sciences. He is a foreign member of the Royal Bohemian Academy of Sciences and Fine Arts, of the Royal Flemish Academy of Sciences in Amsterdam, and of the Academy of Sciences in Lisbon.

In 1938 the Netherlands government knighted Dr. Kolthoff an Officer in the Order of Orange-Nassau, and in 1947 he was made a Commander in that Order. He holds the Charles Medal of Charles University in Prague. In 1949 the New York Section of the American Chemical Society conferred on him its Nichols Medal, and in 1950 he was the recipient of the Fisher Award in Analytical Chemistry of the American Chemical Society. In 1954 he became an Honorary Professor of San Marcos University, and in 1955 he was awarded an honorary doctor's degree by the University of Chicago. He received the Anachem Award of the Association of Analytical Chemists (Detroit) in 1961.

Happily, this is only a progress report. May God grant Professor Kolthoff many more years of fruitful labour.

GRADUATE STUDENTS OF IZAAK MAURITS KOLTHOFF

1. E. J. Amdur	M.S.	1941
2. Madolyn Youse Babcock	M.S.	1950
3. Cyrus P. Barnum	Ph.D.	1940
4. Gordon H. Bendix	M.S.	1938
5. R. A. Bovey	Ph.D.	1948
6. R. C. Bowers	Ph.D.	1953
7. Stanley Bruckenstein	Ph.D.	1954
8. Albert H. Bushey	Ph.D.	1940
9. Marion Bushey	Ph.D.	1940
10. E. M. Carr	M.S.	1952
11. Chi Chang	Ph.D	1958
12. M. K. Chantooni, Jr.	Ph.D.	1960
13. J. F. Coetzee	Ph.D.	1955
14. Frank T. Eggertsen	Ph.D.	1939
15. William von Fischer	Ph.D.	1937
16. C. E. Gracias	Ph.D.	1961
17. W. F. Graydon	Ph.D.	1949
18. Frank S. Griffith	Ph.D.	1937
19. L. S. Guss	Ph.D.	1938
20. W. E. Harris	Ph.D.	1944
21. A. C. Holler	B.S.	1947
22. David N. Hume	Ph.D.	1943
23. R. A. Johnson	Ph.D.	1949

24. W. F. Johnson	Ph.D.	1949
25. S. E. Khalafalla	Ph.D.	1953
26. C. A. Kelly	Ph.D.	1958
27. L. A. Knecht	Ph.D.	1959
28. Herbert A. Laitinen	Ph.D.	1940
29. W. D. Larson	Ph.D.	1936
30. Thomas S. Lee	Ph.D.	1949
31. D. J. Lehmicke	Ph.D.	1945
32. D. L. Leussing	Ph.D.	1952
33. James J. Lingane	Ph.D.	1938
34. William M. MacNevin	Ph.D.	1936
35. George Matsuyama	Ph.D.	1948
36. D. R. May	Ph.D.	1944
37. Walter J. McCoy	M.S.	1938
38. D. C. McWilliams	Ph.D.	1955
39. A. I. Medalia	Ph.D.	1948
40. Carl S. Miller	Ph.D.	1940
41. I. K. Miller	Ph.D.	1950
42. H. Minato	M.S.	1958
43. D. C. Nelson	M.S.	1957
44. E. R. Nightingale	Ph.D.	1955
45. George Noponen	Ph.D	1936
46. Stephen S. Ober	M.S.	1952
47. Albert S. O'Brien	Ph.D.	1938
48. Y. Okinaka	M.S.	1957
49. Edward F. Orlemann	Ph.D.	1941
50. D. A. Otterson	M.S.	1947
51. Lyle G. Overholser	Ph.D.	1938
52. E. P. Parry	Ph.D.	1950
53. R. W. Perlich	M.S.	1938
54. Thomas B. Reddy	Ph.D.	1960
55. Warren Reynolds	Ph.D.	1955
56. Bart van't Riet	Ph.D.	1957
57. Ernest B. Sandell	Ph.D.	1932
58. I. Shapiro	Ph.D.	1944
59. Maurice E. Stansby	M.S.	1933
60. Vernon A. Stenger	Ph.D.	1933
61. Nora Tamberg	M.S.	1956
62. C. N. Thompson	M.S.	
63. Paul E. Toren	Ph.D.	1953
64. William J. Tomicek	Ph.D.	1934
65. James I. Watters	Ph.D.	1943
66. D. Weiblen	M.S.	
67. Henry C. Yutzy	Ph.D.	1936

For a complete list of the publications of I. M Kolthoff see p. 351.

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THE STATUS OF AND TRENDS IN ANALYTICAL CHEMISTRY

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THE DEVELOPMENT OF ANALYTICAL CHEMISTRY AS A SCIENCE

BEFORE a subject becomes a science its development is empirical in nature. Facts must be collected before generalisations in the form of laws and interpretations of the facts can be made. Before chemistry had reached the stage of a science, the empirical work in its early days was mainly analytical in nature. With the spectacular development of physical chemistry in the last quarter of the nineteenth century, analytical chemistry started to lose its historic lustre because analytical chemists continued to practice their subject in an empirical way, without making use of the new laws and theories developed by physical chemists. Academically, analytical chemistry became discredited. It was the famous German chemist Wilhelm Ostwald who, at the end of the last century, established analytical chemistry as a scientific discipline. In the preface of his stimulating book, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, published in 1894, Ostwald made it clear that analytical chemistry was doomed to continue to occupy the subordinate position of a maid-servant for the other branches of chemistry unless the analytical chemists would discontinue teaching their subject solely as an empirical technique and art which requires skill, and would start making use of the experimental developments and theories of physical chemistry. Infrequently physical chemists would describe analytical applications of certain physico-chemical principles, but analytical chemists in those days lacked the background to comprehend their significance. At the end of the last century papers describing the principles of voltammetry, of amperometric, potentiometric and conductometric titrations already were found in the chemical literature, to be "rediscovered" and developed much later, after education in analytical chemistry had become scientific in nature. In fact, most of the early scientific fundamentals of analytical chemistry and the analytical applications of theoretical chemistry have been developed by non-analytical chemists. In addition to the early papers on what is now modern electroanalytical chemistry, the development and understanding of acid-base indicators may be mentioned. At the very beginning of this century analytical chemists empirically knew that weak acids are titrated with a strong base using phenolphthalein as an indicator and weak bases with a strong acid using methyl orange as an indicator. It was only after the introduction of the concept of pH and the detailed description of its colorimetric and potentiometric determination in 1909 by the famous Danish *bio*chemist, S. P. L. Sörensen, that the fundamentals of aqueous acid-base titrations could be understood. Sörensen's paper still belongs to the most fundamental publications on the concept and determination of pH with the hydrogen electrode and with acid-base indicators, and it is as important now as it was in those days. Sörensen also made clear the significance and the meaning of buffer action and he developed a set of buffer solutions, covering the entire pH range in aqueous medium. For many years Sorensen's buffer solutions have served as standards for the colorimetric determination of pH and several other purposes. Again, analytical chemists did not comprehend the significance of Sorensen's pioneer work, and it was not until 1914 when the famous Danish *physical* chemist Niels Bjerrum published his classical monograph, *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*, that a quantitative interpretation of acid-base equilibria and titration errors in aqueous media became available. In the same year the German *bio*chemist L. Michaelis published his book, *Die Wasserstoffionenkonzentration*, and soon thereafter a monograph on oxidation and reduction potentials. This latter book allowed us to give a quantitative interpretation of oxidation-reduction titrations. It was the well known American *physical* chemist, Joel H. Hildebrand, who published in 1913 his important paper on potentiometric titrations with the hydrogen electrode. It was not an analytical chemist but the American *physiological* chemist, W. Mansfield Clark, who in 1917 added the sulphophthaleins to the series of acid-base indicators.

It is not surprising that the fundamentals of analytical chemistry in those early days were developed by non-analytical chemists. Analytical chemistry was still looked down upon as a maid-servant for the other disciplines of chemistry, and no formal education in analytical chemistry was offered by European universities. All students in chemistry had to learn the practice of gravimetric and titrimetric analysis, which was offered as a laboratory course under the supervision of a teaching assistant. Technical universities in Europe and in several American universities had a chair for analytical chemistry, but the subject was taught in a classical way and its aims were mainly to provide instruction in the technique of the analysis of inorganic constituents and of ores, rocks, industrial products, food stuffs, *etc.*

It was only after about 1920 that analytical chemistry gradually became established as a scientific discipline of chemistry. With some notable exceptions, most universities in the world have chairs now in analytical chemistry, and all students in chemistry now receive education both in classical analytical chemistry and—after a course in physical chemistry—in the principles of physicochemical methods of analysis. Those students who major in analytical chemistry for the Ph.D. are exposed to all aspects of modern analytical chemistry, which includes the determination and study of such properties and quantitative characterisation of such systems which aid, and often are essential in, the solution of analytical problems, and which guide in the development of new analytical methods. "Theory guides and experiment decides."

Complaints are sometimes heard that there is overlapping between teaching and research in analytical and other fields of chemistry. Actually, this is not only an unavoidable but rather a desirable situation. A few examples may illustrate this claim. Chemical equilibria is a subject of importance to inorganic, physical, organic, industrial and biochemists. Its principles are now taught in beginning general chemistry, but the significance of this subject in the various specific fields of chemistry is taught in courses for students specialising in these fields. Before scientific analytical chemistry was recognised in the academic curriculum, principles of chemical equilibria were being taught by physical chemists; such courses did not emphasise their primary importance in, and application to, analytical chemistry. Nowadays the subject has rightfully become part of the curriculum in modern analytical chemistry.

Quite generally, in quantitative chemical analysis we make use of properties which can be measured. All other chemists are interested in properties, but again, courses in modern analytical chemistry must include instruction in the understanding of properties which are important analytically, and laboratory instruction on the measurement of these properties.

All experimental scientists must be acquainted with the fundamentals of instrumentation. In view of the fact that an instrument is needed for the measurement of a property, the subject of instrumentation is of special importance to analytical chemistry. Instruction in instrumentation is now a recognised subject in the analytical curriculum.

All chemists are concerned with various aspects of separations, a subject completely analytical in nature. The Dutch word for chemistry is "Scheikunde," meaning the art and ability of separating. It originated in the sixteenth century when chemistry was mainly analytical in nature. The present chemical literature is replete with papers by organic, inorganic, analytical, industrial, and biochemists dealing with the application of chromatography, ion-exchange, distillation, extraction and other methods of separation in the preparation of pure compounds and the identification and determination of constituents. All chemists, including physical chemists, for their own purposes are concerned with an understanding of the factors which determine the degree of completeness of separations. Would it not be desirable that the theoretical and experimental principles of separation—a subject which is analytical chemistry *par excellence*—be taught to all chemists by analytical chemists? The late Professor Ehrenfest once said that everything which is understood in chemistry is physics. Considering the various disciplines of chemistry it is fair to state that the theoretical fundamentals of analytical, inorganic and organic chemistry are physicochemical in nature. But for obvious reasons we need chemists with a major interest in analytical chemistry to teach analytical chemistry, just as we need inorganic chemists to teach inorganic and organic chemists to teach organic chemistry.

THE STATUS OF MODERN ANALYTICAL CHEMISTRY

It seems fair to state that analytical chemistry started to develop as a science towards the end of the first quarter of this century. Analytical chemists became fully conscious of the fact that for the further growth and expansion of analytical chemistry they had to remain up to date with the discoveries and new theories by other classes of chemists and of physicists, and had to consider their significance for and applicability to analytical chemistry. In the last quarter of a century a host of new nuclear, subatomic, atomic and molecular properties have been discovered, most of which already find analytical applications. Radioactive methods, especially activation analysis in trace analysis, are becoming more and more popular. Nuclear techniques have been introduced for analytical purposes. For example, a new instrument has been made available commercially for the rapid and continuous measurement of moisture in bulk materials, based on the reflection of two different kinds of nuclear radiation. X-ray spectroscopy and fluorescence, microwave spectrophotometry, ion-scattering methods, mass spectroscopy and nuclear and electronic magnetic resonance are some of the modern developments which find analytical use. Most of these new techniques originate with physical chemists or physicists, but analytical chemists play an important part in their further development. Numerous symposia organised jointly by physical and analytical chemists are indicative of the role which analytical chemists play in the development of these new techniques.

These advances in techniques are being made possible, not only by new discoveries and theories, but also by the phenomenal progress of instrumentation. This progress has its impact both on the development of techniques based on new discoveries, and also on the development of techniques based on the measurement of a host of classical properties. Many of these properties were known and measured more than a century ago. However, their application to analytical chemistry remained limited, mainly for the reasons that a thorough knowledge and understanding of the instruments was necessary, and the measurements themselves were very time-consuming. Modern instrumentation has changed all this and has even provided us with a host of automatically indicating instruments.

A few examples may illustrate how modern instrumentation has made possible daily measurement of classical properties and their much expanded use in analytical chemistry. Some twenty-five years ago many of us strained our eyes with a Duboscq or another visual colorimeter, or with a polarimeter or refractometer. Accurate spectrophotometers were available as far as colorimetry was concerned, but they were not suitable for routine work. Nowadays modern spectrophotometers for measurements in ultraviolet, visible and infrared light, and also self-recording instruments, are found in all modernly equipped analytical laboratories. Similarly, the analytical application of emission spectroscopy probably dates back to Fraunhofer, who in 1817 combined a slit, a glass prism and a theodolite. This same scientist may be considered the father of atomic absorption (Fraunhofer lines). Bunsen is usually credited as the chemist who introduced spectroscopy in analytical chemistry when he wrote with Kirchhof his classical paper in 1860 entitled *Chemische Analyse durch Spektralbeobachtung*. Much later the spectrograph was developed, but did not acquire popularity until 1939 when excellent optical instruments were produced which allow comparison of spectra with a microphotometer that can be coupled to a recorder—the latter in turn automatically recording the intensity of a whole series of lines.

Quite generally, recorders are now being used in analytical chemistry for automatic registration. Classical photometric, potentiometric, coulometric, conductometric, amperometric, turbidimetric and thermometric titrations are now being carried out with automatic end-point determination. Principles of coulometry, including stripping analysis, and coulometric titrations were laid down more than a hundred years ago in Faraday's second law, but their practice has become popular only after the development of convenient instruments.

Most modern methods of separation are classical in nature. The first evidence of the use of paper chromatography as a separation technique is found in the dye industry of the 1800's. Dyes were tested by spotting vat solutions on paper and observing the number of concentric rings formed as the liquid migrated. The German dye chemist, F. Runge, developed this technique and described the results in two books, *Farbenchemie* (1850) and *Der Bildungstrieb der Stoffe*, the latter being prefaced by actual chromatograms developed by Runge.

Schönbein, around 1860, showed that if a paper is dipped into an inorganic salt solution the liquid migrating through the paper carries the salt with it. However, the water moves faster than the inorganic salts, which travel with different rates. F. Goppelsröder developed the method further for the detection and determination of inorganic and organic constituents, and called the technique capillary analysis. This technique is closer to adsorption than to partition chromatography. Columnar chromatography was discovered in 1897 by the American, J. T. Day, who used it for fractionating petroleum by preferential adsorption on columns of Fuller's earth. Ion-exchange chromatography is classical in nature, and has been made use of in soil studies since the middle of the last century. Liquid-liquid extraction was used already in the 19th century as a method of separation. All these methods of separation have been greatly perfected in the last 25 years, and new techniques, like partition chromatography (Martin and Synge, 1941) and gas chromatography (James and Martin, 1952) have been added. In spite of the great popularity of all these methods of separation, and the great number of papers on the subject in contemporary chemical literature, many phases of these techniques are still incompletely understood.

It is hardly necessary to mention that modern analytical chemistry is still actively engaged in the further development of classical analytical principles. Organic reagents for the detection and determination of inorganic constituents had already been introduced in the 19th century. Many analytical chemists have been searching since for organic reagents with such functional groups that they become selective and/or specific for any given cation. That goal probably never will be reached because, considering the structure of the ions, it would seem impossible that there is a reagent which is truly specific for one particular ion and the reaction of which is not interfered with by some other element. However, the ideal goal may be approached with the aid of masking reagents and modern methods of separation. There is already a considerable literature on the use of ethylenediaminetetra-acetate (EDTA) and similar compounds for masking purposes. Frequently, reports on the discovery of known reagents, or the introduction of known compounds as reagents for use in various types of methods of chemical analysis, are found in the modern literature. Some of these reagents may have been known for years but had not been tested for their analytical usefulness. With our increasing knowledge and understanding of chemical bonding, of steric hindrance and of co-ordination in particular, it is now often possible to predict which groups may have desirable properties for particular analytical purposes, for example, for complexation. Although EDTA and related compounds had been known for some time, it is only as a result of the pioneer work of Gerold Schwarzenbach that they are now in daily use in complexometric titrations and for masking purposes. A large chapter has been added to analytical chemistry after the introduction of these reagents.

RESEARCH IN ANALYTICAL CHEMISTRY

Academic and industrial analytical research deals with the theoretical and experimental development of classical and modern techniques, including micro and submicro techniques, the interpretation and improvement of existing methods of analysis, the development of new methods of analysis to replace existing ones, and the assay and evaluation of new industrial products.

As far as research dealing with theoretical fundamentals is concerned, there naturally is again overlapping with some phases of research carried out by physical, inorganic and organic chemists. As a matter of fact, in the last quarter of a century there has been a definite shift of the activities of classical physical chemistry to analytical chemistry. In the beginning of this century the determination of the dissociation constants of acids and bases by potentiometric, conductometric and colorimetric methods, the determination of distribution equilibria, of solubility products, of the stability constants of complexes, of oxidation-reduction equilibria, of electrode potentials, *etc.*, belonged to the activities of the physical chemists. Nowadays this type of information is obtained mainly by analytical and inorganic chemists. A great many phases of electrochemistry have become the domain of the analytical chemist. In order to interpret and further develop empirical methods of analysis it is essential that the physical chemistry involved in the behaviour of the components of the systems under consideration be fully understood. For example, acid-base titrations in non-aqueous media have experienced wide analytical application after the publication of the fundamental papers by Conant *et al.* on the behaviour of bases in pure acetic acid. Titrations of acids and of bases in a host of other solvents have been described since. However, although the results can be understood qualitatively, much work on acid-base equilibria remains to be done to arrive at a quantitative understanding. The same is true for many phases of extraction analysis as far as a quantitative interpretation of distribution equilibria is concerned. Electroanalytical methods in non-aqueous media, including fused salts, require much fundamental research before they can be fully developed. A host of problems in all kinds of solvents demands much fundamental research before they are completely understood and the results can be applied to further improvement of analytical methods.

Consider, for example, our understanding of the formation and growth of precipitates, of coprecipitation and aging. In spite of the numerous publications dealing with these subjects, a quantitative understanding of the factors determining or affecting the size of the particles of a precipitate and of coprecipitation is still lacking. This is also true with regard to an understanding of the value of the distribution coefficient (or constant), λ, in the formation of heterogeneous mixed crystals. Theoretically, λ should be equal to the thermodynamically defined homogeneous distribution coefficient, D. But even under conditions of *kinetically controlled precipitation*, a term which I prefer to "precipitation from homogeneous solution," λ can be much greater or much smaller than D, even though in many systems studied, especially by L. Gordon, λ is found to be sensibly constant during the precipitation. Apparently, supersaturation during the growth of crystalline particles is mainly responsible for the difference between D and λ (J. A. Hermann, 1956). In unpublished work we have found that λ closely approaches D in the kinetically controlled formation of mixed crystals of barium and lead sulphate, with barium sulphate as the host crystal, when the system is seeded with a relatively large amount of small and well aged crystals of barium sulphate. These crystals serve to overcome to a large extent the supersaturation during the formation of mixed crystals.

In the development of new chelating agents, including metal ion indicators, the modern investigator is actively interested in the nature of reactive groups and the structure of chelates. In order to predict and interpret complexometric titration curves he must have data on stability constants and quantitative knowledge of the effect of pH and other constituents on equilibria. In addition, knowledge of the kinetics of formation of the dissociation of metal chelates, of the chromatographic (ion exchange) and other characteristics of metal chelates, are essential in the further development of the application of complexation in analytical chemistry. Research on ion exchange, chromatography, solvent extraction, electrodialysis and migration, again, is being carried out not only by analytical chemists but also by physical, inorganic, organic, industrial and biochemists. This overlapping of research activities is a fortunate situation, because all disciplines of chemistry profit from each other's contributions, and together we can fill up the gaps in our understanding of the fundamentals of chemistry. It would be deplorable if the scope of research in analytical chemistry were limited to the more typically classical topics.

ACADEMIC AND INDUSTRIAL ANALYTICAL CHEMISTRY

From what has been said in previous sections we may define academic analytical chemistry as the science concerned with the study and interpretation of all aspects of existing methods of analysis and the development of new methods of analysis. This definition apparently has neither the sympathy nor the approval of industrial analytical chemists. In his thought-provoking Fisher Award Address, H. A. Liebhafsky[1] refers to a definition of analytical chemistry which I stated twelve years ago:[2] "The aims and objectives of analytical chemistry are to determine the composition of any complex compound or mixture of compounds." Generously Liebhafsky adds: "From a university point of view of twelve years ago, this is an excellent definition," I would like to maintain that academically the definition is as valid now as it was a century ago. Liebhafsky then refers to R. C. Chirnside's interesting address[3] entitled *The Enlargement of Horizons in Analytical Chemistry*, in which Chirnside quotes E. B. Hughes as having defined our discipline to be "the examination of a material to ascertain its composition, its properties, its qualities." Liebhafsky finds this definition too restrictive and sees "modern analytical chemistry as the characterisation and control of materials—no more, and certainly no less." Liebhafsky further makes the statement (p. 26A): "Analytical chemistry has lost prestige as a research activity and has not yet gained prestige commensurate with its great and growing importance as a *service in industry*." (Italics mine). I would infer from this statement that Liebhafsky expresses himself on the *role* of analytical chemistry and the *use* of analytical chemistry in *industry*. His views are in close sympathy with those of Chirnside, another recognised analytical-chemical leader in industry, who states: "... he would be a brave man who would today attempt a proper definition of analytical chemistry or chemical analysis, or indeed a description of the analyst himself."

If it is admitted that the classical definition of analytical chemistry has remained unchanged but that the aims and objectives for which the analytical chemist is used in industry have changed and are continuing to change, the question arises whether our education of majors with an advanced degree in analytical chemistry satisfies the needs of industry. If the present education of our majors for the Ph.D. in analytical chemistry does not provide adequate background for the industrial analytical chemists, our institutions of higher learning might consider the introduction of a new minor in "materials characterisation and control" for our majors in analytical chemistry. As far as the loss of prestige as a research activity is concerned, I would like to claim that particularly during the last twenty-five years analytical chemistry has gained great prestige as a research activity, thanks to fundamental contributions by both academic and industrial analytical chemists. To a large extent the empiricism has gone out of analytical chemistry.

RECENT AND FUTURE TRENDS IN ANALYTICAL CHEMISTRY

Education in chemistry

In this era of spectacular advances in the natural sciences, and in chemistry in particular, each discipline of chemistry must periodically reappraise and modify its curriculum in order to keep it up to date with the developments. During the last few years we have witnessed and are still witnessing such a reappraisal and modernisation of courses, especially in the U.S.A. In order not to extend the number of years required now for earning a bachelor's or an advanced degree, all disciplines must curtail their "classical" programmes so that justice can be done to the teaching of modern developments. Reluctantly, analytical chemists internationally agree that the scope of the classical programme in gravimetric and titrimetrc analysis, and in particular the laboratory work, must be curtailed, in order to include the theoretical and experimental fundamentals of physicochemical methods of analysis in the curriculum of all students in chemistry. With further scientific developments periodic modernisation of courses will remain necessary.

However, training in elementary gravimetric and titrimetric analysis should remain a requirement in the curriculum for all chemists, as these subjects have not outlived their usefulness. In experimental research in all fields of chemistry these methods find frequent application, *e.g.*, in testing for purity of and assaying reagents, and in following the course and rate of reactions. Moreover, gravimetric and titrimetric analysis are still indispensable in the accurate determination of major constituents in many types of samples. Also, in several physicochemical methods standards are necessary whose composition is often determined by classical analysis, while some "instrumental methods" also involve classical methods, like gravimetry in activation analysis.

As far as majors for the Ph.D. in analytical chemistry are concerned, it is still desirable to include the essentials of classical analytical chemistry and it is possible to cover the essentials of modern analytical chemistry in the curriculum. Considering however, the almost frightening expansion of the literature, the appearance of a host of new journals in specialised fields of analytical chemistry, it will become necessary to add more specialists to the teaching staff. Even so, the education should remain fundamental in nature, and should provide such background that the Ph.D. can later become a specialist in particular fields. Many of us know by experience that education does not stop at the Ph.D. level. A recent Ph.D. is a novice in the field who has such knowledge and understanding of all aspects of analytical chemistry that it serves him to develop into a creative academic or industrial analytical chemist. Only those of our graduate students who exhibit great ability and creativity in research—and their percentage is rather small—should be encouraged to work for the doctor's degree. Society has a great need for advanced technicians who might be encouraged to earn a new degree of "Chem.D." (chemical doctor).

Future trends in analytical chemistry

The Dutch have a saying: "In the past lies the present, and in the present what is going to be." Considering the past and present development of analytical chemistry it is possible to forecast future trends without becoming speculative. In this era of concentration on the natural sciences, discoveries of new properties, especially in the field of radiation, will continue to be made. Modern instrumentation will quickly provide the instruments with which these properties can be measured and recorded. Thus, we will experience a further expansion of "physical analysis." This, combined with continued automation of new and classical methods of analysis may create social problems. However, for the development of scientific analytical chemistry the further perfection of instrumentation is most welcome, because the results of measurements will become more readily available and more time and effort can be devoted to the solution of unsolved problems.

More and more use will be made of computers in the solution of several analytical problems. In titrations involving complicated equilibria exact equations can be derived for the calculation of the titration error and titration curves, for example, in many complexation reactions or acid-base equilibria and titrations in solvents of low dielectric constant. Such equations may be so involved that they require computers for their exact solution. The same is true in the analysis of complex organic mixtures by measuring a host of physical properties, or in the further development of "kinetic" analysis based on different rates of reaction of various constituents, or the determination of particle size and particle size distribution by light scattering and other methods.

In the previous sections a few examples of the application of chemical reactivity have been given. Several methods based on reactivity are awaiting further development; others have hardly been explored yet. The search for more selective reagents, including complex-formers, particularly those with mixed ligands, and for metal ion indicators is not nearly finished. In organic analysis, research continues on specific reagents for functional groups, and on making more analytical use of the kinetics of formation of compounds obtained by reaction of functional groups with suitable reagents, and of the kinetics of the dissociation of these reaction products into the original reactants. Further studies on the expansion of oxidation-reduction analysis to solutions in solvents much more difficult to oxidise and/or reduce than water, remain to be done.

Our quantitative knowledge of the fundamentals of the titration of Lewis acids with bases is still extremely incomplete. The formation constant of the "neutralisation product" AB formed by reaction of the Lewis acid A with a base B, its ionic dissociation constant, its molecular dissociation constant, and the association constants of the ionic dissociation products of AB with AB in a variety of solvents, should be known before a successful interpretation and exhaustive development of thermometric, conductometric, potentiometric (search for indicator electrodes), amperometric, coulometric and visual titrations of Lewis acids (including many inorganic ions or compounds) with bases can be made.

For further development of extraction analysis, much more research remains to be done on formation constants of ion pairs, of ion triplets and quadruplets in solvents used for extraction, and on the effects of pH and of structural characteristics of the cations and anions on distribution and extraction coefficients.

Little work has been done on reactivity at very high and at very low temperatures, on the use of various radiations to bring about chemical reactions, on the quantitative measurement for analytical purposes of the energy involved in breaking chemical bonds.

Organic, inorganic and industrial chemists continue to make available a host of new organic and inorganic compounds. In consequence, analytical chemists are being called upon continuously to devise methods of analysis for these compounds. In addition, analytical chemists are interested in the possible use as reagents of the new products, like organo-metallic compounds. Continuously industry is producing new complex products, like inorganic and organic polymers, and semiconductors, which demand the development of analytical methods for their characterisation and evaluation, and the solution of analytical problems during the production process. Semiconductors are an example *par excellence* to illustrate the increasing demand for the development of new methods for trace analysis, and for the preparation of substances of extremely high degree of purity. Modern biochemistry requires the further development of sub-micro techniques of analysis.

The above review of present and future activities in analytical chemistry is sketchy in nature. In an essay of this kind it is not possible to present either an exhaustive or complete discussion of these activities. However, the examples given substantiate the thesis that analytical chemistry will continue to flourish as one of the scientific disciplines of chemistry as long as there are unsolved chemical problems and the chemistry remains in chemistry.

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DETERMINATION OF URANIUM AT MICROGRAM LEVELS BY DERIVATIVE POLAROGRAPHY*

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Summary—The incremental method of derivative polarography has been applied to the low-level analysis of uranium in acetate-buffered EDTA electrolyte. Optimum conditions are shown for the rapid determination of $2 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ bismuth and of $5 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ molybdenum, with a precision $\leq 2\%$ and without prior separation Uranium in amounts $\leq 10\,\mu g$ may be detected in a 10^4-fold excess of bismuth. The method has been used successfully for the analysis of a bismuth alloy containing 0·1% of uranium.

URANYL ion is one of the few electroactive species which are only weakly complexed by ethylenediaminetetra-acetate (EDTA) and related chelating agents. This fact has prompted Přibil and Blažek,[1] in the course of systematic studies, to investigate the polarography of uranium in an EDTA-containing medium; procedures were reported for determining uranium in the presence of several elements whose half-wave potentials are markedly displaced towards negative values by virtue of chelation with EDTA. Davis[2] has made a more fundamental study of the uranyl-EDTA system. Conventional techniques were used in these earlier investigations and the various elements were present at comparable levels. Derivative polarography, on the other hand, with its enhanced sensitivity and resolving power, has proved ideally suited for the determination of minor constituents in the presence of a less easily reduced major constituent. It was felt, therefore, that derivative polarography in solutions containing EDTA could be made the basis of a simple and rapid analytical method for micro amounts of uranium in a variety of matrices, without prior separation. It is shown in the present paper that the incremental polarograph[3] may be used to determine less than $5 \times 10^{-6}M$ uranium in the presence of $0{\cdot}01M$ bismuth or molybdenum, with a precision $\leq \pm 2\%$. This application is typical of the analytical problems created by developments in nuclear technology.

EXPERIMENTAL

Apparatus

The incremental polarograph has been described in detail,[3] and shown to provide an excellent novel approach to derivative polarography. The present work was carried out using a modified version, which includes transistorised operational amplifiers (Philbrick P2) of exceptionally low inherent noise level and a timing section of greatly improved precision and versatility. The current amplifier provides sensitivities ranging from 0·25 to 50 μA full-scale, and the current differences stored in the memory capacitor can be amplified by factors ranging from 10 to 500. The modified instrument also incorporates optional circuitry for controlled-potential polarography,[4] involving the use of a three-electrode system.

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In the present work, unless otherwise specified, the current was sampled during the period from 3 0 to 3 6 sec after drop fall (drop time *ca* 5-5 5 sec, m = 1 46 mg/sec). The voltage was scanned in 10-mV increments Polarograms were recorded by means of a Leeds and Northrup Speedomax recorder (Model G, 0 25-sec pen speed), using the duplex readout mode, which allows simultaneous recording of the current amplifier output over the sampling period and of the difference amplifier output corresponding to the end of the sampling period. This feature is of interest because it allows measurements, on the same polarogram of both the peak incremental response (*i e*, the slope of the current-voltage curve at the half-wave potential) and the instantaneous diffusion current, at the same instant in the drop life, the relationship between these quantities is useful either as a criterion of reversibility or as a means for determining *n* in reversible systems

Reagents

Stock solutions of uranyl perchlorate were prepared from U S Bureau of Standards U_3O_8 and standardised coulometrically Bismuth stock solutions were obtained by dissolving analytical reagent bismuth trioxide in excess nitric acid, and $(NH_4)_6Mo_7O_{24}$ $4H_2O$ served as a source of molybdenum. Solutions of EDTA were standardised titrimetrically against standard magnesium chloride Triple distilled mercury was passed through a nitric acid purification column before use.

Because of the necessity for minimising the level of copper impurities (*vide infra*), the available distilled water was purified further using a commercial distilling-refluxing unit

General procedure

The polarographic cell consisted of a jacketed beaker, placed on a triple shock mount and maintained at 25° by water from a circulating constant temperature bath. This was preferable to direct immersion in a water bath because it was found essential to minimise sources of electrical noise The cell was covered with a polyethylene stopper containing appropriate openings. Contact to the saturated calomel reference electrode was made through a fine porosity frit The three-electrode configuration, with a platinum spiral counter electrode, was used in most of the work, although *iR* corrections were, as expected, wholly negligible at concentrations less than $2 \times 10^{-4}M$. Oxygen was removed from the solutions with prepurified nitrogen which was bubbled through dilute vanadium[11] perchlorate.

Incipient maxima interfered with measurements of the peak incremental response even in $2 \times 10^{-5}M$ uranium solutions; thymol was therefore used at a concentration of 0 001%, which suppressed the maxima without producing distortion in the diffusion current region. Use of Triton X-100 cannot be recommended, despite its masking effect on the interfering copper wave[8] (*vide infra*), because it was found to attenuate the uranium wave markedly as well.

In order to minimise introduction of impurities, no effort was made to maintain the ionic strength constant by adding excess inert salt. The work was performed at ionic strengths varying from 0 1 to about 0·3, and it was ascertained that this variation had no noticeable effect on the behaviour of uranium. All EDTA concentrations quoted refer to the excess over the stoichiometric amount required by the metal ion(s) present Potentials are referred to the saturated calomel electrode.

RESULTS AND DISCUSSION

Uranium alone

Some of the interesting aspects of the polarography of uranyl-EDTA complexes have been discussed by Davis,[2] who worked in a self-buffered 0·1*M* EDTA-1*M* sodium perchlorate supporting electrolyte. He obtained a single wave, the shape of which points to a reversible *one-electron* reduction. His results in a weakly acidic medium, however, led to diffusion current constant values substantially larger than would be expected on this basis, and he also found that massive reduction at a mercury pool proceeds by a *two-electron* step, *i.e.*, to uranium^{IV}. We have observed similar behaviour in a supporting electrolyte consisting of either 0·001*M* or 0·01*M* excess EDTA and 0·1*M* acetic acid—0·1*M* sodium acetate buffer (referred to hereafter as "0·1*M* acetate buffer"). In fact, the presence of acetate buffer was found to enhance the diffusion current constant still further. This is shown in Table I; the diffusion current constants, *I*, were calculated from instantaneous diffusion currents, i_d, corresponding to time t (the end of the sampling period), and converted to average values

$$I = \frac{\frac{6}{7} i_d}{Cm^{2/3}t^{1/6}}.$$

From an analytical viewpoint, a medium containing 0·1M acetate buffer provides an appreciable gain over the sensitivity attainable with EDTA alone, and it was used throughout most of this work. The half-wave potentials of uranium under these conditions are —0·30 V and —0·31 V in 0·01M and 0·001M excess EDTA, respectively. Indications are that the slight negative shift is caused by competing acetate complexation at the lower EDTA concentration. Further work is in progress on the significance of these findings.

The relationship between peak incremental response and concentration was found to be linear over a range of uranium concentrations from 5 × $10^{-6}M$ to 8 × $10^{-4}M$, the slope being (0·47 ± 0·01) μA/mM per 10-mV step. Within this range, concentrations were determined with a precision of ±1%. Below 5 × $10^{-6}M$ the presence of copper impurities in the water interfered to a degree with the quantitative determination of uranium, although concentrations as low as 1 × $10^{-6}M$ could be detected. Copper forms an EDTA complex which is reversibly reduced to the metal;[6] thus, copper peaks were observed in the supporting electrolyte at —0·24 V and —0·27 V, respectively, with 0·001M and 0·01M EDTA. Regular distilled water proved entirely inadequate for work below 2 × $10^{-5}M$ uranium. Even by using redistilled water it was impossible to reduce the height of the residual copper peak beyond a value about 40% in excess of the base line level (0·0015–0·002 μA per 10-mV step[8]). This corresponds to an estimated decrease in copper concentration from 5 × $10^{-6}M$ to 8 × $10^{-7}M$. The limitation introduced by residual copper is illustrated in Fig. 1. In 0·001M EDTA, where the half-wave potentials differ by 0·07 V, an indication of a copper shoulder can be seen on the ascending edge of the uranium peak, producing slight asymmetry. In 0·01M EDTA, however, the half-wave potentials are separated by only 0·03 V; here the waves essentially overlap, and copper definitely contributes to the uranium peak height. It should be noted that the 0·03 V separation in half-wave potentials produces a shift of the observed peak from —0·30 V towards —0·27 V as the uranium concentration approaches the residual copper level; errors will result under such conditions if the incremental response is measured at the composite peak location rather than at the true half-wave potential as established at higher concentrations.

TABLE I.—POLAROGRAPHY OF URANIUM IN EDTA-CONTAINING MEDIUM (pH = 4·55 ± 0·05; 0·001% OF THYMOL PRESENT)

U × 10^3, M	EDTA, M	I	Remarks
0·82	0·01	2·52	0·1M acetate buffer present
0·82	0·01	2·27	0·1M $NaClO_4$ present[a]
0·41	0·1	2·18	No additional supporting electrolyte present[a]

[a] pH adjusted using HCl and NaOH

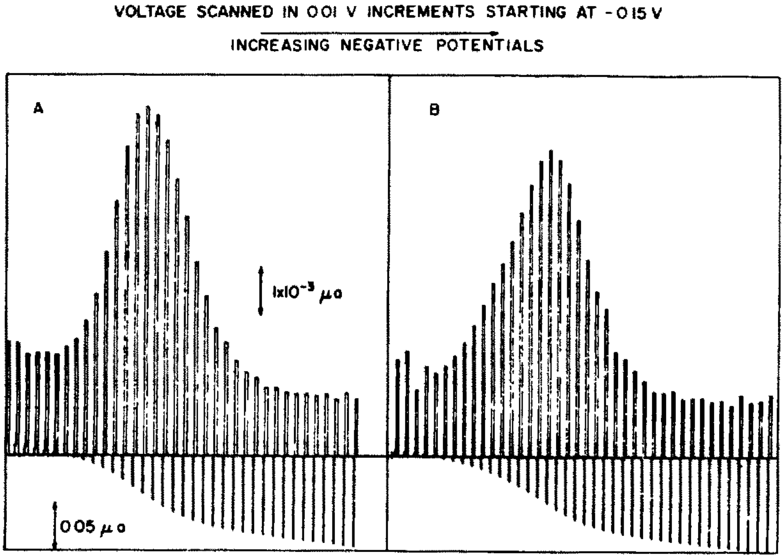

FIG 1.—Effect of EDTA Concentration on Polarography of Uranium ($1 \times 10^{-5} M$ U, 0·1M CH_3COOH–0·1M CH_3COONa; 0·001% thymol):
(A) 0·01M EDTA, (B) 0·001M EDTA.
Current-voltage curve is recorded below base line, simultaneously with incremental curve

Uranium-bismuth and uranium-molybdenum-mixtures

Fig. 2 shows a polarogram of a solution containing $1 \times 10^{-4} M$ each of uranium and of bismuth in the EDTA electrolyte. The bismuth wave is seen to be composed of two separate waves under these conditions; the same behaviour was observed with $1 \times 10^{-3} M$ bismuth. It may be noted that, although the bismuth-EDTA complex is known to be reduced irreversibly,[7] the existence of two nearly overlapping waves of this type can only be established by a derivative technique. Neither location nor height of the uranium peak, however, were affected by the presence of bismuth, and the separation between the uranium half-wave potential and the first bismuth peak is more than 0·2 V. The irreversible nature of the bismuth wave makes quantitative calculations difficult, but it is apparent that large bismuth/uranium ratios can be tolerated without causing appreciable interference with the uranium peak. Fig. 3 illustrates the polarographic behaviour of a solution containing $1 \times 10^{-5} M$ uranium in the presence of 0·01M bismuth and 0·01M excess EDTA. Excellent resolution is achieved between the uranium peak and the ascending edge of the bismuth wave. The resolution is slightly less satisfactory with 0·001M EDTA, where the uranium half-wave potential is 0·01 V more negative. No further improvement was noted at EDTA concentrations higher than 0·01M in either the presence or absence of acetate buffer.

Curve (A) in Fig. 3 shows the extent of interference of the aforementioned residual copper wave. In the presence of 0·01M bismuth the copper wave was found to behave irreversibly; the copper peak was displaced to —0·29 V, *i.e.*, to within 0·01 V of the uranium peak, and its location became independent of the excess EDTA concentration. This observation was not investigated further at this time; however, the effect facilitates low-level uranium analysis, as does the relatively flat region beyond the

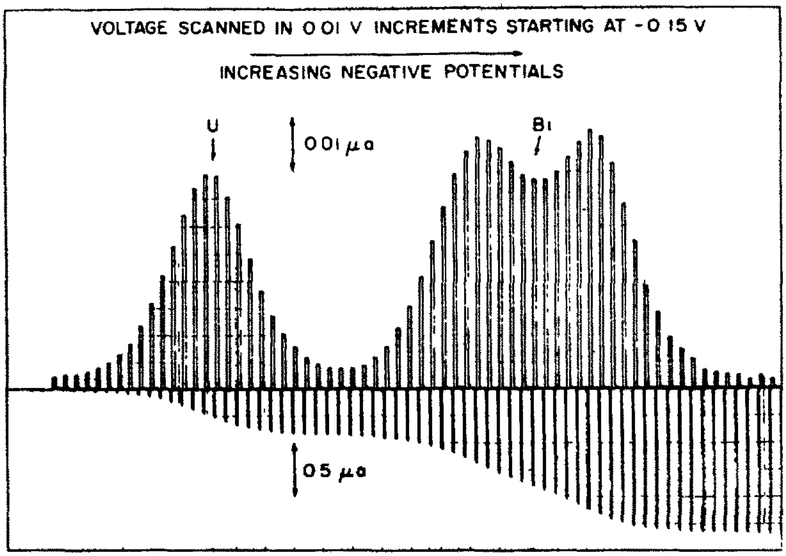

FIG. 2.—Polarogram of a Uranium-Bismuth Mixture (0·82 × 10^{-4}*M* U, 1 × 10^{-4}*M* Bi; 0·01*M* EDTA, 0·1*M* CH_3COOH–0·1*M* CH_3COO Na, 0·001% thymol)

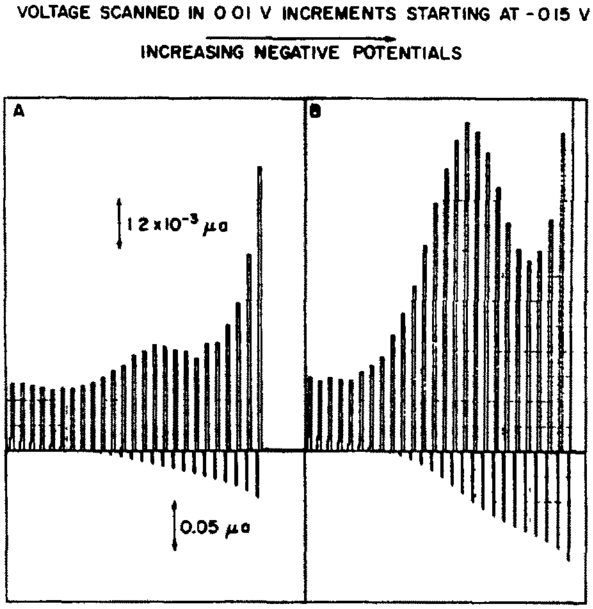

FIG. 3.—Polarogram of Uranium in Presence of Excess Bismuth:
(A) Supporting electrolyte: 0·01*M* Bi, 0·01*M* EDTA,
0·1*M* CH_3COOH–0·1 *M* CH_3COONa, 0·001% thymol
(B) Same, plus 1 × 10^{-5}*M* U.

copper peak, caused by the onset of the bismuth wave Thus, $2 \times 10^{-6}M$ uranium in $0{\cdot}01M$ bismuth could be determined with a precision of ±1%, and $1 \times 10^{-6}M$ uranium (corresponding to a 25% increase over the residual copper peak) could easily be detected. Linearity of the peak incremental response, to within ±2%, was established over the $2 \times 10^{-6}M - 1 \times 10^{-4}M$ concentration range, the slope was found to be *ca.* 7% lower than in the absence of bismuth

Molybdenum in the same supporting electrolyte was found to give two fairly well-resolved peaks, between −0·55 V and −0·75 V. This observation basically confirms the findings of Pecsok and Sawyer,[8] and again serves to demonstrate the utility of the incremental approach in analysing complex waves. The presence of $10^{-5}M$ molybdenum did not affect either location or height of the uranium peak. Molybdenum at a concentration of $10^{-2}M$, however, caused difficulties because of the onset of a drawn out wave at −0·26 V, *i.e.*, 0·04 V more positive than the uranium peak. The situation could be improved by increasing the excess EDTA concentration to $0{\cdot}05M$ ($0{\cdot}1M$ acetate buffer), thereby shifting the onset of the molybdenum wave to −0·33 V. Under these conditions $5 \times 10^{-6}M$ uranium could be determined in the presence of $10^{-2}M$ molybdenum with ±2% precision, using the peak observed at −0·31 to −0·32 V; this corresponded to a 50% increase over the residual response. Linearity was established up to $1 \times 10^{-4}M$ uranium, with a slope of 0·42 μA/mM, *i.e.*, 10% lower than for uranium alone.

Practical application

To test the practical utility of the technique described, uranium was determined in an alloy containing more than 99·8% bismuth. This material has been studied extensively as a potential liquid homogeneous reactor fuel. It also contains 0·035% of zirconium, 0·025% of magnesium and smaller traces of steel corrosion products. The following procedure was employed:

Dissolve a 6 to 8-g sample in excess nitric acid Transfer the solution to a 200-ml volumetric flask and make up to volume. The final solution should contain *ca.* $1M$ nitric acid to prevent hydrolysis of bismuth on standing Transfer a 5·0-ml aliquot to a 100-ml volumetric flask containing 10 ml of $1M$ acetate buffer. Add enough $1M$ sodium hydroxide to neutralise excess nitric acid. Add 10 ml of $0{\cdot}10M$ EDTA *in excess* over the amount required (*ca.* 10 ml) to dissolve the precipitate formed in the neutralisation step. Add 0·5 ml of 0·2% alcoholic thymol solution and dilute to the mark The final pH should be 4·6 ± 0·1 Transfer a portion to the polarographic cell, de-aerate and obtain the incremental polarogram. Measure the incremental response at −0·30 V *vs.* S.C.E Calculate the uranium concentration with the aid of a blank and appropriate uranium standards, both containing the same concentrations of bismuth, EDTA and buffer as the sample. Double or triple distilled water should be used for both preparation of reagents and all other operations.

Four separate portions of an alloy of this type (kindly provided by Dr. J. R. Weeks) were analysed by the above procedure, yielding 0·096% of uranium with an average deviation of ±2%. A modified version of the spectrophotometric dibenzoylmethane method[9] gave 0·102%, with comparable precision. It should be noted that the spectrophotometric procedure includes a preliminary extraction step. By contrast, the present method involves only the most elementary chemical steps; it is therefore easily applicable to a highly radioactive material, as would be exemplified by the above prospective reactor fuel.

In conclusion, it is shown that the incremental technique of derivative polarography can be applied to rapid and precise low-level uranium analysis in systems of high electrochemical complexity, without the need for prior separations.

Zusammenfassung—Die Methode der Inkremente in der Derivativpolarographie wurde auf die Bestimmung geringer Uranmengen in acetatgepuffertem EDTA-Elektrolyten angewandt. Die optimalen Bedingungen fur die Schnellbestimmung von 2 10^{-6}m Uran neben 0,01m Wismut und 5 10^{-6}m Uran neben 0,01m Molybdan werden angegeben Die Genauigkeit ist besser als 2%, vorherige Abtrennung nicht notwendig Uranmengen unter 10 μg lassen sich neben der 10^4-fachen Menge Bi nachweisen. Die Methode wurde mit Erfolg auf die Analyse einer 0,1% U enthaltenden Wismutlegierung angewandt

Résumé—La méthode à incréments de la polarographie dérivée a été appliquée à l'analyse de traces d'uranium dans un électrolyte constitué par de l'EDTA tamponné par de l'acétate. Les conditions optimales sont indiquées pour la détermination rapide d'uranium 2 . 10^{-6} M en présence de bismuth 0,01 M et d'uranium 5 . 10^{-6} M en présence de molybdène 0,01 M avec une précision <2% et sans séparation préalable. L'uranium en quantité inférieure ou égale à 10 μg peut être détecté dans un excès de 10^4 de bismuth La méthode a été utilisée avec de bons résultats dans le cas de l'analyse d'un alliage de bismuth contenant 0,1% d'uranium

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PROPERTIES OF BASES IN ACETONITRILE AS SOLVENT—III*

HYDROGEN BONDING BETWEEN PROTONATED AND FREE NITROGEN BASES

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Summary—In acetonitrile as solvent, the stronger nitrogen bases, *B*, form 1:1 and also higher hydrogen-bonded complexes with their conjugate acids, BH^+. Formation constants for these complexes have been determined by glass-electrode measurements in buffer solutions consisting of a constant concentration of the perchlorate or picrate of the base and varying concentrations of free base. The results show that the degree of complexation increases with increasing strength of the base and increasing number of hydrogen atoms in the ammonium group of the conjugate acid, and also that it has severe steric requirements, as expected. Thus, complexation is most extensive for the lower aliphatic primary amines and aliphatic cyclic secondary amines, such as piperidine, and does not occur with non-cyclic tertiary amines, except trimethylamine. The significance of these complexation reactions in potentiometric and conductimetric titrations and in studies concerned with the relative strength of bases is discussed.

INTRODUCTION

NON-AQUEOUS solvents have been used extensively in acid-base titrations, mainly in those cases where replacement of water by another solvent results in a desirable increase in solubility of the (organic) solutes, or improved sensitivity of the titration, or better differentiation of the components of mixtures, or where the use of a non-aqueous solvent avoids undesirable hydrolytic reactions. The subject has been thoroughly reviewed on several occasions by Riddick, and recently by Streuli.[1]

In the majority of cases the selection of solvent and titrant involved largely an empirical procedure of trial and error, because little theoretical information was available about the exact nature of the various solute species present and their interactions in these solvents. However, in recent years there has been an increasing interest in the theoretical aspects of acid-base reactions in non-aqueous solvents, particularly in solvents such as acetic acid and ethylenediamine, and in non-hydrogen bonding solvents of intermediate dielectric constant, such as the nitriles. Evidence is accumulating that probably no solvent is truly inert, and non-aqueous solvents provide a broad spectrum of conditions over which such solute-solvent interactions can be studied. However, certain non-aqueous solvents are much more inert in particular respects than water, and therefore provide suitable media for the investigation of the more subtle intrinsic properties of solutes, which are masked in water. Acetonitrile is such a solvent. It is a weaker base and a much weaker acid than water,

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* Part II: see reference 2.

and its dielectric constant is lower (36·0, as compared to 78·5 for water). The cumulative effect of these three factors is that acetonitrile is a much more differentiating solvent than water, as is reflected by its much smaller autoprotolysis constant (3×10^{-27}, as compared to 1×10^{-14} for water[2]). Nevertheless, the dielectric constant of acetonitrile is sufficiently high to allow extensive electrolytic dissociation of ionic solutes and to permit the study of such solutions by conductimetry and other electrometric methods.

An important consequence of the extremely weak acidic (hydrogen bonding) properties of acetonitrile is the fact that in solutions of many weak Brönsted acids, HA, the anions, A^-, are not stabilised sufficiently by solvation (which for the majority of anions must occur mainly by hydrogen bonding) and therefore resort to hydrogen bonding with undissociated acid instead, producing complexes such as $A^- \ldots HA$. Naturally, if such complexation reactions occur, the treatment of data obtained with hydrogen ion indicator electrodes, and by methods involving conductimetry, spectrophotometry, *etc.*, will be more complex than for the same solutes in water. The complexation reactions of Brönsted acids in acetonitrile have been studied thoroughly by Kolthoff and his coworkers.[3]

Analogous hydrogen bonded complexes between free and protonated amine-type bases are also produced in acetonitrile, although not to the same extent as for Brönsted acids. Nevertheless, some of these complexes are sufficiently stable to be important in acid-base titrations and particularly in theoretical studies concerned with the relative strength of bases. This communication is concerned with the formation of such complexes.

EXPERIMENTAL

Apparatus

Electromotive force measurements were made with a Beckman Model G pH meter and an *H*-type cell containing a Beckman "general purpose" No. 1190-80 glass electrode in conjunction with an Ag/(0 010*M* $AgNO_3$ in acetonitrile) reference electrode, and with 0·1*M* tetra-ethylammonium perchlorate in acetonitrile as salt bridge. This apparatus has been described elsewhere.[2]

Reagents

Technical grade acetonitrile (from two sources, Matheson and Sohio) was purified by a sequence of operations described before,[4] including fractional distillation, first from phosphorus pentoxide and then from calcium hydride.

The bases used were generally purified by distillation from sodium hydroxide and sodium metal (under reduced pressure for high-boiling bases). Full details will be presented elsewhere.[5] Boiling points agreed with literature values.

The perchlorates and picrates of the bases studied were generally prepared by potentiometric titration with the appropriate acid to the equivalence point (glass electrode) in water or ethanol as solvent, followed by evaporation of the solvent if necessary, and recrystallisation of the product from ethanol, isopropanol or ethyl acetate. Again, detailed information will be given elsewhere.[5]

RESULTS AND DISCUSSION

Cells containing glass electrodes in acetonitrile give a reversible response, provided the solutions are adequately buffered, a proper reference electrode is used, and liquid junction potentials are controlled, as described before.[2] For each base (B) studied, we have measured the potential of a glass electrode in a series of 8 to 14 buffer solutions consisting of a constant concentration ($C_s = 5 \times 10^{-4}M$) of the perchlorate or picrate of the base and varying concentrations (C_b) of free base. The salt concentration was deliberately kept low to minimise activity effects, changes in liquid junction potential and complications from $BH^+ClO_4^-$ and BH^+Pi^- ion pair formation, even though a higher concentration of salt would facilitate (qualitative) detection of B·BH$^+$ and higher complexes.

For the dissociation of a protonated amine in a solvent *S* which has some proton acceptor power, the following equilibrium relationships apply:

$$\mathrm{BH^+_{solvated}} + \mathrm{S} \rightleftharpoons \mathrm{SH^+_{solvated}} + \mathrm{B_{solvated(?)}}$$

$$K_a = a_{SH^+} \cdot \frac{[B]}{[BH^+]} \cdot \frac{f_B}{f_{BH^+}}$$

where K$_a$ is the thermodynamic dissociation constant of *BH*$^+$, and [X] denotes the molar concentration, a_X the activity and f_X the molar activity coefficient of species *X*. At constant ionic strength, f_B/f_{BH^+} is constant, so that

$$\frac{[B]}{[BH^+]} = \frac{\text{constant} \times K_a}{a_{SH^+}}.$$

If the electrode responds reversibly to a_{SH^+}, it follows from the Nernst equation that a plot of *E vs.* log ([B]/[BH$^+$]) or *vs.* log [B] at constant [BH$^+$], will be linear with a slope of 59 mV at 25°. If no complexation occurs between *B* and *BH*$^+$ and if the degree of dissociation of *BH*$^+$ is negligible compared to unity (as it is in all cases studied), [B] and [BH$^+$] are given by the total (analytical) concentrations C_b and C_s, respectively. However, if some *BHB*$^+$ formation occurs, it follows that

$$[B] = C_b - [BHB^+]$$

and

$$[BH^+] = C_s - [BHB^+]$$

so that a plot of *E vs.* log (C_b/C_s) will deviate from linearity. In the limiting case where formation of *BHB*$^+$ is virtually complete over the range of base concentrations studied, the plot will again be linear, but now with a slope of 118 mV.

In all cases formation constants of B·BH$^+$ and B$_2$·BH$^+$ complexes were evaluated from *E vs.* log (C_b/C_s) plots, such as those given in Figs. 1–4. In a relatively ideal case, such as that of piperidine (Fig. 2), only one complex (*BHB*$^+$) is produced and, furthermore, formation of this complex is virtually complete over a wide range of free base concentrations, so that calculation of the formation constant is straightforward. However, with the majority of bases studied the situation is more complicated, because either the species *BHB*$^+$ is insufficiently stable to be formed virtually exclusively even at the highest base concentrations studied (see below, pyridine), or else higher complexes such as B$_2$·BH$^+$ (Fig. 1, n-butylamine) and even B$_4$·BH$^+$ (Fig. 3, hydrazine) also are produced.

As an illustration of the calculations carried out, the case of pyridine will be considered. Pyridine forms a relatively weak complex B·BH$^+$, and gives no evidence of forming higher complexes. Experimental data are given in Table I. For the last measurement listed, it follows from the Nernst equation that

$$\log \frac{0{\cdot}812 - x}{5 \times 10^{-4} - x} - \log \frac{0{\cdot}812}{5 \times 10^{-4}} = \frac{39}{59} = \log 4{\cdot}58$$

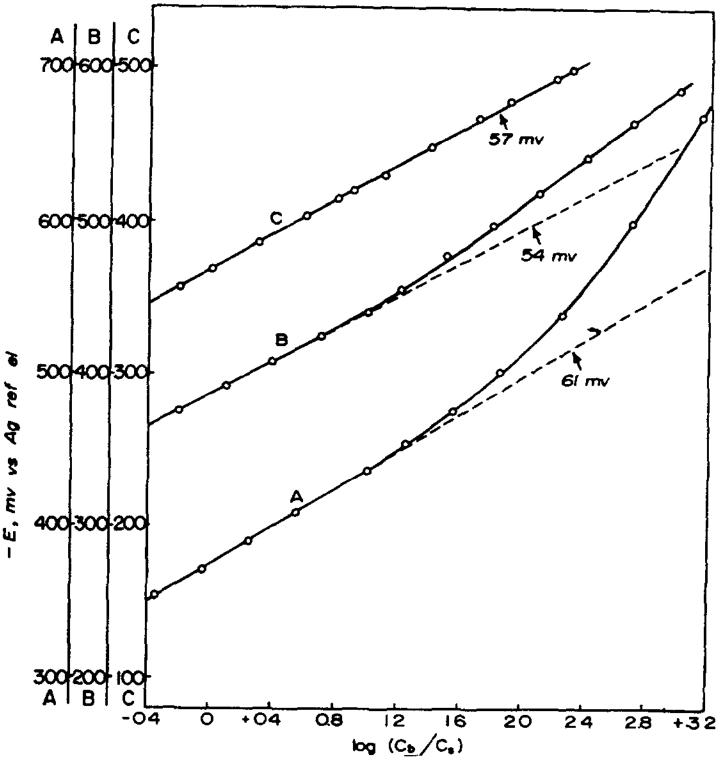


Fig. 1.—Potential of glass electrode in buffer solutions of n-butylamines and their perchlorates at a constant salt concentration of $5 \times 10^{-4}M$. (*A*) n-Butylamine, (*B*) Di-n-butylamine, (*C*) Tri-n-butylamine.

where x represents the molar concentration of the BHB^+ complex. Hence,

$$\frac{0{\cdot}812 - x}{5 \times 10^{-4} - x} = 1624 \times 4{\cdot}58 = 7{\cdot}44 \times 10^3$$

so that

$$x = [BHB^+] = 3{\cdot}91 \times 10^{-4}$$

and

$$[BH^+] = 5{\cdot}00 \times 10^{-4} - 3{\cdot}91 \times 10^{-4} = 1{\cdot}09 \times 10^{-4}.$$

Hence,

$$K = \frac{[BHB^+]}{[B][BH^+]} = \frac{3{\cdot}91 \times 10^{-4}}{0{\cdot}812 \times 1{\cdot}09 \times 10^{-4}} = 4{\cdot}4.$$

Considering a more complicated example, that of n-butylamine, similar calculations give values of K that increase with increasing concentration of base: $K = 26{\cdot}3$, $25{\cdot}4$, $32{\cdot}2$, $41{\cdot}6$ and $70{\cdot}4$ for $C_b = 0{\cdot}0174, 0{\cdot}0348, 0{\cdot}087, 0{\cdot}261$ and $0{\cdot}696M$, respectively. It is clear that (weak) higher complexes also are formed. In such cases the stepwise constants were computed by a series of approximations. For example, assuming as a first approximation that for n-butylamine $K_1 = 26$, it follows for the last measurement listed ($C_b = 0{\cdot}696M$) that

$$[B{\cdot}BH^+] = 26\,[B][BH^+].$$

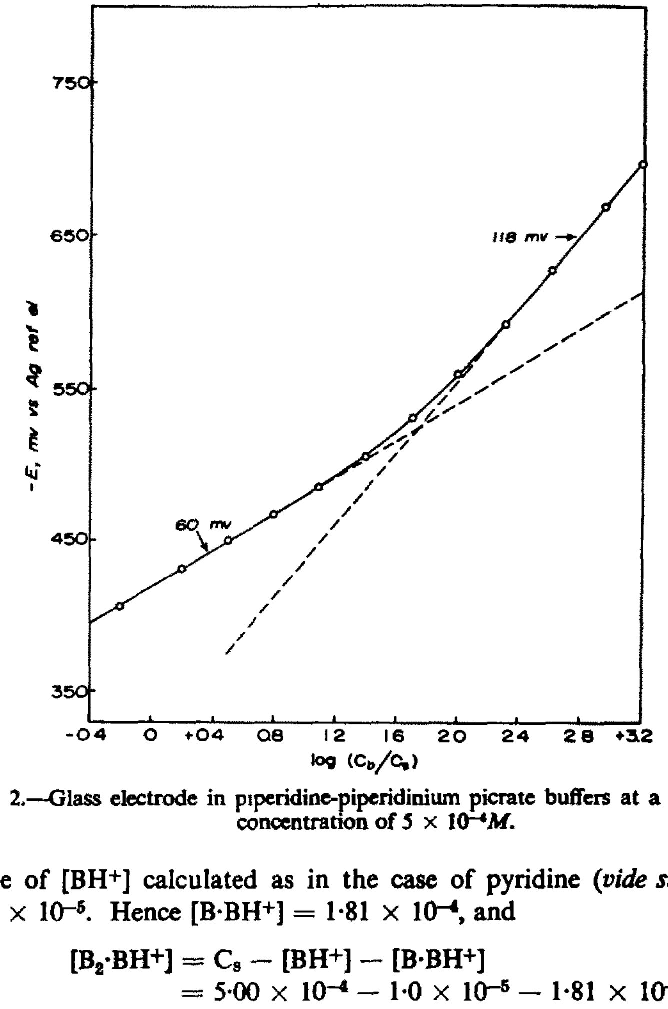


FIG 2.—Glass electrode in piperidine-piperidinium picrate buffers at a constant salt concentration of 5 × $10^{-4}M$.

The value of $[BH^+]$ calculated as in the case of pyridine (*vide supra*) was found to be 1·0 × 10^{-5}. Hence $[B{\cdot}BH^+] = 1{\cdot}81 \times 10^{-4}$, and

$$\begin{aligned}[B_2{\cdot}BH^+] &= C_s - [BH^+] - [B{\cdot}BH^+]\\ &= 5{\cdot}00 \times 10^{-4} - 1{\cdot}0 \times 10^{-5} - 1{\cdot}81 \times 10^{-4}\\ &= 3{\cdot}09 \times 10^{-4}\end{aligned}$$

so that

$$K_2 = \frac{[B_2{\cdot}BH^+]}{[B][B{\cdot}BH^+]} = \frac{3{\cdot}09 \times 10^{-4}}{0{\cdot}696 \times 1{\cdot}81 \times 10^{-4}} = 2{\cdot}5.$$

Similar calculations are carried out for all other points where formation of $B_2{\cdot}BH^+$ is apparent. For $C_b = 0{\cdot}261$ and 0·087, $K_2 = 2{\cdot}3$ and 2·7, respectively. The average value of K_2 (2·5) is then used to correct all preliminary values of K_1, which yields even for the last 3 measurements listed above a reasonably constant value of $K_1 = 26{\cdot}6$, 25·8 and 26·3, respectively. For cases where it was necessary, this sequence of calculations was repeated until (self-consistent) constant values of K_1 and K_2 were obtained. In the case of hydrazine (Fig. 3), where even higher complexes are also formed, an approximate value of K_2 was obtained by using the data for intermediate concentrations of base. Evaluation of K_3 and K_4 for hydrazine is too uncertain to be reported. More precise e.m.f. measurements (perhaps with a vibrating-reed electrometer as null detector) would be required for this purpose.

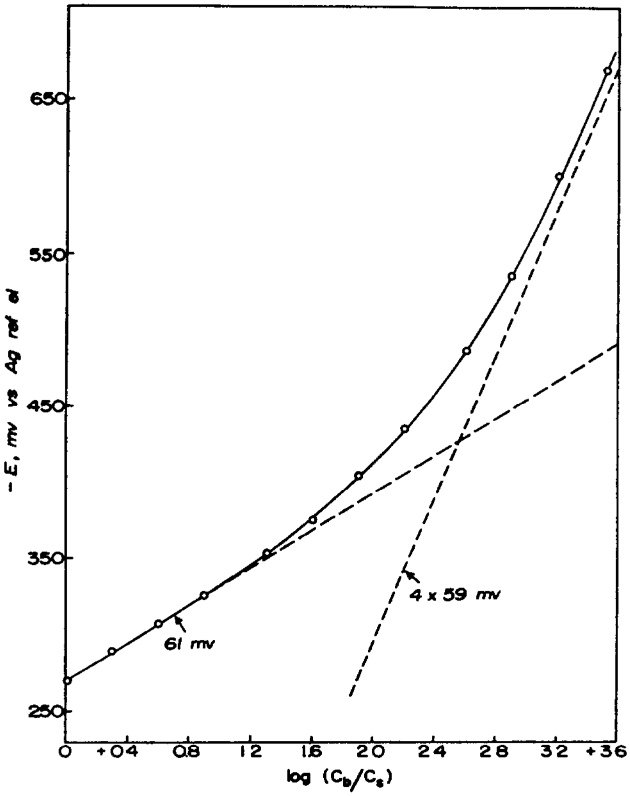


FIG. 3.—Glass electrode in hydrazine-hydrazonium monoperchlorate buffers at a constant salt concentration of 5 × $10^{-4}M$.

Formation constants for the complexes produced by a variety of nitrogen bases in acetonitrile as solvent are reported in Table II.

The main features of the results listed in Table II and in Figs. 1–4 are the following.

A. Non-cyclic aliphatic amines

1. The tendency of these amines to form 1:1 hydrogen bonded complexes, BHB^+, increases in the order tertiary, secondary, primary.

2. The tendency of the same amines to form higher complexes increases in the same order. Furthermore, it is to be expected that the highest complex that can be formed in any given case will be the species $B_n \cdot BH^+$, where n is the number of hydrogen atoms in the ammonium group and therefore represents the maximum number of hydrogen bonds that can be formed. The results are in agreement with this requirement.

3. However, steric factors are very important, as is most apparent from the behaviour of tertiary amines. Thus, while trimethylamine does form a 1:1 complex, triethylamine and its higher homologues form none. Similarly, the higher non-cyclic secondary amines do not form complexes.

B. Aromatic and cyclic aliphatic amines

1. The strength of the complex formed increases with increasing strength of the base. Thus, the relatively weak primary amines aniline and *p*-toluidine do not form

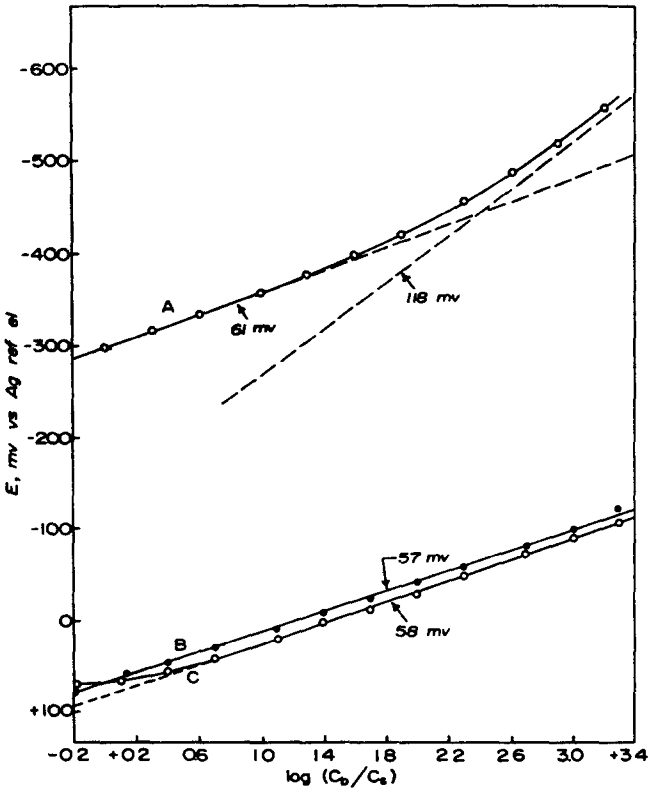


FIG. 4.—Glass electrode in benzylamine and aniline buffers at a constant salt concentration of 5 × $10^{-4}M$.

(*A*) Benzylamine and its picrate, (*B*) Aniline and its perchlorate, (*C*) Aniline and its picrate.

TABLE I.—EXPERIMENTAL DATA FOR PYRIDINE

C_b*	ΔE, *mV*†	[BHB^+] × 10^4	[BH^+] × 10^4	K‡
0·101	11	1·75	3·25	5·3
0·125	11	1·75	3·25	4·3
0·250	17	2·43	2·57	3·8
0·304	22	2·88	2·12	4·5
0·500	27	3·26	1·74	3·8
0·812	39	3·91	1·09	4·4

* Total molar concentration of base added; concentration of salt (perchlorate) kept constant at 5·00 × $10^{-4}M$ for all 6 measurements.

† Difference from line of slope = 59 mV extrapolated from initial linear section of curve, which in the case of pyridine extended from the first point measured (C_b = 2·5 × $10^{-4}M$) through the seventh (C_b = 0·020*M*).

‡ Formation constant of BHB^+ complex. Omitting the first measurement, the average value is 4·2

TABLE II.—FORMATION CONSTANTS OF HYDROGEN-BONDED COMPLEXES FORMED BETWEEN FREE AND PROTONATED BASES IN ACETONITRILE

Base	pK_a in water	Concn. range of base*		Salt	K_1†	K_2†
		Min., $M \times 10^4$	Max, $M \times 10$			
Ammonia	9 26	3	10	Perchlorate	11	2
Methylamine	10 64	3	11	Perchlorate	35	2
Dimethylamine	10 61	5	17	Perchlorate	31	0·5
Trimethylamine	10 72	2	2	Perchlorate	6	—
Ethylamine	10 75	4	8	Perchlorate	25	2
Diethylamine	11·00	4	7	Perchlorate	3	—
		5	8	Picrate	1	—
Triethylamine	10 74	1	1	Picrate	None	
n-Propylamine	10·59	3	8	Perchlorate	19	2
Tri-n-propylamine	10 70	3	0·8	Perchlorate	None	
n-Butylamine	10 61	2	7	Perchlorate	26·$_{2}$	2·$_{5}$
Di-n-butylamine	11 31	2	4	Picrate	None	
		2	5	Perchlorate	None	
Tri-n-butylamine	10 89	3	1	Perchlorate	None	
		2	0·8	Picrate	None	
t-Butylamine	10 45	2	8	Picrate	20	1
Di-isobutylamine	10 59	1	4	Picrate‡	None	
Tri-isoamylamine	—	4	0·7	Picrate‡	None	
Piperidine	11 20	2	9	Picrate	25·$_{0}$	—
Pyrrolidine	11 31	3	10	Picrate	33	2 $_{5}$
		3	9	Perchlorate	30	2
Pyridine	5 17	2	8	Perchlorate	4·$_{2}$	—
Aniline	4 58	3	11	Picrate	None	
		3	11	Perchlorate	None	
p-Toluidine	5·30	3	8	Perchlorate	None	
Benzylamine	9 30	3	9	Picrate	15	—
Monoethanolamine	9 45	3	8	Picrate	24	1·$_{6}$
Morpholine	8·36	3	10	Picrate	10	—
Hydrazine	7·99	4	12	Perchlorate	30	6§
Ethylenediamine	10 03	3	8	Perchlorate	40	1 $_{5}$
1,3-Propanediamine	10 64	3	8	Perchlorate	22	1 $_{5}$
1,4-Butanediamine	10·82	3	8	Perchlorate	10	1 $_{5}$
Triethylenediamine¶	8 19	3	8	Perchlorate	16	—

* Range over which total added base concentration was varied, while keeping salt concentration constant (at $5 \times 10^{-4}M$, except where indicated otherwise).

† K_1 and K_2 are stepwise formation constants:

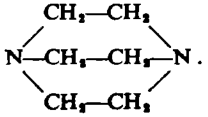
$$K_1 = \frac{[BHB^+]}{[B][BH^+]} \quad \text{and} \quad K_2 = \frac{[B_2BH^+]}{[B][BHB^+]}.$$

For diamines, the data refer to monoprotic species only.

‡ Salt concentration $= 5 \times 10^{-2}M$.

§ Higher complexes, up to $B_4.BH^+$, also formed. Value of K_2 uncertain.

¶ Triethylenediamine:



complexes, while pyridine and especially benzylamine (Fig. 4) do. A similar correlation between the base strength and hydrogen bonding ability (acceptors: chloroform and methanol) has been observed with pyridines in the pure bases as solvent.[6]

2. The cyclic amines pyrrolidine and piperidine form complexes that are much more stable than those of the corresponding non-cyclic secondary amines. Similarly

the cyclic tertiary amine triethylenediamine (Table II) and even the relatively weak base pyridine form 1:1 complexes. Clearly, in these cases steric hindrance is less marked than for the corresponding non-cyclic amines.

C. Other generalisations

1. For the diamines, $H_2N{\cdot}(CH_2)_n{\cdot}NH_2$, *BHB*$^+$ formation decreases as *n* increases from 2 to 4, even though the base strength *increases* in this sequence (in both water and acetonitrile). In the cases where $n = 3$ and 4 internal hydrogen bonding (N—H . . . N) may stabilise the cation, thereby reducing its desire to form hydrogen bonds with free base. The diamines are an interesting series of compounds, exhibiting quite different relationships between hydrazine and the remaining members in acetonitrile and in water. These differences will be discussed elsewhere.[5]

2. Generally, the slopes of the *E vs.* log (C_b/C_s) plots in the early region, before complexation becomes significant, were within 1 or 2 mV from the theoretical value of 59 mV. However, in the case of di-n-butylamine (Fig. 1) the slope was considerably less (average of 4 series of measurements = 54 mV). The reason for this behaviour is unknown. In the case of aniline in picrate buffers (Fig. 4) there is marked curvature in the initial region of the plot. This is because of reversion of the salt to the weak parent acid and base:

$$BH^+ + Pi^- \rightleftharpoons B + HPi.$$

Titration curves

The complexation reactions of nitrogen bases in acetonitrile not only are interesting *per se*, but are also important in the interpretation of acid-base titration curves. Clearly, in the titration of an amine with perchloric acid the largest effect of complexation will occur in the early stages of the titration, and again just before the equivalence point, where either the base or the salt is in considerable excess over its conjugate species. It can be shown readily that complexation should result in a decrease of the buffer capacity of the solution and a reduction in the break at the equivalence point of a potentiometric titration. These generalisations were verified experimentally. For example, in a titration of 0·1*M* pyrrolidine in acetonitrile with 0·5*M* perchloric acid dissolved in methylene chloride the potential of the glass electrode deviated from the hypothetical values calculated from the dissociation constant of pyrrolidinium ion in acetonitrile[5] on the assumption that no complexation, no ion pair formation and no interference by methylene chloride occurs, by −12, −5, +6 and +10 mV at 10, 30, 70 and 90% titrated, respectively, where negative values indicate that the solution is more basic than the hypothetical value, and *vice versa*. The formation constants reported for pyrrolidine (Table II) account for the major part of this variation.

The influence of complexation on the titration curves of amines with *weak* acids is more striking. Fig. 5 gives the conductimetric titration curves of n-butylamine with salicylic acid. The pronounced curvature before the equivalence point is from the *BHB*$^+$ complex (*BH*$^+$*A*$^-$ ion pair formation is also important), and that after the equivalence point from the *AHA*$^-$ complex (studied in detail for similar systems by Kolthoff and Chantooni[8]). In a masking solvent, such as water, the two branches of the curve are virtually linear, and the section after the equivalence point is nearly horizontal. We will discuss elsewhere the conductimetric titration curves of a variety of amines with *ortho*-substituted benzoic acids.

CONCLUSIONS

It has been shown that many of the stronger amines, particularly aliphatic primary and cyclic secondary amines, form hydrogen-bonded complexes with their conjugate acids in acetonitrile as solvent. One may speculate that this behaviour is likely to be the norm, rather than the exception, in the majority of solvents which have very weak-base properties. A formation constant near 30, which is typical for a number of these bases in acetonitrile, corresponds to a free energy of formation given by

$$\Delta F = -10^{-3}\,RT \ln K = -10^{-3} \times 2{\cdot}0 \times 298 \times 2{\cdot}3 \times 1{\cdot}48 = -2{\cdot}0 \text{ kcal/mole.}$$

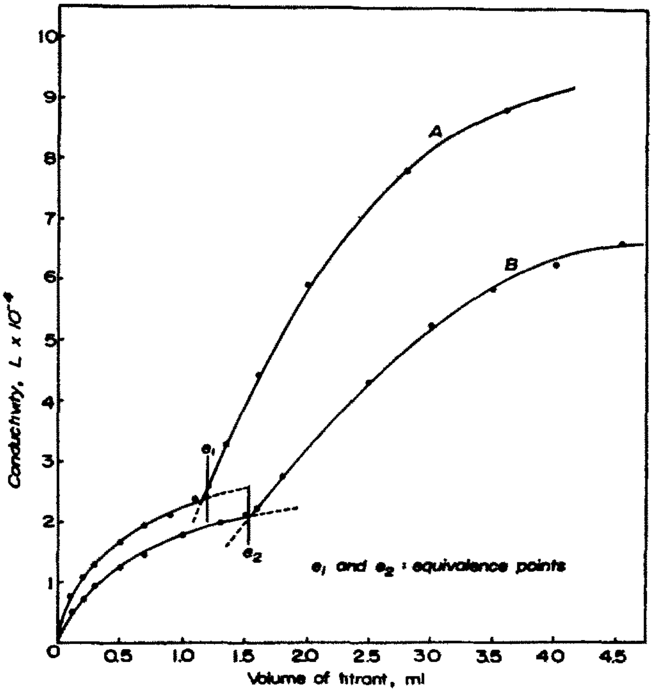


FIG. 5.—Conductimetric titration of n-butylamine with salicylic acid:
(*A*) 0·0287*M* base with 0 478*M* acid,
(*B*) 0·0191*M* base with 0 249*M* acid.

The corresponding complexes, AHA^-, formed between a number of Brönsted acids and their anions[3] are more stable, with formation constants ranging up to 10^3, corresponding to $\Delta F = -4$ kcal/mole. This difference reflects the fact that acetonitrile is more reluctant to solvate anions than cations, as compared to analogous solvation by water.

It is necessary to consider the possible formation of BHB^+ complexes in any exact determination of the relative strength of amines (with the proton as reference acid) in acetonitrile and similar solvents. If the potential of a hydrogen-ion indicator electrode at the "half-neutralisation" point in the titration of an amine with a relatively strong acid is regarded as an index of the strength of the base,[7] an error will be introduced if complexes higher than the 1:1 species are produced. We have determined the pK_a values of a series of nitrogen bases in acetonitrile by measurements similar to those described in this communication, but with provisions to maintain the absolute value of the net liquid junction potential constant for the entire series, and by making due allowance for complexation reactions. The results will be presented elsewhere.[5]

Acknowledgments—We thank the National Science Foundation for financial support under grant number NSF-G14502. We also wish to express our indebtedness to Professor Kolthoff, whose classical investigations of many facets of the chemistry of non-aqueous solutions have created widespread interest in this field.

Zusammenfassung—In Acetonitril als Lösungsmittel bilden stärkere Stickstoffbasen *B* mit einem oder mehreren Molekülen ihrer konjugierten Säuren BH^+ Wasserstoffbrückenkomplexe. Bildungskonstanten solcher Komplexe wurden durch Messungen mit Glaselektroden in Pufferlösungen aus konstanten Mengen des Perchlorats oder Pikrats der Base und variablen Mengen der freien Base bestimmt. Die Ergebnisse zeigen, daß der Komplexbildungsgrad mit steigender Basenstärke und steigender Anzahl von Wasserstoffatomen in der Ammoniumgruppe der konjugierten Säure wächst. Ferner sind erwartungsgemäß strenge sterische Bedingungen zu erfüllen. So ist die Komplexbildung am stärksten bei den niedrigen aliphatischen primären und den cyclischen sekundären Aminen wie Piperidin und bleibt bei nichtcyclischen tertiären Aminen außer Trimethylamin überhaupt aus. Die Bedeutung dieser Komplexbildungsreaktionen bei potentiometrischen und konduktometrischen Titrationen und bei Untersuchungen über die relative Stärke von Basen wird diskutiert.

Résumé—Dans l'acétonitrile, les bases fortes azotées, B, forme des complexes 1/1 et plus élevée par liaison hydrogène avec leurs acides conjugués BH^+. Les constantes de formation des ces complexes ont été déterminées par mesure au moyen d'électrode de verre en solution tamponnées constituées par un perchlorate ou un picrate de la base étudiée en concentration constante et en présence de concentrations variables de base libre. Les résultats montrent que le taux de complexation augmente avec l'accroissement de la force de la base et avec le nombre d'atomes d'hydrogène du groupement ammonium dans l'acide conjugué, et également que les impératifs stériques jouent un grand rôle, comme il faut s'y attendre. Ainsi, la formation de complexe est plus accentuée pour les amines aliphatiques primaires légères et les amines secondaires aliphatiques cycliques, comme la pipéridine, et n'apparaît pas avec les amines tertiaires non-cycliques, excepté la triméthylamine. Discussion de la signification de ces réactions de formation de complexes dans les dosages par potentiométrie et conductimétrie et dans les études relatives aux diverses forces de ces bases.

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A.C. POLAROGRAPHIC STUDIES ON THE INFLUENCE OF TENSAMMETRIC WAVES ON REDUCTION PEAKS OF INORGANIC CATIONS AND *VICE VERSA*

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Summary—This investigation deals with the studies on the effect of the nature and concentration of surface active substances (s.a.s) on the a c. reduction peaks of Cd^{2+} and Zn^{2+} ions and *vice-versa* by a.c. polarography. The magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s., but with concentrations higher than this, the magnitude of the reduction peak progressively decreases; a concentration of 1·3% of n-amyl alcohol completely removes the $10^{-3}M$ Cd^{2+} peak. Neither magnitude nor the peak potential of the tensammetric peak of n-amyl alcohol are influenced by the presence of Cd^{2+} ions. There is a linear relation between the concentration of the electroactive species and the optimum concentration of the s.a.s., and also the concentration of the s.a.s. just required to remove the reduction peak. These observations are further supported by the curve which gives the linear relation between the concentration of the electroactive species and the amount of the s.a.s. required to reduce the magnitude of the reduction peak to half its value. The amount of the surfactants required to remove the reduction peak completely is in the order n-amyl alcohol > Cerfak [sodium napthalene (2-dodecyl)3-sulphonate] > cetylpyridinium bromide. These results are discussed.

INTRODUCTION

SURFACE active substances usually employed to eliminate maxima on polarographic waves often cause undesirable effects such as suppression of a diffusion current, shift of a half-wave potential, splitting of a wave into two or more waves; in some cases the entire wave is obliterated, or a combination of these effects occurs. Breyer and Hacobian[1] studied the influence of tensammetric waves on a.c. and d.c. polarography. They showed, however, that in the presence of cyclohexanol the discharge of Cd^{2+} ions was rendered irreversible, as shown by the absence of an a.c. polarogram, only the tensammetric wave of cyclohexanol appearing. In contradistinction to Cd^{2+} the discharge of Mn^{2+} (−1·5v *vs.* S.C.E.) was completely unaffected by the presence of cyclohexanol.

The purpose of the present investigation was to study in detail the effect of the nature and concentration of surface active substances, *viz.*, n-amyl alcohol, Cerfak [sodium napthalene(2-dodecycl)3-sulphonate] and cetylpyridinium bromide, on the a.c. reduction peaks of Cd^{2+} and Zn^{2+} ions and *vice versa*. It is also to be seen if there is a possible correlation between the optimum concentration of the surface active substance and the amount of reducible species before any of the above undesirable effects are operative was also sought. This would be of great significance in removing polarographic maxima in d.c. polarography.

EXPERIMENTAL

Reagents

Cadmium sulphate and *zinc sulphate* used as reducible species were AnalaR quality (B.D.H.) *Normal amyl alcohol* of "Baker analysed reagent grade" was used as non-ionic surface active substance Pure samples of *Cerfak* and *cetylpyridinium bromide* were used as anionic and cationic agents respectively. All other chemicals used were of analytical quality, B.D.H.

Mercury used for the pool and the dropping electrode was passed through a Meyer's column[3] washed several times with distilled water, dried, passed through a sintered-glass filter and finally distilled under vacuum.

Apparatus

The apparatus employed in the present investigation is the same as that described before,[3,4] the only modification being as much reduction as possible of series resistance. This is done by applying to a dropping mercury electrode a 50-cycle a.c. ripple of 40 mV (r.m.s.) over the d.c. potentials and observing the alternating component of the resulting pulsating current. The d.c. potentials have been expressed with reference to the saturated calomel electrode. The constants of the d.m.e were as follows.

$$m = 3{\cdot}559 \text{ mg per sec.}$$

$$t = 2{\cdot}3 \text{ sec per drop in } 0{\cdot}1M \text{ KCl (open circuit).}$$

Potassium chloride solution (0·1*M*) was used as the supporting electrolyte, and was invariably shaken and kept in contact with mercury and mercurous chloride. In each case the measurements were taken with the indifferent electrolyte, and the effect has been expressed in terms of the per cent increase (with sign) of the alternating current. The d.m.e. was cathodic throughout the measurements. All the experiments were done at a pH of 3·3 and a temperature of 30 ± 0·5°.

RESULTS

Fig. 1 shows the effect of various concentrations of n-amyl alcohol on the Cd^{2+} ($10^{-3}M$) reduction peak. It is seen, in general, that the magnitude of the reduction peak is not influenced up to a certain concentration, known as the optimum concentration of the s.a.s., but with concentrations higher than this the magnitude of the reduction peak progressively decreases, so much so that a concentration of 1·3% of n-amyl alcohol completely removes the $10^{-3}M$ Cd^{2+} peak. The magnitude and the peak potential of the tensammetric peak of n-amyl alcohol shows the normal behaviour that would be expected without the presence of Cd^{2+} ions. These observations are further supported by Fig. 2, which gives the effect of various concentrations of Cerfak on the $10^{-3}M$ Cd^{2+} reduction peak. In this case, 0·066% of Cerfak is sufficient to remove the Cd^{2+} peak completely.

Fig. 3 shows the effect of various concentrations of Cd^{2+} ions on the tensammetric peak of 1·3% n-amyl alcohol. It is again confirmed that the $10^{-3}M$ Cd^{2+} peak is completely suppressed by 1·3% n-amyl alcohol, whereas, with higher concentrations of Cd^{2+}, the reduction peak reappears; its magnitude then increases with increase in the concentration of Cd^{2+} ion without affecting either the magnitude or the peak potential of the tensammetric peak of 1·3% n-amyl alcohol.

Fig. 4 gives the curve which relates the amounts of n-amyl alcohol required just to remove the Cd^{2+} peak completely using different concentrations of the electroactive species. It can be seen that the curve is linear within the concentration range $10^{-4}M$–$10^{-3}M$ of the electroactive species. From this curve one can see directly the amount of s.a.s. just required to remove completely the reduction peak of an electroactive species corresponding to any particular concentration. In other words, it gives the concentration of the s.a.s. which is sufficient to make the discharge process completely irreversible.

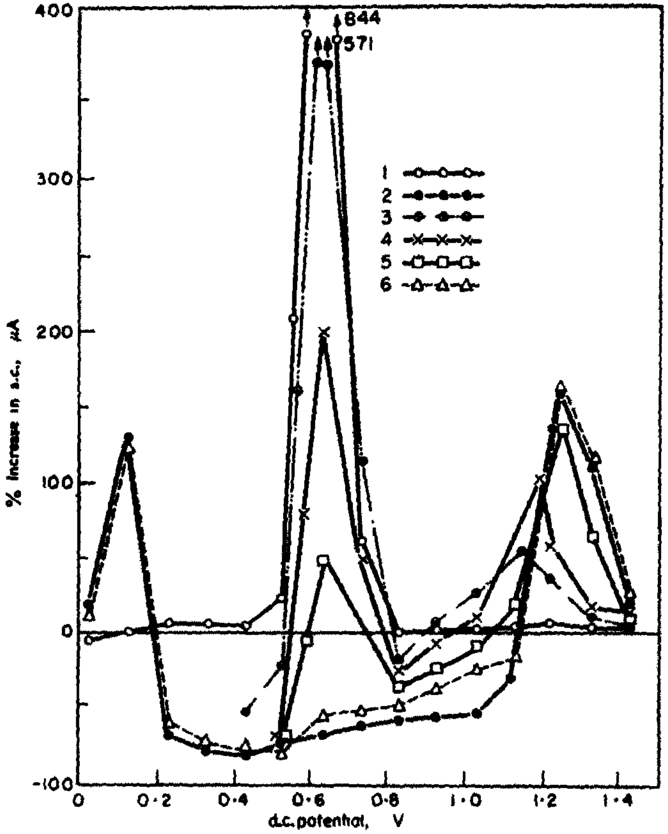

FIG. 1.—The effect of various concentrations of n-amyl alcohol on the Cd^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Cd^{2+}
2. 1·3% n-amyl alcohol
3. $10^{-3}M$ Cd^{2+} + 0·4% n-amyl alcohol
4. $10^{-3}M$ Cd^{2+} + 0·7% n-amyl alcohol
5. $10^{-3}M$ Cd^{2+} + 1·0% n-amyl alcohol
6. $10^{-3}M$ Cd^{2+} + 1·3% n-amyl alcohol.

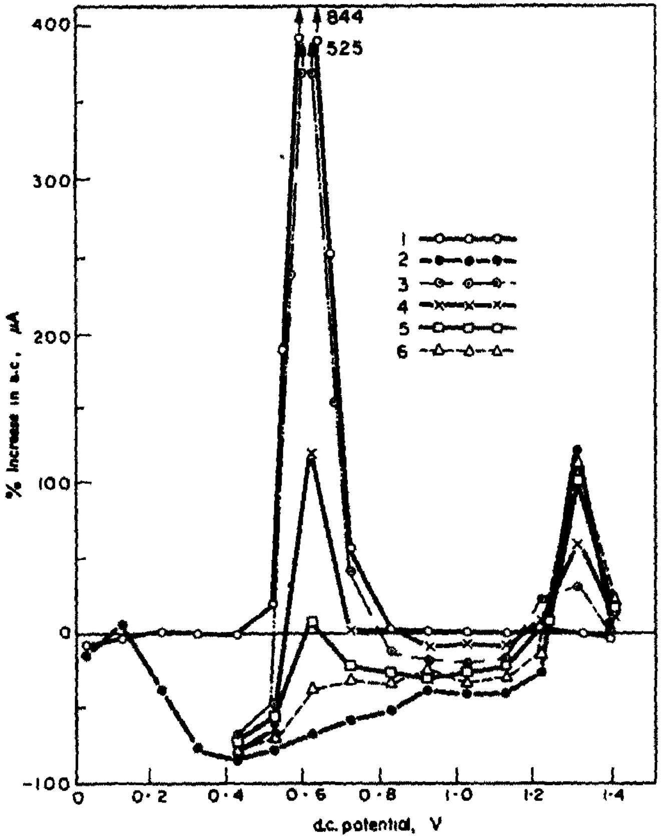

FIG. 2.—The effect of various concentrations of Cerfak on the Cd^{2+} ($10^{-3}M$) reduction peak.

1. $10^{-3}M$ Cd^{2+}
2. 0·066% Cerfak
3. $10^{-3}M$ Cd^{2+} + 0·02% Cerfak
4. $10^{-3}M$ Cd^{2+} + 0·04% Cerfak
5. $10^{-3}M$ Cd^{2+} + 0·06% Cerfak
6. $10^{-3}M$ Cd^{2+} + 0·066% Cerfak.

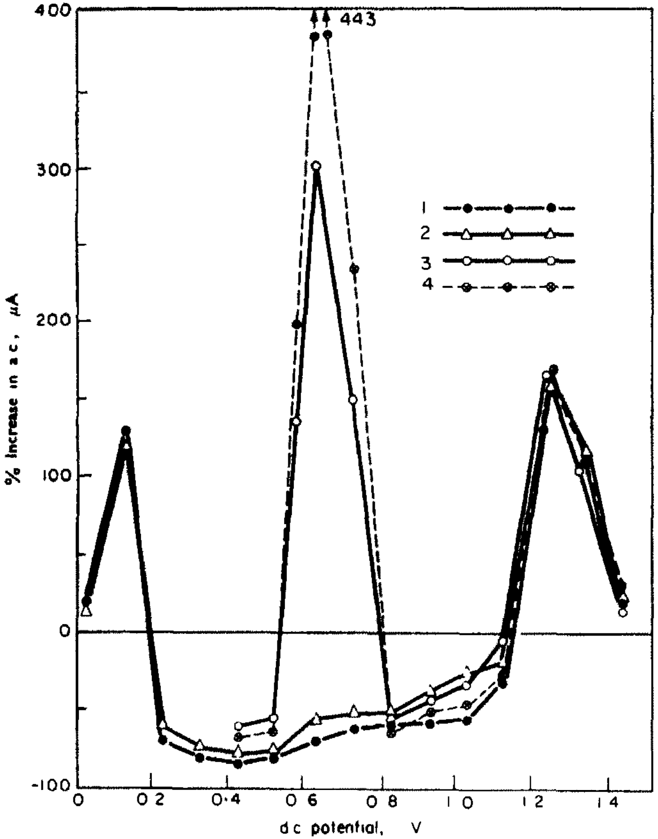

FIG. 3.—The effect of various concentrations of Cd^{2+} ion on the tensammetric peak of 1·3% n-amyl alcohol

1. 1·3% n-amyl alcohol
2. 1·3% n-amyl alcohol + $10^{-3}M$ Cd^{2+}
3. 1·3% n-amyl alcohol + 3 × $10^{-3}M$ Cd^{2+}
4. 1·3% n-amyl alcohol + 5 × $10^{-3}M$ Cd^{2+}

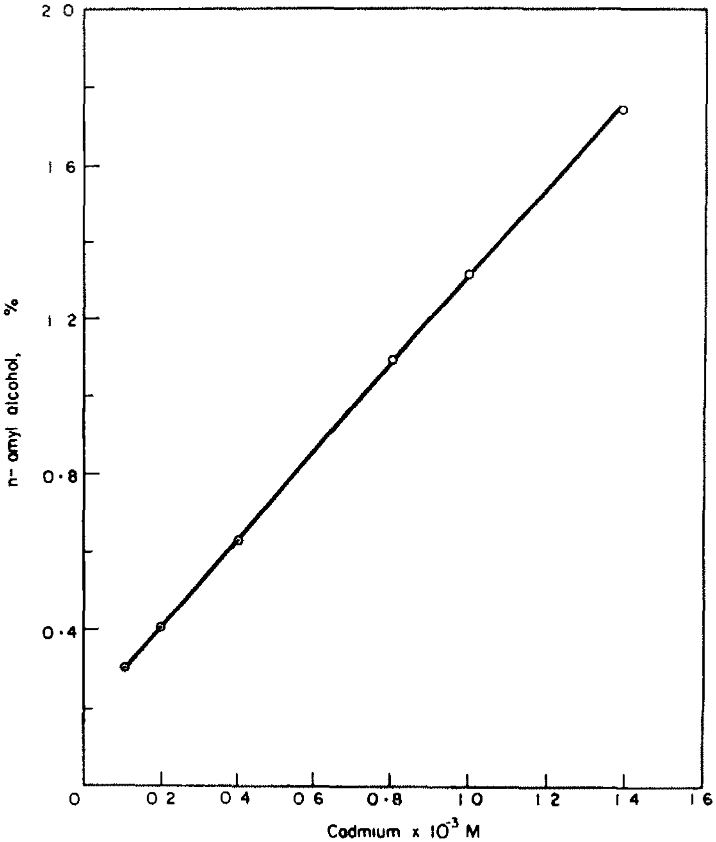

FIG. 4 —Relation between the amounts of n-amyl alcohol required to remove the Cd^{2+} peaks completely for various concentrations of Cd^{2+} ion.

Fig. 5 relates the optimum concentrations of n-amyl alcohol used for various concentrations of Cd^{2+} ion to produce the reduction peak. Here again it can be seen that the relation is linear in the concentration range $10^{-4}M$–$10^{-3}M$ of Cd^{2+}. This relation should be of particular interest in connection with d.c. polarography, where the optimum concentration of the s.a.s. is of significance in suppressing the polarographic maxima.

These observations are further substantiated by Fig. 6, which shows the linear relation between the concentration of the electroactive species and that of the surface active substance required to reduce the magnitude of the reduction peak to half its value. This linear relation holds good for the electroactive species between $10^{-4}M$ and $10^{-3}M$. The relation between the magnitude of the reduction peak and the molar concentration of the Cd^{2+} ion is linear within the above range.[5]

Fig. 7 shows the effect of various concentrations of n-amyl alcohol on the reduction peak of $10^{-3}M$ Zn^{2+} ions. Here, also, as in the case of Cd^{2+} ions, up to a certain concentration of n-amyl alcohol, the magnitude of the Zn^{2+} peak is not affected at all; but with concentrations greater than this optimum concentration, the magnitude of the peak decreases progressively till it is completely removed by 1 0% n-amyl alcohol. Further, the peak potential and the magnitude of the tensammetric peak of 1·0% n-amyl alcohol remain unaffected by the presence of $10^{-3}M$ Zn^{2+} ions.

These observations are further confirmed by Fig. 8 and Fig. 9, which show the effect of various concentrations of Cerfak and cetylpyridinium bromide on the reduction peaks of $10^{-3}M$ Zn^{2+} ion The concentrations of Cerfak and cetylpyridinium bromide required for completely removing the reduction peak are 0·056% and 0·008%, respectively. Therefore to remove completely the reduction peak of $10^{-3}M$ Zn^{2+}, the quantities of s.a.s. required are in the order n-amyl alcohol > Cerfak > cetylpyridinium bromide; this is supported by the effect of these s.a.s. on the reduction peak of Cd^{2+} ion.

DISCUSSION

Tensammetric peaks[1] are the outcome of the electrode processes which have their origin in adsorption/desorption processes occurring at the d.m.e. when a small sinusoidal a.c. voltage is superimposed upon the direct potential applied to a d.m.e. in the presence of s.a.s. and the resultant a.c. current is measured. They differ fundamentally from the a.c. reduction peaks of inorganic cations which are produced as a consequence of depolarisation processes occurring at the d.m.e., in the sense that in the former case no electron transfer takes place across the electrode boundary, whereas in the latter case it does.

In the absence of s.a.s. the reduction of inorganic cations takes place unhindered at the d.m.e. at the corresponding peak potential, and gives very high peaks which are reversible and diffusion-controlled. If s a.s is added, by virtue of the hydrophobic groups in the molecule it is preferentially adsorbed on the electrode surface, and hinders the electrode process either by film formation or by chemical interaction with the electroactive species in the immediate vicinity of the electrode surface. This adsorption is maximum at the electrocapillary zero (e.c.z), and diminishes on either side of the e.c.z. giving rise to tensammetric peaks arising from sudden desorption of the s.a.s. at higher cathodic or anodic potentials It is obvious, therefore, that the electrode processes whose reduction potentials lie within the adsorption range of the

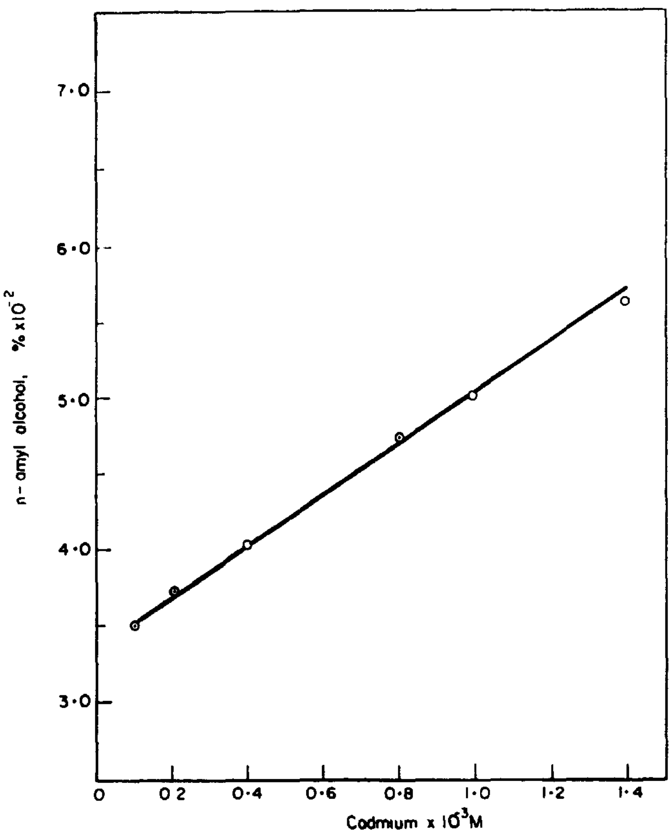

FIG. 5.—Relation between the optimum concentrations of n-amyl alcohol required, for various concentrations of Cd^{2+} ion

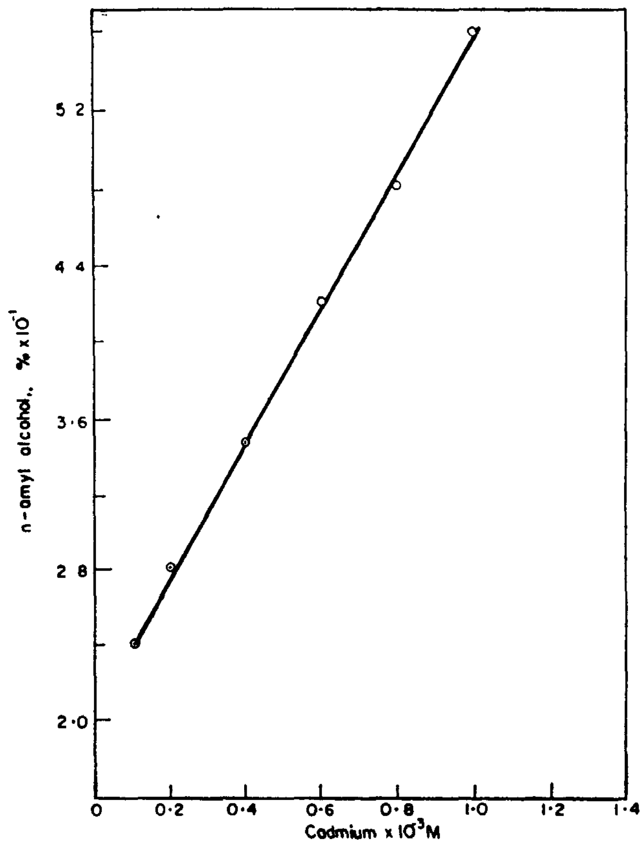

FIG. 6.—Relation between the concentrations of Cd^{2+} ion and n-amyl alcohol required to reduce the magnitude of the reduction peak to half its value.

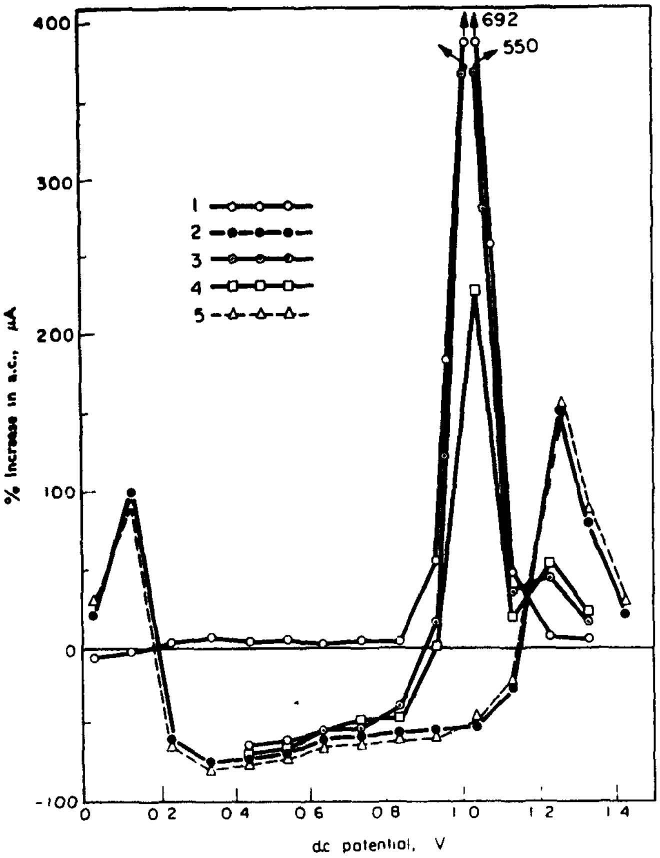

FIG. 7.—The effect of various concentrations of n-amyl alcohol on the Zn^{2+} ($10^{-3}M$) reduction peak

1. $10^{-3}M$ Zn^{2+}
2. 1·0% n-amyl alcohol
3. $10^{-3}M$ Zn^{2+} + 0·2% n-amyl alcohol
4. $10^{-3}M$ Zn^{2+} + 0·4% n-amyl alcohol
5. $10^{-3}M$ Zn^{2+} + 1·0% n-amyl alcohol

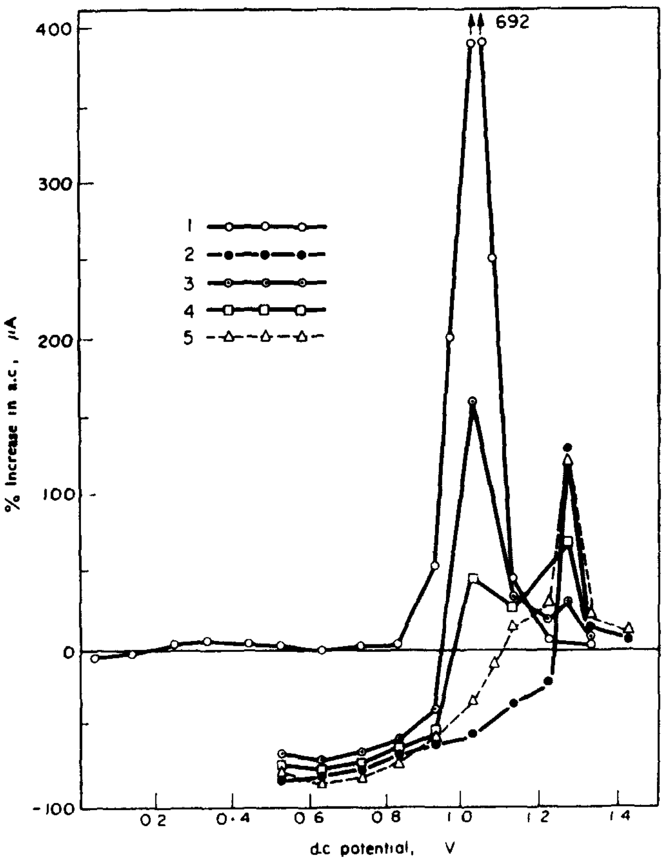

FIG. 8.—The effect of various concentrations of Cerfak on the Zn^{2+} ($10^{-3}M$) reduction peak

1. $10^{-3}M$ Zn^{2+}
2. 0 056% Cerfak
3. $10^{-3}M$ Zn^{2+} + 0 02% Cerfak
4. $10^{-3}M$ Zn^{2+} + 0·04% Cerfak
5. $10^{-3}M$ Zn^{2+} + 0 056% Cerfak

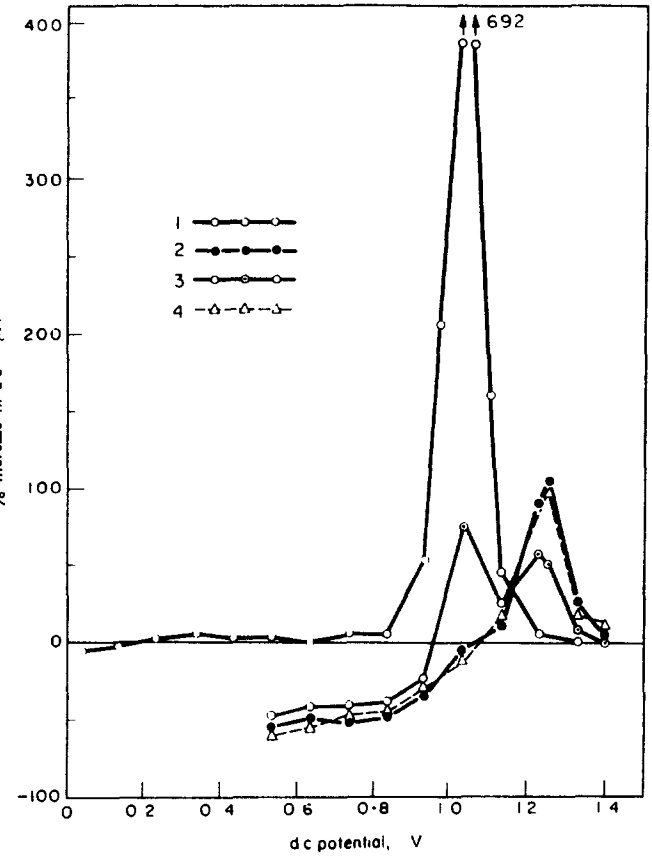

FIG. 9.—The effect of various concentrations of cetylpyridinium bromide on the Zn^{2+} ($10^{-3}M$) reduction peak

1. $10^{-3}M$ Zn^{2+}
2. 0 008% cetylpyridinium bromide
3. $10^{-3}M$ Zn^{2+} + 0 004% cetylpyridinium bromide
4. $10^{-3}M$ Zn^{2+} + 0 008% cetylpyridinium bromide.

s.a.s. will be affected by the presence of s.a.s., whereas outside this range there will be no significant influence on the electrode processes.

Because the peak potential and the magnitude of the tensammetric peak corresponding to any particular amount of s.a.s. remain constant with and without electroactive species, this suggests that the hindrance of the electrode process probably arises from film formation at the electrode surface and not from any chemical interaction between s.a s. and the electroactive speices. This is further supported by Fig. 3, in which both the peak potential and the amount of 1·3% n-amyl alcohol are unaffected by adding various amount of Cd^{2+} ions in the solution . It appears that with concentrations up to the optimum concentration of the s.a.s., the amount of s.a.s. is not sufficient to cover the electrode surface to a sufficient extent to hinder the electrode process, but concentrations greater than the optimum concentration progressively increase the extent of surface coverage within the life of the drop, and increase the degree of hindrance of the electrode process, thereby diminishing the magnitude of the reduction peak At higher concentrations of the s.a.s., corresponding to the removal of the reduction peak, it appears that most of the surface is covered with a unimolecular film; this hinders the rate of electron transfer from the electrode surface so much that it becomes slower than the diffusion rate, and hence the limiting current is no longer diffusion controlled. Thus a decrease in the rate of the electron transfer corresponds to an increase in irreversilibity of the electrode reaction, thereby producing no peak in a c. polarography.

With larger amounts of a particular reducible species, the quantity of the s.a.s. needed to make the rate of electron transfer slower than the rate of diffusion will be more than when smaller amounts of the same reducible species are present. Hence it is seen that the amount of n-amyl alcohol required for removing the reduction peak of Cd^{2+} using larger concentrations of Cd^{2+} ions are more than those for smaller amounts of Cd^{2+} ions. It may be mentioned that although the concentration of surfactants below the optimum concentration do not show any adverse effects on the kinetics of the electrode process, they are nevertheless capable of suppressing the polarographic maxima, probably because of preferential adsorption of the s.a s. at the neck of the mercury drop.[6]

The extent of inhibition on the kinetics of the electrode process depends, amongst other factors, on the structure of the adsorbed film, which in turn depends both on the nature of the s.a.s., especially its charge, and on the nature of the reducible species. On the cathodic side of the e.c.z., cationic surfactants will be adsorbed more strongly than anionic surfactants, and therefore the amount of cetylpyridinium bromide (which is cationic) required to remove Cd^{2+} and Zn^{2+} peaks is much less than the amount of Cerfak (which is anionic in nature.)

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Zusammenfassung—Diese Arbeit befaßt sich mit dem Effekt von Art und Konzentration oberflächenaktiver Stoffe auf die Wechselstromreduktionsspitzen von Cd^{2+} und Zn^{2+} in der Wechselstrompolarograp hiesowie den umgekehrten Effekten. Die Größe der Reduktionsspitze wird bis zu einer gewissen Konzentration des oberflächenaktiven Stoffes nicht beeinflußt, daruber nimmt die Spitze ab; eine Konzentration von 1,3% n-Amylalkohol unterdruckt die Spitze bei 10 ^{3}m Cd^{2+} ganz Große und Potential der tensammetrischen Spitze von n-Amylalkohol werden durch Cd^{2+} nicht beeinflußt. Es besteht eine lineare Beziehung zwischen der Konzentration des reduzierbaren Ions und der Optimalkonzentration des oberflächenaktiven Stoffes und der Konzentration, die zur Unterdruckung der Spitze eben ausreicht Diese Beobachtungen werden weiter gestuzt durch die lineare Beziehung zwischen Konzentration des reduzierbaren Ions und der Menge des oberflächenaktiven Stoffes, die die Große der Spitze halbiert. Die zur volligen Unterdruckung der Reduktionsspitze notwendige Menge oberflachenaktiven Stoffes fällt von n-Amylalkohol uber Cerfak zu Cetylpyridiniumbromid Diese Ergebnisse werden in dieser Arbeit diskutiert.

Résumé—Cette recherche traite des études sur l'effet de la nature et de la concentration des substances tensioactives (s t.a) sur les pics de réduction en c.a des ions Cd^{2+} et Zn^{2+} et vice-versa par polarographie en c.a. On voit que l'amplitude du pic de réduction n'est pas influencée jusqu'à une certaine concentration en s t.a., mais à des concentrations supérieures à celle-ci, l'amplitude du pic de réduction décroît progressivement de sorte qu'une concentration de 1,3% en alcool n-amylique supprime complètement le pic 10^{-3}M Cd^{2+}. L'amplitude, ainsi que le potentiel de pic du pic tensammétrique de l'alcool n-amylique ne sont pas influencés par la présence d'ions Cd^{2+}. Il y a une relation linéaire entre la concentration de l'espèce électroactive d'une part, et la concentration optimale de la s.t.a., ou les concentrations de s t.a. juste nécessaires pour annuler le pic de réduction d'autre part. Ces observations sont en outre étayées par la courbe qui donne la relation linéaire entre la concentration de l'espèce électroactive et la quantité de s.t a nécessaire pour diminuer de moitié l'amplitude du pic de réduction La quantité de surfactant nécessaire pour supprimer totalement le pic de réduction se classe dans l'ordre. alcool n-amylique > cerfak > bromure de cétylpyridinium. Ces résultats sont discutés dans le mémoire

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SOME TEMPERATURE EFFECTS IN GAS CHROMATOGRAPHY

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Summary—The expected effects of temperature on column efficiency are considered in detail for typical compounds of low, intermediate and high retention Situations involving various relative values of the resistances to mass transfer in the gas and liquid phases are analysed. One conclusion reached is that flow conditions cannot be chosen at any one temperature which will result in maximum efficiency for all solutes It would also be expected that column efficiency generally should increase with increasing temperature although under some conditions, of high mass transfer resistances in the liquid phase relative to that in the gas phase, a decrease or virtual independence of temperature may be found. The effect of variation of column temperature on pressure drop across the column is also examined briefly.

THE early work of Van Deemter *et al.*[1] immediately led to a greater understanding of the theory and practice of gas chromatography. Significant progress has been made with regard to theory since then by a number of persons of whom Jones,[2] Giddings[3] and Golay[4] might be mentioned. Much of the effort has been in relation to isothermal chromatography. It has been shown[5] that a knowledge of isothermal behaviour is important to an understanding of programmed temperature gas chromatography. In this paper some of the effects of temperature on isothermal gas chromatography, particularly with respect to column efficiency are examined. Because column efficiency is intimately related to the flow rate of the eluent gas and the distribution coefficients of the sample components, the effect of temperature on these two variables will first be briefly considered.

Flow rate and pressure drop

The effect of temperature on flow rate is primarily through its influence on gas viscosity which relates the flow rate to the pressure drop. There is a further strong effect from direct gas expansion if comparisons are made for conditions of constant mass flow rate.

The viscosity of most gases at ordinary pressures is approximately proportional to the temperature raised to a power somewhat less than one.[6] At high temperatures the limiting value of the slope shows a temperature dependence to the 0·63-power. At lower temperatures the coefficient is somewhat larger and no great error is incurred if the viscosities of gases of chromatographic interest are assumed to vary as the 0·7-power of the temperature.

It is noteworthy that the viscosity of hydrogen is about 0·84 × 10^{-4} g/sec cm at 0° and 1 atmos, whereas all other gases of chromatographic interest have viscosities which are about twice this value. Therefore, the absolute change in viscosity with temperature as well as the viscosity itself is least for hydrogen. Thus hydrogen is unquestionably the preferred eluent gas, both from the point of view of minimum pressure drop and of least change in pressure drop with temperature

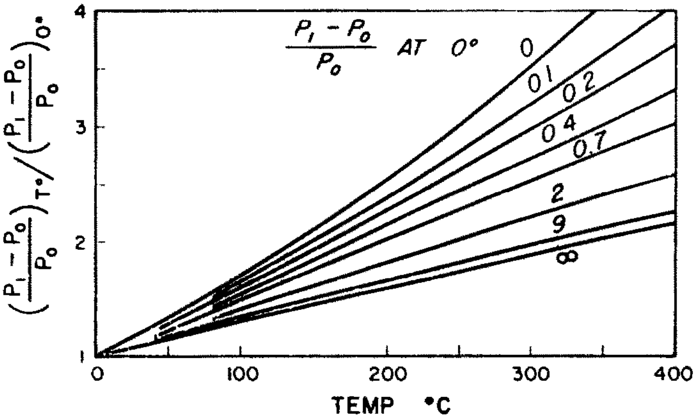

FIG. 1 -Change in relative pressure drop with temperature for columns with various pressure gradients (P_i is the inlet pressure, P_o is the outlet pressure and T is the temperature).

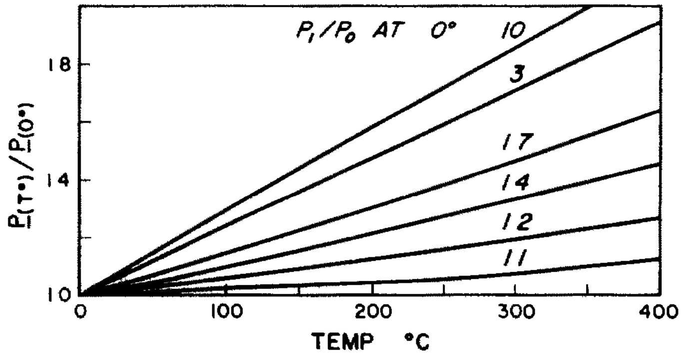

FIG. 2 --Change in inlet to outlet pressure ratio with temperature for columns with various pressure gradients

If one assumes that the flow rate, expressed at column outlet pressure and at a constant temperature of 0°, is maintained constant (constant mass flow rate) while the temperature of the column is changed, then some pressure drop relationships which can be calculated are shown in Figs. 1 and 2. Fig. 1 indicates that the relative change in pressure drop with increased temperature is greatest when the absolute pressure drop across the column is smallest. It can be deduced that when the pressure drop is small, *i.e.*, $P_o - 1$ approaches zero, then the temperature dependence of $\underline{P} - 1$ varies according to $(T/273)^{1·7}$, where $\underline{P}$ is the ratio of inlet to outlet pressure, P_i/P_o, and T is the column temperature. The power 1·7 arises from the 0·7 viscosity dependence and the 1·0 from thermal expansion. When the pressure drop is large $\underline{P} - 1$ varies according to $(T/273)^{0·85}$. In Fig. 2 the actual changes in the ratio of inlet to outlet pressure with temperature are illustrated. As expected, this ratio changes most when it is high initially. The principal significance of these changes for the present work are in connection with the James and Martin[7] compressibility correction to flow-rates, *i.e.*, $j = \frac{3}{2}\frac{(\underline{P}^2 - 1)}{(\underline{P}^3 - 1)}$.

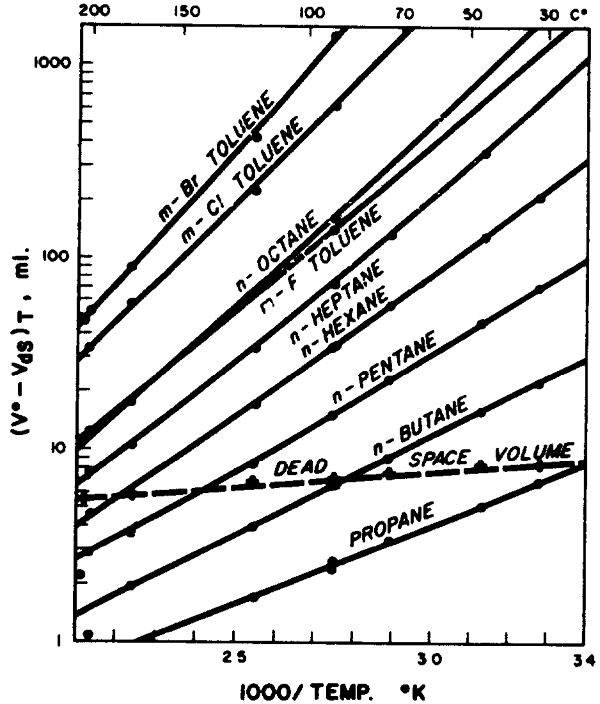

FIG. 3.—Dependence of net retention volume, ($V° - V_{ds}$), per g of column liquid, on temperature for a variety of solutes on Apiezon L on firebrick (2-m, 0·25-inch coiled copper column).

Distribution coefficient

The most important effect of temperatures is on the distribution coefficients of the sample components between the eluent gas and the stationary liquid and is reflected primarily in the retention volumes and secondarily in the relative peak broadenings. The variation in distribution coefficient with temperature is dependent principally upon the exponential change of vapour pressure with temperature and to a small extent on changes in activity coefficients.[8] This leads to the well-known linear relationship between the logarithm of the net retention volume and the reciprocal of the absolute temperature, such as shown in Fig. 3.

Column efficiency

Column efficiency, or the number of theoretical plates, is commonly expressed in terms of the theoretical plate height, *H*, as a function of eluent gas velocity for any particular system at constant temperature. The spreading of a chromatographic band in a column has been shown to be caused by a number of factors. These may be summarised in the following expression involving eluent gas velocity

$$H = A + B/u + C_{liq}\,uj + C_{gas}\,u \qquad (1)$$

A, B, C_{liq} and C_{gas} are constants at any given temperature, u is defined here as the eluent gas velocity at the outlet, and j is the compressibility correction.

The first and controversial term A in equation (1) is the contribution from eddy diffusion It is a term which is limited to packed columns and is ascribed to the multiple paths followed by the eluent gas. It is small and is considered negligible by some authors. If real, it should be independent of temperature and therefore need not concern us further.

The second term, B/u, which is most important at low flow velocities, describes the spreading because of diffusion in the flowing gas along the direction of flow. The constant B is $2\gamma D_g$, where D_g is the gas phase diffusion coefficient at column outlet conditions and γ is a tortuosity factor equal to somewhat less than 1 for a packed column To assess the importance of this term it is necessary to know the diffusion coefficients and their change with temperature. The equation of Chen and Othmer[9] appears to agree with experimental measurements better than any other general equation yet proposed and the constants involved are the readily accessible critical constants

$$D_{gas} = \frac{0{\cdot}43\left(\frac{T}{100}\right)^{1{\cdot}81}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^{0{\cdot}5}}{P\left(\frac{T_{C_1}\;T_{C_2}}{10{,}000}\right)^{0{\cdot}1405}\left[\left(\frac{V_{C_1}}{100}\right)^{0{\cdot}4}+\left(\frac{V_{C_2}}{100}\right)^{0{\cdot}4}\right]^2} \qquad (2)$$

D_{gas} is the diffusion coefficient in cm^2/sec, T is the absolute temperature, P is the pressure in atmospheres, M_1 and M_2 are the molecular weights of eluent gas and diffusing solute, and T_{C_1}, T_{C_2}, V_{C_1} and V_{C_2} are the critical temperatures and volumes. This equation indicates that the diffusion coefficient is inversely proportional to pressure and, important for our present purposes, proportional to the 1·81-power of temperature. Thus, the gaseous diffusion coefficient increases strongly with temperature and, for instance, could be expected to double in going from 25° to 160°. For conditions of constant mass flow rate, the actual velocity at the column outlet is proportional to temperature to the first power. Hence, for constant mass flow rate conditions the B/u term increases with temperature according to only the 0·81-power.

The third and fourth terms in equation (1) refer to band broadening, which results from the finite time taken for equilibrium to be reached across any column section between the gas and liquid phases. The third term, $C_{liq}\,uj$, describes the effects of resistance to mass transfer in the liquid phase. The C_{liq} coefficient of this term is generally agreed to have the form

$$C_{liq} = \frac{2}{3}\frac{k}{(1+k)^2}\frac{d_{liq}^2}{D_{liq}} \qquad (3)$$

where k is the ratio of moles of solute in the liquid to moles of solute in the gas, d_{liq} is the effective thickness of the liquid phase on the solid support and D_{liq} is the diffusion coefficient. In contrast to the second term, high diffusion coefficients minimise band broadening while high eluent gas velocities increase band broadening.

Experimental measurements of the diffusion coefficients of small solute molecules in high molecular weight viscous liquids are not very extensive, particularly over a range of temperatures. An estimate of the temperature dependence of diffusion coefficients may be made from viscosity measurements using the general relation that the diffusion coefficient is proportional to the absolute temperature divided by the viscosity. This quantity is plotted in Fig 4 for a variety of solvents.[10] Variations over many orders of magnitude are clearly indicated The temperature coefficient of viscosity, and hence of diffusion, appears to be particularly large for highly viscous liquids.

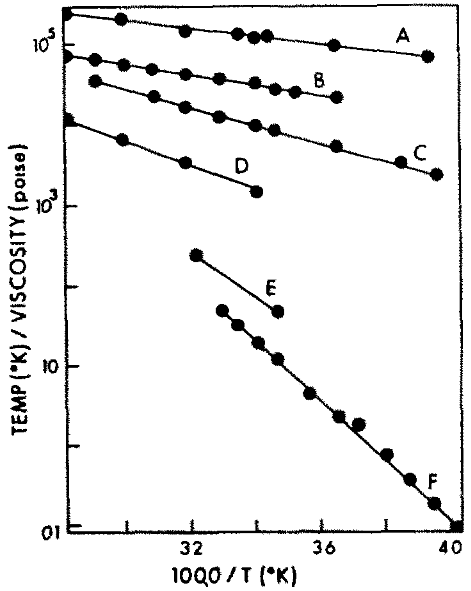

Fig 4 —Viscosity-temperature relations for various substances
A—ether, D—glycol,
B—carbon tetrachloride, E—heavy machine oil,
C—n-butyl alcohol, F—glycerol

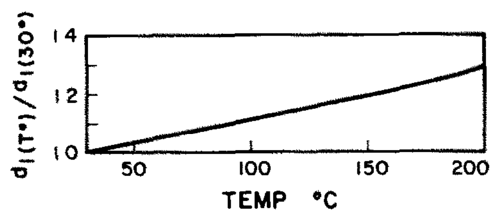

Fig. 5.—Relative thermal expansion of dinonylphthalate [$d_l(T°)$ is the effective thickness of liquid film at $T°$, $d_l(30°)$ is the effective thickness of film at 30°]

The absolute magnitude of the diffusion coefficient in liquids is very much smaller than in gases. Thus, Scott and Hazeldean[11] reported a value of $1{\cdot}1 \times 10^{-7}$ cm^2/sec for n-heptane in dinonylphthalate, which can be compared with a value of about 0·4 cm^2/sec for n-heptane in helium at a pressure of 1 atmos.

The remaining two factors contributing to C_{liq} [equation (3)] are also temperature dependent. The temperature dependence of the term d_{liq} is because of the thermal expansion of the liquid and Fig. 5 shows the relatively minor change in the relative value of d_{liq} as a function of temperature for dinonylphthalate.[12] Even though this factor is squared in equation (3) its temperature effect is still small.

Finally, the distribution ratio, k, as noted in the preceding section, varies exponentially with the reciprocal of the absolute temperature and hence will decrease strongly with increasing temperature. This is shown in Fig. 6 for three typical cases which are derived from the data of Fig. 3 and are chosen to represent cases of a substance with a very low retention volume, propane; one with an intermediate value, pentane; and one with a large retention volume, octane. The quantity $k/(1 + k)^2$ will have a maximum at k equal to 1 and thus starting from a high value of k at low temperature, $k/(1 + k)^2$ will first rise and then fall with temperature as shown in Fig. 7 for the same three examples. Normally k is somewhat greater than 1 for optimum chromatographic behaviour and, hence, the usual effect of increasing temperature will be to increase this factor.

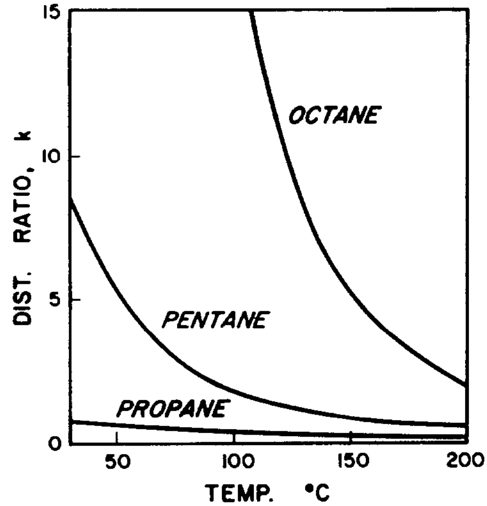

FIG. 6.—Distribution ratio, k, as a function of temperature for three hydrocarbons on an Apiezon L column using the data of Fig. 3.

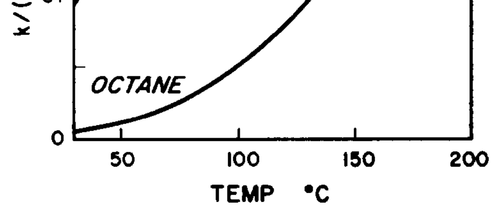

FIG. 7.—The factor $k/(1 + k)^2$ as a function of temperature for the three hydrocarbon systems.

When the temperature effects for all three factors of the third term are combined, the relative values of C_{liq} for the three hydrocarbon systems of Figs. 6 and 7 are obtained as functions of temperature (Fig. 8). In this figure it has been arbitrarily assumed that D_{liq} changes in the same way with temperature as does glycol, Fig. 4, and also that all three solutes have equal diffusivities. It can be seen that the highly volatile propane has a C_{liq} term decreasing strongly with temperature. For the more typical case of a strongly retained substance, such as octane, the factor is low and may even increase slightly with temperature. The contribution to plate height is equal to $C_{liq}\, uj$. For operation at constant mass flow rate u increases in proportion to temperature, while j decreases to an extent dependent upon the initial pressure drop across the column as explained in the first section. The product uj will increase with temperature and this effect must be considered along with the data of Fig. 8. The joint and competing effects of these various factors results in a complex temperature behaviour for the third term of equation (1).

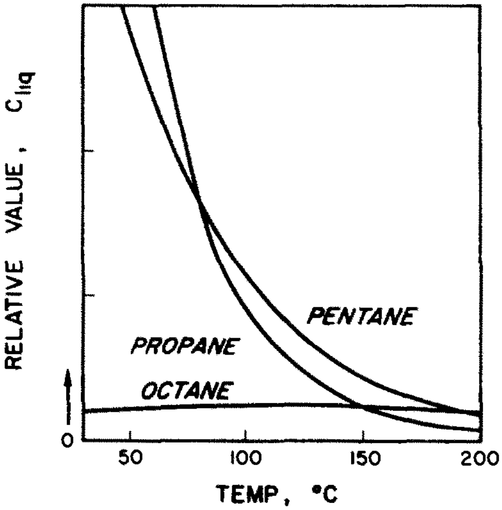

FIG. 8 —The relative value of the coefficient of resistance to mass transfer in the liquid phase, C_{liq}, as a function of temperautre.

Finally, the fourth term, $C_{gas}\, u$, refers to band broadening from resistance to mass transfer in the gas phase, where C_{gas} is a constant expressed in terms of the outlet conditions of the column. This term is probably the least well understood except for capillary columns.[3,13] As a general expression, Jones[2] has proposed that

$$C_{gas} = C_2 \frac{k^2}{(1+k)^2} \frac{d_{gas}}{D_{gas}} + C_3 \frac{d_p^{\,2}}{D_{gas}} + 2\rho(C_2C_3)^{\frac{1}{2}} \frac{k}{(1+k)} \frac{d_p\, d_{gas}}{D_{gas}} \tag{4}$$

where C_2 and C_3 are constants, d_{gas} is the average diffusion path length in the gas phase, d_p is the packing particle size and ρ is a factor between 0 and 1. These three factors refer to diffusion in the gas phase, mixing of streams of gas with different velocities and to interactions between these two effects. On the other hand, Giddings[14] has suggested that the major effect arises from the interactions of relatively high velocity portions of the gas stream in the large interparticle spaces with the relatively stagnant or low velocity portions, such as in intraparticle pores. Qualitatively, all of these contributions to the plate height show a decrease with increasing temperature, primarily because of the D_{gas} factor which increases according to the 1·81-power of the temperature [equation (2)] Factors involving k vary between 1 and 0, while d_{gas} would be expected to be essentially independent of temperature. To illustrate the magnitudes of the proposed effects Figs 9, 10 and 11 show relative values of the three gaseous resistance terms proposed by Jones for the widely variant situations represented by propane, pentane and octane cited before. It can be seen that the first and third factors decrease sharply with temperature, whereas the second decreases more slowly. The relative change in a factor, such as the one proposed by Giddings,[14] would be nearly identical with the curves for Jones' second factor. The over-all contribution of the fourth term, C_{gas} u, includes the contribution of the gas velocity. At constant mass flow rate it must be borne in mind that u increases in direct proportion to the temperature.

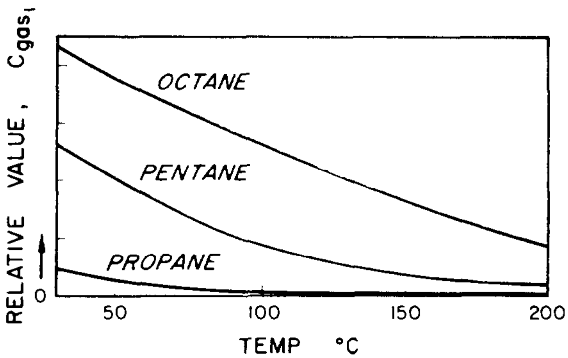

Fig 9.—The relative value of C_{gas_1}, the first term in equation (4), as a function of temperature

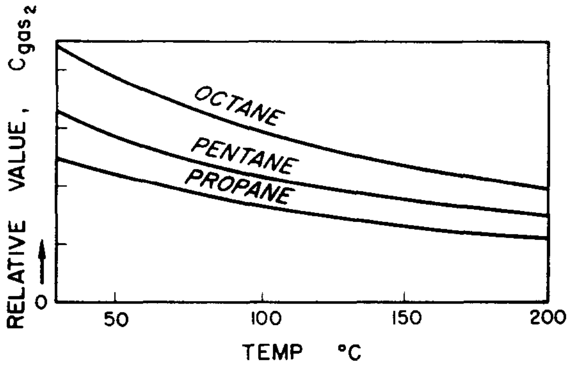

Fig. 10.—The relative value of C_{gas_2}, the second term in equation (4), as a function of temperature.

The contributions of the various terms of equation (1) to the final value of plate height for a particular column can vary independently over wide ranges. The data of the preceding figures and equations have been used to produce various sets of plate height—gas velocity curves (Fig. 12) for these same three hydrocarbon systems, propane, pentane and octane on Apiezon L, as representative of substances with low, intermediate and relatively high retention volumes. In order to combine the various terms of equation (1) the following conditions were specified:

1. The second term is 0·6 cm for propane at 30° and a value of u of 1 cm/sec. This is a reasonable value for a packed column at this low velocity.

2. The total contribution of the third and fourth terms is 0·1 cm for propane at the above conditions. This value for the mass transfer terms is arbitrary and would depend on the column packing.

3. The three contributions to C_{gas} in equation (4) apply in the ratio of 1·20·1. The proportions are arbitrary, but are influenced considerably by Giddings' conclusion.

4. Parts A, D and G of Fig. 12 are based on the term C_{liq} equal to the term C_{gas} for propane at 30°; parts B, E and H are based on C_{liq} equal to 10 C_{gas}; and parts C, F and J are based on C_{liq} equal to 100 C_{gas}, again for propane at 30°.

The results are further limited by the assumptions implied previously: helium carrier gas, outlet pressure of 1 atmos, negligible pressure drop, the term A equal to zero and a column liquid with the viscosity characteristics of glycol and the retention characteristics shown in Fig. 3. Following a usual convention the flow velocities shown are those measured at column temperature and at outlet pressure If the velocity is expressed at some standard temperature in order to make comparisons under conditions of constant mass flow rate, then the figures are qualitatively similar but with the high temperature curves compressed towards the vertical axis.

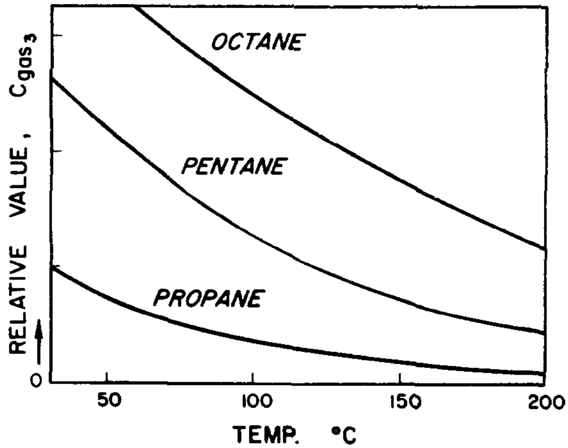

FIG. 11.—The relative value of C_{gas_3}, the third term in equation (4), as a function of temperature.

Fig. 12 illustrates most of the characteristics identifiable in experimentally observed curves. If one bears in mind that most chromatographic separations are based on k values in the range of 1 to 5, it can be seen from Fig. 6 that the three systems illustrated in Fig. 12 cover a much wider range of conditions than are usually employed in practice. Even at the lowest temperature of 30°, propane is still at the lower limit of useful retention while octane is only within this range in the upper 50° of the temperatures chosen.

At low velocities the predominant contribution to plate height arises from the term B, which decreases with decreasing temperature or increasing molecular weight of the sample component. The contribution of the term B becomes small at high velocities and for this reason will not be discussed in further detail.

At high velocities the mass transfer terms predominate. The general effect obvious from the various charts is a decrease in mass transfer resistance with increasing temperature although the curves in J are approaching the opposite behaviour.

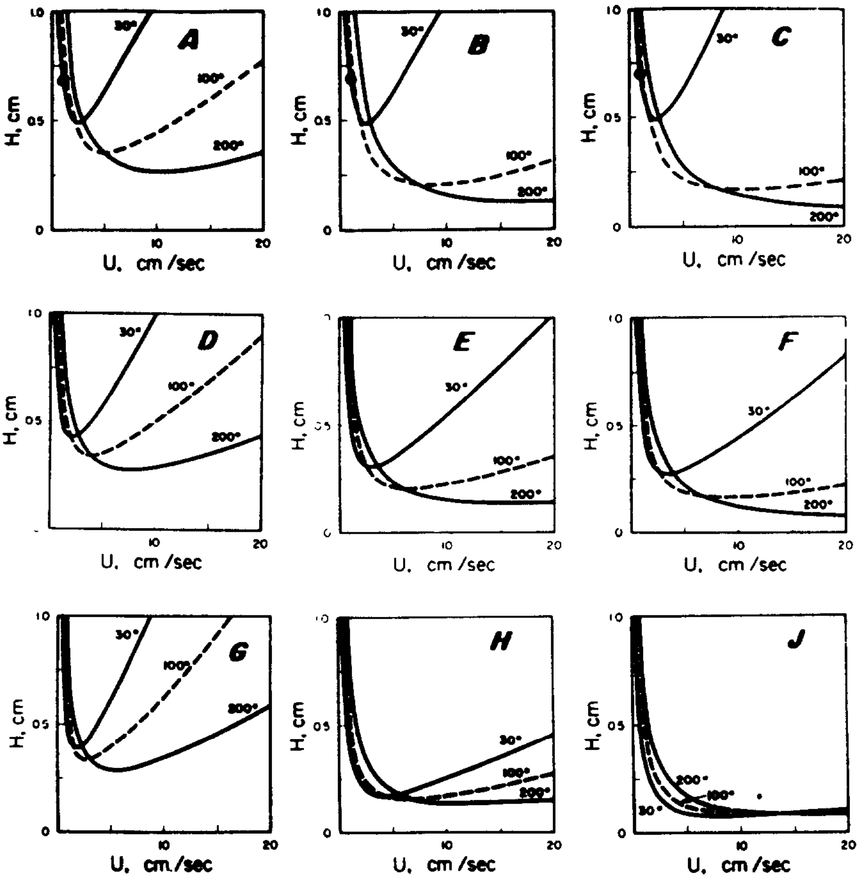

Fig. 12.—Calculated plate height—gas velocity curves for the same three systems of the previous figures at three temperatures and based on three arbitrary ratios of 1, 10 and 100 for C_{liq} to C_{gas} for propane at 30° [B/u of equation (1) taken as 0·6 cm and ($C_{liq}\,u + C_{gas}\,u$) taken as 0·1 cm for propane at 30° and u of 1 cm/sec]:

Temperature		30°		100°		200°	
Chart	Compound	C_{liq}	C_{gas}	C_{liq}	C_{gas}	C_{liq}	C_{gas}
A	propane	50	50	4·7	39	0·5	20
B	propane	91	9·1	8·6	7·1	0·8	3·7
C	propane	99	1·0	9·4	0·8	0·9	0·4
D	pentane	20	78	5·8	48	1·0	28
E	pentane	35	14	10	·87	1·8	5·1
F	pentane	38	1·6	12	0·9	2·0	0·5
G	octane	1·0	109	1·3	71	1·0	42
H	octane	1·9	20	2·4	13	1·8	7·6
J	octane	2·1	2·2	2·6	1·4	2·0	0·8

C_{liq} and C_{gas} given in sec × 10^3.

Charts A, D and G are based on equal contributions of the liquid- and gas-phase resistance to mass transfer for propane at 30°. The initial high temperature coefficient of C_{liq} for propane as well as the relative positions of the curves in Figs. 8 and 10 mean that the gas-phase contribution predominates at most temperatures and at all temperatures for the higher hydrocarbons. Thus, for instance, in A at 200° the contribution of liquid resistance to mass transfer is only about 2% of the gas-phase resistance. Charts A, D and G therefore illustrate the case of gas resistance being the major contribution to plate height. Under these conditions it is clearly advantageous to work at high temperatures. Furthermore, because of the relatively small effect of the distribution ratio on the value of C_{gas}, the curves for the different hydrocarbons are very similar to each other and high efficiencies may be attained at high temperatures for all components in an analysis. This type of operation is characteristic of most capillary columns which would therefore be expected to show a marked increase in efficiency with higher temperatures. This has been clearly demonstrated by Scott.[13]

At the other extreme in charts C, F and J, which are based on C_{liq} equal to 100 C_{gas} for propane at 30°, one sees curves in which liquid-phase resistance is generally predominant. At 200° both liquid and gas resistance to mass transfer are of the same order. Other generalisations are difficult because of the competing effects involved in the temperature coefficient of C_{liq}. With propane the decrease in $k/(1 + k)^2$ and of $1/D_{\mathrm{liq}}$ with temperature combine to show marked increases in efficiency with increasing temperature in the range 30° to 100°. With pentane the large change in the factor $1/D_{\mathrm{liq}}$ over-rides the increase in $k/(1 + k)^2$ in this same temperature interval and the curves are similar to those for propane. For octane the factors approximately compensate at all temperatures. Under these conditions the efficiencies may vary widely for the different components in a sample.

A case presumably similar to that in chart F has been described by Duffield and Rogers.[15] These authors have shown that liquid-phase viscosity affected plate height as would be expected for a column in which C_{liq} is controlling.

In a comparison of different ratios of liquid and gas resistances, such as shown in any horizontal row in Fig. 12, the effects to be expected will depend mostly on the type of temperature behaviour of the C_{liq} factor. Thus, for propane where C_{gas} and C_{liq} are qualitatively similar the temperature effects are not grossly different. For octane where the temperature coefficients of C_{gas} and C_{liq} are of the opposite sign over a wide temperature range, profound changes in the curves become evident in going from G to J.

It is not feasible to attempt to describe all of the possible extrapolations of the data shown in Fig. 12 to other possible conditions involving changes in gas and liquid properties. One case of possible interest would involve greater predominance of liquid-phase resistance, relatively high retention volume and possibly a lower temperature coefficient of liquid viscosity. A combination of these effects could lead to a marked decrease in column efficiency with increasing temperature, such as was almost reached in chart J. The curves shown in Fig. 13 may be an example of this sort. This figure shows the usual behaviour between 30° and 50°, but above 50° the efficiency appears to decrease with increasing temperature.

Further analysis of the relationships depicted in Fig. 12 may be made by considering the minimum plate height or maximum efficiency values and the corresponding velocities. The gas velocity at the minimum[16] in the plate height—velocity curves

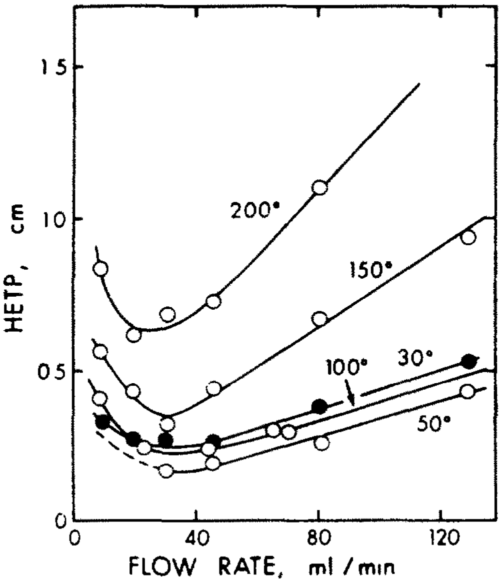

Fig 13.—Plate height—gas velocity curves for n-hexane at a series of temperatures on a 2-M Apiezon L column using hydrogen as the carrier gas

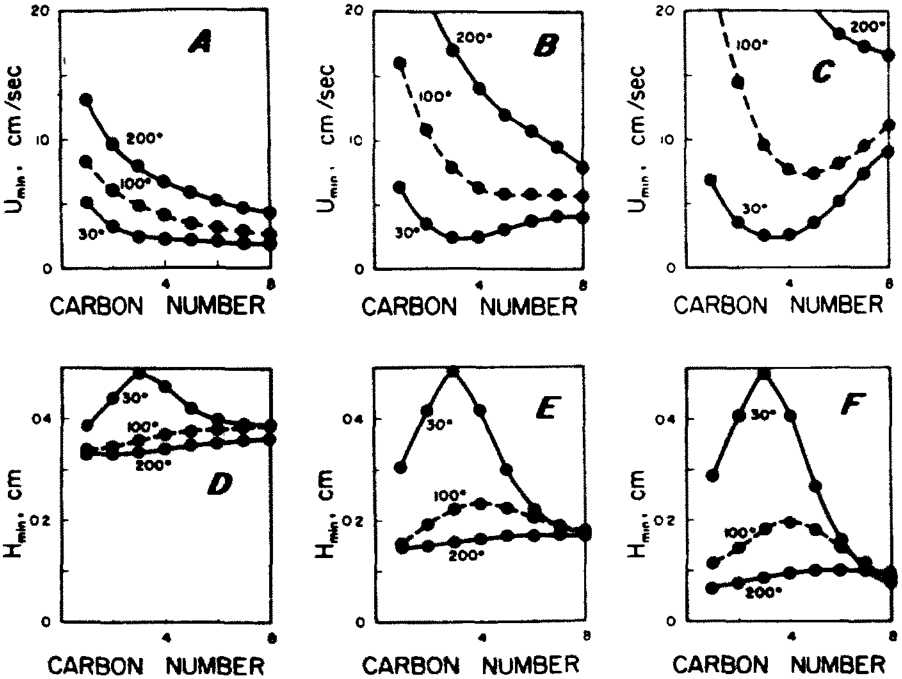

Fig 14 —Optimum velocity and minimum plate height as a function of carbon number and temperature for hydrocarbons under conditions specified in Fig 12·

A and D—Based on C_{liq} equal to C_{gas} for propane at 30°,
B and E—Based on C_{liq} equal to 10 C_{gas} for propane at 30°,
C and F—Based on C_{liq} equal to 100 C_{gas} for propane at 30°

at any one temperature is equal to $\sqrt{B/(C_{\text{liq}} + C_{\text{gas}})}$ and the value of the plate height at this minimum velocity is equal to $A - 2\sqrt{B(C_{\text{liq}} + C_{\text{gas}})}$. In Fig. 14 these two quantities are shown as a function of carbon number at three column temperatures and for the three $C_{\text{liq}}/C_{\text{gas}}$ conditions illustrated in Fig. 12. Reasonable estimates of the values of the retention characteristics of hydrocarbons not shown in Fig. 3 have been made. One may say generally that, for any one hydrocarbon, with increasing temperature the gas velocity at the minimum increases (charts A, B and C) and the H_{min} decreases (charts D, E and F). These effects are independent of the ratio of liquid- and gas-phase mass transfer resistances, although for octane in chart F a slight reverse trend in H_{min} is apparent. As indicated in the earlier discussion and possibly suggested in Fig. 13, this decrease in optimum efficiency with increasing temperature may occasionally be of some practical significance. At constant temperature the optimum velocity may decrease regularly with carbon number where gas phase resistances tend to predominate as in chart A; or it may show a more complex behaviour when liquid phase resistances become significant as in charts B and C. The H_{min} values are relatively independent of carbon number at higher temperatures but vary considerably through a maximum at lower temperatures. The variations in both U_{min} and H_{min} are greatest when liquid-phase resistances predominate.

It is obvious from Figs. 12 and 14 that flow conditions cannot be chosen at any one temperature which will result in maximum efficiencies for all solutes. This is recognised in chromatographic practice in that a gas velocity greater than the minimum is usually chosen.

It should be emphasised that while the conditions assumed for the construction of the curves in Figs 12 and 14 may exemplify actual chromatographic conditions there are innumerable alternatives. For example, the mass transfer terms may be larger or smaller compared to the longitudinal diffusion term, the gaseous mass transfer term may be more or less important, *etc*. Normally, one attempts by appropriate selection of design and operating variables to minimise both mass transfer contributions to plate height. Thus, changing the carrier gas to one with low diffusivity will decrease the longitudinal diffusion term but increase the term C_{gas} and leave the term C_{liq} unchanged. The relative values of C_{gas} and C_{liq} will also depend on column or particle dimensions and on the manner in which the liquid is distributed on the support. The effects of various combinations can be deduced from reasonable extensions of the data given by the curves shown in Fig. 12 For example, a ten-fold decrease of the terms C_{liq} and C_{gas} of A, D and G would produce three new figures all very similar to H.

Zusammenfassung—Der zu erwartende Temperatureinfluß auf die Wirksamkeit von Säulen wird im einzelnen fur typische Verbindungen niedriger, mittlerer und hoher Retention erörtert. Es werden Fälle mit verschieden großer Hemmung des Massenüberganges in Gas- und flüssiger Phase betrachtet. Es wird gefolgert, daß bei einer Temperatur keine für alle gelosten Stoffe optimal wirksamen Strömungsbedingungen zu finden sind. Es ist auch zu erwarten, daß die Wirksamkeit der Säule im allgemeinen mit steigender Temperatur zunehmen sollte, obwohl unter gewissen Bedingungen, nämlich starker Hemmung des Massenüberganges in der flüssigen Phase relativ zur Gasphase, ein Abfall oder scheinbare Unabhängigkeit von der Temperaturge funden werden kann. Außerdem wird kurz der Einfluß der Säulentemperatur auf den Druckabfall längs der Säule untersucht.

Résumé—On étudie en détail les effets de la température sur l'efficacité d'une colonne dans le cas de composés caractéristiques de haute, moyenne et basse rétention. On analyse des exemples comportant diverses valeurs relatives de la résistance au transfert de masse tant en phase liquide qu'en phase vapeur. On montre qu'on ne peut trouver des conditions de reflux à une température donnée, telles qu'on puisse obtenir l'efficacité maximale pour tous les solutés. On montre également que l'efficacité de colonne croit généralement avec la température. Cependant, dans certaines conditions, si le rapport des résistances au transfert de masse en phase liquide et en phase gazeuse est grand, on peut rencontrer une décroissance ou une pseudo-indépendance par rapport à la température. On examine également brièvement la variation de la température de la colonne sur la chute de pression le long de la colonne.

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THERMOMETRIC TITRATIONS IN ACETONITRILE

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Summary—The use of acetonitrile as a medium for thermometric acid-base titrations has been studied. Satisfactory titrations are obtainable for a wide variety of amines and organic acids, but the instability of the solvent in the presence of strong bases greatly limits its practical applicability. Data are given on the heats of neutralisation of various acids in acetonitrile, and the results for *m*- and *p*-substituted benzoic acids are shown to correlate well with their Hammett σ-values.

INTRODUCTION

THE advantages of performing acid-base titrations in non-aqueous systems are well known. The limitations of conventional methods of end-point detection have led to the exploration of alternatives. One of these, automatic thermometric titrations, introduced by Linde, Rogers and Hume,[1] is particularly well adapted to non-aqueous systems because of its independence of the chemical nature of the solvent and reactant. A general review has been given by Zenchelsky.[2] The applicability of thermometric titration to non-aqueous acid-base titrations in glacial acetic acid has been studied by Keily and Hume.[3] The present paper describes the investigation of acid-base titrations in acetonitrile.

Acetonitrile is a good solvent for a wide variety of organic acids and bases. Being very weakly basic and having negligible acidic properties, it permits titrations to be made over a very wide range of acidity as compared to water. Fritz,[4] carrying out potentiometric titrations with a glass-calomel electrode pair, showed that acetonitrile was a suitable solvent for differentiating titrations of strong and weak bases. Critchfield and Johnson[5] demonstrated acetonitrile to be a satisfactory solvent for differentiating potentiometric titrations of relatively strong acids. This lack of leveling action also shows in its range between the half-neutralisation potentials of strong acids and strong bases which Van der Heijde and Dahmen[6] observed to be one of the widest among the solvents which have been studied, being better in this respect than acetic acid, dimethylformamide, ethanol or amines. In practice, however, the range is limited somewhat by the effect of very strong bases, such as hydroxide ion or alkoxide, which catalyse the polymerisation of solvent.

EXPERIMENTAL

Apparatus

The instrumental set-up used was that designed, built and employed by Keily.[7] A constant-flow, motor-driven syringe burette delivers titrant into the sample, which is contained in a half-pint Dewar flask. The flask carries a Plexiglass cover insulated with cork, which holds the measuring thermistor, a glass-covered wire heater, and has holes for the burette tip and the shaft of a 600-rpm stirrer. The temperature of the titration mixture is measured continuously by a thermistor in a Wheatstone bridge circuit and recorded on a Speedomax G, 2-mV potentiometer-recorder. Pen displacement has been shown to be linear with temperature changes over a range of several tenths of a degree, and the instrument at the highest sensitivity responds to a change of 0 001 Titrations were performed by first adjusting the temperature of the sample to that of the titrant, then running in the titrant at constant speed with a continual recording of the temperature

Reagents

Acetonitrile Material obtained from Carbide and Carbon Chemicals Co was used throughout this work The water content of the material as received was of the order of 0 1% (by Karl Fischer titration) and, occasionally, small amounts of weakly acid impurities appeared in individual batches The presence of acidic impurity was tested for by the addition of 1 drop of thymol blue (salt form) to about 5 ml of solvent In satisfactory material the colour should be yellow (red indicates acidic impurity) and should change to blue upon the addition of not more than 1 drop of 0 1*M* sodium methoxide in methanol [7] Water and other impurities were removed in either of two ways One method consisted of predrying with anhydrous potassium carbonate, then distilling over phosphorus pentoxide This gave an excellent product at the expense of considerable time and effort. Another method which was employed throughout the bulk of this work involved drying the solvent by placing it in contact with Type 4A molecular sieves (Linde Air Products Co.) for at least 15 min before use The solvent treated in this way was found to contain less than 0·01% of water and the absorbant properties of these sieves were sufficient to remove small amounts of acid impurities.

Substances titrated Most of the bases titrated were subjected to some preliminary treatment or purification. They were of the best grades readily available, and all were Eastman White Label products unless otherwise noted Compounds used without further purification were *p*-toluidine, *p*-bromaniline, *m*-nitro-aniline, ethylamine (anhydrous), trimethylamine (anhydrous), isopropylamine and urea (Merck U S.P.).

Compounds distilled under vacuum were *o*-chloraniline, *N,N*-dimethylaniline, *N,N*-diethylaniline, *N*-methylaniline, aniline (Fisher Reagent), *p*-chloraniline (Eastman Practical), tri-n-butylamine (over sodium hydroxide) and tri-isobutylamine (Kahlbaum over sodium hydroxide).

Compounds subjected to simple distillation were isobutylamine (over calcium oxide), tert-butylamine (over calcium oxide), n-butylamine (over calcium oxide), 1-ethylpiperidine, pyridine (Mallinckrodt Reagent over sodium hydroxide), morpholine (Carbide and Carbon Co. over sodium hydroxide), n-propylamine (over sodium hydroxide), di-n-butylamine (over sodium hydroxide), diethylamine (Sharples Commercial over sodium hydroxide), triethylamine (Sharples Commercial over sodium hydroxide), sec-butylamine (Sharples over sodium hydroxide), di-sec-butylamine (Sharples over sodium hydroxide), and di-isopropylamine (Eastman Yellow Label over sodium hydroxide).

Ammonia (Matheson Co, Anhydrous) was passed through No. 4A Molecular Sieves (Linde Air Products Co.), then dissolved by passing it over a stirred volume of acetonitrile The *p*-nitroaniline and *p*-chloraniline were recrystallised from ethanol and air-dried, while *p*-anisidine was recrystallised once from water and once from 10% methanol-water solution and finally washed with iced water and air-dried

Compounds titrated as acids were prepared or purified in the following ways. No further purification was given to benzoic acid, *p*-toluic acid, *m*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-chlorobenzoic acid, *m*-chlorobenzoic acid, *m*-bromobenzoic acid, glacial acetic acid (duPont 99 7%), formic acid (Baker and Adamson 98–100%) or sulphuric acid (duPont 98%).

Monochloracetic acid was dried over phosphorus pentoxide for 24 hr, then vacuum-sublimed at about 60°. Dichloracetic acid (Eastman technical grade) was vacuum-distilled and trichloracetic acid (Mallinckrodt Reagent) was dried for 1 week over magnesium perchlorate and vacuum-sublimed at about 60°. The water content of the compounds before solution in acetonitrile was determined by Karl Fischer titration and found to be 0 25%, 0 12% and 0·09% for the mono-, di- and trichloracetic acid, respectively.

Titrants Hydrogen bromide solutions in acetonitrile were used for the titration of organic bases The titrant was usually made up to a concentration of approximately 0·1*M*. Solutions were prepared by passing anhydrous hydrogen bromide (Matheson Co.) through a drying tower containing anhydrous magnesium perchlorate and silica gel and then over the surface of the acetonitrile, which was being stirred vigorously with a magnetic stirrer. The resulting solutions generally developed a yellow colour in a period of 1–2 hr, but appeared to be stable thereafter A similar colour developed when anhydrous solutions of hydrogen chloride were prepared, or when attempts were made to prepare anhydrous solutions of perchloric acid in acetonitrile. Hydrogen bromide appears to have a considerable vapour pressure over acetonitrile solutions: standard solutions were observed to decrease in strength by about 1% per day For this reason the titrants were standardised daily by diluting aliquots with water and titrating with standard sodium hydroxide using a potentiometric end-point.

Diphenylguanidine solutions were used to titrate acids. Eastman White Label 1,3-diphenylguanidine was recrystallised successively from toluene, ethanol and again from toluene before being dried at 110° over-night. The resulting product was found to be 99·7+% pure by titration with standard aqueous hydrochloric acid. Titrant solutions made with this product were colour-stable and did not change titre appreciably over a period of at least 1 month.

Procedure

The bases listed previously were all titrated with approximately 0·1*M* hydrogen bromide in acetonitrile. The solutions titrated were made up to about ten-fold more dilute than the titrant. In each instance, 15-ml portions were titrated. No corrections were made for density variations because all titrations were performed in an air-conditioned room with temperature fluctuations $> \pm 1^{\circ}$. In order to estimate the accuracy of the method, comparison was made between concentrations determined thermometrically and those determined by conventional methods. The concentration of aliphatic amines was determined by diluting aliquots about five-fold in water and titrating with standard aqueous hydrochloric acid, using either a glass-calomel potentiometric end-point or a methyl red-methylene blue mixed indicator. Aromatic amine concentrations were determined by dissolving aliquots in glacial acetic acid and titrating with perchloric acid in glacial acetic acid. The perchloric acid was standardised against potassium hydrogen phthalate using a glass-calomel electrode pair for potentiometric end-point determination.

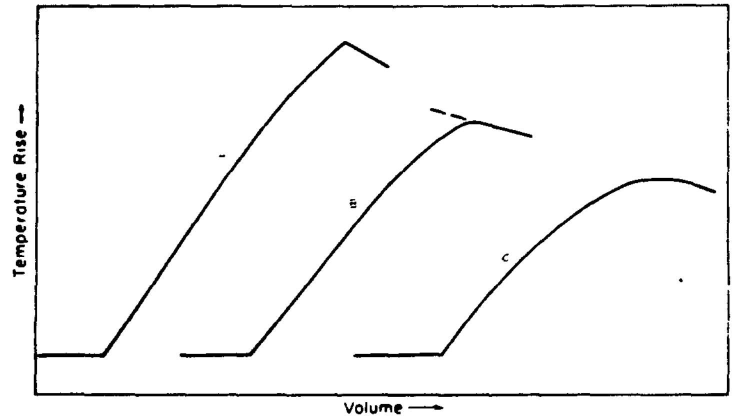

FIG. 1.—Typical titration curves of bases with a strong acid in anhydrous acetonitrile medium.

(A) aliphatic amines, (B) aromatic amines, (C) very weak bases

RESULTS

Thermometric titration end-points consist of a change in slope of a temperature *vs.* volume curve. Typical curve shapes for the systems studied in this investigation are illustrated in Fig. 1. The ease of end-point estimation is evidently dependent upon the sharpness of the slope change. This, in turn, is related to two fundamental factors: the magnitude of the free-energy change of the reaction and the change in enthalpy which accompanies the reaction. Because it is the free-energy change which determines whether and how far a reaction will go towards completion, the magnitude of this term is of fundamental importance. Assuming a favourable free-energy change, the sharpness of the end-point break will be determined by the magnitude of the enthalpy change: the larger the change, the more acute the change in slope at the equivalence point. If the free-energy change in not favourable, there will be a rounded end-point because of the incompleteness of the reaction at the equivalence point, regardless of the magnitude of the enthalpy term. Because the temperature rise in thermometric titrations is nearly linear, rounded end-points may be estimated by extrapolation of the slopes before and after the highly curved portion of the plot. The general theory of the shape and characteristics of thermometric titration curves has been discussed by Keily and Hume.[9]

Titration of bases

Fig. 1 illustrates the general shapes of titration curves obtained for the titration of strong, weak and very weak bases with hydrogen bromide solution. It demonstrates the rough rule that sharpness of the end-point depends on the strength of the base titrated. This generalisation held in a qualitative sense for all of the bases titrated in this study. It is evident, however, from the data of Table I showing the precision and accuracy obtained in the titration of 17 non-aromatic amines that sharpness of the end-point is not the only factor which affects the precision and accuracy. The bases in Table I are listed in the general order of decreasing strength as determined by ionisation constant in water. It was noted that the precision for a number of the more volatile compounds was lower than that for the average, and this is probably a factor which contributes to the considerable range in standard deviations observed. The over-all percentage standard deviation from the pooled data of all of the titrations of bases is ±0·52%. This precision is poorer than the ±0·2% reported by Linde, Rogers and Hume for thermometric titrations in water[1] and by Keily and Hume for glacial acetic acid.[3] The observed precisions are similar to those reported by Fritz for potentiometric titrations.[4] It is of interest to note that the precision of titration of very weak bases was not significantly different from that of the over-all precision, even though the accuracy was lower. Table II shows results for aromatic and heterocyclic amines. With the exception of the values for *p*-bromaniline and *m*-chloraniline, the average accuracy is 99·2%. The latter compound defined the limits of practical titrability using the thermometric end-point in acetonitrile. All weaker bases, as measured by their pK_B values in water, gave thermometric curves which were so rounded that no significant change in slope could be seen to define the end-point. The weakest bases with discernible end-points have aqueous pK_B values in the range of 10–10·5. As is evident in the accuracy values for *p*-brom- and *m*-chloraniline, the tendency is for the observed end-point to err on the high side in the titration of very weak bases. A similar tendency is apparent in Keily's data for the titrations of the very weak bases, urea and acetanilide, in glacial acetic acid.[3]

TABLE I.—TITRATION OF NON-AROMATIC AMINES

Compound	No. of detns.	Present, *mmole*	Found *mmole*	Accuracy, %	Std. devn., %
Di-n-butylamine	4	0·600	0·598	99·7	0·14
Diethylamine	3	0·595	0·598	100·5	0·40
Di-sec-butylamine	4	0·285	0·281	98·6	0·76
Di-isopropylamine	3	0·130	0·129	99·2	1·56
Tri-n-butylamine	4	0·598	0·595	99·5	0·56
Ethylamine	3	0·535	0·529	98·9	0·93
Triethylamine	4	0·439	0·436	99·3	1·10
Isopropylamine	2	0·700	0·693	99·0	1·64
n-Butylamine	4	0·540	0·537	99·4	1·0
n-Propylamine	4	0·445	0·440	98·9	0·40
Sec-butylamine	2	0·535	0·531	99·3	0·0
Tert-butylamine	4	0·449	0·446	99·3	0·35
Iso-butylamine	3	0·995	0·983	98·3	0·70
1-Ethylpiperidine	4	0·111	0·110	99·1	0·97
Tri-isobutylamine	4	0·365	0·361	98·9	0·26
1,3-Diphenylguanidine	4	0·7079	0·7057	99·7	0·57
Ammonia	4	1·320	1·316	99·7	0·95

TABLE II.—TITRATION OF AROMATIC AMINES AND OTHER WEAK BASES

Compound	No. of detns.	Present, *mmole*	Found, *mmole*	Accuracy, %	Std devn., %
Morpholine	4	0·424	0·420	99·1	0·85
N,*N*-Diethylaniline	4	0·457	0·449	99·1	1·03
p-Anisidine	3	0·640	0·634	99·1	0·40
Pyridine	4	0·590	0·584	99·0	0·74
p-Toluidine	4	0·828	0·824	99·5	0·23
N,*N*-Dimethylaniline	3	0·610	0·604	99·0	0·94
N-Methylaniline	3	0·640	0·628	98·1	1·14
Aniline	4	0·930	0·918	98·7	0·78
p-Chloraniline	4	1·028	1·033	100·5	1·23
p-Bromaniline	4	0·794	0·823	103·6	0·21
m-Chloraniline	4	0·820	0·853	104	1·12
o-Chloraniline	5		too weak to titrate		
m-Nitroaniline	3		too weak to titrate		
p-Nitroaniline	6		too weak to titrate		
Urea	4		too weak to titrate		

The effect of precipitation of insoluble hydrobromides during the titration is seen in Fig. 2. The sudden appearance of the heat of precipitation distorts the curve but need not affect the accuracy of locating the end-point if the onset of precipitation is not too close to the end-point. The heat of neutralisation may, of course, be estimated independently of the precipitation by the use of the initial slope.

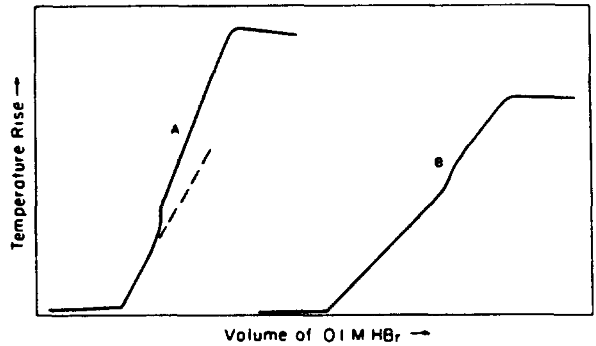

FIG. 2.—The effect of delayed precipitation during titration:
(A) aniline with hydrogen bromide,
(B) *p*-toluidine with hydrogen bromide

Differentiating titration of bases

The criteria for a good differentiating end-point are evident from a consideration of the factors affecting the thermometric end-point in general. For successful thermometric differentiation, not only must the free-energy change for each component in the mixture be great enough to assure completeness of reaction, and the free energies be sufficiently different that the reactions take place consecutively, rather than simultaneously, but the enthalpy change for each component must be sufficiently different that a significant change in slope can be recognised. It is difficult to say exactly how much of a difference in ΔH is essential to end-point discernment because in real titrations extraneous factors, such as heats of dilution, heat loss and changing heat capacity from addition of titrant, also act to obscure end-points. It appears that roughly a slope ratio of the order of 3 2 for the components is necessary in order that the break be clearly defined It has been shown that in acetonitrile there is a remarkably constant proportionality between ΔH and pK_B for amines of similar type [10] Because the slopes of thermometric titration curves are proportional to ΔH, this means that two bases which are sufficiently different in strength to be titrated consecutively are likely to have thermometric slope ratios favourable for differentiating titration in acetonitrile. As an illustration of the types of curves obtained, Fig. 3 shows the titration of mixtures of 1,3-diphenylguanidine (ΔH = 20·7 Kcal/mole) plus pyridine (ΔH = 14·4 Kcal/mole), and mixtures of *N*-butylamine (ΔH = 25·8 Kcal/mol) plus pyridine. The titration of the diphenylguanidine-pyridine mixture is illustrative of borderline conditions of titrability. The precisions of the two end-points (standard deviation) are 1·14 and 1·16%, respectively The titration curve for butylamine and pyridine is an example of an easily differentiated mixture Precisions of these end-points are 0 5% and 0·61%, respectively.

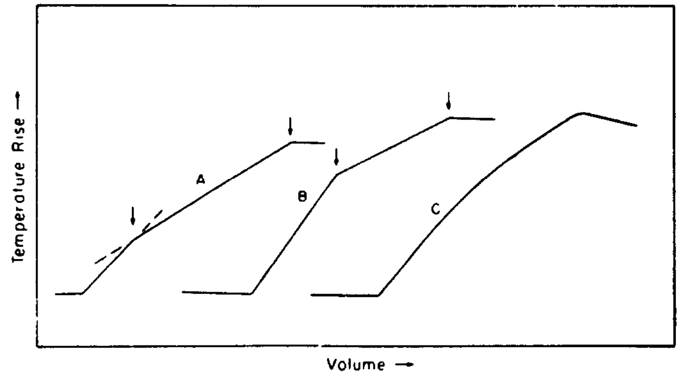

FIG 3 —Differentiating titrations·
(A) 1,3-diphenylguanidine and pyridine with hydrogen bromide,
(B) *n*-butylamine and pyridine with hydrogen bromide,
(C) Sulfuric acid with 1,3-diphenylguanidine.

Titration of acids

The list of acids titrated with diphenylguanidine solution is given in Table III. The weakest acid that showed a distinct end-point was benzoic (pK_a in water 4·20). Acetic acid and *p*-toluic acids were too weak to be estimated thermometrically, in agreement with Kilpatrick,[8] who found that acetic acid could not be titrated in acetonitrile using indicators The reason for the limitation to relatively strong acids is related to the instability of the solvent in the presence of strong bases. Presumably, if one could titrate with bases stronger than diphenylguanidine or aliphatic amines, the range of titrability could be greatly extended. This is indicated by the work of Bruss and Wyld,[11] who claimed that acids as weak as the phenols could be titrated in acetonitrile if tetrabutylammonium hydroxide in isopropyl alcohol was used as titrant. Attempts to dissolve bases such as potassium hydroxide or sodium methoxide in acetonitrile resulted in the formation of a reddish-brown gelatinous residue, presumably polymeric in nature. The over-all pooled percentage standard deviation for the titration of acids was found to be 0·99%.

TABLE III.—TITRATION OF ACIDS WITH 1,3-DIPHENYLGUANIDINE

Acid	No. of detns	Present, *mmole*	Found, *mmole*	Accuracy, %	Std Devn, %
Benzoic	3	0·302	0·309	102·3	1·21
p-Chlorobenzoic	3	0·269	0·275	102·3	2·4
m-Chlorobenzoic	3	0·0910	0·0903	99·2	1·55
m-Bromobenzoic	3	0·240	0·243	101·3	1·35
m-Nitrobenzoic	3	0·449	0·445	99·1	1·05
p-Nitrobenzoic	3	0·296	0·300	101·4	2·18
p-Toluic	6		too weak for end-point estimation		
Acetic	4		too weak for end-point estimation		
Chloracetic	2	0·470	0·476	101·3	1·58
Dichloracetic	3	0·313	0·311	99·4	0·60
Trichloracetic	3	0·114	0·113	99·1	2·08
Hydrogen chloride	3	0·606	0·603	99·5	0·47
Hydrogen bromide	4	0·428	0·424	99·1	0·77
Sulphuric[a]	3	0·426	0·424	99·5	0·33
Perchloric[b]	3	0·350	0·348	99·4	0·13
				pooled = ±0·99%	

[a] Both protons

[b] Filtrate from barium perchlorate plus sulphuric acid reaction.

The titration of sulphuric acid with 1,3-diphenylguanidine is also shown in Fig. 3. Critchfield and Johnson showed that the two protons of sulphuric acid can be distinguished potentiometrically by titration with morpholine in acetonitrile solution. In the present instance, the free energy criterion appears to be fulfilled, but the difference in the heats of neutralisation of the two protons is not sufficiently great to allow a distinct evaluation of the first end-point.

Effect of water

Unfavourable effects from the presence of water in non-aqueous titration systems have been noticed by many authors. For the most part, interference from water is associated either with its acid-base properties or its high dielectric constant. Keily and Hume have also pointed out the problems from the heats of dilution and mixing that may result from the presence of even minute amounts of water.[3]

The situation is even more complex in acetonitrile where the possibility of acid- or base-catalysed hydrolysis of the solvent must also be considered. In the titration of solutions of hydrogen chloride with diphenylguanidine, there is little effect from the presence of 1–2% of water added immediately before the titration. If, however, as short a time as 1 hr elapses between the addition of water to the acid solution and the titration, as little as 0·5% of water can result in sufficient hydrolysis of the solvent to obscure the entire titration curve. On the other hand, there appears to be little perceptible effect of water on the titration of bases with hydrogen bromide.

In contrast with the behaviour of dry acetic acid systems, the presence of small amounts of water was found to have very little effect on the heat of dilution of the titrants. On running 0·1*M* hydrogen bromide into 50-ml portions of acetonitrile containing varying amounts of water, linear dilution curves of low slope were obtained. Even with 1% of water present, the temperature rise did not exceed 0·08°. Mixing studies with diphenylguanidine titrant and acetonitrile-water mixtures yielded similar results.

TABLE IV—HEATS OF REACTION OF ACIDS WITH 1,3-DIPHENYLGUANIDINE

Acid	No of detns	$-\Delta H_{150}$, *Kcal/mole*	Std devn, *Kcal/mole*	$pK_{A(H_2O)}$
Benzoic	3	12 4	0 2	4 20
p-Chlorobenzoic	4	12 8	0 8	3 98
m-Chlorobenzoic	4	12 8	0 3	3 82
m-Bromobenzoic	3	12 8	0 1	3 81
m-Nitrobenzoic	5	15 4	0 6	3 49
p-Nitrobenzoic	7	13 4	0 4	3 42
Chloracetic	5	13 6	0 9	2 86
Dichloracetic	3	15 7	0 5	1 30
Trichloracetic	3	19 2	0 6	0 89
Hydrogen bromide	3	20 3	0 2	—
Hydrogen chloride	7	25 3	0 7	—
Sulphuric[a]	6	20 4	1 4	—
Perchloric[b]	4	17 4	0 8	—
Perchloric[c]	4	17 6	0 5	—

[a] First proton

[b] Filtrate from barium perchlorate plus sulphuric acid reaction

[c] Contains excess glacial acetic acid

DISCUSSION

Although satisfactory titrations may be obtained both for the titration of acids and of bases, the use of acetonitrile as a medium for acid-base titration with a thermometric end-point has no real advantage from a practical standpoint. The instability of the solvent in the presence of strong bases makes the determination of weak acids impractical, and the difficulty of preparing stable anhydrous acetonitrile solutions of strong acids is a drawback for the determination of bases. Attempts to prepare anhydrous acetonitrile solutions of perchloric acid by metathetical reactions were unsuccessful. For example, although barium sulphate is very insoluble in acetonitrile, a mixture of barium perchlorate and sulphuric acid continued to deposit a precipitate after equilibration for 6 months. Hydrogen bromide, in spite of its volatility, was the most satisfactory of the strong acids investigated. The utilisation of reagent solutions in solvents other than acetonitrile (*e.g.*, higher alcohols, ketones, dioxan) for titrations in an acetonitrile medium may generally be expected to give rise to heats of mixing and dilution which distort the titration curves and may not always be compensatable by differential temperature measurements.

The heats of reaction of carboxylic and mineral acids in acetonitrile with 1,3-diphenylguanidine are given in Table IV. It was of interest to see if the same sort of relationship existed between the heats of neutralisation of the carboxylic acids in acetonitrile and their acid strengths as was found to exist between the heats of neutralisation and basic strengths of amines in the same solvent.[10] The plot of $-\Delta H_{150}$ in acetonitrile *versus* the Hammet σ-value for benzoic acid and five *m*- or *p*-substituted benzoic acids (Fig. 4) shows that such a correlation does exist except for *m*-nitrobenzoic acid. The anomalously high value for the heat of neutralisation of this compound remains unexplained. The equation of the line in Fig. 4 is $-\Delta H_{150} = 1{\cdot}23\ \sigma + 12{\cdot}4 \pm 0{\cdot}1$ Kcal/mole. Data on the heats of neutralisation of 32 amines with hydrogen bromide in acetonitrile and their theoretical interpretation have been published elsewhere[10]

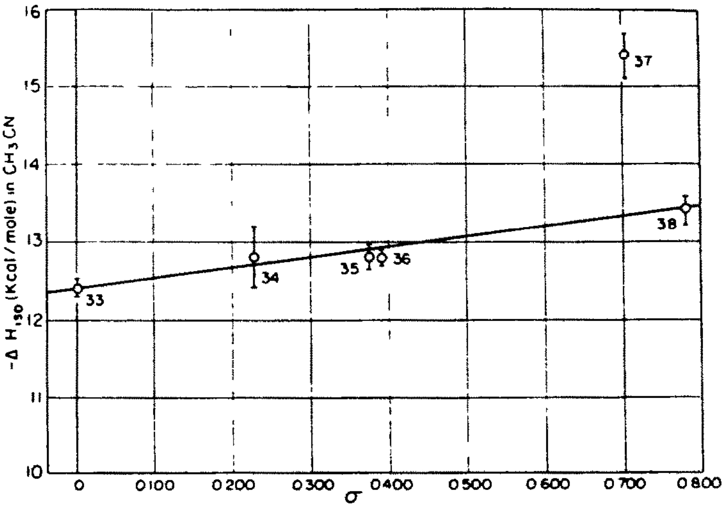

FIG 4.— $-\Delta H_{iso}$ in acetonitrile *vs* σ for substituted acids (33) benzoic, (34) *p*-chlorobenzoic, (35) *m*-chlorobenzoic, (36) *m*-bromobenzoic, (37) *m*-nitrobenzoic, (38) *p*-nitrobenzoic

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Zusammenfassung—Acetonitril als Medium für thermometrische Säure-Basen-Titrationen wurde untersucht Sehr viele Amine und organische Säuren lassen sich befriedigend titrieren, aber die Zersetzlichkeit des Lösungsmittels in Gegenwart starker Basen begrenzt die praktische Anwendbarkeit. Es werden Neutralisationswärmen verschiedener Säuren in Acetonitril angegeben, die Ergebnisse an m- und p-substituierten Benzoesäuren entsprechen ihren Hammettschen σ-Werten

Résumé—On étudie l'utilisation de l'acétonitrile comme milieu pour des titrages thermométriques acide-base Les resultats sont satisfaisants pour de nombreux acides organiques et de nombreuses amines, mais l'instabilité du solvant en présence de bases fortes limite grandement son application pratique On donne des resultats sur les chaleurs de neutralisation de différents acides dans l'acétonitrile, les resultats pour les acides benzoiques m- et p- substitués se corrèlent bien avec les valeurs de leurs σ de Hammett

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POLAROGRAPHY OF COPPER IN DIETHYLENE-TRIAMINEPENTA-ACETIC ACID SOLUTIONS

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Summary—The polarographic behaviour of copper in the presence of excess DTPA has been studied by means of the dropping mercury electrode In an acidic medium the $copper^{II}$ complex is reversibly reduced to the amalgam At pH values above 5 the wave is broken into two parts and a new irreversible wave appears at a more negative potential An increase in pH of the supporting electrolyte results in an increase of the second wave at the expense of the original one, the limiting current of the total wave remaining constant. The effect of temperature, pressure of mercury, pH and the concentration of DTPA on the limiting current and the half-wave potentials of the two waves have been investigated and the stability constant of the copper-DTPA complex has been redetermined. The double wave is assumed to be the result of an inhibited electrode reaction, the inhibition being caused by the deposition of the reduction product at the electrode surface When the applied potential is increased above −0·7 V *vs* S.C.E., the film is desorbed and the current rises to its original value

INTRODUCTION

DIETHYLENETRIAMINEPENTA-ACETIC acid (DTPA) forms stable complexes with $copper^{II}$ In the presence of excess DTPA three complexes with the formulae CuH_2DTPA, CuHDTPA and CuDTPA, respectively, are formed at various pH. The complexes have been investigated by spectrophotometric and potentiometric methods and the stability constants determined.[1–4]

The polarographic behaviour of the copper-DTPA chelates has not previously been investigated. Preliminary experiments with the dropping mercury electrode (D.M.E.) showed that copper in the presence of excess DTPA is reduced in two steps in an alkaline medium, and that the ratio of the two waves was highly dependent on the pH of the supporting electrolyte. The present work was carried out in order to study this effect of pH on the reduction of the copper-DTPA complexes.

EXPERIMENTAL

Reagents

Diethylenetriaminepenta-acetic acid Obtained from Geigy Chemical Corp., New York, U.S.A. The commercial DTPA was recrystallised twice from a minimum amount of hot water and dried in the air. The purity of the product was checked by infrared analysis. A $0{\cdot}05M$ stock solution was prepared by dissolving 19·7 g of DTPA and 6 g of sodium hydroxide in distilled water and diluting to 1 litre The solution was standardised against dipyridozincthiocyanate according to Buděšinsky [5]

Standard $copper^{II}$ solution: Prepared by dissolving an accurately weighed amount of electrolytic copper in nitric acid. Part of the excess acid was evaporated and the residue diluted to appropriate volume.

The remaining chemicals were of reagent grade quality and they were used without further purification.

Two-tenths molar acetate- phosphate- and ammonia-buffers were used as supporting electrolytes. The pH of the electrolytes was adjusted to the desired value by adding hydrochloric acid or potassium hydroxide to the solution and its pH measured with a pH meter. Triton X-100, obtained from Rohm and Haas Co., Philadelphia, U.S.A., was used as maximum supressor in some experiments

Apparatus

Polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen Germany). The conventional type of dropping mercury electrode and of electrolysis cell was used The capillary characteristics, measured in 0·1*M* potassium nitrate (open circuit) at a mercury height of 52 4 cm were. m = 2 998 mg/sec and t = 3 52 sec An external saturated calomel electrode (S C E), connected to the cell by means of an agar bridge, served as reference electrode Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis All experiments were performed at 25 ± 0 1°

The reversibility of the electrode reactions was tested by determining the temperature coefficient of the half-wave potentials and the slopes of the curves of log $i/(i_d - i)$ *vs* potential Corrections were made for the residual current and IR-drop in the circuit Data for the logarithmic plots were taken by manual operation of the polarograph, measuring the applied potential with a Hartman and Braun (No. 10018) potentiometer. Half-wave potentials of the reversible waves were taken from the logarithmic plots and were reproducible to ±1 mV

RESULTS

Preliminary experiments

Current-voltage curves of DTPA in supporting electrolytes of different pH showed that the reagent is not reduced at the D.M.E. An anodic wave, however, probably from the oxidation of mercury to a mercury-DTPA complex, was observed on all polarograms. The wave was shifted to more negative values with an increasing pH of the supporting electrolyte and the height of the wave was found to be proportional to the concentration of DTPA.

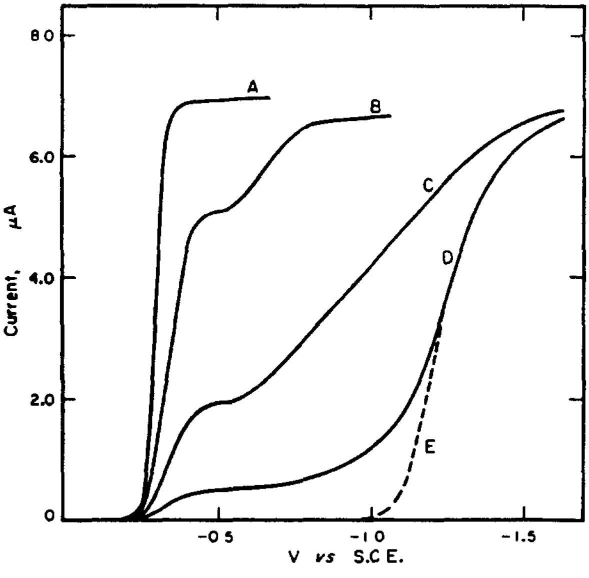

FIG. 1.—Polarograms of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA in acetate buffer pH 4 60 with various amounts of Triton X-100 present. (a) 0%, (b) 0 002%, (c) 0 003%, (d) 0·006%, and (e) >0 01%.

Polarograms of copper in the presence of DTPA exhibited a maximum when recorded from solutions with low pH values. The maximum was easily suppressed by the addition of a minute amount of Triton X–100. Larger amounts of Triton had, however, a marked effect on the reduction wave, which was split into two waves and the limiting current was strongly decreased over a considerable potential range. A few polarograms recorded in the presence of various amounts of Triton X–100 are shown in Fig. 1. Experiments showed that the presence of 0·0005% of Triton was

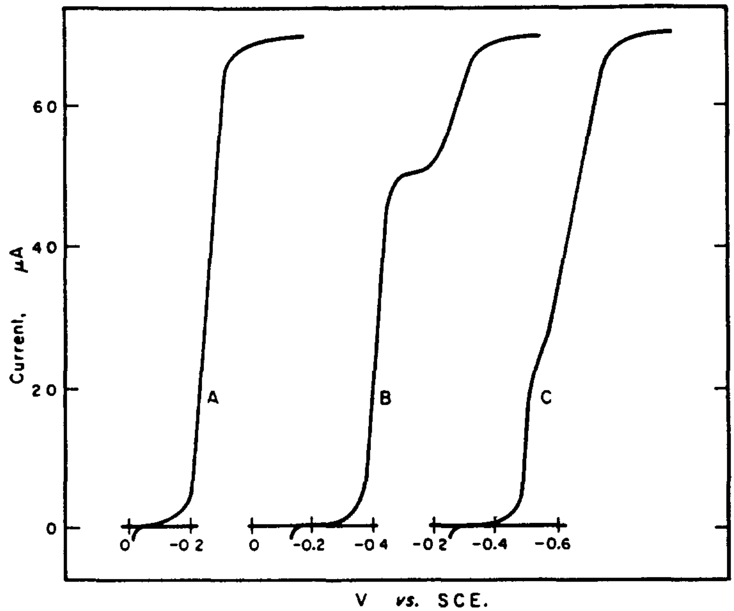

FIG. 2.—Polarograms of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA: (A) acetate buffer pH 4·65, (B) phosphate buffer pH 6 80, and (C) phosphate buffer pH 9·60.

sufficient to suppress the maximum and this low concentration had no undesirable effect in an acidic medium. No maximum was observed on polarograms recorded from solutions with a pH greater than 4, and in the following experiments no surface active substances were added to the supporting electrolytes in the pH range 4–12.

Effect of pH

The effect of pH on the cathodic wave of copper^{II} in the presence of excess DTPA was investigated, using acetate and phosphate buffers as supporting electrolytes. Polarograms recorded from solutions with a pH less than 5 consisted of a single well-defined wave, whereas a second wave appeared on polarograms recorded at higher pH. An increase in pH of the supporting electrolyte resulted in an increase of the second wave at the expense of the first one, the total limiting current remaining constant. A few typical polarograms are shown in Fig. 2. The half-wave potential of the first wave was shifted to more negative values with increasing pH as indicated in Fig. 3. The half-wave potential of the second wave, however, remained practically constant ($E_{\frac{1}{2}} = -0{\cdot}68$ V *vs.* S.C.E.) in the entire pH range 5–12. The lower limit of pH in these measurements is restricted by the solubility of DTPA and the dissolution wave of mercury which interfered at pH values less than 3. The variation of the height of the first and second wave with the pH of the supporting electrolyte, is plotted in Fig. 4. The above results were perfectly reproducible. At a given pH identical polarograms were obtained, independent of the supporting electrolyte used (*i.e.*, acetate, phosphate or potassium nitrate/potassium hydroxide). The ratio between the first and second wave increased, however, in the presence of ammonia (Fig. 4). This is probably because of a mixed ligand complex and will be discussed below.

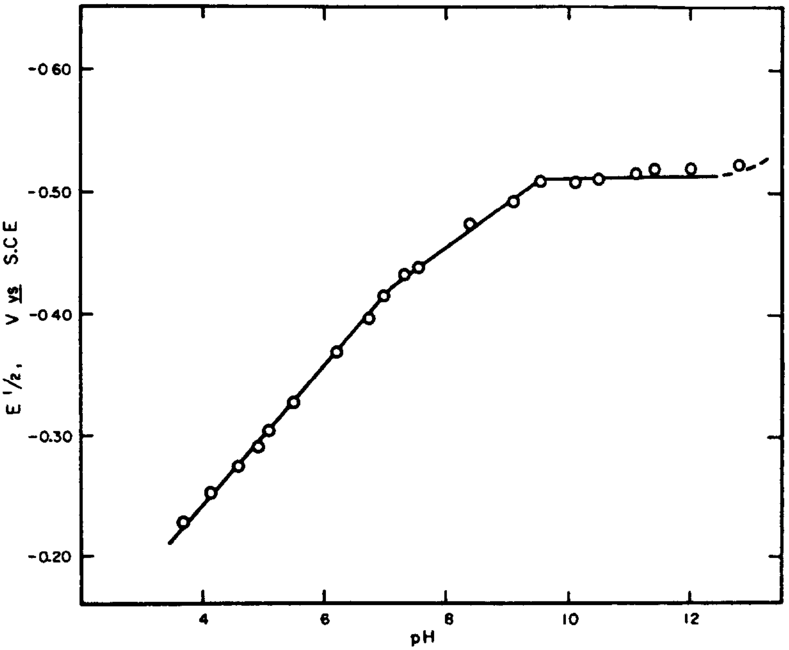

FIG 3.—Half-wave potentials of the first wave of $10^{-4}M$ copper^{II} and $10^{-2}M$ DTPA at various pH values

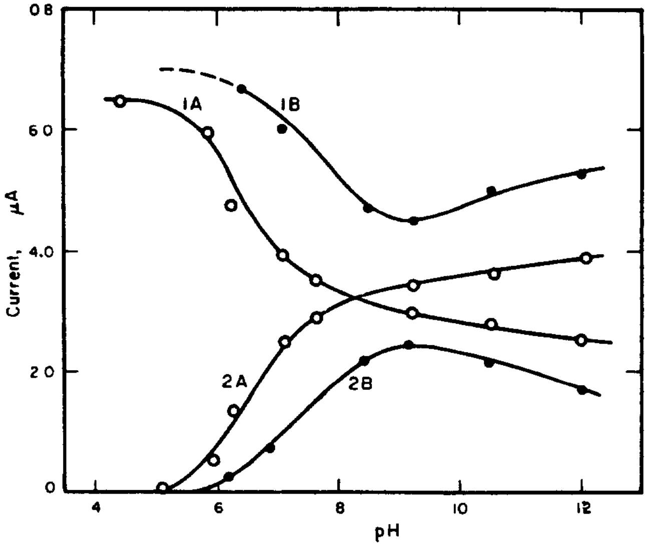

FIG. 4.—Limiting currents of the first (1) and second (2) wave of $10^{-3}M$ copper^{II} and $10^{-2}M$ DTPA at various pH values: (A) acetate and phosphate buffers, (B) ammonia buffers.

Reversibility of the electrode reactions

The reversibility of the electrode reactions was tested by plotting log $i/(i_d - i)$ *vs.* the potential. The plots yield straight lines at all pH for the first wave, and the slope of the lines indicated a reversible two-electron reduction of copper to the amalgam.

The half-wave potential of the first wave shifted to more negative values with an increasing concentration of DTPA, and the plot of the values of $E_{\frac{1}{2}}$ *vs.* the corresponding values of log C_x, resulted in straight lines. The slope of the lines indicated that only one group is co-ordinated in the complex. In the concentration range 5×10^{-4} to $10^{-2}M$ DTPA, the half-wave potential of the first wave may be expressed by the equation:

$$E_{\frac{1}{2}} = -0{\cdot}576 - 0{\cdot}029 \log C_x.$$

The concentration C_x of the free ligand available for complex formation was calculated using the dissociation constants of DTPA reported by Anderegg and coworkers.[2]

The second wave, which appeared on polarograms recorded from solutions with a pH greater than 5, showed an irreversible reduction. The plot of log $i/(i_d - i)$ *vs.* the potential yields curved lines at all pH from 5 to 12. The half-wave potential of this wave, taking $E_{\frac{1}{2}}$ as the point on the curve where $i = i_d/2$, was constant (—0·68 V *vs.* S.C.E.) and independent of the pH of the supporting electrolyte and the excess of DTPA present.

Effect of temperature

The effect of temperature on the cathodic waves of copper in the presence of excess DTPA was tested in acetate and phosphate buffers. In the region 20–45° the temperature dependence of both the half-wave potential and the height of the first wave was linear. The temperature coefficient of the half-wave potential, —0·3 mV/degree, is of the proper sign and magnitude for that of a reversible process.

TABLE 1 —EFFECT OF TEMPERATURE

Temp., °*C*	First wave		Second wave	
	$-E_{\frac{1}{2}}$, *V*	Current, μA	$-E_{\frac{1}{2}}$, *V*	Current, μA
20	0·396	0·53	0·68	0·16
25	0·397	0·56	0·68	0·16
30	0·399	0·60	0·68	0·16
35	0·400	0·64	0·68	0·16
40	0·402	0·68	0·68	0·15
50	0·403	0·73	0·68	0·15

$10^{-4}M$ copper^{II} and $10^{-3}M$ DTPA in phosphate buffer of pH 6·60.

The temperature coefficient of the diffusion current was 1·3% per degree, indicating a diffusion-controlled process. The data obtained from phosphate buffer pH 6·6 are reported in Table I. At this pH the two waves are very well separated and the temperature dependence of the second wave could also be measured. As seen from the table, the half-wave potential and the height of the second wave were found to be independent of the temperature within the experimental error.

Diffusion current constant

The diffusion current constant at different pH was determined by measuring the limiting current of 2×10^{-5} to $2 \times 10^{-3}M$ copper in the presence of $10^{-2}M$ DTPA. In the pH range 3–10, using acetate and phosphate buffers as supporting electrolytes, the limiting current of the *total wave* was independent of pH and it increased proportionally to the concentration of copper at all pH. The diffusion current constant in these media was found to be $I = 2{\cdot}42 \pm 0{\cdot}06$. In ammonia buffers of pH 10–12 the diffusion current constant was somewhat larger, $I = 2{\cdot}55 \pm 0{\cdot}05$. Comparison of these values with the diffusion current constant of the copper EDTA-complex determined by Pecsok,[6] $I = 2{\cdot}85$, indicates that the total wave is caused by a two-electron reduction of copper to copper amalgam.

Effect of drop time

The effect of drop time was investigated by recording polarograms of $10^{-4}M$ copper and $10^{-2}M$ DTPA in acetate and phosphate buffers at various heights of the mercury column. The height of the single wave obtained at pH <5 and the first wave obtained at higher pH values, increased with the height of the mercury, the value $i/\sqrt{h}$, where h is the height of the column after correction for the "back-pressure", was constant, indicating that the electrode reaction is diffusion controlled. The height of the second wave was found to increase proportionally to the height of the mercury column and indicates that this wave is from an adsorption on the electrode and that the current is controlled by the rate of penetration of the copper complex through an adsorbed film.[7] The data obtained at pH 6·65 are given in Table II.

TABLE II.—EFFECT OF PRESSURE OF MERCURY

h_{corr}, *cm*	First wave		Second wave	
	i_d, μA	$i_d/\sqrt{h}_{corr.}$	i, μA	i/h_{corr}
45·6	4·65	0·69	1·40	0·031
50·6	4·95	0·68	1·55	0·031
55·6	5·15	0·69	1·70	0·031
60·6	5·35	0·68	1·85	0·031

$10^{-3}M$ copper^{II} and $10^{-2}M$ DPTA in phosphate buffer of pH 6·65.

The drop time of the capillary was also measured as a function of the applied potential. The electrocapillary maximum was not shifted and the general shape of the curve did not change upon the addition of $10^{-3}M$ copper and $10^{-2}M$ DTPA to the supporting electrolyte, but a 2% decrease in drop time was observed over a considerable potential range.

DISCUSSION

It is evident from the experimental data that the first wave is from a reversible, diffusion-controlled, two-electron reduction of the copper-DTPA complex. The observed half-wave potentials are linear functions of the pH in the regions 4–7, 7–10 and 10–12·5 (Fig. 3). The slopes of the curves are −0·060, −0·035 and 0

V/pH unit, respectively, indicating that the following reactions take place at the electrode:

$$CuA^{3-} + 2H^+ + 2e^- \xrightarrow{pH\ 4-7} Cu(Hg) + H_2A^{3-}$$
$$CuA^{3-} + H^+ + 2e^- \xrightarrow{pH\ 7-10} Cu(Hg) + HA^{4-}$$
$$CuA^{3-} + 2e^- \xrightarrow{pH\ 10-12\cdot5} Cu(Hg) + A^{5-}$$

where H_5A represents DTPA.

At pH <4, the conditional constant[4] of $CuHA^{2-}$ is of the same order as that of CuA^{3-}, and the following reaction will probably take place in that pH region:

$$CuHA^{2-} + 2H^+ + 2e^- \xrightarrow{pH<4} Cu(Hg) + H_3A^{2-}.$$

The stability constants of the CuA^{3-} complex, calculated from the half-wave potentials of the first wave, was $pK_c = 20\cdot4$. Considering the great difference in ionic strength, this value compares favourably with the values 21·0, 21·5, 21·1 and 20·5 previously determined by potentiometric titration.[1-4]

The interpretation of the second wave is more difficult. The half-wave potential of this wave was constant, independent of excess reagent, pH and the kind of supporting electrolyte. Consequently, the double wave is not from the reduction of two copper complexes of different composition or mixed ligand complexes. The effect of temperature and the height of the mercury column on the second wave, indicates that the current is controlled neither by diffusion nor by kinetic reactions. At a given pH, the height of the second wave is proportional to the concentration of copper and to the height of the mercury column. The current did not, however, reach a limiting value with increasing concentration as in the case of catalytic and classical adsorption waves.

The double wave may, however, be the result of an inhibited electrode reaction.[8,9,10] The DTPA liberated at the electrode during the electrolysis is therefore assumed to be surface active and to accumulate on the electrode surface during the life of the drop. The effect will then be similar to the addition of Triton (Fig. 1), and the reaction will be partly inhibited until the desorption potential is reached. When the applied potential is increased above this value (about −0·7 V *vs.* S.C.E.), the film is desorbed and the current will rise to its original value.

Equipment for oscillographic current/time curves[8] was not available in this laboratory, but a detailed inspection of undamped polarograms indicated that an inhibition mechanism occurred at the electrode and the height of the second wave increased proportional to the height of the mercury column, as in the case of limiting penetration currents.[7]

At a given pH value the ratio of the two waves, and hence the degree of inhibition, was found to be independent of excess DTPA in the solution, indicating that only the DTPA species liberated at the electrode during the electrolysis is surface active. Hence, the electrode reaction cannot be completely inhibited as by the addition of a large amount of Triton X-100 (Fig. 1). The DTPA anions are desorbed at a less negative potential (−0·7 V) than the neutral Triton X-100 molecule (−1·3 V), indicating that the desorption potential depends on the charge and type of inhibitor present in the electrolyte.

It is of interest to note that the second wave does not appear on polarograms recorded from solutions of pH less than 5. In this pH range H_3A^{2-} is formed during the reduction and is probably less surface active and not so strongly adsorbed as the HA^{4-} and A^{5-} species liberated at higher pH values.

The co-ordination number of copper is six in the copper-EDTA complex and according to Kirson and Citron the complex exists as a polymer in solution.[11] By the addition of ammonia to the solution, the polymer is disrupted into single

$$[Cu(NH_3)_2EDTA]^{2-}$$

units.[12] A similar polymer with hexaco-ordinated copper is probably also formed in DTPA solutions, the six co-ordination being completed by weak intermolecular $C = O \cdots Cu$ linkages. When ammonia or ethylenediamine was added to the copper-DTPA chelate in phosphate buffer of pH 9–12, the blue colour of the complex increased in intensity. Polarograms of these solutions exhibited two waves as in phosphate buffers, but the height of the first wave increased at the expense of the second one upon addition of ammonia or polyamines to the supporting electrolyte, whereas the half-wave potentials remained practically constant. At a given pH and excess ammonia or ethylenediamine, the ratio of the two waves was constant and independent of other electrolytes present (Fig. 4). These experiments indicate that the DTPA species liberated at the electrode is less surface active and that a smaller amount is adsorbed in the presence of ammonia. It is possible that this effect is caused by a disruption of the polymer and the formation of a mixed ligand complex similar to that in EDTA solutions. No mixed ligand DTPA complexes have yet been reported in the literature, but the existence of a copper-ammonia–DTPA complex may probably be verified by infrared experiments as in the case of the EDTA complexes.[11,12]

Zusammenfassung—Das polarographische Verhalten von Kupfer in Gegenwart von überschüssiger DTPA wurde an der Quecksilbertropfelektrode untersucht. In saurem Medium wird der Kupfer (II)-Komplex reversibel zum Amalgam reduziert. Bei p_H-Werten über 5 spaltet die Welle in zwei auf und eine neue irreversible Welle erscheint bei negativerem Potential Ansteigen des p_H des Leitelektrolyten läßt die zweite Welle auf Kosten der ersten ansteigen, wobei der Gesamt-Grenzstrom konstant bleibt. Der Einfluß von Temperatur, Quecksilberdruck, p_H und DTPA-Konzentration auf Grenzstrom und Halbwellenpotential der beiden Wellen wurden untersucht und die Stabilitätskonstante des Cu-DTPA-Komplexes neu bestimmt. Die Doppelwelle wird als Folge einer gehemmten Elektrodenreaktion gedeutet, wobei die Hemmung in der Abscheidung des Reaktionsproduktes an der Elektrodenoberfläche besteht. Wenn die angelegte Spannung über −0,7V gegen die gesättigte Kalomelektrode gesteigert wird, wird der Film desorbiert, und der Strom steigt auf seinen ursprunglichen Wert an.

Résumé—Le comportement polarographique du cuivre en présence d'un excès de DTPA (acide diéthylène triamine pentaacétique) a été étudié au moyen de l'électrode à gouttes de mercure. En milieu acide le complexe du cuivre(II) est réduit réversiblement en amalgame. A un pH supérieur à 5 la vague se dédouble et une nouvelle vague irréversible apparaît à un potentiel plus négatif. A une augmentation de pH de l'électrolyte support correspond une augmentation de la hauteur de la deuxième vague aux dépens de la vague initiale, la somme des courants de diffusion restant constante. L'effet de la température, de la pression du mercure, du pH et de la concentration de DTPA sur le courant de

diffusion et sur les potentiels de demi-vague des deux vagues a été étudié et la constante de stabilité du complexe Cu-DTPA a été déterminée à nouveau. La double vague est supposée être le résultat d'une réaction à l'électrode inhibée, cette inhibition étant due au dépot du produit de réduction sur la surface de l'électrode Quand le potentiel appliqué devient plus négatif que $-0{,}7$ V/E C.S le film est désorbé et le courant reprend sa valeur initiale

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GEOMETRY-RELATED ERRORS IN INSTRUMENTAL NEUTRON-ACTIVATION ANALYSIS

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Summary—Geometry-related errors in instrumental neutron-activation analysis are defined and evaluated. Neutron-flux distributions, variations in counting geometry, and intra-sample neutron moderation and reflection are discussed in relation to these errors. Devices for error control are described.

NEUTRON ACTIVATION when combined with γ-ray spectrometry and decay-rate analysis offers a purely instrumental, non-destructive approach to elemental analysis. Because of the high penetrativeness of neutrons and of γ-rays, matrix effects are exceptionally small. In many cases, samples as large as 25–30 ml are analysed. Furthermore, in most cases, the results are relatively insensitive to differences in composition, sample volume or bulk density. With the introduction of accelerator systems for neutron production, this method, called instrumental neutron-activation analysis here, comes within the budgetary, space and manpower limitations of many laboratories, and shows promise of taking a place among the established instrumental analytical tools of the modern laboratory.

The physical concepts of the method, its instrumentation and some typical applications to routine analyses have been presented by Guinn and Wagner[1] for the system used in the Emeryville Research Center of Shell Development Company. Using this system, Guinn and Johnson[2] have found instrumental neutron activation to be a reliable and convenient tool for routine analysis and to be especially valuable in quickly solving new or unusual analytical problems which by other methods would require considerable research and development.

In seeking the greatest power and efficiency for this new method, it is the task of analytical research and development to explore its variables systematically and to relate them to such analytical characteristics as sensitivity, precision and selectivity. As a part of this exploration, the present study has to do with errors related to sample-source geometry and to sample-counter geometry. In the typical activation determination, results are calculated on the basis of a comparison of the respective count rates of a sample and a standard. Implicit in this comparison are the assumptions that sample and standard are exposed to the same neutron flux and are counted with the same counting efficiency. In practical activation sources, however, the neutron-flux distribution is non-uniform, and presents significant differences between and within sample spaces. Furthermore, for the detectors and samples used, the counting efficiency varies significantly over the sample space. Thus the assumptions of constant flux and constant counting efficiency are not simply and exactly met. In an evaluation of the analytical consequences of this situation, this study presents surveys of neutron distributions and of counting efficiencies, relates these variables to certain errors in activation analysis, and describes methods for control of these errors.

Although the results are specific for the actual source used, the principles evolved and the approach taken to control the geometry-related errors are expected to be generally applicable to other systems for instrumental neutron-activation analysis

EXPERIMENTAL

Apparatus

Neutron source The neutron source used is a modification of the source described by Guinn and Wagner[1] and illustrated in Fig. 1. Neutrons are generated by the action of bremsstrahlung, from a 3-MeV Van de Graaff electron accelerator with a gold target, on beryllium in a 6-inch cube of the metal. The moderator is Santowax, a radiation-resistant wax Neutron shielding is accomplished by a Boral cover and by boric acid around the side and bottom of the assembly

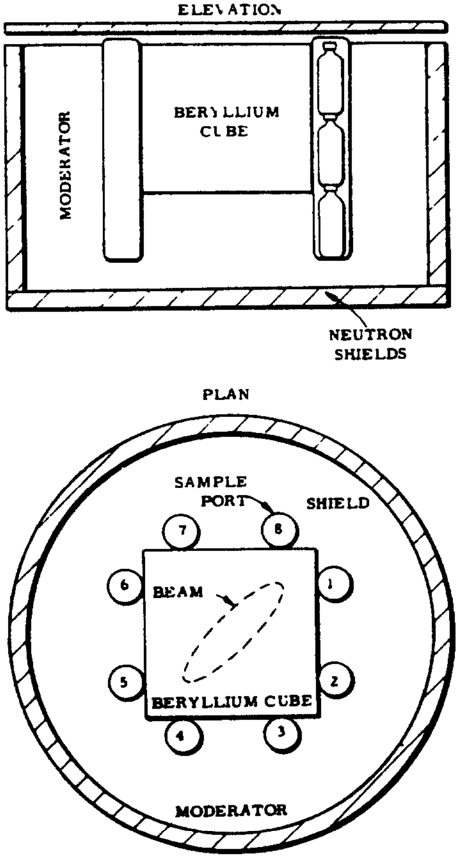

FIG. 1.—The photoneutron source.

Scintillation counter: Well-type NaI(Tl) crystal is used to yield maximum counting efficiency and to achieve the smallest variation in counting geometry with sample volume. The well accommodates commercially available 1-oz polyethylene bottles, as shown in Fig. 2. The over-all dimensions of the crystal, diameter × depth, is 3″ × 3″.

Procedure

Flux-distribution patterns are determined by activating and counting gold foils (usually about 20 mg of 0·5 mil gold sheet) supported in appropriate positions on pressure-sensitive cellophane tape.

The position of the X-ray beam relative to the beryllium block is determined photographically with the aid of X-ray sensitive polyvinyl chloride sheet.[2]

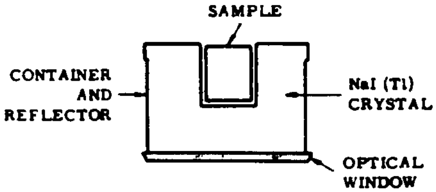

FIG. 2.—Cross-section of scintillation well detector with sample in well

The neutron-flux levels in different sample ports are determined by activating and counting a set of nearly identical standards, *e g* , gold foils, or suitable solutions, such as 0 1% manganous nitrate, at a given level in sample ports around the core.

Volume effects and height effects are determined in an analogous way using monitors irradiated and counted under the conditions being tested

RESULTS AND DISCUSSION

Positioning errors

Positioning errors are defined as errors attributable to differences in neutron flux at a given level from sample port to sample port. A typical positioning error pattern is given in Fig. 3. Also shown in this figure is the corresponding beam-to-core orientation, according to the photograph for this positioning run. A comparison of the pattern and the diagram illustrates the main dimensional and geometric effects on the pattern. In particular, positions 5–8 show a generally higher flux than positions 1–4, which correlates with the beam being located closer to the former positions than to the latter. Furthermore, a geometric correlation is observed in the similarity of the pattern for positions 1–4 to that for positions 4–8; thus the symmetry of the beam scan is reflected in the symmetry of the positioning pattern.

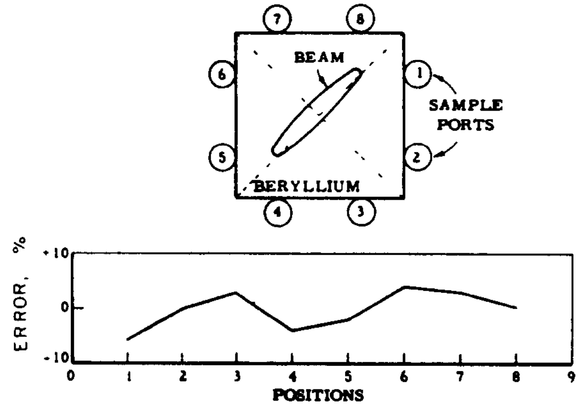

FIG. 3.—Positioning error with an uncentred beam

The correlations observed above are generally found throughout a series of positioning runs. However, the variability of the patterns from run to run is great enough to reduce the value of any single pattern as a calibration standard.

The position-to-position variation and the run-to-run variability are largely attributed to the strong dependence of the neutron flux on beam-to-sample distance. An illustration of this effect is given in Fig. 4, which presents the changes in neutron flux in the sample space with changes in the distance from the beam centre to the sample (see inset in Fig. 4). According to Fig. 4, the gradient for the centred beam, *i.e.*, at a beam-sample distance of 3·5 inches, is 16–20 relative % per inch. For a beam which is 0·25 inch off centre, this gradient corresponds to a difference of 8–10% between fluxes in ports on opposite sides of the core and, therefore, yields a positioning pattern like that of Fig. 3. In terms of precision, the above effects yield an error component of about 3% relative standard deviation.

Another view of the effect of flux distribution is given in Fig. 5, which shows how the flux varies with distance from the beam axis for a centred beam (see inset in Fig. 5).

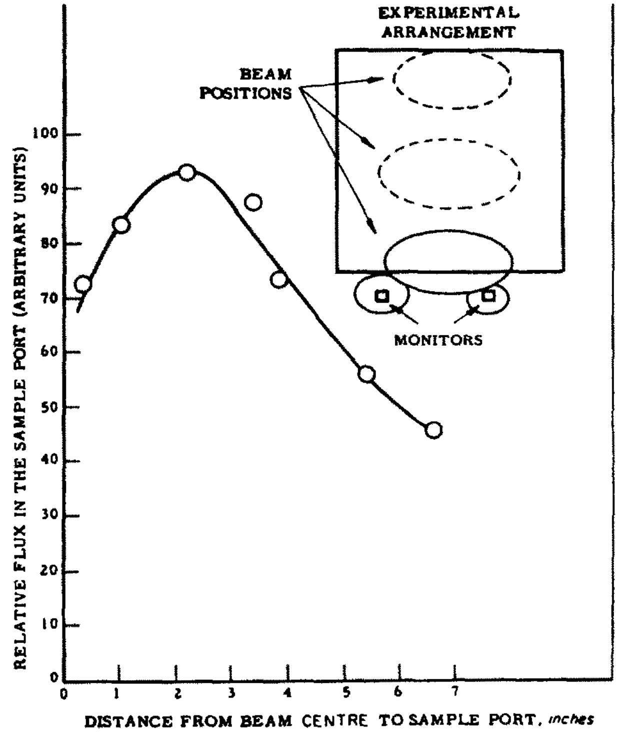

FIG. 4.—Effect of beam-to-port distance of flux in the sample port (beam position variable).

The sharp flux-distance gradient has the same implications as in the preceding discussion. A small maximum in the flux distribution is found in the reflector near its interface with the core. This maximum, signifying a local accumulation of neutrons in the reflector, is attributed to the fact that in comparison with the beryllium of the core the wax moderator has greater moderating power and a smaller neutron capture cross section.[4] The distribution of Fig. 5 is measured at the top of the source, *i.e.*, above the level of Sample C in Fig. 1. Experimental determination of distributions at lower levels are not feasible in this system, but results from other systems, to be described elsewhere, indicate that maxima at lower levels are less sharp. The development of the maximum near the interface has the effect of reducing the error from inhomogeneity within a cross-section of the sample.

Devices for controlling the positioning error

Foil monitors. Flux monitors of gold foil are attached to the tops of the containers of samples and standards, carried through the irradiation, and counted to yield a position-to-position flux calibration for the respective irradiation. Use of monitors is simple, but it contributes an additional counting error to the result.

"*Lazy susan*" *sample rotation.* If the sample ports and core are radially symmetrical with respect to an axis, rotation of samples about that axis eliminates errors from beam wandering and core-to-beam eccentricity. In practice, some variation is usually found from position-to-position because of dissymmetries in the rotating assembly, *i.e.*, in the interrelationship of ports, core, and axis of rotation. However, if the axis of rotation is accurately centred with respect to the ports, the pattern of flux variation from these dissymmetries is reproducible and, once determined, may be used as a calibration curve.

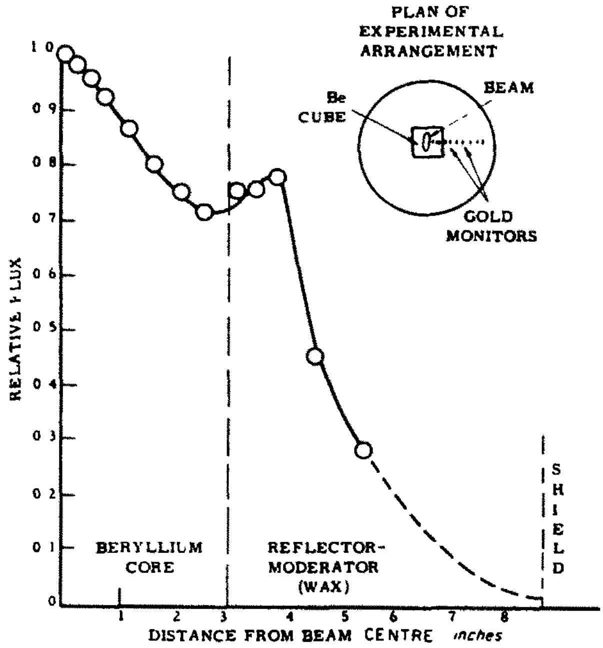

FIG. 5.—Effect of beam-to-monitor distance of flux distribution transverse to the beam (beam position fixed).

The off-centre beam position. If only one sample and one standard are to be irradiated, excellent flux uniformity can be achieved by scanning the beam parallel to and about 1 inch from one edge of the core, as shown by the beam position with the solid outline in Fig. 4. In this beam-to-core orientation, two effects compensate each other to form a maximum in the plot of flux available to the sample *vs.* beam-to-port distance as shown in Fig. 4. The compensating effects which result in the maximum are (1) a decrease in flux with increase in beam-to-port distance resulting from inverse square attenuation and neutron capture and (2) an increase in flux with increase in beam-to-port distance because of an increase in the fraction of bremsstrahlung beam falling within the beryllium core.

Volume errors

The volume errors in this discussion are those errors in activation analysis attributable to differences between the volumes of samples and the volumes of their respective comparison standards. In this investigation of these errors, the variables studied are: (1) differences in neutron flux at different levels within the ports, (2) enhancement of intra-sample neutron flux with increase of sample volume, and (3) differences in counting efficiency at different levels in the detector well.

The relationship between neutron flux and height within the sample port is shown in Fig. 6. The three sample positions indicated in Fig. 6 correspond with the sample levels shown in Fig. 1, the diagram of the neutron source assembly. It is evident from Fig. 6 that the neutron flux available to the sample depends strongly on the height at which it is situated in the sample port. It is also evident that both the sign and magnitude of the intra-sample flux-to-height gradient depend strongly on the choice of height at which the sample is irradiated. For example, for a sample in position A or position B of this source, the neutron flux increases with increasing height, *cf.*, Curve 1, Fig. 7; however, for a sample in position C, the neutron flux decreases with increasing height.

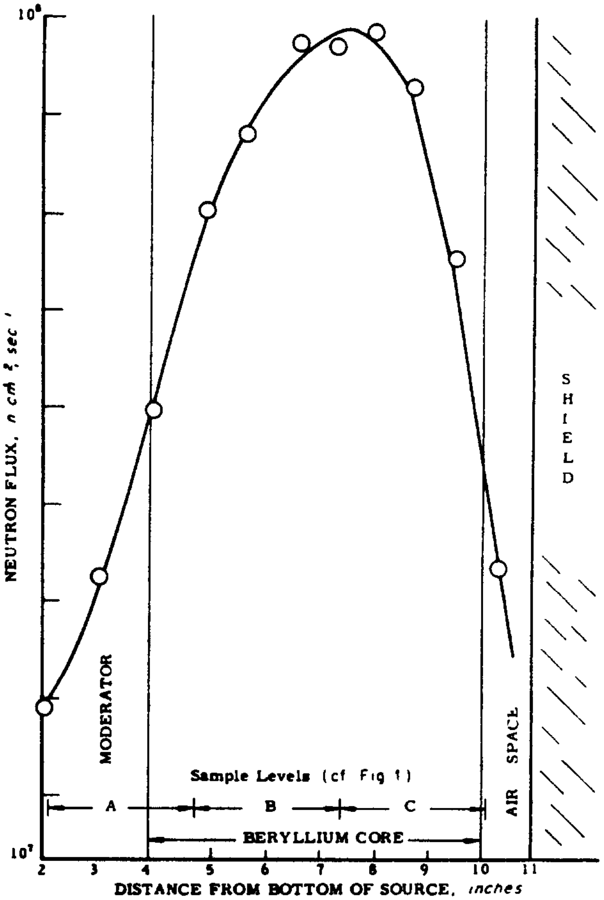

FIG. 6.—Flux distribution parallel to the beam axis (vertical distribution).

In instrumental neutron-activation analysis, the counterpart of the flux-to-height variation is the variation of counting efficiency with height in the detector. The latter relationship, shown in Curve 2 of Fig. 7, is largely determined by the sample-well geometry.

The count rate measured in a practical activation analysis, which is called the activation count rate here, is a function of the product of the neutron flux and the counting efficiency. Correspondingly, the variation of activation count rate with height in a given sample space varies with the product of the respective flux- and counting efficiency-height variations. This inter-relationship is illustrated in Fig. 7 for irradiation in the B position of the present source (Figs. 1 and 6). In this situation, the height-flux gradient (Curve 1, Fig. 7) is opposite in sign, but nearly equivalent in magnitude to the height-counting efficiency gradient (Curve 2, Fig. 7). Thus these two effects in an activation analysis may approximately cancel each other to yield a relatively small dependence of activation-induced count rate on height, as shown in Curve 3, Fig. 7. However, a quite different relationship may be found for irradiations carried out at a different height in the sample port. For example, samples irradiated in the C-position of the present source (Figs. 1 and 6) are exposed to a neutron flux which decreases with increasing height in the port. In this situation the flux-height gradient and the counting efficiency-height gradient enhance each other to yield a relatively strong dependence of activation count rate on sample height. It is clear, therefore, that the magnitude of errors possible from discrepancies between respective sample and standard volumes varies widely with differences in the height at which irradiations are carried out.

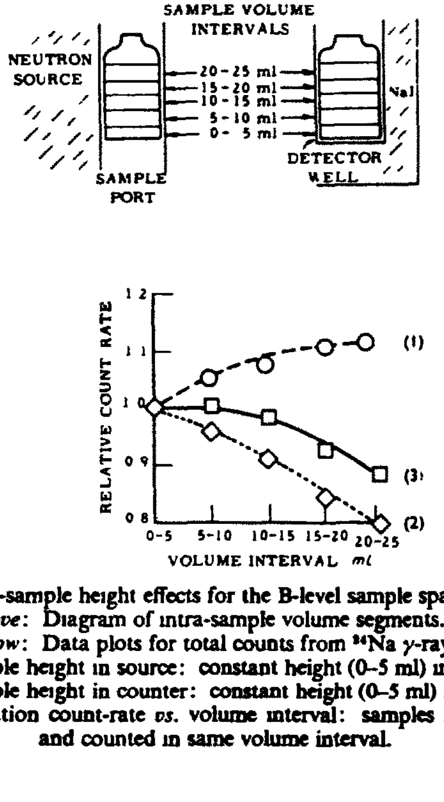

FIG. 7.—Intra-sample height effects for the B-level sample space of Fig. 6.
Above: Diagram of intra-sample volume segments.
Below: Data plots for total counts from ^{24}Na γ-rays.
○—Variable height in source: constant height (0–5 ml) in counter.
◇—Variable height in counter: constant height (0–5 ml) in source.
□—Activation count-rate *vs.* volume interval: samples irradiated and counted in same volume interval.

The preceding discussion deals with changes accompanying the displacement of a small volume segment along the vertical axis of the counter well and/or the sample port of the neutron source. On the basis of these effects, estimates may be made of the corresponding changes accompanying increases in sample volume. These estimates may be obtained by calculating the averages of the effects for the respective small volume displacements, *e.g.*, the counting efficiency of a 10-ml sample is approximately the average of the counting efficiencies of the 0–5 ml segment and the 5–10 ml segment in the crystal well. Thus the effect of increasing volume on activation count rate may be estimated as the averages of the activation count rates for the appropriate small volume segments. For the results given in Curve 3, Fig. 7, these averages are given in Column 2, Table I. For comparison, the experimentally-determined count rates for the indicated sample volumes are given in Column 3 of this Table The results in these two columns reveal that with increasing sample volume the experimental count rates exceed by progressively greater amounts the rates based on experiments with small volume segments. This difference is attributed to a third factor in the volume effect, namely, the effect of flux enhancement with increasing volume from intra-sample neutron moderation and reflection. This effect is more specifically demonstrated by the experiment and results shown in Fig. 8. Here it is shown that an increase in activation count rate is obtained in a sample segment without changing its radiation position or counting position if the sample segment is flanked by segments of water as a reflector. This enhancement, as indicated above, is attributed to neutron moderation and reflection within the sample. In general, the magnitude of this effect for samples ranging in volume from 2–25 ml is smaller than the flux-height and counting efficiency-height effects. Nevertheless, it is important enough to be considered in setting up the irradiation geometry for activation analysis of samples varying over a wide volume range such as this.

TABLE I —EFFECT OF SAMPLE VOLUME ON SPECIFIC COUNT RATE OF ^{24}Na γ-RAYS IN INSTRUMENTAL ACTIVATION ANALYSIS
Samples are irradiated in the position indicated as "B" in Fig. 1 and 6 and counted in a well-type scintillation detector

Sample volume, *ml*	Relative specific count rates	
	Averages of rates from corresponding 5-ml segments. Results of Curve 3, Fig. 7	Experimental rate for volume indicated
5	1·00	1·00
10	1·00	1·02
15	0·99	1·03
20	0·98	1·03
25	0·96	1·04

A similar effect observed in activation analysis in the ORNL graphite reactor is described by Reynolds and Mullins[6] as a neutron perturbation attributable to enhancement of the thermal flux by moderation of epithermal neutrons within the sample.

By using the above considerations as guide lines in choosing the irradiation positions in the present activation system, good uniformity of specific count rate over a relatively large volume range, 5–25 ml, has been obtained. This uniformity is evident in the results of Column 3, Table I. Although the examples given here are from one neutron source and one detector, the principles and general approach described have usually been successful in analyses with other neutron sources, *e.g.*, sources with beryllium cores of other shapes and sizes and fast neutron sources using the deuterium-tritium reaction to produce 14-MeV neutrons.

It should be noted that volume effects other than those which are geometry-related exist, and may cause large errors. These other effects are principally radiation absorption effects, *i.e.*, variations in self-shielding of neutrons and self-absorption of β rays and γ rays with variation in sample volume. These effects will be described elsewhere.

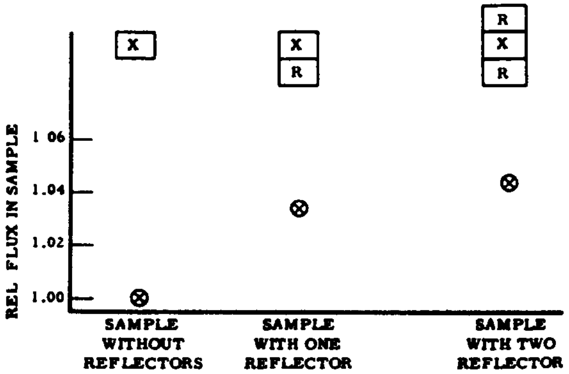

Fig. 8.—Effect of intra-sample neutron reflection.
Boxes show sample(X)-reflector(R) arrangements. For the samples irradiation position and counting geometry are held constant.

CONCLUSIONS

Geometry-related errors in instrumental neutron activation analysis are of two types, *viz.*, positioning errors and volume errors. Positioning errors are those which arise if samples and their comparison standards yield different specific count rates because of a variation in neutron flux from port-to-port around the source. In studies of this error, the port-to-port flux variations are found to correlate with small variations in beam-to-port distance. Furthermore, considerable variability among port-to-port flux patterns is found as small accidental changes in the beam-to-source geometry are made from run to run. These effects are attributed to the relatively large flux gradients shown to exist in neutron flux distributions normal to the beam axis. In the control of the positioning error, port-to-port flux patterns are usually too variable to permit the use of a single pattern as a calibration standard. However, satisfactory results have been obtained by (1) using gold foils attached to each container as flux monitors; (2) rotation of samples about the beam axis on a "lazy susan" to produce a uniform average flux to the samples; or (3) irradiation in an off-centre beam position chosen to yield excellent flux uniformity to a single sample-standard pair.

Volume errors are those which arise if the specific count rates of sample and standards are different because of differences in their volumes. The effects found to be the sources of geometry-related volume errors are the following:

(1) variation in counting efficiency with height in the detector well, which is found to be in general agreement with the variation predicted on the basis of solid geometry;

(2) variation in neutron flux with height in the port of the neutron source, which is characterised by a maximum flux near the midline of the core; and

(3) enhancement of neutron flux with increase in sample thickness, which is smaller than the preceding effects and is attributed to intra-sample neutron moderation and reflection.

From surveys of these effects on a particular system, an optimum irradiation position may be chosen in which respective height gradients compensate each other so as to yield a minimum variation of activation-induced count rate with changing volume.

This approach to control of the volume error is especially important in analysis in which large volume ranges are involved, *e.g.*, 2–25 ml. The principles and methods are expected to be applicable to instrumental activation analyses with other source-counter combinations

Zusammenfassung—Geometrisch bedingte Fehler bei der Neutronenaktivierungsanalyse werden definiert und berechnet. Neutronenfluß-verteilung, Veränderungen der Zählgeometrie und Bremsung und Reflexion von Neutronen in der Probe werden in Bezug auf diese Fehler diskutiert Vorrichtungen zur Fehlerkontrolle werden angegeben

Résumé—On définit et évalue les erreurs dues à la géométrie des instruments dans l'analyse par activation neutronique. On discute la distribution du flux de neutrons, la variation de la géométrie de comptage, la modération et la réflection des neutrons à l'intérieur de l'échantillon On décrit des dispositifs pour contrôler les erreurs.

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BIVALENT THALLIUM AND THE MECHANISM OF THE ELECTRODE REACTION $Tl^{3+} + 2e \rightleftharpoons Tl^{+}$*

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Summary—The thallium^{I}-thallium^{III} electrode reaction has been studied by hydrodynamic voltammetry at platinum anodes and cathodes. Conclusive evidence is presented that the electro-oxidation of the aquo ion Tl^{+} and the electroreduction of Tl^{3+} proceed via a bivalent thallium species. Thallium^{II} is a stronger oxidant than thallium^{III} ion. In 1*M* aqueous perchloric acid the rate of the disproportionation process

$$2Tl^{II} \rightarrow Tl^{+} + Tl^{3+}$$

is relatively fast compared to the electron transfer steps

$$Tl^{II} + e \rightarrow Tl^{+}$$
$$Tl^{3+} + e \rightarrow Tl^{II}.$$

THE investigation described below was devoted to the heterogeneous electron-transfer process

$$Tl^{3+} + 2e \leftrightarrows Tl^{+} \tag{1}$$

occurring at a platinum indicator electrode in a 1*M* aqueous perchloric acid supporting electrolyte, where the aquo-ions of univalent and tervalent thallium are the overwhelmingly predominating stable species. In view of this situation, equation (1) is of fundamental significance, as a possible example of a "single-stage two electron transfer" mechanism in an electrode reaction. In terms of a corresponding physical picture, this implies that the transfer of both electrons be completed during a single vibrational transition of the activated complex, *i.e.*, within a time interval of the order of 10^{-13} sec. For "purely chemical" electron-transfer processes occurring in homogeneous solution (*e.g.*, electron exchange between tagged and untagged ions involving two oxidation states of the same element; "cross reactions" involving two different couples, such as the oxidation of chromium^{II} by cobalt^{III}) this question has been the subject of a historic controversy. On the one hand, the Haber-Weiss school argued *a priori* that *all* electron transfer processes must necessarily be resolvable into ultimate "single electron transfer steps";[2,3] on the other hand, experimental evidence to the contrary was adduced.[4] As far as the thallium^{III}-thallium^{I} couple in perchloric acid is concerned, rate studies of the homogeneous electron-exchange process

$$Tl^{+} + \overset{\bullet}{Tl}{}^{3+} \xrightarrow{\text{aq. HClO}_4} Tl^{3+} + \overset{\bullet}{Tl}{}^{+} \tag{2}$$

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* Based on a doctoral thesis by H. A. C. The senior author (J. J.) has had the benefit of the inspired guidance of Professor Kolthoff in an earlier study devoted to the voltammetry of thallium.[1] It is fitting that he contribute to this Honour Issue a paper on a related topic.

did not permit discrimination between the two alternatives.[5] However, kinetic data involving the oxidation of iron^{II} by tervalent thallium were interpreted[6] as being consistent with the formation of a bivalent thallium intermediate in accordance with the equations:

$$Fe^{2+} + Tl^{3+} \rightarrow Fe^{3+} + Tl^{II} \tag{3}$$

$$Tl^{II} + Fe^{2+} \rightarrow Fe^{3+} + Tl^{+} \tag{4}$$

The elucidation of the mechanism of the thallium^{I}-thallium^{III} electrode reaction is timely, because it has been suggested that similar transition states may be involved in electrode processes and in homogeneous electron-exchange reactions.[7] Vetter and Thiemke[8] have presented experimental evidence which is compatible with the assumption, that in 0·5–7·5 *M* aqueous sulphuric acid, reaction (1) proceeded *via* the two-step sequence.

$$Tl^{III} \overset{e}{\leftrightarrow} Tl^{II} \overset{e}{\leftrightarrow} Tl^{I} \tag{5}$$

In the investigation described in this paper, it has been shown *conclusively* that in 1*M* perchloric acid the thallium^{I}-thallium^{III} electron transfer at platinum electrodes occurred by the following mechanism.

Electroreduction of aquo-thallium^{III} ion.

$$2[Tl^{3+} + e \xrightarrow[\text{rate determining}]{k_{3,2}} Tl^{II}] \tag{6a}$$

$$2\,Tl^{II} \xrightarrow[\text{fast}]{k_{dispr}} Tl^{+} + Tl^{3+} \tag{7}$$

Electro-oxidation of aquo-thallium^{I} ion:

$$2[Tl^{+} \xrightarrow[\text{rate determining}]{k_{1,2}} Tl^{II} + e] \tag{6b}$$

$$2\,Tl^{II} \xrightarrow[\text{fast}]{k_{dispr}} Tl^{3+} + Tl^{+} \tag{7}$$

Implicit in equation (7) is direct evidence that the standard potential of the couple Tl^{II}/Tl^{+} must necessarily be more anodic than that of the Tl^{3+}/Tl^{+} couple. This accounts satisfactorily for the fact that bivalent thallium has never been prepared as a stable species in quantities amenable to chemical characterisation.

EXPERIMENTAL

The methodological approach employed for elucidating electrode kinetics was the technique of "hydrodynamic voltammetry", developed in these laboratories and previously described.[9–11] Current-voltage (c.v.) curves were recorded in a rotated electrolysis cell in which the electrolyte solution streamed past a stationary indicator electrode under judiciously controlled conditions of laminar flow.[11] The rates of the prevailing mass transport (between the bulk of the electrolyte solution and the indicator surface) corresponded within 1% to a forced convection model discussed in an earlier paper,[10] and characterised by the following equations:

$$I = \pm nFAm_i(a_i - a_i^0) \tag{8}$$

$$I_l = \pm nFAm_ia_i \tag{9}$$

$$m_i = \rho V^{1/2}D_i^{2/3}\nu^{-1/6}L^{-1/2} \tag{10}$$

which were verified in the present study. The symbols in equations (8)–(10) have the following meaning: I = net current (A), assigned a positive or negative sign to denote reduction or oxidation, respectively; nF = number of coulombs/mole involved in the over-all electrode reaction; I_l = limiting current (anodic or cathodic); A = effective area of indicator electrode (cm^2), m_i = mass transport coefficient (cm/sec) for the species identified by the subscript, a_i, a_i^0 = activity (moles/ml) of species i in the bulk of the solution and at the electrode surface, respectively; ρ = a dimensionless friction drag coefficient; v = linear velocity of solution (cm/sec) past the indicator electrode, D_i = a diffusion coefficient (cm^2/sec) defined in terms of activity gradients,[12] ν = kinematic viscosity (cm^2/sec), L = characteristic dimension (cm) of electrode, parallel to flow Concentrations of reactants and products at the indicator electrode interface (which are not accessible to direct experimental determination and are of critical importance in determining the values of the rate parameters in electrode reactions) were calculated on the basis of this mass transfer model Two indicator electrode geometries which yielded similar results were employed, viz, a conical micro electrode described previously[10] (L = the slant height of the cone) and a planar wedge electrode illustrated in Fig. 1.

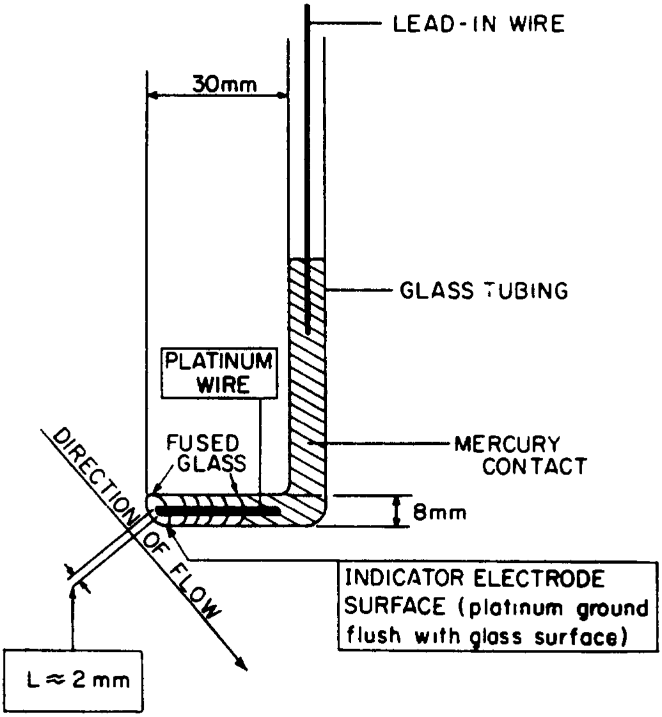

FIG. 1.—Planar wedge microelectrode
{L = characteristic dimension [see equation (10)]}

All c.v. curves were recorded in a range of potentials between 0 2 and 1 7 V versus the normal hydrogen electrode (NHE), where the platinum surface existed invariably in a reproducible "semi-oxidised" form, Pt(OH)$_n$, characterised by Feldberg.[13] As a working reference electrode, a saturated silver-silver chloride half cell (0·198 V *vs.* NHE), described by Lingane was used in conjunction with an agar gel salt bridge.[14] Appropriate precautions were taken to eliminate any consequential contamination of the electrolysis cell from the reference electrode. The electrolysis cell was constructed of polyethylene. It was ascertained, with the aid of *ad hoc* experiments carried out in all-glass apparatus, that the results obtained in this study were not affected by the polyethylene.

Voltammograms were recorded with conventional automatic polarographs, including a Sargent Model XXI instrument, and a Leeds and Northrup Electrochemograph, Model E. Potentials were scanned at rates customary in conventional polarography, *i.e.*, 1·24 to 3 33 mV/sec.

All experiments were carried out at 25·0°. Reagent-grade chemicals and triply distilled water were used. Current measurements were reproducible to within ±1%. Potential measurements were

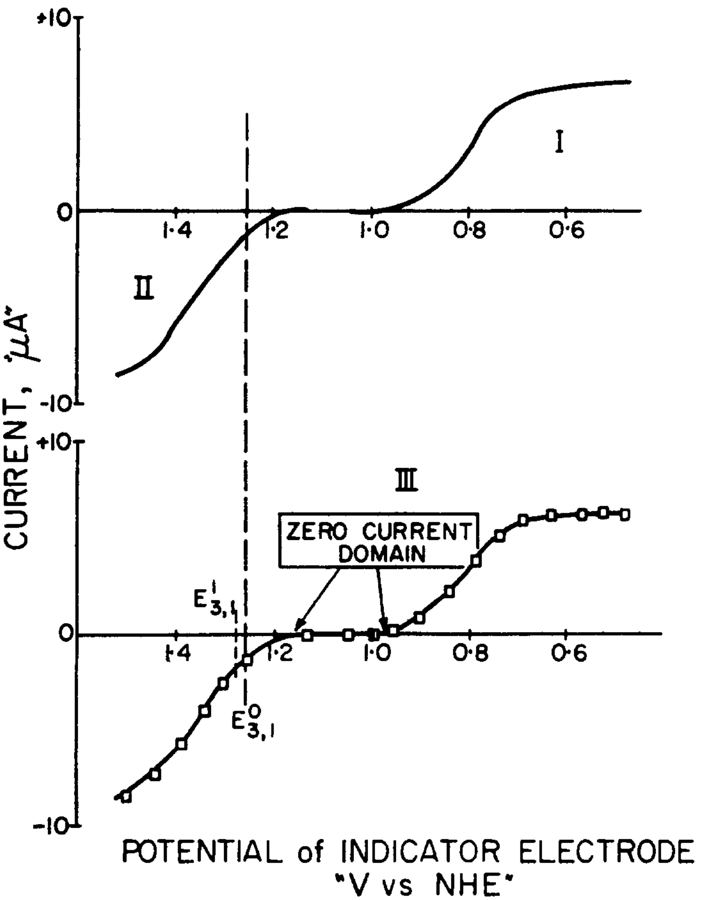

Fig. 2.—Examples of current-voltage curves obtained experimentally (flow velocity = 7·0 cm/sec): I—cathodic wave obtained in $10^{-3}M$ Tl^{3+}, in the absence of Tl^+;
II—anodic wave obtained in $10^{-3}M$ Tl^+, in the absence of Tl^{3+};
III—voltammogram obtained in mixture of $10^{-3}M$ Tl^{3+} plus $10^{-3}M$ Tl^+; smooth curve recorded experimentally, points calculated theoretically on basis of Mechanism C.
[Supporting electrolyte: $1M$ aqueous $HClO_4$; E_3^0: standard potential of Tl^{3+}/Tl^+ couple; $E_{3,1}'$: genuine equilibrium potential in presence of $10^{-3}M$ Tl^{3+} plus $10^{-3}M$—Tl^+ (= formal potential)]

precise and accurate to 0·005 V. Because the resistance of the electrolysis cell was 350 Ω and the maximum current measured was 50 μA, corrections for iR drops were not necessary. All potentials have been referred to the normal hydrogen electrode (NHE), using the Stockholm Sign Convention. All rate parameters reported in this paper have been consistently defined in terms of the activities of the reactants involved. This applies to the rate constants used to characterise electron transfer, as well as to mass transport coefficients [*m* in equations (8)–(10)] and diffusion coefficients. The choice of "activity rate constants", in preference to the more commonly used conventional "concentration rate constants", was predicated by considerations of fundamental consistency and general applicability (as well as convenience in correcting for electrical double layer effects, when applicable).[15]

Careful consideration was given to the magnitude of possible corrections from effects of the electric double layer.[16,17,18,19,20] At the high ionic strength used in this study ($\mu = 1$), corrections for "non-specific adsorption" proved unnecessary within the precision of the rate parameters determined (±30% for electron-transfer rate constants and ±10% for transfer coefficients). The experimental conditions were such that specific adsorption (as far as it can be assessed) was minimised.

All studies were carried out in a voltage domain which was more positive than the potential of zero charge on platinum ($\approx 0{\cdot}2$ V in $1M$ perchloric acid), where cations are generally not adsorbed.* The sole anion present in appreciable concentrations was perchlorate, the specific adsorption of which is known to be negligible in our working range of potentials.

RESULTS

Altogether, approximately 100 voltammograms were recorded at several concentrations and at 15 selected flow velocities in the ranges specified below:

(a) bulk concentrations of Tl^{3+}:

$5 \times 10^{-3} M$ to $5 \times 10^{-4} M$ [$3 \times 10^{-7} < a_{Tl^{3+}} < 3 \times 10^{-6}$ moles/ml]†

(b) bulk concentrations of Tl^+:

$5 \times 10^{-3} M$ to $5 \times 10^{-4} M$ [$3 \times 10^{-7} < a_{Tl^+} < 3 \times 10^{-6}$ moles/ml]†

(c) flow velocities:

5 to 90 cm/sec.

Values reported in this paper for rate parameters represent appropriately weighed averages of all of the relevant results, whose precision is indicated in terms of the standard deviation of the mean. The voltammograms illustrated in Fig. 2 are typical of the results obtained. As is evident from the figure, the cathodic wave was virtually unaffected by the presence of thallium^{I} ion and *vice versa*. Between the waves there exists a "zero current domain" (ZCD), in the potential range $1{\cdot}0 < E < 1{\cdot}2$‡. Such a situation is characteristic of "totally irreversible voltammograms",[22] indicating that at voltages corresponding to the cathodic wave, the rate of the over-all reaction

$$Tl^+ \rightarrow Tl^{3+} + 2e \tag{12}$$

was negligible compared to the rate of the converse process

$$Tl^{3+} + 2e \rightarrow Tl^+ \tag{13}$$

and *vice versa* for the anodic wave. The interesting effect of flow velocity on voltammograms is illustrated by a typical "family of curves" shown in Fig. 3.

DISCUSSION

In interpreting the experimental current voltage curves, three plausible mechanisms were considered for the electrode reaction (1);

(A) *A single stage two-electron transfer, viz.*

$$Tl^{3+} + 2e \xrightarrow{k_{s,1}} Tl^+ \tag{14}$$

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* As a notable exception, Frumkin has recently reported[21] that thallium^{I} ion was adsorbed on black platinised anodes when present at a concentration of $1M$ in the bulk of the solution. The effect was appreciable at potentials between $0{\cdot}3$ and $0{\cdot}7$ V, but decreased abruptly when the voltage was made either more positive or more negative. The only potential domain where adsorption of thallium^{I} ions may have been of significance in the present study was $>1{\cdot}2$ V (*vide infra*). Extrapolation of Frumkin's data suggests that it would have been negligible in that voltage range, even under his own experimental conditions. However, in the present investigation the maximum concentration of Tl^+ was $5 \times 10^{-3}M$ (as compared to $1M$ in reference 21) and the electrodes we used were blank (rather than black) platinum. These factors can reasonably be expected to have reduced the adsorption of thallium^{I} ion (if any) to negligible proportions. Accordingly, it was ignored.

† Concentrations were converted into corresponding activities, with the aid of applicable molarity activity coefficients, *viz.*, $f_{Tl^{3+}} = 0{\cdot}65$, $f_{Tl^+} = 0{\cdot}54$.

‡ Actually, the ZCD is a region where c.v. curve III had a very small slope, which coincided with the zero current axis within the precision of the present investigation.

for the cathodic wave of thallium^{III} ion; and for the anodic wave of thallium^{I} ion:

$$Tl^{+} \xrightarrow{k_{1,a}} Tl^{3+} + 2e \qquad (15)$$

(B) *Two successive one-electron transfer steps, viz.**

$$Tl^{3+} \overset{e}{\longleftrightarrow} Tl^{II} \overset{e}{\longleftrightarrow} Tl^{+} \qquad (16)$$

(C) *A rate determining one-electron transfer followed by fast disproportionation of the intermediate* in accordance with equations (6)–(7).

These three schemes are examined critically below, with a view to ascertaining whether they can account for the results obtained in this study. The applicable assumption was made that under the experimental conditions a steady state prevailed at any given potential (*i.e.*, there was no transient variation of the measured currents), and rate laws characteristic of each particular mechanism were derived accordingly.[9,22,23]

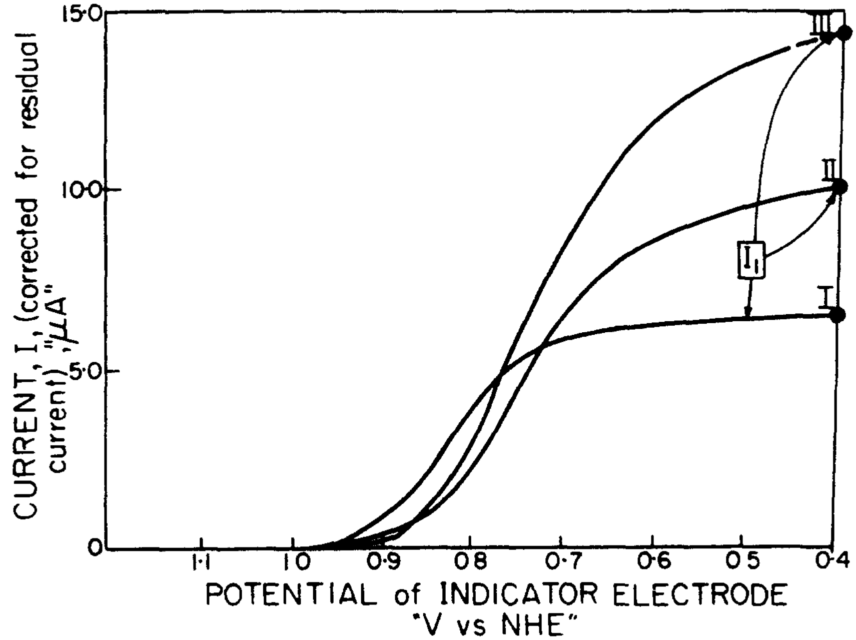

FIG. 3.—Typical "family of voltammograms" (of $10^{-3}M$ Tl^{3+} in $1M$ $HClO_4$), illustrating over-all effects of flow velocity: I—13·7 cm/sec; II—36·6 cm/sec; III—91·0 cm/sec (I_l = limiting current)

The following general observations, common to all current-voltage curves obtained, were taken into account:

(*a*) All cathodic and anodic voltammograms exhibited "shifts" as a function of flow velocity. The nature of these "shifts" is illustrated in the "normalised" voltammograms, shown in Fig. 4. These represent a replot of the data shown in Fig. 3 using as ordinate the quantity I/I_l instead of I.

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* The symbol ⟷ is used to denote a "kinetically discrete" electron-transfer step, *i.e.*, one which proceeds in the forward (reduction) or reverse (oxidation) directions via the same activated complex.

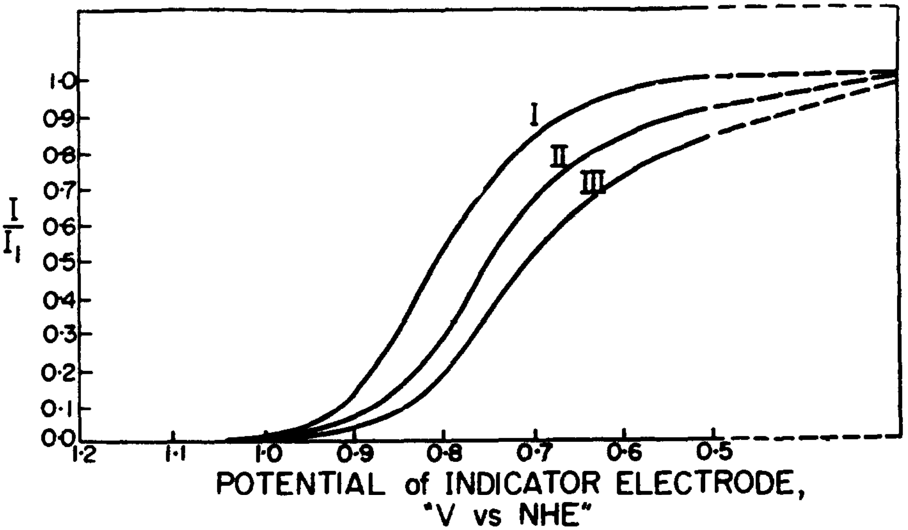

FIG 4.—Normalised voltammograms illustrating potential shifts as function of flow velocity. Replot of data shown in Fig. 3, using the dimensionless quantity $\left(\frac{I}{I_l}\right)$ as ordinate (I = current at a given potential; I_l = limiting current)

Shifts of the type illustrated in Fig. 4 are characteristic of situations where the ascending portion of c.v. waves is controlled concomitantly by rates of electron transfer and by mass transport. Consequently, only those mechanisms were considered, in which the rate of at least one electron-transfer step is a kinetically controlling factor of the over-all reaction.

(*b*) Without exception, in all of the voltammograms recorded in this investigation, the standard potential of the thallium^{III}-thallium^{I} couple was located on the ascending part of the anodic wave, rather than in the ZCD (see Fig. 2, Curve III), *i.e.*, the apparent "overvoltage" of the cathodic wave was considerably greater than that of the anodic wave. This remarkable feature proved an important clue in the elucidation of the electrode mechanism.

Mechanism A

From the viewpoint of formal "mathematical kinetics", this is a well-known case. With respect to electron transfer, the following equations apply:

$$I = I_+ + I_- \tag{17}$$

$$I_+ = 2\,F\,A\,k_{3,1}\,a_3{}^0 \tag{18}$$

$$I_- = -2\,F\,A\,k_{1,3}\,a_1{}^0 \tag{19}$$

$$k_{3,1} = k^0{}_{3,1}\exp\left[\alpha_{3,1}(E^0_{3,1} - E)\frac{2F}{RT}\right] \tag{20}$$

$$k_{1,3} = k^0_{3,1}\exp\left[(1 - \alpha_{3,1})(E - E^0_{3,1})\frac{2F}{RT}\right] \tag{21}$$

where I_+ and I_- denote the cathodic and anodic current components; $k_{3,1}$ and $k_{1,3}$ are electron-transfer rate constants (cm/sec) effective at the potential E, for reactions (14) and (15), respectively; subscripts $_3$ and $_1$ identify activities of the thallium^{III} and thallium^{I} ions, and $E^0_{3,1}$ denotes the standard potential of the thallium^{III}-thallium^{I} couple. A crucial consideration characterising Mechanism A is that the values of the specific rate constant, $k^0_{3,1}$, and of the transfer coefficient, $\alpha_{3,1}$, must be identical irrespective of whether they are calculated form cathodic currents [equations (14) and (20)] or anodic currents [equations (15) and (21)]. *The "sameness" of these two rate parametres represents an unambiguous test as to whether only one transition state is involved, which is mandatory whenever a genuine single-stage process prevails.*

The prevailing mass transfer model requires that the following equations hold:

$$\frac{I}{2FA} = m_3(a_3 - a_3{}^0) = m_1(a_1{}^0 - a_1) \tag{22}$$

$$I_{1,+} = 2\,F\,Am_3a_3 \tag{23}$$

$$I_{1,-} = -2\,F\,Am_1a_1 \tag{24}$$

where the subscripts + and − denote cathodic and anodic limiting currents, respectively. In accordance with the steady state assumption, the a's were eliminated between equations (17)–(19) and (22)–(24) yielding the following "general wave equation", which is applicable to voltammograms expected in the presence of either Tl^+ or Tl^{3+}, or both:

$$I = \frac{\dfrac{k_{3,1}}{m_3}\,I_{1,+} + \dfrac{k_{1,3}}{m_1}\,I_{1-}}{1 + \dfrac{k_{3,1}}{m_3} + \dfrac{k_{1,3}}{m_1}} \tag{25}$$

Theoretical c.v. curves, computed [from equations (20), (21) and (25)] for a solution which contains 10^{-3} M Tl^{3+} plus 10^{-3} M Tl^+, by assigning a variety of reasonable sets of values to the rate parameters $k^0_{3,1}$, α, m_3 and m_1, yielded the plots shown in Fig. 5. These represent a family of curves of a well-known type,[22] ranging in shape from

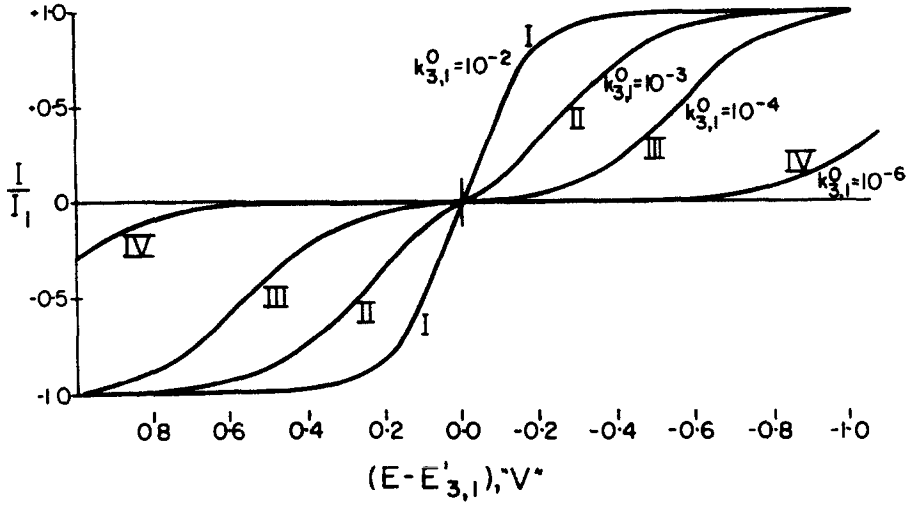

FIG. 5.—"Theoretical normalised voltammograms", calculated in accordance with Mechanism A, for a solution containing equimolar concentrations of Tl^+ plus Tl^{3+}. (E = potential of indicator electrode; $E_{3,1}{}'$ = same as in Fig. 2. Values assigned: $\alpha_{3,1} = 0{\cdot}50$; $m_3 = m_1 = 10^{-3}$ cm/sec; $k^0_{3,1}$–as shown on each curve)

a "reversible" composite wave (Curve I) via a "totally irreversible" split wave (Curve III), to Tafel plots (Curve IV). Comparisons of Fig. 5, on the one hand, with the corresponding experimental voltammogram (Fig. 2, Curve III) on the other, revealed irreconcilable differences: For instance, $E'_{3,1}$ in Fig. 5 is invariably in the ZCD, while in Fig. 2 it is located on the sigmoid section of the anodic wave. Quite generally, it was found that for all possible assignments of

$$0 < k^0_{3,1} < \infty$$

and

$$0 < \alpha^0_{3,1} < 1$$

calculations based on Mechanism A yielded c.v. curves which were significantly at variance with the experimental results.

The utter incompatibility of Mechanism A with our experimental data has been substantiated further, using the following argument. Assuming that Mechanism A did prevail, the rate parameters $k^0_{3,1}$ and $\alpha_{3,1}$ were evaluated separately from experimentally obtained cathodic and anodic c.v. waves. Using a procedure recommended in a classical paper by Laitinen *et al.*,[24] equations (18)–(21) were applied to the "foot" of the waves where concentration polarisation was negligible. This yielded two discrete sets of values, one obtained from cathodic voltammograms of Tl^{3+}, and the other from anodic voltammograms of Tl^+. The relevant data are listed in Table I. As can be seen in the table, the precision of the means *in each set* was better than ± 10% for $\alpha_{3,1}$ and better than ±30%, for $k^0_{3,1}$. However, the mean $k^0_{3,1}$ of the "cathodic set" differed by three orders of magnitude from that of the

TABLE I.—KINETIC PARAMETERS EVALUATED FROM THE EXPERIMENTAL DATA ON THE ASSUMPTION THAT MECHANISM A WAS OPERATIVE

Set of values obtained from cathodic waves of Tl^{3+} using equation (20)

Flow velocity, *cm/sec*	$2\alpha_{3,1}$	$k^0_{3,1}$, *cm/sec*
13·7	0·60	$1{\cdot}14 \times 10^{-6}$
25·4	0·55	$1{\cdot}25 \times 10^{-6}$
36·6	0·55	$0{\cdot}45 \times 10^{-6}$
58·0	0·50	$1{\cdot}07 \times 10^{-6}$
70·8	0·59	$1{\cdot}00 \times 10^{-6}$
91·6	0·58	$0{\cdot}61 \times 10^{-6}$

Averages: $\alpha_{3,1} = 0{\cdot}28 \pm 0{\cdot}02$, $k^0_{3,1} = (0{\cdot}9 \pm 0{\cdot}2) \times 10^{-6}$

Set of values obtained from anodic waves of Tl^+ using equation (21)

Flow velocity, *cm/sec*	$2(1 - \alpha_{3,2})$	$k^0_{3,1}$, *cm/sec*
6·96	0·45	$4{\cdot}8 \times 10^{-4}$
13·0	0·60	$9{\cdot}0 \times 10^{-4}$
24·8	0·51	$5{\cdot}8 \times 10^{-4}$
35·5	0·60	$5{\cdot}8 \times 10^{-4}$
47·0	0·63	$5{\cdot}9 \times 10^{-4}$
48·9	0·59	$6{\cdot}3 \times 10^{-4}$
72·9	0·50	$7{\cdot}1 \times 10^{-4}$
85·4	0·51	$6{\cdot}3 \times 10^{-4}$
91·0	0·51	$9{\cdot}1 \times 10^{-4}$

Averages $\alpha_{3,1} = 0{\cdot}72 \pm 0{\cdot}03$; $k^0_{3,1} = (7 \pm 1) \times 10^{-4}$

"anodic set". The mean $\alpha_{3,1}$ values of the two sets were discrepant by a factor of three. All this indicated compellingly that more than one transition state was involved in Reaction 1.

Mechanism B

Current knowledge of the chemistry of thallium suggests strongly that the reversible standard potentials defined by equations (26) and (27) [where the subscript $_2$ identifies the bivalent thallium species in equation (16)]

$$E = E^0_{3,2} + \frac{RT}{F} \ln \frac{a_3}{a_2} \tag{26}$$

$$E = E^0_{2,1} + \frac{RT}{F} \ln \frac{a_2}{a^1} \tag{27}$$

do not differ too much (unless $E^0_{2,1} > E^0_{3,2}$, which requires a spontaneous disproportionation of bivalent thallium and leads to Mechanism C). If they did, it should have been easy to prepare bivalent thallium either by electro-oxidation of thallium^{I} ion or by the electroreduction of thallium^{III} ion. Furthermore, if

$$E^0_{2,1} \ll E^0_{3,2} \tag{28}$$

the anodic and cathodic waves shown in Fig. 2 should have each been split in two, corresponding to the appropriate discrete one-electron transfer steps. The precision and accuracy of the experiments was such that a corresponding resolution into a total of four one-electron transfer waves (in lieu of the two waves shown in Fig. 2, Curve III) would have been observed experimentally, whenever $(E^0_{3,2} - E^0_{2,1}) > 0{\cdot}05$ V.

The electron-transfer rate equations pertaining to Mechanism B are

$$I_+ = F A\, k_{3,2}\, a_3{}^0 + F A\, k_{2,1}\, a_2{}^0 \tag{29}$$

$$I_- = -F A\, k_{1,2}\, a_1{}^0 - F A\, k_{2,3}\, a_2{}^0 \tag{30}$$

Equation (31) holds concomitantly because a steady state exists

$$\frac{da_2}{dt} = 0 \rightarrow k_{3,2}\, a_3{}^0 + k_{1,2}\, a_1{}^0 = k_{2,3}\, a_2{}^0 + k_{2,1}\, a_2{}^0 \tag{31}$$

Relevant rate constants, transfer coefficients and potentials are correlated as follows:

$$k_{3,2} = k^0_{3,2} \exp\left[\alpha_{3,2}(E^0_{3,2} - E)\frac{F}{RT}\right] \tag{32}$$

$$k_{2,3} = k^0_{3,2} \exp\left[(1 - \alpha_{3,2})(E - E^0_{3,2})\frac{F}{RT}\right] \tag{33}$$

$$k_{2,1} = k^0_{2,1} \exp\left[\alpha_{2,1}(E^0_{2,1} - E)\frac{F}{RT}\right] \tag{34}$$

$$k_{1,2} = k^0_{2,1} \exp\left[(1 - \alpha_{2,1})(E - E^0_{2,1})\frac{F}{RT}\right] \tag{35}$$

$$E^0_{3,1} = \frac{E^0_{3,2} + E^0_{2,1}}{2} \tag{36}$$

Elimination of all activity terms between equations (22)–(24) and (29)–(31) yielded the "general wave equation":

$$I = \frac{\dfrac{k_{3,2}\,k_{2,1}}{m_3}\,I_{l,+} + \dfrac{k_{1,2}\,k_{2,3}}{m_1}\,I_{l,-}}{k_{2,3} + k_{2,1} + \dfrac{k_{3,2}\,k_{2,1}}{m_3} + \dfrac{k_{1,2}\,k_{2,3}}{m_1}} \tag{37}$$

Theoretical voltammograms corresponding to equations (32)–(35) and (37) were constructed with the aid of calculations similar to those employed in obtaining Fig. 5. Judicious comparison with experimental c.v. curves indicated unambiguously that Mechanism B could not account satisfactorily for the experimental observations, regardless of the values assigned to the rate parameters $k^0_{3,2}$, $k^0_{2,1}$, $\alpha_{3,2}$ and $\alpha_{2,1}$. That Mechanism B was indeed not operative is evident from the fact that in an equimolar solution of Tl^{3+} and Tl^{+}, where

$$\frac{a_3}{f_3} = \frac{a_1}{f_1} \tag{38}$$

equation (37) requires that

$$I = 0 \; at \; E = E'_{1,3} = E^0_{1,3} + \frac{RT}{2F} \ln \frac{f_3}{f_1} \tag{39}$$

Mathematical proof, that requirement (39) is mandatory for Mechanism B whenever Tl^{3+} plus Tl^{+} are present in equimolar bulk concentrations, is offered in the *Appendix*. It can be seen in Fig. 2, Curve III (which is a typical example of a voltammogram actually recorded in an equimolar solution of Tl^{3+} plus Tl^{+}) that the results obtained in this investigation were strikingly at variance with requirement (39). Consequently, Mechanism B has been ruled out.

Mechanism C

In accordance with equations (6)–(7) the following rate laws apply:

$$I_{+} = 2\,F A\,k_{3,2}\,a_3^0 \tag{40}$$

$$I_{-} = -2\,F A\,k_{1,2}\,a_1^0 \tag{41}$$

Concomitantly, rate and potential parameters must conform with equations (32)–(36), mass transport is governed by equations (22)–(24), and the following Steady State Requirement [based on equations (7), (40), (41)] must be met:

$$\frac{da_2^0}{dt} = 0;\; k_{3,2}\,a_3^0 + k_{1,2}\,a_1^0 = \delta k_{\text{dispr.}}\,(a_2^0)^2 \tag{42}$$

where δ denotes the thickness of the reaction layer at the electrode surface. The corresponding general wave equation (obtained by appropriate elimination of the activity terms) has the form:

$$I = \frac{\dfrac{k_{3,2}}{m_3}\,I_{l,+} + \dfrac{k_{1,2}}{m_1}\,I_{l,-}}{1 + \dfrac{k_{3,2}}{m_3} + \dfrac{k_{1,2}}{m_1}} \tag{43}$$

Theoretical voltammograms computed in accordance with equation (43) gave plots which proved, in all instances, identical with the corresponding experimental c.v.

curves. The excellent agreement is exemplified by the "calculated points", superimposed on Fig. 2, Curve III.

Numerical estimates of rate parameters, calculated from experimental voltammograms on the basis of equation (43) are listed in Table II

TABLE II—KINETIC PARAMETERS CALCULATED FROM THE EXPERIMENTAL DATA ON THE ASSUMPTION THAT MECHANISM C WAS OPERATIVE

Set of values obtained from cathodic waves of Tl^{3+} using equations (40) and (43)

Flow velocity. *cm/sec*	$\alpha_{3,2}$	$k_{3,2}$ (at 1·25 V)[a]
13·7	0·60	$1·14 \times 10^{-6}$
25·4	0·55	$1·25 \times 10^{-6}$
36·6	0·55	$0·45 \times 10^{-6}$
58·0	0·50	$1·07 \times 10^{-6}$
70·8	0·59	$1·00 \times 10^{-6}$
91·8	0·58	$0·61 \times 10^{-6}$

Average $\alpha_{3,2} = 0·56 \pm 0·03$; $k_{3,2} = (0·9 \pm 0·2) \times 10^{-6}$

Set of values obtained from anodic waves of Tl^{+} using equations (41) and (43)

Flow velocity *cm/sec*	$(1 - \alpha_{2,1})$	$k_{1,2}$ (at 1·25 V)[a]
6·97	0·45	$4·8 \times 10^{-4}$
13·0	0·60	$9·0 \times 10^{-4}$
24·8	0·51	$5·8 \times 10^{-4}$
35·5	0·60	$5·8 \times 10^{-4}$
47·0	0·63	$5·9 \times 10^{-4}$
48·9	0·59	$6·3 \times 10^{-4}$
72·9	0·50	$7·1 \times 10^{-4}$
85·4	0·51	$6·3 \times 10^{-4}$
91·0	0·51	$9·1 \times 10^{-4}$

Average: $\alpha_{2,1} = 0·45 \pm 0·05$; $k_{1,2} = (7 \pm 1) \times 10^{-4}$

[a] Because $E^0_{3,2}$ and $E^0_{2,1}$ are not known, values of $k_{3,2}$ and $k_{2,1}$ effective at $E^0_{2,1}$ (= 1·25 V) have been reported.

It is apparent that the values obtained at fifteen different flow velocities exhibited satisfactory "internal consistency" and the transfer coefficients $\alpha_{3,2}$ and $\alpha_{2,1}$ approximate 0·5 in agreement with reasonable *a priori* considerations. This confirms that under the experimental conditions prevailing in this investigation, the thallium^{I}-thallium^{III} electron transfer occurred via Mechanism C [equations (6)–(7)].

The finding, that in 1 *M* perchloric acid the thallium^{I}-thallium^{III} reaction involves a fast disproportionation of the bivalent intermediate, invites an interesting comparison with the report of Vetter and Thiemke.[8] In the presence of sulphuric acid in appreciable concentration, the same process was compatible with Mechanism B. It is noted in this context, that Vetter and Thiemke's experimental results are also compatible with Mechanism C. In other words, their data did not permit discrimination between Mechanisms B and C. The possibility, that the shape of d.c. voltammograms may be sometimes inconclusive for the purpose of identifying mechanisms of electrode processes, has been pointed out by Riddiford.[25] The experimental situation in the present investigation was fortunate in this respect. The genuine equilibrium potential of the thallium^{I}-thallium^{III} couple ($E'_{3,1}$ in the presence of equimolar concentrations of Tl^{+} plus Tl^{3+}) was invariably located *outside the ZCD* (see Fig. 2). This has permitted us to select *Mechanism C* as *uniquely applicable*, without ambiguity. However, we desire to emphasise that there is no necessary contradiction between Vetter and Thiemke's conclusions and ours. Quite possibly, the rates and mechanism of the thallium^{I}-thallium^{III} electrode reaction may be entirely different in perchloric and in sulphuric acids. Appreciable sulphato-complexation of thallium^{I} and thallium^{III} ion is known to occur in sulphate media.[8,26] Consequently, the electroreactive species are not necessarily the same in the presence of sulphate as in perchloric acid (where the aquo ions prevail). Furthermore, the presence of sulphate and/or perchlorate may quite radically change the rates and the mechanism if, for instance, a "bridged" transition state were involved. It should be noted, in this context, that Mechanism C may readily be converted into B if the rate of disproportionation [equation (7)] is slow compared to the rate of the electron-transfer steps (6a) and (6b). This is evident from the following scheme.

$$\text{PATH I: } \underbrace{Tl^{3+} \xleftrightarrow{\ e\ } \underbrace{Tl^{II}}_{} \xleftrightarrow{\ e\ } Tl^{+}}_{} \qquad (44)$$

PATH IIa PATH IIb
Oxidation of Tl^{II} Reduction of Tl^{II}

If the rate of reaction (7) is slow compared to the electron-transfer processes

$$Tl^{II} \xleftrightarrow{e} Tl^{+} \qquad (45)$$

$$Tl^{II} \xleftrightarrow{e} Tl^{3+} \qquad (46)$$

the over-all electrode reaction [equation (1)] must proceed via "PATH I" (as may have been the case in Vetter and Thiemke's work). Alternative PATH II would be operative (as was the case in the present investigation) in the following situations

$$r_7 \gg r_{45} \qquad (47)$$

$$r_7 \gg r_{46} \qquad (48)$$

where the symbol *r* denotes the rate of the reaction identified by the subscripts (which are identical with the serial numbers of the corresponding chemical equations listed earlier in this article).

The possibility of a mechanism where $r_7 \approx r_{45} \approx r_{46}$ was rejected, on the grounds that it would be characterised by a gradual changeover from Mechanism C to Mechanism B as a function of the concentration of the "primary reactants" Tl^{3+} and Tl^{+}: reaction (7) is second order with respect to Tl^{II}, while reactions (45) and (46) both have first order kinetics. Consequently, Mechanism B would be expected to predominate at low concentrations of Tl^{+} and Tl^{3+}, and Mechanism C at high concentrations. No such trend was evident in the present investigation.

In conclusion, it is apparent that the thallium^{III}-thallium^{I} electrode reaction proceeds via a bivalent intermediate which is a stronger oxidant than Tl^{3+}. In aqueous solution, and in the absence of complexing ligands, the relevant redox potentials [identified in expression (49)]

$$\underbrace{Tl^{3+} \xleftrightarrow{E^{0}_{3,2}} Tl^{II} \xleftrightarrow{E^{0}_{2,1}} Tl^{+}}_{E^{0}_{3,1}} \qquad (49)$$

are characterised by the following relative properties:

$$E^0_{2,1} > E^0_{3,1} \qquad (50)$$

$$2E^0_{3,1} = E^0_{3,2} + E^0_{2,1} \qquad (51)$$

Disproportionation of bivalent thallium into Tl^{3+} plus Tl^{+}, as required by relation (50), occurred in the presence of perchloric acid at a rate which was fast compared to reactions (45) and (46).

APPENDIX

Proof of requirement (39)

Because the denominator of equation (37) is finite, the necessary and sufficient condition for

$$I = 0 \qquad (A1)$$

is that the numerator be equal to zero, *viz.*:

$$\frac{k_{3,2} \, . \, k_{2,1}}{m_3} I_{1,+} + \frac{k_{1,2} \, . \, k_{2,3}}{m_1} I_{1,-} = 0 \qquad (A2)$$

Substituting for k the appropriate potential dependent expressions [equations (32)–(35)] and rearranging equation (A2), yielded

$$\exp\left\{[2E - (E^0_{3,2} + E^0_{2,1})] \frac{F}{RT}\right\} = -\frac{m_1 I_{1,+}}{m_3 I_{1,-}} \qquad (A3)$$

Expressing $(E^0_{3,2} + E^0_{2,1})$ and the quotient on the right side in terms of equivalent quantities via equations (36), (23) and (24), equation (A4) was obtained.

$$\exp\left\{(E - E^0_{3,1}) \frac{2F}{RT}\right\} = \frac{a_3}{a_1} \qquad (A4)$$

Applying equation (38) and taking logarithms, equation (39) was readily obtained:

$$(38) \rightarrow \frac{a_3}{a_1} = \frac{f_3}{f_1}; \qquad (A4) \rightarrow E_{I=0} \, E^0_{3,1} + \frac{RT}{nF} \ln \frac{f_3}{f_1}$$

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Zusammenfassung—Die Thallium(I)- Thallium(III)- Elektrodenreaktion wurde mit Hilfe der hydrodynamischen Voltammetrie an Platinanoden und -kathoden untersucht. Es werden schlüssige Beweise dafür angegeben, dass die Elektrooxydation des hydratisierten Tl^{+} und die Elektroreduktion von Tl^{3+} über eine zweiwertige Thalliumstufe verlaufen Tl(II) ist ein stärkeres Oxydationsmittel als Tl(III). In 1m wässriger Überchlorsäure war die Geschwindigkeit der Disproportionierung

$$2\,Tl(II) \rightarrow Tl^{+} + Tl^{3+}$$

schnell im Vergleich den Elektronenübergängen

$$Tl(II) + e \rightarrow Tl^{+}$$

und

$$Tl^{3+} + e \rightarrow Tl(II).$$

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* Preliminary assignments of values for two-electron transfer rate constants were made available to Dr. Marcus while the investigation described in this paper was still in progress. They have been incorporated for documentation purposes in a recent theoretical paper[7] and identified as "unpublished results". The values given in the present article are considered definitive assignment, superseding the preliminary data reported by Marcus.

This investigation was supported in part by Public Health Service Research Grant HE-02342 from the National Heart Institute

Résumé—La réaction Tl^{3+}/Tl^{+} aux électrodes a été étudiée par voltampérométrie hydrodynamique sur cathodes et anodes de platine. On montre que l'électrooxydation de l'ion Tl^{+} en milieu aqueux et l'électroréduction de Tl^{3+} font intervenir une forme divalente du thallium. Tl(II) est un oxydant plus fort que l'ion thallique. Dans l'acide perchlorique 1 M la vitesse de la réaction de dismutation

$$2\,Tl(II) \rightarrow Tl^{+} + Tl^{3+}$$

est relativement rapide comparée aux étapes du transfert électronique.

$$Tl(II) + e \rightarrow Tl^{+}$$

$$Tl^{3+} + e \rightarrow Tl(II)$$

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POLAROGRAPHIC DETERMINATION OF CERTAIN MEDICINAL COMPOUNDS CONTAINING DICHLORACETAMIDO GROUPS*

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Summary—A polarographic study has been made of a variety of compounds containing dichloracetamido groups, including *N*-(2,4-dichlorobenzyl)-*N*-(2-hydroxyethyl)dichloracetamide (chlorbetamide), *N*-(4-methylsulphonylphenyl)-1,3-dihydroxy-2-propyldichloracetamide(raceophenidol), *N*,*N*′-bis-(2-ethoxyethyl)-*N*,*N*′-*p*-xylylene-bis-dichloracetamide (teclozan), *N*,*N*′-octamethylene-bis-dichloracetamide and their corresponding analogues. Analytical results are discussed from a quantitative and qualitative point of view with special emphasis on the stability of the compounds at various pH and the effect of various elements or groups in the molecule on the half-wave potentials of the two resulting cathodic waves.

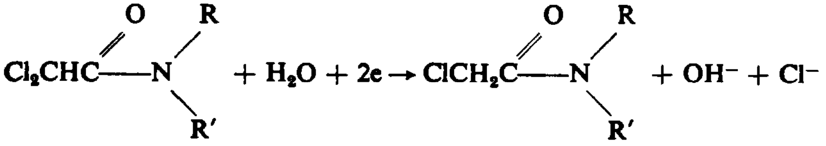
INTRODUCTION

In the past, little attention has been given polarographically to the dichloracetamido group in medicinal compounds. Chloramphenicol, D(−)-threo-2,2-dichloro-*N*-[β-hydroxy-α-(hydroxymethyl)-*p*-nitrophenethyl]-acetamide, has been studied polarographically by Hess[1], Varela,[2] and Knobloch and Svatek[3] The emphasis was, however, on the reduction characteristics of the nitro group rather than the dichloracetamido group. Elving and Ching-Siang Tang[4,5,6] have shown the polarographic characteristics of mono-, di- and trichloracetic acid as well as esters of these acids. In many respects the compounds described in the present paper are like the esters of dichloracetic acid in that as long as they remain intact two cathodic waves result when polarographed.

If the compounds are split by hydrolysis, only one cathodic wave develops, showing all of the polarographic characteristics of dichloracetic acid. These compounds, being amides, are not as susceptible to hydrolysis as are the esters of dichloracetic acid.

The mechanism for these polarographic reductions, representing the successive removal of chlorine from the dichloracetyl portion of the molecule, would be the same as Elving has stated and for the same reasons:—

First Cathodic Wave:



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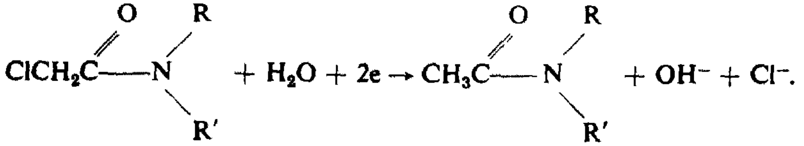
† Fellow of the American Foundation for Pharmaceutical Education.

Second Cathodic Wave



$$\mathrm{ClCH_2C(=O)NRR'} + H_2O + 2e \rightarrow \mathrm{CH_3C(=O)NRR'} + OH^- + Cl^-.$$

It is the purpose of this communication to show the polarographic characteristics of a variety of compounds containing the dichloracetamido group. The compounds have been divided into four major groups (Table I).

EXPERIMENTAL

Reagents

All chemicals and organic solvents were reagent grade. Nitrogen was Edison's dry high-purity nitrogen. Distilled water was used throughout as a solvent as well as in rinsing the polarographic cell.

The buffers were constant ionic strength (1*M*) McIlvaine pH 3, 4, 5, 6, 7 and 8 buffers[7] and a 2·5*M* constant ionic strength aqueous ammonia–ammonium chloride buffer pH 8·2. Unless otherwise stated, the ionic strength of the polarographic media was 0·5*M*. The buffers were adjusted to the stated pH ± 0·1. On addition of these buffers to the polarographic medium the pH of the resulting medium was changed:

in 10% methanol the pH was 0·2–0·3 unit higher;
in 50% methanol the pH was nearly 1 unit higher;
in 70% methanol–10% *N,N*-dimethylformamide (DMF) the pH was 0·5–0·6 unit lower.

Because the polarographic waves resulting from the dichloracetamido groups are independent of pH in the pH range studied, the pH mentioned in the text will refer to that of the aqueous buffer.

Sample solutions: Stock solutions of Group I, II and IV compounds (0·005, 0·005 and 0·0025*M*, respectively) were prepared in 50 ml of methanol. Because of their poor solubility in methanol, 0·0025*M* solutions of the compounds of Group III were prepared in 50 ml of DMF.

Apparatus

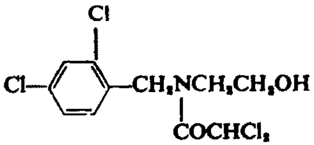
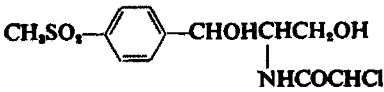
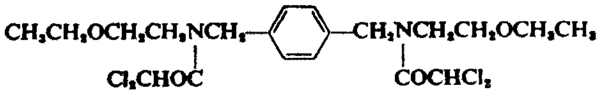
A Sargent Recording Polarograph Model XXI with a conventional dropping mercury electrode (DME) and an aqueous saturated calomel electrode (SCE) were used throughout these studies at a sensitivity setting of 0·06 μA/mm of scale. The damping switch was set at number one. The polarographic cell was a Lingane and Laitinen H-type cell with an agar potassium chloride salt bridge. Unless otherwise stated, all polarograms were recorded in a Sargent constant temperature bath set at 25·0 ± 0·1°. The capillary used in these studies had the following characteristics in 0·5*M* pH 8 McIlvaine buffer in 50% methanol (open circuit): $m = 1{\cdot}861$ mg/sec and $t = 4{\cdot}28$ sec for $h = 50$ cm.

All polarograms were recorded with the mercury height (h) at 50 cm. All diffusion currents were corrected for residual current, which never exceeded 0·2 μA for any potential at which the diffusion current was measured. Maxima were occasionally observed with the second wave but never the first. No maximum suppressors, which might distort the resulting waves, were added to any of the solutions. The half-wave potentials reported are not corrected for iR drop (cell resistance). A Beckman pH meter, Model G, was used to measure pH of the various buffers and solutions.

General procedure for recording the current-voltage curves

Five ml (by pipette) of the appropriate stock solution were added to a 50-ml volumetric flask containing the desired buffer and methanol concentration. For Groups I, II and IV the medium consisted of 25 ml of the 1*M* buffer and 20 ml of methanol. For Group III the medium consisted of 10 ml of 2·5*M* aqueous ammonia–ammonium chloride buffer pH 8·2 and 35 ml of methanol. In each case the solvent mixture was allowed to cool to room temperature before addition of the sample. After the sample addition, the solution was diluted to volume with water and mixed. About 20 ml of this buffered solution was then polarographed within 15 min and the remaining portion after standing 3 days at room temperature. Nitrogen was first passed through a wash bottle containing the same solvent and buffer as the sample, then through the polarographic cell containing the sample for 5 min to deaerate the medium. During the recording of the polarogram (0·0 to −2·0 V) nitrogen was passed over the surface of the solution but without disturbing it. From the resulting polarograms, the half-wave potentials were determined by the intersecting point method[8] and the diffusion current was determined by subtracting the extrapolated residual current from the extrapolated limiting

TABLE I

Group	Structure and chemical name of representative medicinal compound	Generic name	Major medicinal activity
I	 *N*-(2,4-dichlorobenzyl)-*N*-(2-hydroxyethyl) dichloracetamide	Chlorbetamide	Amebicidal
II	 *N*-(4-methylsulphonylphenyl)-1,3-dihydroxy-2-propyldichloracetamide	Raceophenidol	Antibacterial
III	 *N*,*N*′-bis(2-ethoxyethyl)-*N*,*N*′-*p*-xylylene-bis-dichloracetamide	Teclozan	Amebicidal
IV	 $Cl_2CHOC\text{-}N(H)(CH_2)_8N(H)\text{-}COCHCl_2$ *N*,*N*′-octamethylene-bis-dichloracetamide	None	Antispermatogenic

current at the half-wave potential of the first wave. The diffusion current of the second wave was determined by subtracting the extrapolated limiting current of the first wave from the extrapolated limiting current of the second wave Using this approach a satisfactory method was applicable. on a comparative basis, to all of the waves obtained. The diffusion current constant (I) was calculated from data obtained from these polarograms: $I = i_d/Cm^{2/3}t^{1/6}$ where i_d is expressed in μA, C in mmoles (of the given compound)/litre, m in mg (of mercury)/sec and t in sec (length of time for 1 drop of mercury at the stated potential at which the diffusion current was measured).

RESULTS AND DISCUSSION

General

The polarographic waves of these dichloracetamido compounds are well-defined irreversible waves, in that they do not comply with the accepted criteria for reversibility. The change in slope for both waves is gradual and usually over a 0·3-V span. The half-wave potentials vary with concentration (become more negative with increasing concentration). The average diffusion current constant (I) values are in good agreement, as shown in Table II. The I values for the bisdichloracetamido compounds (Groups III and IV) are about twice the values of the mono-dichloracetamido compounds (Groups I and II). This is added evidence that the resulting polarographic waves are from the amount of the dichloracetamido in the given compound. Even though the second wave is not as well-defined as the first, its average I value is in close agreement with that of the first wave. This again is evidence for the reduction of the chlorines individually, from the dichloracetamido group

TABLE II

$$I^* = \frac{i_d}{Cm^{2/3}t^{1/6}}$$

Group	Average I-Value for first wave	Average I-Value for second wave
I	1 55	1 72
II	1 49	1 42
III	2 92	3 32
IV	2·90	3 01

* I is the diffusion current constant where i_d is expressed in μA, C in mmoles/litre, m in mg/sec and t in sec.

The temperature coefficient for these dichloracetamido compounds is 1·5 to 2·0% between 20° and 40°. On changing the mercury column height from 30 to 90 cm, the ratio of $i/h^{1/2}$ was found to be constant. The current resulting from the reduction of these chlorine atoms is diffusion controlled current (i_d) according to the existing criteria.

With none of the compounds did pH (in the pH 3–8 range) affect the wave-height or the half-wave potential of the freshly prepared solution of a given compound.

The ionic strength of the media was varied from 0·1 to 0·5*M* without affecting any of the polarographic wave characteristics of the compounds The methanol content in the polarographic media was varied from 10 to 80%. With most of the compounds, the current decreases about 20% when the methanol content is increased from 10 to 50%. The half-wave potentials usually become more negative (of the order of 0·03 to 0·3 V) as the methanol content increased from 10 to 50%.

With the Group I and II compounds, the diffusion current (corrected for residual current) for the first wave is proportional to concentration from 0·0002 to 0·001*M* (the highest concentration tested). For the bis-dichloracetamido compounds (Groups III and IV) the range is 0·0001 to 0·001*M*.

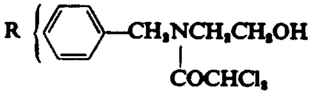
When related compounds were available, containing the several amido groupings (acetyl, mono-, di- or trichloracetyl), it was found that the polarographic waves are very closely related. With the trichloracetamido group, three polarographic waves result. The first appearing to be nearly reversible with a half-wave potential between 0·1 and 0·2 V. The second wave has the same half-wave potential as the first wave of the dichloracetamido group. The third wave has the same half-wave potential as the second wave of the dichloracetamido group and the same as the single wave of the monochloracetamido group. The simple acetamido group results in no wave other than that of the residual current. With the various waves the diffusion current constants are quite similar.

When polarographed, all of the compounds containing the dichloracetamido group resulted in two cathodic waves which are well suited for both the qualitative and quantitative analysis of the intact compounds as well as the main hydrolysis product, the dichloracetate ion. It is from this approach that the compounds will be discussed under their respective groupings.

Group I

Effect of ring substituents. The positioning of the halogen atoms on the benzyl nucleus (Table III) alters the half-wave potential of the first reduction wave of this group of compounds. The 3,4-dichloro analogue's half-wave potential is nearly 0·2 V more positive (thus making the first chlorine of the dichloraceto group easier to reduce) than the 2,6-dichloro analogue. Between these extremes the half-wave potentials of the other halogen compounds are found.

TABLE III.—POLAROGRAPHIC REDUCTION OF GROUP I COMPOUNDS IN BUFFERED 50% METHANOL



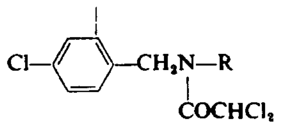
R	First wave		Second wave		Hydrolysed after 3 days at pH 8, %
	$-E_{1/2}$	I	$-E_{1/2}$	I	
1 3,4-dichloro	0·46	1·38	1·20	1·41	72
2 2,4-dibromo	0·49	1·29	1·12	1·57	42
3 4-chloro	0·50	1·38	1·19	1·40	47
4 2,4-dichloro	0·51	1·58	1·16	1·88	64
5 2,6-dichloro	0·63	1·34	1·28	1·26	54
6 4-C_2H_5O—	0·51	1·07	1·18	1·27	82
7 4-C_4H_9O—	0·54	1·13	1·18	1·44	83
8 3,4-diCH_3O—	0·55	1·21	1·18	1·52	76
9 3,4-CH_2O_2—	0·55	1·34	1·20	1·50	89

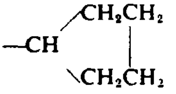
The presence of various alkoxy groups on the benzyl nucleus (Table III) does not appreciably change the polarographic characteristics of the dichloracetamido group.

Effect of substituents on the amide nitrogen. The changes in half-wave potentials of the dichloracetamido group resulting from the various groups on the tertiary amide are not extreme, as shown in Table IV.

From the values (Hydrolysis, %) in the last column of Tables III and IV, the effect of the adjacent substituents on the hydrolysis of the dichloracetamido group is

TABLE IV.—POLAROGRAPHIC REDUCTION OF GROUP I COMPOUNDS IN BUFFERED 50% METHANOL



	R	First Wave		Second Wave		Hydrolysed after 3 days at pH 8, %
		$-E_{1/2}$	I	$-E_{1/2}$	I	
10	—$CH_2CH_2CH_2OH$	0·46	1·62	1·15	1·87	None
11	—$CH_2CHOHCH_3$	0·47	1·78	1·15	1·88	None
12	—CH_2CH_2OH*	0·51	1·58	1·16	1·88	64
13	—$CH_2CH_2OCH_3$	0·49	1·76	1·13	2·08	None
14	—$CH_2CH_2OC_2H_5$	0·51	1·63	1·14	1·84	None
15	—$CH_2CH_2OCOCH_3$	0·41	1·90	1·10	2·18	60
16	—$CH_2CH_2OCOCH_2CH_2Cl$	0·42	1·66	1·11	1·72	56
17	—CH_2CH_2CN	0·37	1·90	1·07	2·05	None
18	—$CH_2CH_2CONH_2$	0·45	1·77	1·16	1·80	None
19	—CH_3	0·50	1·80	1·14	2·07	None
20	—$CH(CH_3)_2$	0·49	1·70	1·16	1·69	None
21		0·51	1·84	1·11	1·97	None

* This is the same compound as number 4 in Table III.

quite apparent. Only the compounds which contain the 2-hydroxyethyl group (numbers 1–9) or the 2-acyloxyethyl group (numbers 15 and 16) attached to the amide nitrogen show any tendency towards hydrolysis of the dichloracetamido group in the 50% methanol pH 8 medium at room temperature. This hydrolysis of the dichloracetamido group may be followed polarographically through the reduction waves of the chlorine on the dichloracetyl group. As long as the dichloracetyl group is still attached to the nitrogen, the two resulting waves are those characteristic of the individual chlorines from the dichloracetamido group being reduced. When about 10% of the dichloracetamido group is hydrolysed, a third wave is detected in the polarogram. The wave height of this third wave increases as the hydrolysis of the dichloracetamido group proceeds to completion. When the dichloracetamido group is 100% hydrolysed, only one reduction wave remains which has all of the polarographic characteristics of dichloracetic acid in this same medium

With the various compounds containing the 2-hydroxyethyl group there is no apparent correlation between the rate of hydrolysis of the dichloracetamido group and the ease of reduction polarographically of the first chlorine of the dichloracetamido group. It is noted, however, that the amount of hydrolysis taking place in this pH 8 medium at room temperature in 3 days depends on the R-substituent of the molecule. The alkalinity of the medium also plays an important role on the rate of hydrolysis of the dichloracetamido group: if the pH 8 buffer is replaced with 0·1*M* tetramethylammonium hydroxide, the dichloracetamido group of chlorbetamide is 100% hydrolysed within 15 min at room temperature, whereas in the pH 8 buffer only 64% is hydrolysed after 3 days at room temperature. In an acidic medium (pH 3) none of these compounds which hydrolyse at pH 8 showed any polarographic signs of hydrolysis of the dichloracetamido group.

It is of particular interest to note the polarograms of *N*-(4-nitrobenzyl)-*N*-(2-hydroxyethyl)dichloracetamide in that both the nitro group and the two chlorines of the dichloracetamido group are reduced polarographically in 50% methanol at pH 8 (Fig. 1). The freshly prepared solution of this compound results in three waves polarographically (Curve A in Fig. 1). The first is the reduction wave of the nitro group. The second and third waves result from the reduction of the individual chlorines of the dichloracetamido group. Curve B in Fig. 1 represents, polarographically, the same solution only after it had been set aside for 3 days at room temperature. Only two waves are present in this polarogram, the first being identical with the reduction wave of the nitro group in the fresh solution. The second wave does not have the polarographic characteristics of either the reduction wave of the chlorines of the dichloracetamido group but does have the same polarographic characteristics of dichloracetic acid in this medium.

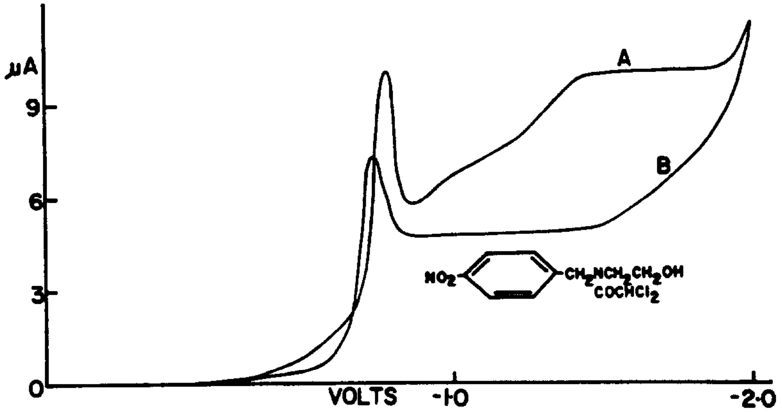


FIG. 1.—Polarograms of 0·0005*M* solutions in 50% methanol and pH 8 buffer:
A—fresh solution,
B—3-day old solution.

This is unequivocal evidence that the dichloracetamido group in the presence of a nitro group does contribute to the resulting polarogram of a freshly prepared solution in 50% methanol and pH 8, and that upon hydrolysis of the compound at room temperature that the dichloracetate ion contributes to the resulting polarogram along with the reduction wave of the nitro group.

With chloramphenicol {D(—)-threo-2,2-dichloro-*N*-[β-hydroxy-α-(hydroxymethyl)-*p*-nitrophenethyl]-acetamide}, in the same polarographic medium as above, three reduction waves result which are similar to those in Curve A in Fig. 1. After 3 days in this medium, the resulting polarogram is identical with the polarogram of the freshly prepared solution. This emphasises the stability of both the nitro and dichloracetamido groups in a compound not having a 2-hydroxyethyl group present on the amide nitrogen to initiate the hydrolysis of the dichloracetamido group at pH 8.

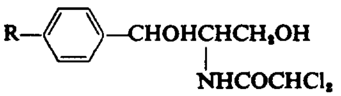
Group II

With the compounds in Group II only the aliphatic group attached to the sulphone or sulphide is varied. With the sulphone homologues, increasing the aliphatic chain from methyl to butyl results in a decrease in half-wave potentials (Table V), while with the sulphide homologues (Table V) an increase in half-wave potentials results.

Comparison of the sulphide, sulphoxide and sulphone analogues (numbers 28, 27, 22 in Table V) shows an increase of half-wave potential with an increase of oxygen content.

With certain isomeric compounds, polarography has shown a difference between the isomers. With the three available isomers of raceophenidol (dl, Dd, and Ll) there is no apparent difference in their polarograms at pH 3 or 8.

TABLE V —POLAROGRAPHIC REDUCTION OF GROUP II COMPOUNDS IN BUFFERED 50% METHANOL



$$R-C_6H_4-\underset{\displaystyle NHCOCHCl_2}{CHOHCHCH_2OH}$$

	R	First wave −$E_{1/2}$	First wave I	Second wave −$E_{1/2}$	Second wave I
22	CH_3SO_2—	1·04	1·62	1·45	1·50
23	$C_2H_5SO_2$—	0·97	1·51	1·41	1·38
24	$C_3H_7SO_2$—	0·93	2·12	1·41	2·04
25	$CH_2{=}CHCH_2SO_2$—	0·93	1·46	1·41	1·21
26	$C_4H_9SO_2$—	0·86	1·29	1·41	1·26
27	CH_3SO—	0·94	1·34	1·42	1·12
28	CH_3S—	0·66	1·30	1·40	*
29	C_2H_5S—	0·69	1·35	1·44	*
30	$CH_2{=}CHCH_2S$—	0·72	1·21	1·40	*
31	C_4H_9S—	0·74	1·47	1·34	*

* Second wave poorly defined

Group III

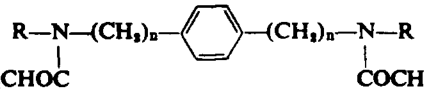
Compounds from the three other groups discussed in this communication dissolve readily in methanol while the compounds in Group III not only dissolve with difficulty but crystallise out of the buffered 50% methanol media within a short period of time at room temperature. This series did dissolve readily in *N,N*-dimethylformamide (DMF), but on mixing with the constant ionic strength buffers, the buffer constituents precipitated in the presence of 50% DMF. With less DMF the compound crystallises out of the media. On using a medium consisting of 70% methanol, 10% DMF and 20% water (containing the buffer) clear solutions with these Group III compounds result for at least 3 days at room temperature. Because of these solubility problems, polarograms were run only at pH 8·2. For a given compound of Group III, the half-wave potentials and the wave heights from the resulting polarograms are the same whether the medium is 70% methanol-10% DMF or the 50% methanol medium (before crystallisation of the compound occurs).

The half-wave potentials decrease about 0·3 V when the structure of the compound is changed from a secondary to a tertiary amide (Table VI).

With the tertiary amide series of compounds, the various substituents did not appreciably affect the polarographic characteristics of the given series of compounds when n = 1 or 0 (Table VI). If the benzene nucleus is replaced with cyclohexane, the polarographic characteristics are not altered appreciably.

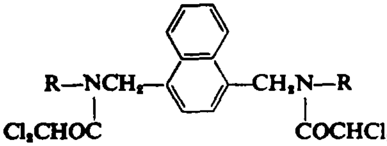
Compounds in Group III which possess the 2-hydroxyethyl group attached to the amide nitrogen, as was the case with chlorbetamide and related compounds in Group I, result in hydrolysis of the dichloracetamido groups. The 2-hydroxyethyl

TABLE VI.—POLAROGRAPHIC REDUCTION OF GROUP III COMPOUNDS IN BUFFERED 70% METHANOL-10% DMF

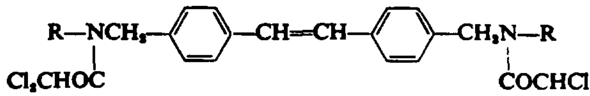


	R	n	First wave $-E_{1/2}$	First wave I	Second wave $-E_{1/2}$	Second wave I
32	—H	1	1·01	2·02	1·49	2·96
33	—CH_3	1	0·70	3·26	1·26	3·47
34	—C_2H_5	1	0·65	2·18	1·24	3·45
35	—$CH(CH_3)_2$	1	0·63	2·22	1·25	2·26
36	—C_3H_7	1	0·61	3·06	1·20	3·42
37	—CH_2CH_2OH	1	0·65	2·27	1·28	2·26
38	—$CH_2CH_2OC_2H_5$	1	0·66	3·33	1·22	3·36
39	—$CH_2CH_2OCOCH_3$	1	0·61	2·95	1·19	2·92
40	—H	0	Single drawn-out wave		1·19	7·70
41	—CH_3	0	0·69	2·82	1·21	3·98
42	—C_2H_5	0	0·67	2·94	1·23	3·73
43	—$CH(CH_3)_2$	0	0·69	3·07	1·28	3·99
44	—$CH(CH_3)(C_2H_5)$	0	0·64	3·51	1·27	4·29

TABLE VII.—POLAROGRAPHIC REDUCTION OF GROUP III COMPOUNDS IN BUFFERED 70% METHANOL-10% DMF



	R	First wave $-E_{1/2}$	First wave I	Second wave $-E_{1/2}$	Second wave I
45	—C_2H_5	0·56	3·07	1·17	3·52
46	—C_2H_4OH	0·62	3·22	1·24	3·08
47	—$C_2H_4OCH_3$	0·55	3·18	1·14	3·63



	R	First wave $-E_{1/2}$	First wave I	Second wave $-E_{1/2}$	Second wave I
48	—CH_3	0·47	3·12	1·15	3·36
49	—C_2H_5	0·47	3·29	1·15	3·42
50	—$CH(CH_3)_2$	0·47	3·21	1·15	3·42

compound (number 37 in Table VI) shows 77% hydrolysis after 3 days at room temperature and pH 8·2. The 2-acetoxyethyl analogue (number 39 in Table VI) shows only 15% hydrolysis under the same conditions. This emphasises again the necessity of the free 2-hydroxyethyl group to initiate the hydrolysis of the dichloracetamido group

Replacement of the benzene nucleus with naphthalene (Table VII) does not change appreciably the general polarographic characteristics. The 2-hydroxyethyl compound (number 46 in Table VII), however, results in 60% hydrolysis of the dichloracetamido groups after 3 days at room temperature and pH 8·2.

Replacement of the benzene nucleus with stilbene results in a series of compounds (Table VII) which are all the same polarographically, even though the aliphatic substituents attached to the amide nitrogen are different.

Group IV

This series of *N*,*N*′-bis-(dichloracetyl)-polymethylenediamines presented the opportunity to study polarographically two homologous series, one with the secondary amide linkage and the other with the tertiary amide linkage of the dichloracetyl group.

With the secondary amide homologous series (Table VIII) the effect of increasing the distance between the two dichloracetamido groups by increasing the methylene groups from 2 to 9 is readily apparent. The half-wave potentials decrease (not linearly though) with the increasing number of methylene groups. The decamethylene homologue is not listed in this table because its first wave is entirely different from any other members of this series (or for that matter from any of the compounds studied). The half-wave potential of the first wave is −0·79 V and has the appearance of a reversible wave (very steep slope). The slope of the second wave (−1·24 V) is similar to the other members of the series (gradual change in slope).

With the tertiary amide homologous series (Table IX) the presence of the ethyl group appears to nullify any appreciable change in the half-wave potentials of these methylene homologues (n = 4 to 12). The trend, however, is the opposite of the striking effect shown by the secondary amide series in that the half-wave potentials increase rather than decrease with the increasing number of methylene groups. It should be noted that with the tertiary amide series the half-wave potentials are 0·1 to 0·3 V lower than the corresponding secondary amide.

With the hexamethylene compounds (Table X) the various substitutions on the nitrogen result in very little change in the half-wave potentials of the two waves of the dichloracetamido groups. Only two of these compounds show, polarographically, hydrolysis of the dichloracetamido groups. Number 70 in Table X which contains the 2-hydroxyethyl group attached to the amide nitrogen and number 73 which contains a potentially available 2-hydroxyethyl group (2-acetoxyethyl analogue of number 70). Both of these compounds are hydrolysed 100% after 3 days at room temperature and pH 8, as determined polarographically by the presence of only the dichloracetate ion reduction wave.

Possible correlation between polarographic findings and biological effectiveness

Groups I, II and III. With the available data there is no clear-cut relationship between the biological activity of these compounds and their polarographic characteristics.[9,10,11,12]

TABLE VIII.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL

$$\begin{array}{ccc} HN & -(CH_2)_n- & NH \\ | & & | \\ Cl_2CHOC & & COCHCl_2 \end{array}$$

	n	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
51	2	1·05	4·42	1·49	4·54
52	3	0·97	3·07	1·44	2·76
53	4	0·87	2·71	1·40	2·39
54	5	0·84	2·94	1·33	2·62
55	6	0·78	2·69	1·32	2·48
56	7	0·75	3·15	1·27	3·73
57	8	0·71	2·48	1·27	2·59
58	9	0·70	2·71	1·23	2·61

TABLE IX.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL

$$\begin{array}{ccc} C_2H_5N & -(CH_2)_n- & NC_2H_5 \\ | & & | \\ Cl_2CHOC & & COCHCl_2 \end{array}$$

	n	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
59	4	0·55	2·94	1·09	3·36
60	5	0·56	3·46	1·09	3·52
61	6	0·56	3·21	1·10	3·32
62	7	0·57	3·09	1·10	3·08
63	8	0·59	2·92	1·14	3·16
64	9	0·60	2·52	1·18	3·06
65	10	0·61	3·20	1·18	3·21
66	12	0·64	2·57	1·21	2·85

TABLE X.—POLAROGRAPHIC REDUCTION OF GROUP IV COMPOUNDS IN BUFFERED 50% METHANOL

$$\begin{array}{ccc} R-N & (CH_2)_6- & N-R \\ | & & | \\ Cl_2CHOC & & COCHCl_2 \end{array}$$

	R	First Wave		Second Wave	
		$-E_{1/2}$	I	$-E_{1/2}$	I
67	—H*	0·78	2·69	1·32	2·48
68	$—CH_3$	0·55	2·76	1·08	2·66
69	$—C_2H_5$†	0·56	3·21	1·10	3·32
70	$—C_2H_4OH$	0·57	2·31	1·16	2·74
71	$—C_2H_4OCH_3$	0·57	2·70	1·13	3·10
72	$—C_2H_4OC_2H_5$	0·57	2·45	1·18	2·86
73	$—C_2H_4OCOCH_3$	0·51	2·43	1·09	2·85

* This is the same compound as number 55 in Table VIII.

† This is the same compound as number 61 in Table IX.

Group IV. With the homologous series of the secondary amide compounds (Table VIII), when n = 2, 3, 4, 5, 6, 7, 9 or 10 the compounds possess amebicidal activity. This amebicidal activity is found to increase with the increase in the number of methylene groups between the two dichloracetamido groups.[13] Polarographically, the half-wave potentials of the first reduction wave of the dichloracetamido group decrease, though not linearly with the increase in the number of methylene groups. When n is 8, however, the amebicidal activity is very low. On the other hand, this homologue (number 57 in Table VIII) has proved to possess the most effective antispermatogenic activity of all of the compounds yet tested in either Group III or IV.[12,13,14] Why the octamethylene homologue has such a singular potency as a spermatocide remains unanswered because the homologues (n = 7 or 9) have little such activity. Polarographically, one does note a uniqueness with the octamethylene compound in that it shows a sharply defined prewave (at 0·71 V) before the first reduction wave. None of the other homologues shows this polarographic characteristic.

With the tertiary amide series (Table IX), even though there is no consistent relationship between the length of the methylene chain and amebicidal activity, they possess (as a group) the greater amebicidal activity on comparing with the secondary amide compounds.[13] Polarographically, the half-wave potentials resulting from the reduction of the first chlorine of the dichloracetamido group in the tertiary amide series are 0·1 to 0·3 V lower than those from the secondary amide compounds.

With the various analogues of the hexamethylene series (Table X) there is little change in amebicidal activity.[13] These different R-groups had little effect on the polarographic characteristics of these analogues.

CONCLUSION

Because the first reduction wave of the chlorine from the dichloracetamido group is so well-defined, its wave height may be utilised in measuring quantitatively the amount of intact dichloracetamido compound in various pharmaceutical formulations (chiefly tablets, injections and feed premixes). The values obtained were within ±2% of label claim. The resulting polarograms, during a stability testing programme, of 1 year, were especially helpful in proving conclusively that the dichloracetamido group is stable in the pharmaceutical preparation as shown by the absence of the dichloracetate reduction wave.

Zusammenfassung—An verschiedenen Verbindungen, die die Dichloracetamidogruppe enthalten, wie N-(2,4-dichlorbenzyl-)N-(2-hydroxyäthyl-) dichloracetamid (Chlorbetamid), N-(4-methylsulfonylphenyl-) 1,3-dihydroxy-2-propyl-dichloracetamid (Raceophenidol), N,N′-bis-(2-äthoxyäthyl-)N,N′-p-xylylen-bisdichloracetamid (Teclozan), N,N′-octamethylen-bisdichloracetamid und analogen Verbindungen, wurden polarographische Untersuchungen angestellt. Die analytischen Ergebnisse werden vom quantitativen und qualitativen Gesichtspunkt aus diskutiert, mit besonderem Nachdruck auf der Stabilität der Verbindungen bei verschiedenen p_H-Werten und auf dem Einfluß verschiedener Elemente oder Gruppen im Molekül auf die Halbwellenpotentiale der beiden kathodischen Wellen

Résumé—L'auteur a étudié par polarographie une série de composés contenant des groupes dichloroacétamide comprenant N-(2,4-dichlorobenzyl)-N-(2-hydroxyéthyl)dichloroacétamide (chlorbetamide), N-(4-méthylsulfonylphényl)-1,3-dihydroxy-2-propyl-dichloroacétamide (raceophenidol), N,N′-bis-(2-éthoxyéthyl)-N,N′-p-xylylène-bis-dichloroacétamide (teclozan), N,N′-octaméthylène-bis-dichloroacétamide et leurs analogues. Les résultats analytiques sont discutés du point de vue qualitatif et quantitatif en insistant particulièrement sur la stabilité de ces composés à différents pH et sur l'influence des éléments ou des groupes variés situés dans la molécule sur les potentiels de demi-vague des deux vagues de réduction

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SCHIFF BASE COMPLEXES

A NUMERICAL STUDY OF THE NICKEL^{II}—PYRUVATE—GLYCINATE SYSTEM USING A HIGH SPEED COMPUTER*

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Summary—A numerical study of the nickel^{II}-pyruvate-glycinate system is undertaken and a computer method of solving the pertinent equations is developed. Theoretical titration curves using trial constants are calculated for conditions corresponding to those used experimentally. The observed inter-relationships between the values of the constants, the concentrations of the reactants and the resulting titration curves yield valuable information regarding the importance of the various mixed complexes under the differing conditions. The "best" set of constants which fits the experimental data according to the minimum value of the sum of the squares of the residuals, $pH_{calc}\, i - pH_{obs}\, i$, is obtained. The results of the study lead to a procedure which should be applicable to determining the constants for mixed complex systems in general.

SCHIFF base complexes partake in many interesting reactions. Pfeiffer and coworkers[1] have demonstrated that enhanced rates of ester exchange and hydrolysis and oxidative de-amination can occur in these systems. The paramagnetic and diamagnetic properties of the nickel^{II} complexes have recently come under intensive study.[2,3] The investigations of Krumholz,[4a] Figgins and Busch[4b,c] and Blight and Curtis[4d] have resulted in interesting compounds having unusual properties. Of special importance is the role these complexes play in non-enzymatic transamination.[5,6,7,8,9] In order to understand more completely the behaviour of Schiff base co-ordination compounds it is desirable to extend our knowledge of the compositions and stabilities of the complexes formed in solution. Such information is a prerequisite to the complete understanding of any equilibrium or kinetic properties of these systems.

One difficulty in the study of equilibria involving Schiff base complexes is the dissociation of the Schiff base itself,[10] *i.e.*, in addition to the Schiff base-metal ion equilibria, there is superimposed the equilibrium between the Schiff base and its component amine and carbonyl compounds. In one approach to the problem a recent communication[11] points out the value of treating these species as "mixed complexes" and using the Bjerrum titration method[12] to obtain the data. In this earlier paper, which concerns the nickel^{II}-pyruvate-glycinate system, Watters' method[13] of obtaining the concentrations of combined and uncombined glycinate was used. This method was feasible because a large difference exists in the basicities of the pyruvate and glycinate ions, and the nickel^{II} "mixed complexes" form predominantly under conditions of pH where pyruvic acid is almost completely dissociated and uncombined glycine is ionized to only a very slight extent. An iterative procedure was used to obtain the formation constants of the species NiPG, $NiPG_2^-$ and $NiP_2G_2^{2-}$ (P^- = pyruvate, G^- = glycinate).

In those systems where the "mixed complexes" are formed under conditions

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where appreciable concentrations of undissociated pyruvic acid are present, Watters' method does not apply. This was found to cause minor difficulties even in the present study and produces a more severe interference when the complexes of copper^{II} are under investigation. Also, in systems of considerable interest, such as those involving pyridoxal or salicylaldehyde and its derivatives, the acidities of the carbonyl compounds approach those of the amino acids, completely obviating Watters' method.

In the present study employing an IBM 7090 computer a numerical investigation of the inter-relationships between the experimental parameters, the concentrations of metal, pyruvate and glycinate ions, the values of the complex formation constants and the shapes of the titration curves, was undertaken. The results led to a general method of obtaining the "best" constants according to a least-squares fit for such systems, and also rendered valuable insight into their equilibrium properties. While the method described below concerns one particular system it can be applied directly to other metal ion-ketoacid-amino acid systems and, with only slight modifications, should even be applicable to those more complicated situations where pyridoxal is involved.

OUTLINE OF COMPUTATIONAL METHOD

In the experiments, solutions containing complexing metal ions, pyruvic acid, sodium pyruvate and inert electrolyte in known concentrations were titrated with a sodium glycinate solution and the equilibrium values of pH were measured after each addition of titrant. A series of titration curves was obtained using solutions with different initial concentrations. The formation constants of the simple complexes, the acid dissociation constants of the ligands and their Schiff base formation constant were determined from the results of similar, separate experiments.

In the computation all of these data, including observed points (pH *vs.* ml) from the experimental titration curves, and the initial concentrations of reactants are first read into and stored in the computer. A predetermined network of trial values of the formation constants of the mixed complexes is then systematically scanned. For each set of constants a theoretical titration curve is calculated pertaining to each of the initial conditions. The residual, $pH_{calc}-pH_{obs}$, is obtained for each of the observed points and the quantity U, which is the sum of the squares of the residuals over all of the points, is computed.

Residuals in pH were minimised because values of pH are measured directly while in mixed complex systems the derived quantity $\bar{n}$, which is more commonly used in calculating equilibrium constants, is not single-valued with regard to the experimental variables, volume and pH. Furthermore, weighting procedures, which may be somewhat involved when $\bar{n}$ values are used,[14] are simplified because each point can be given unit weight. The error is assumed to lie entirely in the measured value of pH and the volume is assumed to be accurately known.

If a sufficiently broad network of constants has been used the region where the minimum value of U lies can be located and passing finer and finer networks through this region the constants which best fit the data can be obtained to the appropriate degree of accuracy. When the calculated N + 1 dimensional surface (N is the number of equilibrium constants being evaluated) is sufficiently wrinkled it is possible for the compution to converge on a "false minimum". One of the purposes of the present approach was to determine if such false minima are apt to interfere with obtaining the "best fit" for these systems.

Considering the bidentate character of pyruvate and glycinate, the tridentate character of their Schiff base and the predominant hexadentate character of the transition metal ions of the first series, the mixed complexes MPG, MP_2G^-, MPG_2^- and MP_2G^{2-} are expected. Considering also the simple species, mass-conservation leads to the following set of equations:

$$M_t = (M^{2+}) + (MP^+) + (MP_2^0) + (MG^+) + (MG_2^0) + (MG_3^-) + (MPG) \\ + (MP_2G^-) + (MPG_2^-) + (MP_2G_2^{2-}) \qquad (1)$$

$$P_t = (HP) + (P^-) + (MP^+) + 2(MP_2^0) + (MPG) + 2(MP_2G^-) + (MPG_2^-) \\ + 2(MP_2G_2^{2-}) + (PG^{2-}) \qquad (2)$$

$$G_t = (H_2G^+) + (HG^\pm) + (G^-) + (MG^+) + 2(MG_2^0) + 3(MG_3^-) + (MPG) \\ + (MP_2G^-) + 2(MPG_2^-) + 2(MP_2G_2^{2-}) + (PG^{2-}) \qquad (3)$$

$$H_t = 2(H_2G^+) + (HG^\pm) + (HP) + (H^+) - (OH^-) \qquad (4)$$

where the quantities on the left-hand side are the known concentrations of complexing metal ions, pyruvate, glycinate and replaceable hydrogen ions and those on the right-hand side are the concentrations of the various species.

Defining the over-all formation constant of the complex MP_pG_g as

$$Q_{pg} = \frac{(MP_pG_g)}{(M)(P^-)^p(G^-)^g}$$

and the formation constant of the Schiff base PG^{2-} as Q_{SB}, substitution into equations (1)–(4) gives:

$$M_t = (M^{2+})[1 + Q_{10}(P^-) + Q_{20}(P^-)^2 + Q_{01}(G^-) + Q_{02}(G^-)^2 + Q_{03}(G^-)^3 \\ + Q_{11}(P^-)(G^-) + Q_{21}(P^-)^2(G^-) + Q_{12}(P^-)(G^-)^2 + Q_{22}(P^-)^2(G^-)^2] \qquad (5)$$

$$P_t = \left[\frac{a_H}{\mathrm{Kap}} + 1\right](P^-) + Q_{10}(M^{2+})(P^-) + 2Q_{20}(M^{2+})(P^-)^2 + Q_{11}(M^{2+})(P^-)(G^-) \\ + 2Q_{21}(M^{2+})(P^-)^2(G^-) + Q_{12}(M^{2+})(P^-)(G^-)^2 + 2Q_{22}(M^{2+})(P^-)^2(G^-)^2 \\ + Q_{SB}(P^-)(G^-) \qquad (6)$$

$$G_t = \left[\frac{a_H^{\,2}}{K_{1aG}K_{2aG}} + \frac{a_H}{K_{2aG}} + 1\right](G^-) + Q_{01}(M^{2+})(G^-) + Q_{02}(M^{2+})(G^-)^2 \\ + Q_{03}(M^{2+})(G^-)^3 + Q_{11}(M^{2+})(P^-)(G^-) + Q_{21}(M^{2+})(P^-)^2(G^-) \\ + 2Q_{12}(M^{2+})(P^-)(G^-)^2 + 2Q_{22}(M^{2+})(P^-)^2(G^-)^2 + Q_{SB}(P^-)(G^-) \qquad (7)$$

$$H_t = \frac{a_H(P^-)}{K_{ap}} + \left[\frac{2a_H^{\,2}}{K_{1aG}K_{2aG}} + \frac{a_H}{K_{2aG}}\right](G^-) + (H^+) - (OH^-) \qquad (8)$$

In equation (8) a_H refers to the hydrogen ion activity whereas (H^+) is the concentration. From blank titrations of the inert electrolyte with hydrochloric acid solutions it was found that $(H^+) = a^{0.96}$ and this relationship was used to make the correction iteratively for free (H^+).

In the experiments, the values of M_t, P_t and H_t are known at each point on the titration curve from the initial concentration and the dilution factor. The value of G_t is also known from the concentration of NaG in the titrant and the volume added.

However, in computing the theoretical curves, because of the higher order equations involved, it is simpler to begin with a value of (G^-) and from this to calculate the corresponding values of pH and G_t than it is to calculate the values of pH and G^- using G_t. Accordingly, the above equations are rearranged in terms of (G^-) and the unknowns (P^-) and a_H.

Solving equation (5) for (M^{2+}) and substituting into equation (6) gives, on rearrangement,

$$F(P^-) = C_3(P^-)^3 + C_2(P^-)^2 + C_1(P^-) - S_0P_t \tag{9}$$

where

$$\begin{aligned}
C_3 &= C_0S_2\\
C_2 &= C_0S_1 + (2M_t - P_t)S_2\\
C_1 &= C_0S_0 + (M_t - P_t)S_1\\
C_0 &= a_H/K_{ap} + Q_{SB}(G^-) + 1\\
S_1 &= Q_{10} + Q_{11}(G^-) + Q_{12}(G^-)^2\\
S_2 &= Q_{20} + Q_{21}(G^-) + Q_{22}(G^-)^2\\
S_0 &= 1 + Q_{01}(G^-) + Q_{02}(G^-)^2 + Q_{03}(G^-)^3
\end{aligned}$$

and the quantities S_i are polynomials depending only on (G^-) and the formation constants.

The correct solution for a given value of G^- is that positive value of (P^-) (and a_H) which causes $F(P^-)$ to become equal to zero.

The value of a_H can be obtained in terms of (G^-) and (P^-) using the quadratic equation

$$a_H = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \tag{10}$$

where, from equation (8),

$$\begin{aligned}
a &= 2(G^-)/K_{1aG}K_{2aG},\\
b &= (G^-)/K_{2aG} + (P^-)/K_{ap},\\
c &= a^{0.96} - H_t.
\end{aligned}$$

The positive root is used because the quantity a_H must be positive.

Once the value of (G^-) is chosen, equation (9) and (10) become two non-linear equations in two unknowns. The equations are solved as follows. First (P^-) is set equal to zero and the corresponding value of a_H is calculated from equation (10) [iteratively when the term resulting from free (H^+) is appreciable with regard to H_t]; these values of a_H and (P^-) are inserted into equation (9) to give a value of $F(P^-)$; (P^-) is incremented by some predetermined amount (usually of the order 0·1 to 0·2 P_t) and a new value of $F(P^-)$ is similarly obtained. A test is made to determine if $F(P^-)$ has changed sign. This process is repeated until a sign change in $F(P^-)$ indicates that a root of equation (9) has been reached. The values of (P^-) and a_H are then refined iteratively using the Newton-Raphson[15] method until any change in (P^-) is less than 0·2% of its value at that time. A test is made to verify that a_H is positive. A negative value signifies an incorrect root and (P^-) is again successively incremented until $F(P^-)$ once more changes sign. In practice it has been observed that the correct root lies at the first sign change. The reason for this can be seen in the data of Table I where $F(P^-)$ and a_H have been computed for various conditions. Only one root appears to exist in the range $0 \leq P^- \leq P_t$. In the region of interest $F(P^-)$ is a smooth curve for which the first, second and third derivatives are all positive. The last appears to be about constant. No troublesome convolutions nor inflections exist in the region F(P⁻) = 0. Also, it can be seen that any error in pH caused by a 0·2% uncertainty in (P⁻) has negligible proportions as far as the present purposes are concerned.

Using the chosen value of (G⁻) and those obtained for (P⁻) and a_H, (M^{2+}) is evaluated from equation (5) and using these results in equation (7), G_{tcalc} is calculated. The volume of titrant necessary to give this value of G_{tcalc} is obtained from the experimentally known concentration of the titrant and the initial volume. The values of M_t, P_t and H_t are corrected for dilution and the last is also corrected for the effect of any excess sodium hydroxide in the titrant. The entire calculation is repeated iteratively until changes in H_t amount to less that 0·2% of its value. In this way one theoretical point on the titration curve (pH *vs.* ml) is obtained. To obtain another point, the value of $-\log(G^-)$ is increased. The final titration curve results when the desired range of (G⁻) values has been covered. The time taken to compute one point is of the order of 25 msec with the IBM 7090 computer.

Only by rare coincidence does an observed and computed volume of titrant agree. Therefore, to obtain the residual for each observed volume it is necessary to interpolate. A second order LaGrange interpolation[16] is performed. Three calculated points bracketing each observed point are used in the interpolation. In the region of interest where the mixed complexes are formed, the buffer capacity of the solutions is large and a higher order equation is not necessary for the interpolation.[17]

The computed points are printed out and the next set of experimental conditions is taken. When the computation for the final experiment has been performed the value of U is also printed out. A new set of constants is then taken. With the IBM 7090 computer the time required to compute a theoretical curve of 16 points, interpolate and obtain the sum of the squares of the residuals is less than 0.6 sec.

In the first version of the programme the constants were varied from initial to final values in fixed steps. To save computer time all of the titration curves were not computed for a given combination of constants if it was found that at any point the absolute value of a residual was greater that 0·15 pH unit. The programme was designed to cease calculations at this point and go on to the next set of constants. Furthermore, because the constants were varied from low to high values, shifting the computed curves to more acid values as the computation progressed, a particular region was considered to be out of range of interest and was no longer investigated if a point on a calculated curve was found to become more acid by 0·15 pH unit than the corresponding experimental point.

DATA AND RESULTS FOR THE NICKEL^{II} PYRUVATE-GLYCINATE SYSTEM

The data from which the $\bar{n}_G$ and log (G⁻) values reported in reference 11 were calculated was taken. In these experiments solutions which contained either 0·0500*M* NiCl$_2$, 0·0500*M* pyruvic acid, (I); 0·0500*M* NiCl$_2$, 0·0500*M* pyruvic acid, 0·0550*M* sodium pyruvate, (II); 0·0500*M* NiCl$_2$, 0·0500*M* pyruvic acid, 0·100*M* sodium pyruvate, (III); 0·0220*M* NiCl$_2$, 0·0500*M* pyruvic acid and 0·100*M* sodium pyruvate, (IV) were prepared. These solutions also contained sufficient potassium chloride to bring the ionic strength to 0·70. Twenty-five ml aliquots were titrated at 25·0° with 0·800*M* sodium glycinate. The pH measurements were made with a Radiometer pHM22 pH meter with a scale expander. Readings were made to the nearest 0·005 pH

TABLE I.—VALUES OF a_H AND THE FUNCTION $F(P^-)_G$
($Q_{11} = 1·25 \times 10^8$, $Q_{12} = 1·00 \times 10^{13}$, $Q_{21} = 0$, $Q_{22} = 2·00 \times 10^{18}$)

Expt. no.	Log $(G^-) = 6·50$				Log $(G^-) = 5·00^{*}$			
(P^-), *moles litre*	$a_H \times 10^6$	$F(P^-)_G$	$\Delta^1F(P^-)_G$	$\Delta^2F(P^-)_G$	$a_H \times 10^7$	$F(P^-)_G$	$\Delta^1F(P^-)_G$	$\Delta^2F(P^-)_G$
0·00000	2·820	−0·05229			8·5313	−0·38359		
			0·01257				0·77957	
0·00750	2·817	−0·03973		0·00773	8·5309	+0·39598		1·7482
			0·02030				2·5277	
0·01500	2·814	−0·01943		0·00824	8·5306	2·9237		2·2545
			0·02854				4·7823	
0·02250	$2·810^{5}$	+0·00911		0·00875	8·5303	7·7060		2·7609
			0·03729				7·5432	
0·03000	2·807	0·04639		0·00926	8·5300	15·5249		3·2673
			0·04654				10·810	
0·03750	2·804	0·09294		0·00977	8·5297	26·060		3·7736
			0·05631				14·584	
0·04500	2·801	0·14925		0·01028	8·5293	40·644		
			0·06659					
0·05250	2·798	0·21584						
Expt. no. III	Log $(G^-) = 6·50$				Log $(G^-) = 5·00$			
0·00000	2·691	−0·15353			8·1497	−1·1283		
			−0·02457				−1·6109	
0·00750	2·688	−0·17839		0·00570	8·1494	−2·7392		−0·1687
			−0·01915				−1·7796	
0·01500	2·685	−0·19754		0·00621	8·1491	−4·5188		+0·3377
			−0·01294				−1·4419	
0·02250	2·682	−0·21048		0·00672	8·1489	−5·9607		0·8440
			−0·00622				−0·5979	

TABLE 1 (*Continued*)

Expt. no. III	Log (G⁻) = 6·50				Log (G⁻) = 5·00			
0·03000	2·679	−0·21670		0·00723	8·1485	−6·5585		1·3504
			+0·001011				+0·7525	
0·03750	2·676	−0·21569		0·00774	8·1483	−5·8060		1·8568
			0·008751				2·6093	
0·04500	2·673	−0·20694		0·00825	8·1479	−3·1967		2·3631
			0·01700				4·9724	
0·05250	2·670	−0·18994		0·00876	8·1477	+1·7757		2·8695
			0·02576				7·8419	
0·06000	2·667	−0·16418		0·00927	8·1473	9·6176		3·3759
			0·03503				4·218	
0·06750	2·664	−0·12915		0·00978	8·1470	20·835		3·8822
			0·04481				15·100	
0·07500	2·661	−0·084343		0·01209	8·1468	35·935		4·3886
			0·05510				19·489	
0·08250	2·658	−0·029248		0·01080	8·1464	55·424		4·8949
			0·06589				24·383	
0·09000	2·655	+0·036643		0·01131	8·1461	79·807		5·4013
			0·07197				29·785	
0·09750	2·652	0·11384		0·01182	8·1458	109·59		5·9077
			0·08901				35·692	
0·10500	2·649	0·20285		0·01232	8·1455	145·28		6·4140
			0·10134				42·106	
0·11250	2·646	0·30419		0·01283	8·1452	187·39		6·9204
			0·11417				49·027	
0·12000	2·643	0·41836			8·1449	236·42		

unit. National Bureau of Standards buffers were used to standardise the glass and calomel electrodes. In the titration curves only those points in the buffer regions where the mixed complexes form, were used in the calculations. As the concentration of pyruvate increases a pronounced break in the titration curve appears where the $Ni^{II}:(G^-)$ ratio is 1:2. This break is informative as far as the stoichiometry is concerned but the points close to the end-point have only slight value as far as determining the constants is concerned.

The constants for the formation of the simple nickel^{II}-glycinate complexes were found to be $4{\cdot}6 \times 10^5$, $3{\cdot}2 \times 10^{10}$ and $9{\cdot}0 \times 10^{13}$ for Q_{01}, Q_{02} and Q_{03}, respectively. For the nickel^{II}-pyruvate system Q_{10} was found to be 14. No evidence for the existence of NiP_2 was observed. The Schiff base formation constant was found to have a value of 2·2–2·3 from the results of a potentiometric titration of glycine in the presence of pyruvate with a solution of sodium hydroxide. This value compares favourably with 2·47 obtained polarographically by Zuman.[18] The value found for the acid dissociation constant of pyruvic acid, K_{aP}, is $4{\cdot}07 \times 10^{-3}$ while K_{1aG} and K_{2aG} for glycine were found to be $3{\cdot}4 \times 10^{-3}$ and $2{\cdot}0 \times 10^{-10}$.

In the previous communication[11] the values reported for Q_{11}, Q_{12} and Q_{22} are $1{\cdot}15 \times 10^8$, $2{\cdot}5 \times 10^{13}$ and $1{\cdot}6 \times 10^{15}$. Ordinarily these results would not be available in which case it is desirable, but not necessary, to make quick preliminary desk calculations to obtain the likely approximate values of the mixed complex formation constants. It is convenient to initiate the computations with the high speed computer using a network of constants with points spaced from about one-third to one-half the preliminary values. In the present series, Q_{11} was first varied from 0 to $3{\cdot}0 \times 10^8$ in steps of $0{\cdot}5 \times 10^8$, Q_{12} was varied from 0 to $4{\cdot}9 \times 10^{13}$ in steps of $0{\cdot}7 \times 10^{13}$ and Q_{22} was varied from 0 to $4{\cdot}5 \times 10^{15}$ in steps of $0{\cdot}5 \times 10^{15}$. Because Q_{20} was found to have a negligibly small value, it seemed reasonable that the same is also likely for Q_{21}. Therefore, in the first series of calculations Q_{21} was set equal to zero.

Complete sets of computed titration curves and values of U were obtained for only a relatively small region of the vector space of trial constants scanned because points for most of the computed curves fell outside the 0·15 pH unit limit. The results are shown in Table IIA. A finer network was then used to obtain the results given in Table IIB.

A final run was made using initial values $Q_{11} = 1{\cdot}15 \times 10^8$, $Q_{12} = 0{\cdot}8 \times 10^{13}$ and $Q_{22} = 1{\cdot}8 \times 10^{15}$, with increments $dQ_{11} = 0{\cdot}10 \times 10^8$, $dQ_{12} = 0{\cdot}20 \times 10^{13}$ and $dQ_{22} = 0{\cdot}20 \times 10^{15}$. The minimum value of U was found to be 0·0229 (43 points)[19] lying at $Q_{11} = 1{\cdot}25 \times 10^8$, $Q_{12} = 1{\cdot}0 \times 10^{13}$ and $Q_{22} = 2{\cdot}0 \times 10^{15}$. A plot of the points obtained for this last set of constants is given in Fig. 1 along with the observed values.

At this stage attempts were made to improve the fit by scanning a four dimensional array of constants using relatively small values of Q_{21} of the order of 10^9. These attempts resulted only in increased U values so it is concluded that as far as the present experimental conditions are concerned any effect of NiP_2G^- is negligible.

It is important to establish whether or not the values found above are meaningful or merely reflect the uncertainties in the pH measurements. Sillén[20] has described methods for obtaining the standard deviations of the constants and the observed points in cases such as the present, where the sum square surface has been obtained. After Sillén[20] a generalised four dimensional paraboloid was fitted to the displacements

TABLE II.—VALUES OF THE SUM-SQUARE AS A FUNCTION OF THE TRIAL CONSTANTS

A Coarse network[a]

	$Q_{22} = 1{\cdot}50 \times 10^{15}$				$Q_{22} = 2{\cdot}0 \times 10^{15}$				$Q_{22} = 2{\cdot}5 \times 10^{15}$	
Q_{11} ╲ Q_{12}	0[c]	7	14	21	0	7	14	21	0	7
0·0[b]	—	—	—	—	—	—	—	—	—	—
1·0	—	0·118	0·114	—	0 174	0·054	0·140	—	0 183	—
1·5	—	—	0·194	—	—	0·101	0·047	—	—	—
2·0	—	—	—	—	—	—	—	—	—	—

B. Medium network[a]

	$Q_{22} = 1{\cdot}50 \times 10^{15}$				$Q_{22} = 1{\cdot}70 \times 10^{15}$				$Q_{22} = 1{\cdot}90 \times 10^{15}$			
Q_{11} ╲ Q_{12}	7[c]	10	13	16	7	10	13	16	7	10	13	16
1·00[b]	0·118	0·094	0·105	0·134	0·062	0·059	0·086	0·135	0·049	0·062	0·103	0 162
1·20	—	0·110	0·088	0·094	0·079	0·043	0·040	0·062	0·036	0·019	0·031	0·065
1·40	—	—	0·153	0·132	—	0·102	0·071	0·068	0·095	0·048	0·035	0·044
1·60	—	—	—	—	—	—	·0102	0 133	—	0·134	0 096	0·085
1·80	—	—	—	—	—	—	—	—	—	—	—	0·175

	$Q_{22} = 2{\cdot}10 \times 10^{15}$				$Q_{22} = 2{\cdot}30 \times 10^{15}$				$Q_{22} = 2{\cdot}50 \times 10^{15}$
Q_{11} ╲ Q_{12}	7[c]	10	13	16	7	10	13	16	
1·00[b]	0·065	0·092	0·142	—	0·104	0 142	—	—	
1·20	0·028	0·026	0·050	—	0 046	0·056	—	—	
1·40	0·060	0·030	0·031	—	0·055	0·039	—	—	All out of range
1·60	—	0·091	0·069	—	0·118	0 078	—	—	
1·80	—	—	0·155	—	—	0·164			

[a] Values of the sum-square were printed out for only those sets of data for which the condition $-0{\cdot}15 \leq \mathrm{pH}_{\mathrm{calc}} - \mathrm{pH}_{\mathrm{obs}} \leq 0{\cdot}15$ is satisfied for all points on the computed titration curves. A total of 41 points was used in this series of calculations.

[b] $Q_{11} \times 10^{-6}$.

[c] $Q_{12} \times 10^{-18}$.

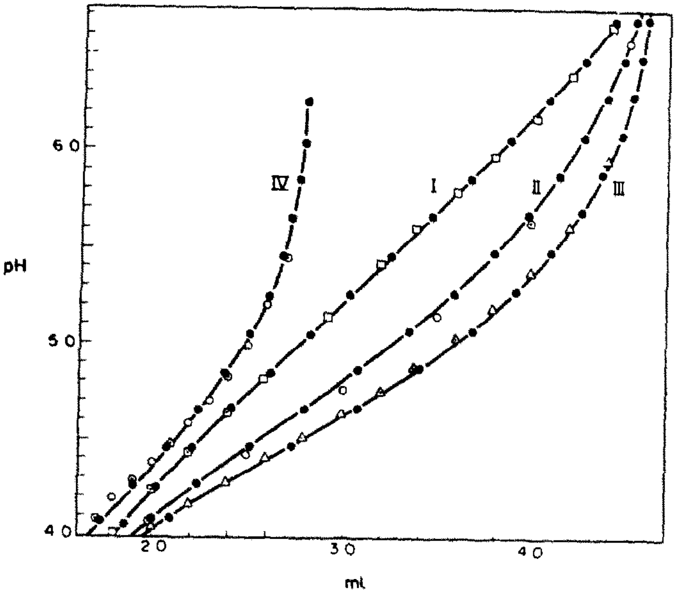

FIG 1.—Computed and Observed Titration Curves.
The roman numerals refer to the experiment number given in the text. The open points are observed and the solid points are computed. The values used in the computation are $Q_{11} = 1{\cdot}25 \times 10^{+8}$, $Q_{12} = 1{\cdot}0 \times 10^{+13}$ and $Q_{13} = 2{\cdot}0 \times 10^{+15}$

in U and in the constants for the last set of calculations taking the observed minimum where $U = 0{\cdot}0229$ as the origin. This gave the equation

$$U = 0{\cdot}0299 + 0{\cdot}0205 \times 10^{-8}x_1 + 0{\cdot}825 \times 10^{-16}x_1^2 - 0{\cdot}0035 \times 10^{-13}x_2 + 0{\cdot}155 \times 10^{-26}x_2^2 + 0{\cdot}0075 \times 10^{-15}x_3 + 0{\cdot}345 \times 10^{-30}x_3^2 - 0{\cdot}445 \times 10^{-21}x_1x_2 - 0{\cdot}625 \times 10^{-23}x_1x_3 + 0{\cdot}280 \times 10^{-28}x_2x_3$$

where $x_1 = Q_{11} - 1{\cdot}25 \times 10^{+8}$, $x_2 = Q_{12} - 1{\cdot}0 \times 10^{+13}$ and $x_3 = Q_{22} - 2{\cdot}0 \times 10^{+15}$. The surface defined by this equation is calculated to have a minimum, $U_{\min}$, equal to 0·0225. Because the values of three constants have been obtained losing three degrees of freedom the standard deviation of the points is calculated to be $\pm 0{\cdot}0225/(43-3) = \pm 0{\cdot}024$. This deviation is only slightly larger than the expected 0·01 – 0·02 unit uncertainty in the measured pH values. From the matrix of the coefficients of the displacements, the constants at the minimum and their standard deviations are calculated to be $Q_{11} = 1{\cdot}23 \pm 0{\cdot}04 \times 10^{+8}$, $Q_{12} = 1{\cdot}01 \pm 0{\cdot}08 \times 10^{+13}$ and $Q_{22} = 1{\cdot}97 \pm 0{\cdot}05 \times 10^{+15}$. The standard deviations are well below the values of the constants.

It is also worthwhile to make plots of various computed curves. In this way visual evidence may be obtained regarding the effects which given species have on the measured parameters under different conditions This information is valuable in the design of experiments. In Fig. 2 are plotted the curves which were obtained using several values of Q_{11}, Q_{12} and Q_{22} for conditions pertaining to experiments I and II. Here it is seen that curve I is sensitive to the values of Q_{11} and Q_{12}, but the variation in Q_{22} has a negligible effect. On the other hand, curve III shows only a slight dependence on the value of Q_{12} but is shown to depend primarily on Q_{11} and Q_{22}. Thus, under the conditions of experiment (I) NiPG and $NiPG_2^-$ are indicated to be important, whereas in experiment (III) $NiP_2G_2^{2-}$ replaces the latter species. For more quantitative

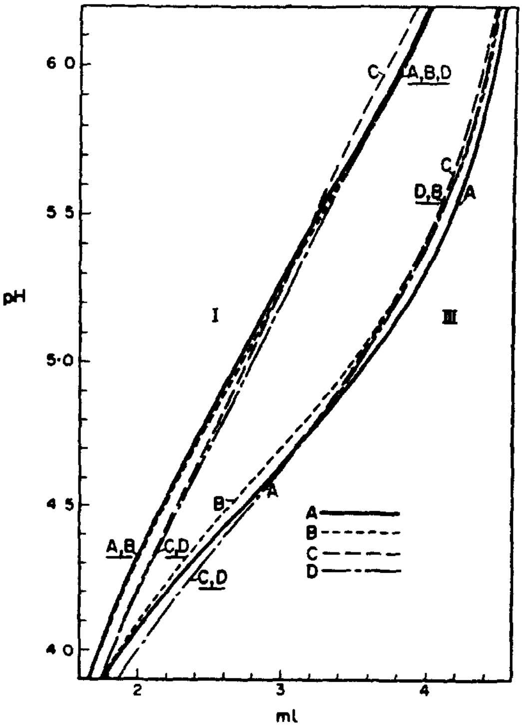

FIG. 2.—The Effect of Variations in Q_{11}, Q_{12} and Q_{22} on the Computed Curves. The roman numerals refer to the experiment number given in the text. The values used in the computation are:

Curve	Q_{11}	Q_{12}	Q_{22}
A	$1·0 \times 10^{+8}$	$0·70 \times 10^{+13}$	$2·0 \times 10^{+15}$
B	$1·0 \times 10^{+8}$	$0·70 \times 10^{+13}$	$1·5 \times 10^{+15}$
C	$1·5 \times 10^{+8}$	$0·70 \times 10^{+13}$	$2·0 \times 10^{+15}$
D	$1·5 \times 10^{+8}$	$1·4 \times 10^{+13}$	$2·0 \times 10^{+15}$

information it is desirable to compute the fractions of each of the species. This can be easily done because (M), (P^-) and (G^-) are known at each point.

The method of obtaining the constants in the present work has the advantages over the iterative procedure used previously[11] in that all of the pertinent data are treated simultaneously and the "best" constants in a "least squares" sense result (see reference 20). Furthermore, by noting the relationships between the experimental conditions and the sensitivities of the curve shapes to the values of the constants, useful information regarding the actual existences of proposed complexes and the proper conditions for studying their properties may be obtained.

SEARCH FOR THE CONSTANTS: A MODIFIED PROGRAMME

The procedure described above is inefficient if all that is desired is the constants for a particular system. The above results indicate that certain modifications in the search procedure can be made to find the minimum more rapidly. The surface $U = F(Q_{11}, Q_{12}, Q_{22})$ is relatively smooth and shows only one important minimum in the region where positive concentrations obtain. Furthermore, in Tables IIA and IIB it is seen that the minimum value of U in each column lies approximately along a downward sloping line which can be drawn across the table. The slope of the line depends on the magnitudes of the increments and the sensitivity of the sum-square to the values of the constants.

To obtain a faster search for the "best" constants the programme has been modified so primarily only those trial sets lying along the valleys shown in Table II are considered. After the preliminary phase where the constants are narrowed down to those giving titration curves falling within some prescribed range, the mapping of the sum-square surface[20] is begun. The value of Q_{11}, at constant Q_{12} and Q_{22}, is incremented until a minimum in U has been reached. This process is then repeated with the next value of Q_{12} but because the valleys slope downward it is not necessary to return Q_{11} to its initial value before starting the new column, but only to reduce it by the value of one increment. As long as the minimum value of U in each new column is found to be smaller than in the preceding column the search at constant Q_{22} continues. Once the lowest value has been reached, ascertained by the simple test that a minimum in a column is larger than that of the preceding column, Q_{22} is increased and Q_{11} and Q_{12} are decreased slightly so as to remain in the vicinity of the minimum.

The search continues in the same manner until the Q_{22} plane having the smallest U has been uncovered. The constants can then be refined either by automatically rescanning the region of minimum U employing smaller and smaller increments until the desired accuracy has been obtained, or by employing procedures based on those described by Hugus[14] or, as illustrated above, Sillén.[20]

Acknowledgement—The author wishes to extend his thanks to the staff of the OSU Numerical Computation Laboratory for their kind assistance and the generous use of their facilities in carrying out this study.

Zusammenfassung—Das Nickel (II)-Pyruvat-Glycinat-System wurde numerisch untersucht. Ein Rechenprogramm zur Lösung der zugehörigen Gleichungen wurde entworfen. Für Bedingungen, die den experimentellen entsprechen, wurden mittels angenommener Konstanten theoretische Titrationskurven berechnet. Die beobachteten Beziehungen zwischen den Werten der Konstanten, den Konzentrantionen der Reaktanten und den sich ergebenden Titrationskurven ergaben wertvolle Informationen über die Bedeutung der verschiedenen gemischten Komplexe unter den verschiedenen Bedingungen. Der "beste" Satz von Konstanten, der gegenüber den experimentellen Daten die kleinste Summe der quadratischen p_H-Abweichungen gibt, wurde erhalten. Die Ergebnisse führen zu einem Verfahren, das auf die Ermittlung der Konstanten in gemischten Komplexsystemen allgemein anwendbar wäre.

Résumé—Une étude quantitative du système Ni(II)-pyruvate-glycinate a été entreprise. On a développé une méthode de résolution des équations correspondantes au moyen d'un calculateur. Les courbes de titrage théoriques correspondant aux conditions expérimentales ont été calculées en utilisant des constantes expérimentales. Les relations observées entre les valeurs des constantes, les concentrations des réactifs, et les courbes de titrage qui en résultent fournissent des renseignements valables concernant l'importance des différents complexes mixtes dans des conditions variées. La "meilleure" série de constantes qui soit en accord avec les données expérimentales est choisie comme étant celle qui donne le minimum pour la somme des carrés des résidus $pH_{calc\,i} - pH_{obs\,i}$. On déduit de ces résultats une méthode qui serait applicable à la détermination des constantes de systèmes de complexes mixtes en général.

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[17] Estimating from the values of the divided differences (ref. 15, p. 147) the error in the interpolation using a second order equation appears to be no more than 0·002 pH unit in the region where the 2nd order approximation is the poorest: the region of negative curvature where the mixed species are beginning to be formed.

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[19] Inadvertently, the two most acid points shown for curve IV in Fig. 1 had been omitted in the first series of computations. These points were included in the last series. As a matter of interest, exclusion of these points yields a minimum U equal to 0·0175 for which the values of the constants are unchanged.

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POTENTIOSTATIC DETERMINATION OF KINETIC PARAMETERS OF ELECTRODE REACTIONS WITH GENERATION OF A REACTANT *IN SITU*

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Summary—It is shown that kinetic parameters of simple, fast electrode reactions of the type $O + ne = R$, where R is soluble in the solution or in the mercury electrode, can be determined by the potentiostatic method with a solution initially containing only the substance O, the substance R being generated *in situ* during electrolysis, provided that the electrode reaction involves only a single rate-determining step. Current-time curves are recorded with a fast response, electronic potentiostat and an oscilloscope upon applying a potential step from the zero-current potential to various potentials on the ascending part of the current-potential curve The forward rate constant k_f at a given potential is calculated from the current at zero time found by extrapolation of the linear portion of the plot of current against square root of time, while the backward rate constant k_b is calculated indirectly from the slope of the same straight line. Plotting log k_f and log k_b against potential allows a simultaneous determination of the formal standard rate constant k_s, both cathodic and anodic transfer coefficients, the number of electrons involved in the rate-determining step and the formal standard potential of the system being studied. This method is considerably simpler than the well-known Gerischer-Vielstich method, and it should be particularly advantageous when R is highly reactive or forms an amalgam which is unstable in air. The upper limit of k_s that can be determined by this method is the same as that determinable by the Gerischer-Vielstich method. The kinetic parameters found by the present method for the electrode reactions zinc ion-zinc amalgam in $1M$ potassium nitrate, copper^{II} ion-copper amalgam in $1M$ potassium nitrate and cadmium ion-cadmium amalgam in $0{\cdot}5M$ sodium sulphate were in fair agreement with the values reported in the literature.

INTRODUCTION

THE potentiostatic method developed by Gerischer and Vielstich[1,2] is a well-established method for the determination of kinetic parameters of fast electrode reactions. In their method, current-time curves are recorded upon applying a potential step from the equilibrium potential of a given system containing initially both oxidised and reduced species at known concentrations, and the exchange current is calculated from the slope at the equilibrium potential of the plot of current at zero time against potential. The standard rate constant and the transfer coefficient are normally

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evaluated by determining the variation of exchange current with the concentration of either oxidised or reduced species. Thus, the Gerischer-Vielstich method suffers experimental complications when the reduced species in solution or in amalgam is highly reactive and subject to air oxidation.

In the method described in this paper, kinetic parameters are evaluated by analysing current-time curves obtained at only one concentration of the oxidised species, the reduced species being absent before electrolysis. Metal ion-amalgam systems can thus be studied by the present method without using an amalgam electrode of accurately known concentration. As expected from theoretical considerations, errors involved in the determination of the backward rate constant are somewhat greater than those involved in the determination of the forward rate constant, particularly at potentials away from the standard potential. Nevertheless, the method should be of practical value, as is evidenced by the fact that the kinetic parameters determined by the proposed method for the few systems are in satisfactory agreement with the values reported in the literature.

CURRENT-TIME RELATIONSHIP

Consider the reduction of a substance O to another substance R in an electrode process involving n electrons at a stationary mercury electrode under the following conditions:

(1) The reduction product R is soluble either in solution or in mercury.
(2) The solution contains the substance O at a known concentration and the concentration of R is negligible before electrolysis.
(3) Because the electrolysis time is very short and the thickness of the diffusion layer is very small in the present potentiostatic method, semi-infinite linear diffusion is the sole mode of mass transfer.
(4) The electrode process involves only a single rate-determining step.
(5) The electrode potential is maintained constant during electrolysis.

The general equation for current-time curves obtained under these conditions is well-known and takes the form[3]

$$i = nFAk_fC_0 \exp(\xi^2)\mathrm{erfc}(\xi) \tag{1}$$

where

$$\xi = st^{1/2} \tag{2}$$

$$s = k_fD_R^{-1/2} + k_bD_R^{-1/2} \tag{3}$$

and i is the current in A, F the Faraday, A the surface area of the electrode in cm^2, k_f and k_b the rate constants for the forward and backward reactions in cm . sec^{-1}, C_0 the concentration of substance O in the bulk of the solution in moles . cm^{-3}, t the time in sec, and D_0 and D_R the diffusion coefficients of 0 and R in cm^2 . sec^{-1}.

For values of ξ smaller than 1, one can write

$$\exp(\xi^2) = 1 + \xi^2 + \frac{\xi^4}{2!} + \dots$$

and for any values of ξ

$$\mathrm{erfc}(\xi) = 1 - \frac{2}{\sqrt{\pi}}\left(\xi - \frac{\xi^3}{3\cdot 1!} + \dots\right).$$

When ξ is so small that the higher terms in the above expansion can be neglected, equation (1) can be written in the following form:

$$i = nFAk_fC_0\left(1 - \frac{2s}{\sqrt{\pi}}t^{1/2}\right) \tag{4}$$

This equation predicts that plotting current against $t^{1/2}$ yields a straight line at sufficiently short times at potentials where the condition $st^{1/2} \ll 1$ is fulfilled. The current at $t = 0$ found by extrapolation of this straight line is directly proportional to k_f, while k_b can be calculated from the slope of this line, provided that the diffusion coefficients are known.

On the other hand, k_f and k_b are related to the standard rate constant k_s and potential E by

$$k_f = k_s \exp\left[-\frac{\alpha n_a F}{RT}(E - E^\circ)\right] \tag{5}$$

$$k_b = k_s \exp\left[\frac{\beta n_a F}{RT}(E - E^\circ)\right] \tag{6}$$

where α and β are the cathodic and anodic transfer coefficients and $\alpha + \beta = 1$, n_a is the number of electrons involved in the rate-determining step, and E° is the formal standard potential. Thus, it is anticipated that plotting $\log k_f$ and $\log k_b$ against E should yield two straight lines, and that it should be possible to find k_s and E° from the intersection of these straight lines. From the slopes of these lines, it should be possible to evaluate separately α, β and n_a.

EXPERIMENTAL

Reagents

All chemicals used were of the highest purity available commercially, and they were used without further purification. De-aeration was carried out by passing highly pure tank nitrogen. Solutions of zinc, copper^{II} and cadmium ions were prepared by dissolution of zinc nitrate, copper^{II} nitrate and cadmium sulphate, respectively. The concentrations were determined polarographically in suitable supporting electrolyte solutions.

Apparatus

Electrodes: A dropping mercury electrode with a drop time of about 10 sec was used as the working electrode, and current-time curves were recorded upon closing the circuit at a certain time (8 to 9 sec) after the beginning of the drop formation. The time when the circuit was closed was measured with a stop-watch, and the switch for closing the circuit was operated manually. Current-time curves were perfectly reproducible, indicating that the error resulting from the manual operation of the switch was quite negligible as compared to that associated with the oscilloscopic recording. Because current-time curves were needed only up to 10 msec after the circuit was closed, the variation of surface area of the mercury drop during the recording was also negligible.

A saturated calomel electrode served as the reference electrode, and it was connected with the dropping electrode through a Luggin capillary.

The counter electrode was a platinum foil, which was placed in the compartment separated by a sintered glass disk.

Potentiostat: The potentiostat used in the present study was an electronic potentiostat constructed by the authors according to the circuit designed and described by Shimodaira, Matsuo, Sugawara and Ebiko[4] of this University. The voltage source for 200 V d.c. described in their paper was found to be unsuitable for this type of work and it was replaced by batteries to minimise disturbances resulting from incomplete rectification. The rise time of the potentiostat was about 6 × 10^{-5} sec, which is one order of magnitude longer than that (2·5 × 10^{-6} sec) of the potentiostat constructed by Electronische Werkstätte of Germany. For the systems studied in this work, however, this was not critical. A micro relay switch was used in the early stages of this investigation. Because this switch generated transients in 0 8 msec, it was later replaced by a sealed-in mercury switch, which was found to give excellent results. The preset potential was read exactly with a potentiometer.

Current-time curves were recorded with a Synchroscope Model SS5151 combined with a high gain differential preamplifier Model SP02-DFH-A, both manufactured by Iwasaki Communication Apparatus Co. Ltd. The calibrated resistances used had a value of 10 to 50 Ω, and the sensitivity of the oscilloscope was always set at the maximum sensitivity of 1 mV. cm^{-1}

All experiments were carried out in a thermostat maintained at 25°.

RESULTS AND DISCUSSION

Experiments were carried out for reductions of zinc ion in 1*M* potassium nitrate, copper^{II} ion in 1*M* potassium nitrate and cadmium ion in 0·5*M* sodium sulphate. Examples of $i - t^{1/2}$ plots are reproduced in Fig. 1. Good straight lines were obtained in all cases at sufficiently short times. The upper limit of t before which a linear $i - t^{1/2}$ is obtained greatly depends on k_s of the system and also on potential. For example, in the vicinity of the standard potential and for the case of $D_0 = D_R(=D)$, we have $s \approx k_s D^{-1/2}$ [*cf.* equations (3), (5) and (6)]. If one prescribes the condition $st^{1/2} \leq 0{\cdot}2$ for a linear $i - t^{1/2}$ plot to be obtained, then one finds $t \leq 10^{-2}$ sec for a reaction with $k_s = 10^{-3}$ cm.sec^{-1} and $t \leq 10^{-3}$ sec for a reaction with $k_s = 10^{-2}$ cm.sec^{-1}. For faster reactions, current-time curves must be recorded at shorter times. At very short times ($<10^{-4}$ sec), however, correction for the capacity current becomes excessive and limits the maximum measurable value of k_s. The discussion given by

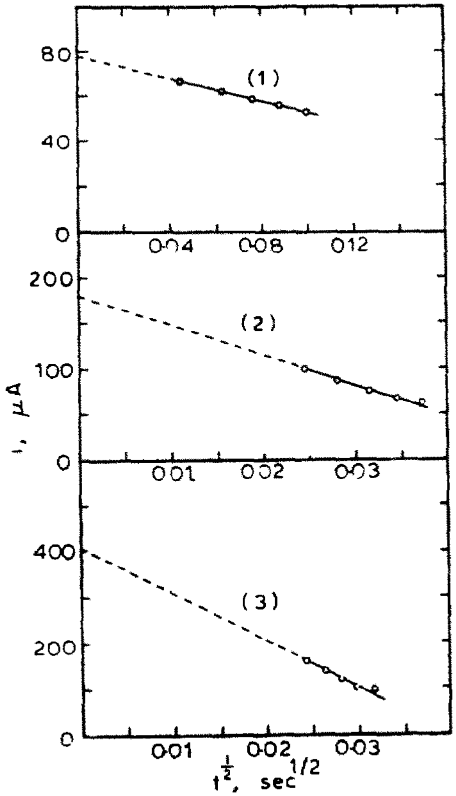

FIG. 1.—Plots of $i - t^{1/2}$: (1) 5 mM Zn^{2+} in 1*M* KNO_3 at −0·986 V; (2) 2 mM Cu^{2+} in 1*M* KNO_3 at +0·034 V; (3) 2 mM Cd^{2+} in 0·5*M* Na_2SO_4 at −0·581 V.

Delahay[5] on this point for the Gerischer-Vielstich method applies directly to the present case, and it can easily be shown that in both methods k_s much greater than 0·2 cm.sec^{-1} cannot be measured. In the experimental examples given in this paper, it was not necessary to measure current at times shorter than 6×10^{-4} sec and the capacity current was quite negligible.

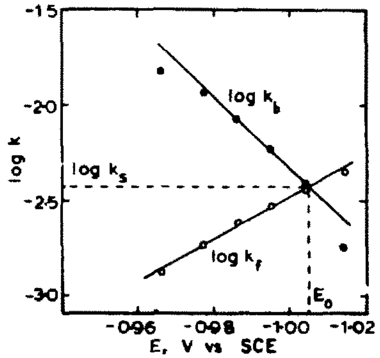

FIG. 2.—Plot of log k − E obtained with 5 mM Zn^{2+} in 1M KNO_3.

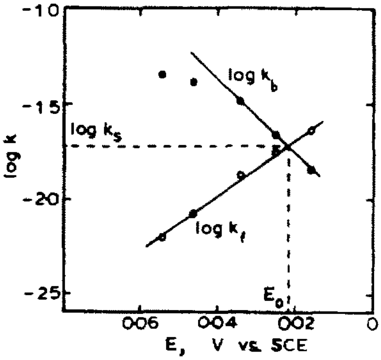

FIG. 3.—Plot of log k − E obtained with 2 mM Cu^{2+} in 1M KNO_3

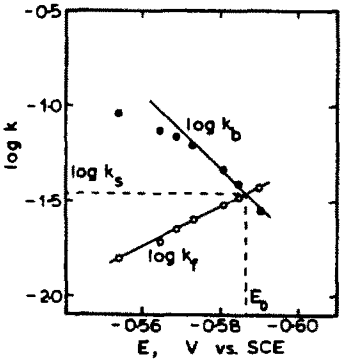

FIG. 4.—Plot of log k − E obtained with 2 mM Cd^{2+} in 0·5M Na_2SO_4.

As is obvious from the theory, a knowledge of diffusion coefficients of both the oxidised and reduced species is required in order to calculate k_b. The values of diffusion coefficients used in the calculation were as follows ($D \times 10^5$ cm^2.sec^{-1}): Zn^{2+} in 1M KNO_3, 0·666; Zn in mercury, 1·57[6]; Cu^{2+} in 1M KNO_3, 0·713[7]; Cu in mercury, 1·06[8]; Cd^{2+} in 0·5M Na_2SO_4, 0·720; Cd in mercury, 2·07[6]. The values for which no literature reference is given were calculated from the average polarographic diffusion current by using the original Ilkovic equation. It is generally recognised that diffusion coefficients calculated in this manner are often in considerable error. For example, the D value of zinc ion calculated by using a modified Ilkovic equation (the numerical constant in the second, correction term being taken equal to 34) was equal to $0·562 \times 10^{-5}$ cm^2.sec^{-1} instead of $0·666 \times 10^{-5}$ cm^2.sec^{-1} found by using the original Ilkovic equation. This difference, however, resulted in only a minor difference in kinetic parameters. For example, the values of k_s for the zinc system calculated with the above two D values were $3{\cdot}6 \times 10^{-3}$ and $3{\cdot}8 \times 10^{-3}$ cm sec^{-1}, respectively.

Plots of log k_f and log k_b against potential for the three systems studied are shown in Figs. 2, 3 and 4. The kinetic parameters found from these plots are summarised and compared in Table I with the values reported in the literature. In general, the agreement between the values found by the present method and the literature values was satisfactory, except that the k_s value for the copper system was somewhat lower than the value found by other methods.

TABLE I —KINETIC PARAMETERS AND FORMAL STANDARD POTENTIALS OF SOME METAL ION–AMALGAM SYSTEMS

System	Temp., °C	$E^{\circ\prime}$, V vs SCE	k_s, cm sec^{-1}	n_a	α	β	Method
Zn^{2+}/Zn(Hg) In 1M KNO_3	25	−1·005	$3{\cdot}8 \times 10^{-3}$	2	0·35	0·56	This study
	25		$3{\cdot}5 \times 10^{-3}$				A C. polarography[9]
Cu^{2+}/Cu(Hg) in 1M KNO_3	25	+0·022	$1{\cdot}9 \times 10^{-2}$	2	0·43	0·53	This study
	25		$4{\cdot}5 \times 10^{-2}$				A.C. polarography[9]
	20		$4{\cdot}5 \times 10^{-2}$				Faradaic impedance[10]
Cd^{2+}/Cd(Hg) in 0·5M Na_2SO_4	25	−0·587	$3{\cdot}6 \times 10^{-2}$	2	0·29	0·62	This study
	25				0·38		A.C. polarography[11]
	25		$2{\cdot}5 \times 10^{-2}$				A.C polarography[12]
	20		$2{\cdot}6 \times 10^{-2}$		0·25		Voltage-step[13]
	20		$4{\cdot}2 \times 10^{-2}$		0·17		Faradaic impedance[14]
	20		$4{\cdot}5 \times 10^{-2}$		0·22		Current-step[15]

In Figs. 2–4, it is noted that the points for log k_b obtained at less negative potentials tended to deviate in the same direction in all three cases. The reason for this deviation is not obvious. At any rate, it is clear from equation (3) that errors involved in the determination of k_b should be minimum at potentials near the standard potential where k_f and k_b are of the same order of magnitude. It should also be noted that as the potential is made more negative, the current-potential characteristics become steeper and this trend is more marked with faster reactions. At such potentials the precision and stability of potential control of the potentiostat become critical. Also, because current becomes larger at more negative potentials, the effect of iR drop between the working electrode and the tip of the Luggin capillary becomes more serious at more negative potentials. For these reasons, satisfactory k_b values could not be obtained at potentials much more negative than the standard potential. While the present method is simpler than the Gerischer-Vielstich method from the experimental viewpoint, it is the disadvantage of this method that the accuracy in the determination of k_b is less than that in the determination of k_f.

If it is desired that k_b be determined with the same degree of accuracy as k_f in a wider potential range and if the reduced species is sufficiently stable, k_b should be calculated from the anodic current at $t = 0$ measured with a system containing the reduced species alone, the oxidised species being generated *in situ* in this case. It also would be of interest to apply the principle of this method to totally irreversible reactions.

Zusammenfassung—Es wird gezeigt, daß kinetische Parameter einfacher schneller Elektrodenreaktionen vom Typ O + *ne* = R, wo R in der Lösung oder in der quecksilbernen Elektrode löslich ist, mit der potentiostatischen Methode bestimmt werden können. Die Lösung enthält dabei zuerst nur O, R wird *in situ* bei der Elektrolyse erzeugt, vorausgesetzt, daß die Elektrodenreaktion nur einen geschwindigkeitsbestimmenden Schritt enthält. Strom-Zeit-Kurven werden mit einem schnell ansprechenden elektronischen Potentiostaten und einem Oszillographen registriert, wobei das Potential sprunghaft vom Potential, bei dem kein Strom fließt, auf ein Potential im ansteigenden Teil der Stromspannungskurve geändert wird. Die Konstante der Hinreaktion k_f bei einem bestimmten Potential wird aus dem Strom zur Zeit Null berechnet, den man durch Extrapolation des linearen Anstiegs des Stromes gegen die Quadratwurzel der Zeit findet. Die Konstante der Rückreaktion k_b wird indirekt aus der Steigung derselben Geraden berechnet. Trägt man log k_f und log k_b gegen das Potential auf, so erhält man gleichzeitig die formale Standard-Geschwindigkeitskonstante k_s, kathodische und anodische Durchtrittsfaktoren, die am geschwindigkeitsbestimmenden Schritt beteiligte Anzahl von Elektronen und das formale Standardpotential des untersuchten Systems. Diese Methode ist beträchtlich einfacher als die bekannte Gerischer-Vielstich-Methode und sollte besondere Vorteile bieten, wenn R sehr reaktionsfähig ist oder ein nicht luftbeständiges Amalgam bildet. Das größte bestimmbare k_s ist hier gleich wie bei der Gerischer-Vielstich-Methode. Die nach der neuen Methode gefundenen kinetischen Parameter für die Reaktionen Zinkion-Zinkamalgam in 1m KNO_3, Kupfer(II)-Ion-Kupferamalgam in 1m KNO_3 und Cadmiumion-Cadmiumamalgam in 0,5m Na_2SO_4 stimmten mit den in der Literatur angegebenen Werten befriedigend überein.

Résumé—On montre que les paramètres cinétiques des réactions aux électrodes, simples, rapides et du type O + *ne* ⇌ R, où R est soluble dans la solution ou dans l'électrode, peuvent être déterminés par une méthode potentiostatique sur une solution qui ne contient initialement que O, la substance R étant fabriquée in situ pendant l'électrolyse. Cette méthode implique qu'une seule réaction détermine la vitesse de la réaction à l'électrode. Les courbes courant-temps sont enregistrées à l'aide d'un potentiostat électronique à réponse rapide et d'un oscilloscope, en appliquant un saut de potentiel allant du potentiel à courant nul jusqu'à divers potentiels de la partie ascendante de la courbe intensité-potentiel. La constante de vitesse directe k_f à un potentiel donné est calculée à partir du courant au [illegible], déterminé par extrapolation de la partie linéaire de la courbe courant-racine carrée du temps, tandis que la constante de vitesse inverse k_b est calculée indirectement à partir de la pente de la même droite. Si l'on trace log k_f et log k_b en fonction du potentiel, on peut déterminer en même temps la constante de vitesse globale k_s, les deux coefficients de transferts cathodique et anodique, le nombre d'électrons mis en jeu au cours de la réaction qui détermine la vitesse, et le potentiel normal du système. Cette méthode est beaucoup plus simple que la méthode bien connue de Gerischer-Vielstich, et devrait être particulièrement avantageuse dans le cas où R est très réactif ou forme un amalgame instable à l'air. La plus forte valeur de k_s que l'on puisse déterminer par cette méthode est la même que celle que l'on détermine par la méthode de Gerischer-Vielstich. Les paramètres cinétiques trouvés par cette méthode pour les réactions à l'électrode: ion zinc-amalgame de zinc dans du nitrate de potassium 1 M, ion cuivre(II)-amalgame de cuivre dans du nitrate de potassium 1 M et ion cadmium-amalgame de cadmium dans du sulfate de sodium 0,5 M sont en bon accord avec les valeurs indiquées dans la littérature.

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THE BORON-CARBON-HYDROGEN SYSTEM

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Summary—Identification of many newly-discovered compounds composed only of the three elements, B, C and H, has been accomplished by use of mass, infrared and nuclear magnetic resonance spectroscopy in conjunction with the isotopic substitution technique. These compounds can be classified into two general categories: (1) the organo derivatives of boron hydrides, and (2) the carboranes (and their organo derivatives) Examples of compounds identified by purely spectroscopic means are given.

THE state of the art of the B-C-H system as of 1942 has been summarised by Schlesinger and Burg.[1] Actually, in addition to the trialkyl boranes, only the alkyldiboranes were prepared and some of their physical properties given. Very little progress in this area was made until 1952, when the present author introduced the isotopic boron technique with spectroscopy as a routine analytical tool for identification of boron-containing compounds. Since that time the organo-substitution compounds of the higher boron hydrides, as well as new boron-carbon systems, have been prepared and identified. It is the purpose of this paper to discuss the various ramifications of these analyses with respect to the identification of the new organoboron compounds.

ANALYTICAL TECHNIQUES

Mass spectrometry

In boron chemistry the mass spectrometer is a particularly useful tool because of the readiness with which compounds of varying isotopic boron composition may be prepared. Isotopically-normal and ^{10}B-enriched organoboranes of the same chemical composition can be prepared by the reaction of unsaturated organic compounds or alkyl halides with corresponding isotopically-normal or ^{10}B-enriched boron hydrides. The exact number of boron atoms in the organoboranes can then be calculated from the shift in peak heights of their mass spectra. The number of carbon and hydrogen atoms can be obtained from the difference of the molecular weight (corresponding to the highest m/e value) and the accountable mass of the boron atoms. No shift in corresponding mass spectra distinguishes pure organic compounds from those containing boron. As an extension of this technique, deuterated compounds can be used to verify the number of hydrogen atoms attached to the carbon and/or boron atoms.

As a matter of historical importance, the discovery (1953) of the carborane series of compounds was a direct application of this isotopic boron technique coupled with mass spectroscopy. Fig. 1 shows the comparison of the mass spectra of products formed by the reaction of acetylene with ^{10}B-enriched and isotopically-normal diboranes. In this case, no fractionation of products was made; consequently, the mass spectra represent a composite spectra of all components in the mixture A high peak at m/e 78 in both spectra must belong to a pure organic compound, subsequent purification and analysis indicated that this pronounced peak at m/e 78 is produced by benzene. The general contour of the three distinct groups of peaks in the high mass range indicates polyboron-containing compounds. This "boron shape" is a function of the number of boron atoms and the isotopic composition[2] For example, the high peak at m/e 95 in the ^{10}B-spectrum shifts to m/e 100 in the normal spectrum, the shift of 5 units indicates a B_5-compound. Similarly, the shift from m/e 109 to m/e 114 also indicates a B_5-compound, and the shift from m/e 114 to m/e 122 signifies a B_8-compound. All of these compounds were later isolated and identified as belonging to the carborane series.

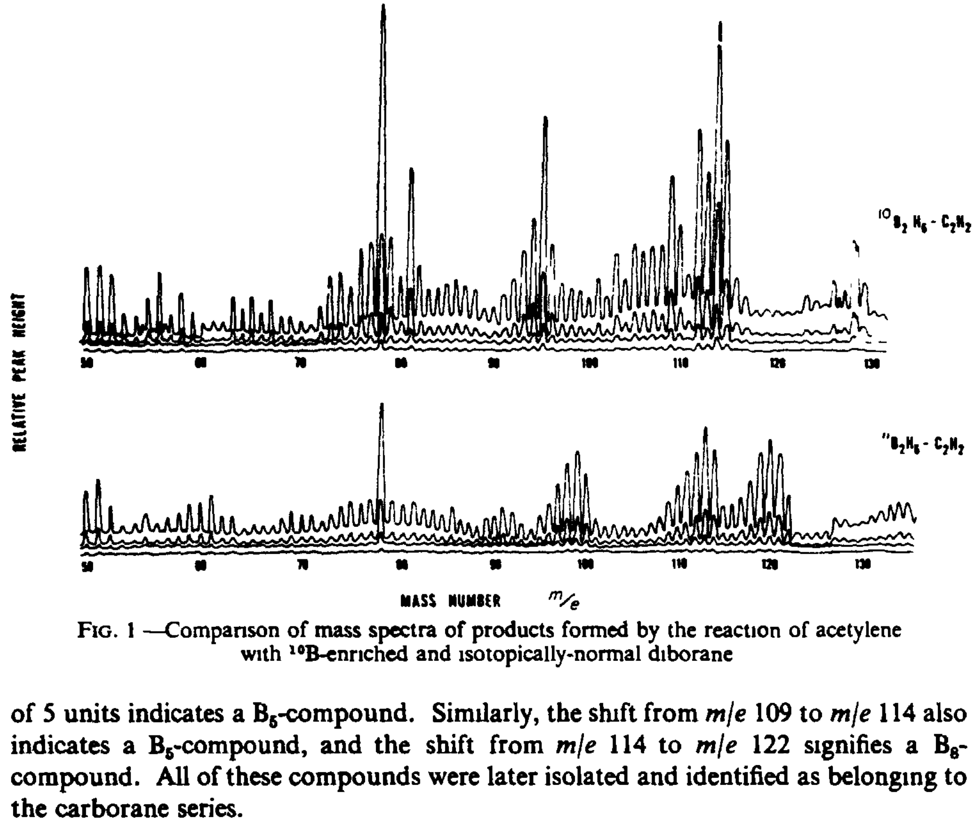


FIG. 1 —Comparison of mass spectra of products formed by the reaction of acetylene with ^{10}B-enriched and isotopically-normal diborane

Infrared spectroscopy

Infrared spectral analysis gives an insight into group arrangements of boron, carbon and hydrogen in the compounds. It is possible, for example, to distinguish between terminal borons (B_t-H) and bridge borons (B-H-B), such as those illustrated in Fig. 2, which shows the absorption peaks for the alkyl diboranes.[3] The bridge-boron absorption frequency is in the 1600 cm^{-1} range; and the terminal boron frequency in the 2500 cm^{-1} range. Further, it is possible to distinguish the number of hydrogen atoms attached to the terminal boron—a single peak indicates one hydrogen and a double peak indicates two hydrogens.

The shift in absorption frequency upon partial deuteration of the organoboron compound can be used to locate the position of the hydrogen (deuterium), *i.e.*, whether it is attached to the boron atom or to the carbon atom.

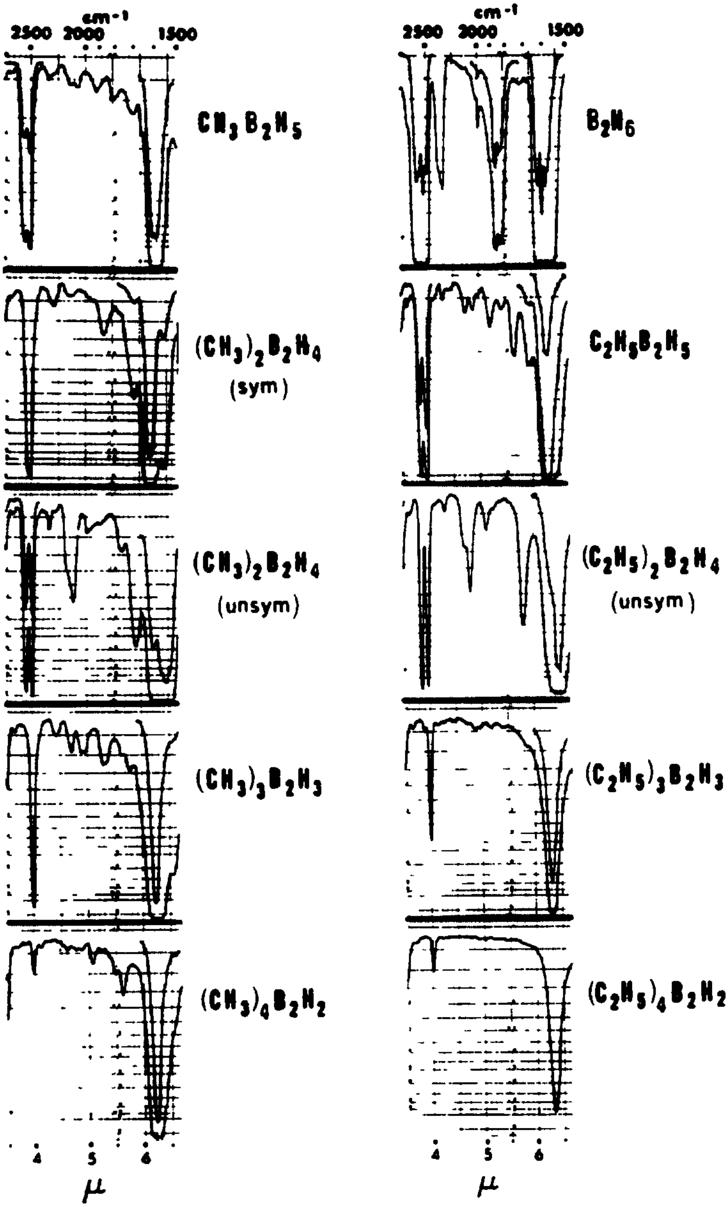


FIG 2.—Infrared region 1500–2850 cm^{-1} showing terminal hydrogen and bridge hydrogen absorptions in alkyldiboranes.

Nuclear magnetic resonance spectroscopy

For complete analysis of organoboron compounds, one should be able to derive the structure of the compound so that one can locate the actual position of, say, an alkyl group, substituted for a hydrogen atom. For example, for a monoalkyl pentaborane, one would like to know whether the alkyl group is located at an apex boron position or on a base boron position. Such information is not readily available from either mass or infrared spectral analyses. By n.m.r. spectroscopy, one can easily distinguish between such positions.

The ^{11}B n.m.r. spectrum yields information of the environment of the boron nucleus. The interaction of a single proton with boron results in a doublet, whereas a BH_2 unit will be represented by a triplet. On the other hand, a boron atom without hydrogen attached will be represented by a singlet. Bridge hydrogens are not observed. Replacement of deuterium for hydrogen collapses the doublet or triplet to a singlet. Because of chemical shift, borons in different positions also can be distinguished. The n.m.r. spectra of the various boron hydrides have been summarised, both by splitting and chemical shift.[4] Alkyl substitution on boron hydrides will manifest itself both by changes in number of peaks and/or relative position in the spectra. Examples of such changes will be given later.

In the proton n.m.r. spectrum, the interaction of the ^{11}B nuclear spin of 3/2 with a proton results in a quartet of (equal size) peaks. On the other hand, the C-H interaction is a single peak. Bridge hydrogens (B-H-B) are manifested by a broad unresolved peak. Because the proton spectrum is the sum of all component peaks, the proton spectrum may at first appear complicated; however, in most instances the spectrum can be reconciled with the structure of the compound, and thus serve as a verification of structure.

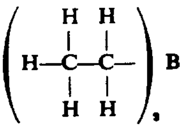
ORGANOBORON COMPOUNDS—COMPOSITION AND STRUCTURE

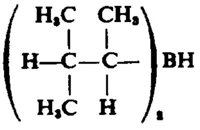
The organoboron compounds (containing only B, C and H) fall into two general categories (1) Derivatives of boron hydrides, and (2) carboranes. In the first category, the organic component (alkyl, aryl, *etc.*) usually is appended to a boron hydride, whereas the term "carborane" was coined to signify that the carbon atom had become an integral part of the boron skeleton. Organo derivatives of carboranes also have been synthesised. In this instance the organic component is appended either to a boron or carbon atom in the carborane. Thus, the number of possible organoboron compounds is large, and new compounds are constantly being discovered. It is apparent that simple elemental analysis no longer suffices in identifying these compounds.

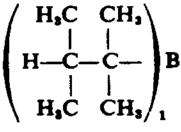
Derivatives of boron hydrides

1. *Monoborane:* The trialkylboranes (BR_3) are well known, and can be prepared by the Grignard reaction or by the addition of diborane to alkenes. If the alkene is a low molecular weight compound, *e.g.*, ethylene, the product will be triethylborane; or in the case of excess diborane, the various ethyl diboranes.

Interestingly, it is not possible to form BHR_2 or BH_2R in the simple compounds because of the great tendency of the boron to be tetrahedrally bonded, thus resulting in dimerisation. However, if the alkene is complex so as to present a large steric hindrance, the monoborane containing one or two hydrogens can be formed,[5] *viz.*,

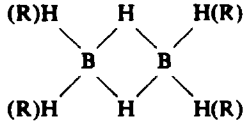

$(H{-}CH_2{-}CH_2{-})_3B$


$(H{-}C(CH_3)_2{-}CH(CH_3){-})_2BH$


$(H{-}C(CH_3)_2{-}C(CH_3)_2{-})_1BH_2$

The alkenylboranes, alicyclic boranes and triarylboranes also are known.[6]

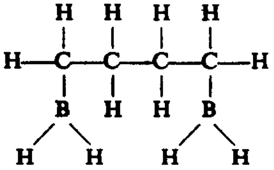
2. *Diborane:* The alkyl diboranes have the same basic boron structure as diborane, *viz.*, two boron atoms held together by two bridge hydrogens with substitution occurring at any of the four terminal hydrogens:

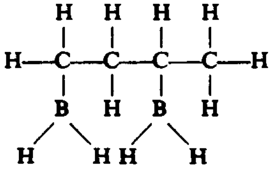


The five possible substituted simple alkyldiboranes had been prepared as early as 1935;[7] however, the purity of some of these compounds may be questionable because of the equilibrium which exists between the various alkyldiboranes. It was not until the advent of spectroscopy that the purity of these compounds could be monitored with any degree of accuracy.[8]

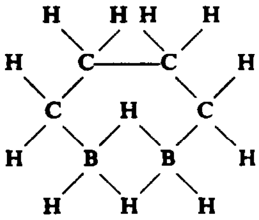
That the molecule contains two boron atoms can be recognised by mass spectral analysis of isotopic variants of the compounds.[9] Infrared analyses[3,8] reveal the presence of B-H-B bridge bonds. The R groups attached to the borons are restricted to low molecular weights; with large sterically hindered groups the molecule dissociates to BH_2R or BHR_2, as mentioned previously.

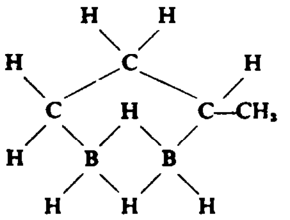
The addition of diborane to alkenes has been studied extensively by H. C. Brown and his school. In the case of the addition of diborane to 1,3-butadiene, Brown[10] reports two possible structures to yield polymeric products:





The reaction of diborane with 1,3-butadiene under different experimental conditions also was carried out in the present author's laboratory.[11] In addition to polymeric products, the product contained an appreciable amount of the 1:1 butadiene diborane addition product. Spectroscopic analyses (mass, infrared and n.m.r.) clearly show two cyclic compounds as follows:

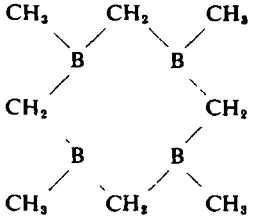




Apparently the presence of two BH_2 groups in the same compound results in tetrahedral boron bond formation. The equivalence of the four hydridic hydrogens (attached to boron) was shown by complete exchange of these hydrogens with deuterium of deuteriodiborane. Such exchanges occur freely in diborane. Interestingly, deuterium in B_2D_6 does not exchange with hydrogen attached to carbon, thus this exchange technique is useful in determining the number of hydrogens attached to boron.[11]

3. *Tetraborane:* To date, there is only one organotetraborane known. This compound formed by the reaction of ethylene with tetraborane has been identified as 2,4-dimethylenetetraborane.[12,13] That the ethylene molecule adds across the 2,4 boron sites is evident in the infrared spectrum by the change of the doublet (BH_2) to a singlet (BH) for the B-H terminal stretching absorption peak. The ^{11}B n.m.r spectrum confirms this conclusion in that the low field triplet (BH_2) of tetraborane changes to a doublet (B-H), whereas the high field doublet remains unchanged (boron sites 1,3) (see Fig. 3).

In the thermal decomposition of trimethylborane, Goubeau[14] reports the formation of a compound containing four boron atoms $[(BCH_2)_4(CH_3)_4]$; however, this compound is visualised as four boron atoms and four CH_2 groups connected alternatively in a ring with a methyl group attached to each boron atom, *viz.*,



Although this compound contains four boron atoms, this compound obviously does not qualify as a tetraborane, but rather as a monoborane.

4. *Pentaborane* Alkyl pentaboranes have been formed in our laboratory by a number of methods, *viz.*, reaction of pentaborane with ethylene or with alkyl halides and aluminum chloride, or by the Grignard reaction. Identification of the various alkylated pentaboranes was made by mass spectral analysis.

Extensive studies on the alkylated pentaboranes also have been carried out at the Explosives Research and Development Establishment in England.[15,16] The various alkylated pentaboranes were separated by gas chromatography and identified by n.m.r. spectroscopy. Up to five ethyl groups have been substituted on pentaborane. Because pentaborane consists of four equivalent boron atoms in a base and one atom in the apex of a tetragonal pyramid, the substitution of alkyl groups gives rise to isomers, and such isomers can be identified by n m.r. spectra. For monoethylpentaborane the ethyl group can be apex or base substituted and its location can be determined by whether the apex doublet or base doublet of pentaborane collapses to a singlet. Diethylpentaborane and tetraethylpentaborane also can have only two isomers, but triethylpentaborane has three possible isomers. All of the possible isomers of the ethylated pentaboranes have been observed [16]

5. *Decaborane* Alkyldecaboranes can be formed by analogous reactions of the alkylpentaboranes. The mass spectrum of monoethyldecaborane already has been given.[17] The various isomers of the alkyldecaboranes can be identified by the changes in the n.m.r. spectrum of decaborane.[18]

The following methyldecaboranes have been prepared and analysed:[19–21] 2-, 5- and 6-methyl-; 1,2-, 2,4-, 5,6- and 6,9-dimethyl-; 1,2,3- and 1,2,4-trimethyl-; 1,2,3,4- and 1,2,3,5-tetramethyldecaborane. For the ethyldecaboranes the following derivatives have been prepared [16,20,22] 1-, 2-, 5- and 6-ethyl-; 1,2- and 2,4-diethyl; at least three isomers of triethyl-, and at least three isomers of tetra-ethyldecaboranes. Benzyldecaborane also has been reported.[23]

6. *Other boron hydrides:* Although not yet reported, organoderivatives of other boron hydrides, such as hexaborane, octaborane, nonaborane, and higher boron hydrides, are anticipated.

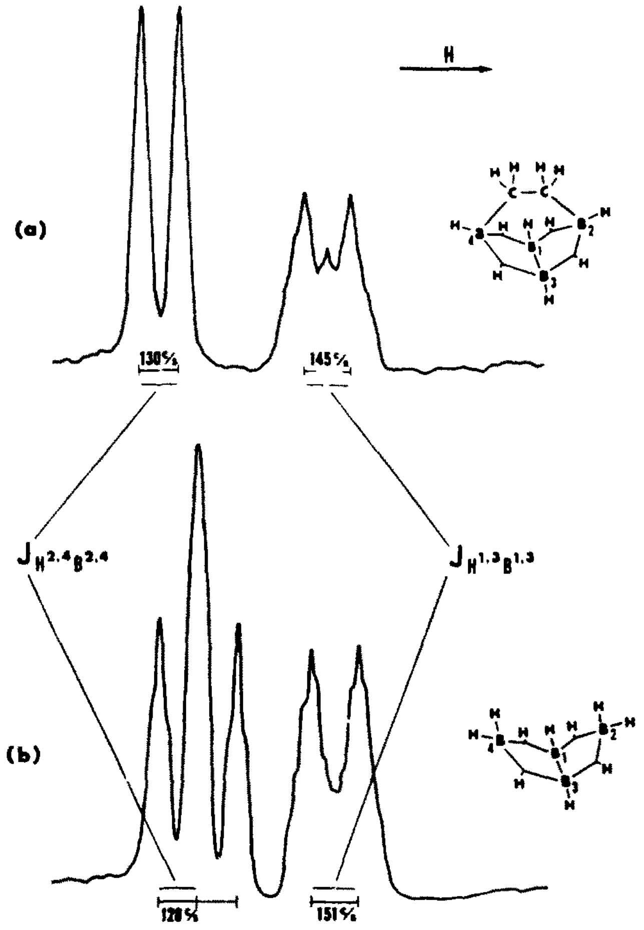


FIG. 3—Comparison of ^{11}B n m r spectra of tetraborane and 2,4-dimethylenetetraborane.

Carboranes

As mentioned previously under the section on *Mass spectrometry*, the study of the reactions of acetylene with various boron hydrides led to the discovery of a new class of organoboron compounds. From spectroscopic identification and characterisation of these compounds, it was shown that they differed from other known boron-carbon compounds. These new compounds have no bridge hydrogens and the carbon atoms are incorporated into the structure of the boron network; consequently, these compounds were named "carboranes". The generic formula for this series of compounds is $B_nC_2H_{n+2}$.[24] Although the entire series of carboranes can be formed by the low pressure flashing reaction of diborane and acetylene, better yields can be obtained by use of the higher boron hydrides as discussed below.

1. *Carborane*-3 ($B_3C_2H_5$): This compound was one of a series of carboranes prepared by the reaction of pentaborane and acetylene in the silent discharge apparatus.[24] Identification was made by comparison of the mass spectra of isotopic variants of the compound, *viz.*, $^{10}B_3C_2H_5$, $B_3C_2H_5$, $B_3C_2H_3D_2$, $B_3C_2D_3H_2$ and $B_3C_2D_5$. From infrared and n.m.r. spectra, the structure of the compound is regarded as a trigonal bipyramid with the three boron atoms in one plane and one carbon above and below the boron plane. The hydrogens attached to the boron and carbon atoms are the same as originally present in the parent compound. The deuterium in deuteriodiborane will exchange with the hydrogens attached to the boron atoms, but not with the hydrogens attached to the carbons. This selectivity of hydrogen-deuterium exchange is common to the boron hydrides and is the basis of a method for determining the location of hydrogen, *i.e.*, whether attached to boron or carbon atoms.

2. *Carborane*-4 ($B_4C_2H_6$): Two isomers of carborane-4 have been identified.[25] The symmetrical isomer is analogous to $B_3C_2H_5$, except that there are four borons in one plane; in the unsymmetrical form, one carbon and one boron atom have interchanged positions. Because of similarities in the vapour pressures of carborane-4 and pentaborane (parent compound), it is not possible to separate the two compounds by direct fractional distillation. However, such separation can be effected by first complexing the pentaborane with triethylamine to change the degree of volatility. The excess triethylamine can be complexed with diborane.

3. *Carborane*-5 ($B_5C_2H_7$): This compound has been identified by comparison of the mass spectra of the ^{10}B-enriched and isotopically-normal variants of the compound.[26] One characteristic feature of the carboranes is the low degree of skeletal breakdown observed in their fragmentation patterns.

4. *Carborane*-8 ($B_8C_2H_{10}$): This compound also has been identified by application of the isotopic boron technique and mass spectrometry.[26] In addition to use of pentaborane as a parent compound, carborane-8 is a product when acetylene is reacted with tetraborane or decaborane.

5. *Carborane*-10 ($B_{10}C_2H_{12}$): Carborane-10 can be prepared conveniently by the reaction of acetylene with decaborane.[26] The n.m.r. spectra of carborane-10 is consistent with the concept that the two carbon atoms replace the four bridge hydrogens of decaborane,[18] thus completing the icosahedron structure.[*] This compound is quite stable.

6. *Alkyl derivatives of carboranes:* In the preparation of the carboranes from acetylene, it has been observed that various alkylated derivatives of the different carboranes are also formed. The alkylated derivatives of the carboranes are also formed by reaction of boron hydrides with alkylated acetylenes, *e.g.*, methylacetylene. The derivatives observed in the mass spectra are as follows: $B_3C_3H_7$, $B_3C_4H_9$, $B_4C_3H_8$, $B_4C_4H_{10}$, $B_5C_3H_9$, $B_5C_4H_{11}$, $B_5C_5H_{13}$, $B_5C_6H_{15}$, $B_8C_3H_{12}$ and $B_8C_4H_{14}$. Numerous derivatives of $B_{10}C_2H_{12}$ also have been formed; these compounds will be the subject of a separate paper.

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[*] The introduction of the two boron atoms of diborane into the decaborane structure results in the unstable $B_{12}H_{12}$ molecule;[27] however, the $B_{12}H_{12}^{-2}$ ion is reported to be stable with an icosahedral arrangement.[28]

Dihydrocarborane

When pentaborane and acetylene react at low pressures, carborane-4 is formed; however, when these same reactants are confined under pressure at elevated temperatures, the product is another organoboron compound whose composition is $B_4C_2H_8$.

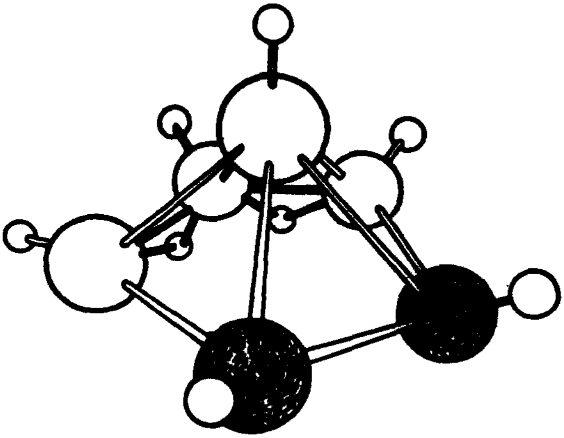

FIG. 4.—Structure of dihydrocarborane-4 ($B_4C_2H_8$).

Before being analysed by n.m.r. spectroscopy, this compound was believed to be "ethenyltetraborane";[29] however, subsequent studies in our laboratory indicate that the compound is structurally similar to hexaborane-10 in which the two carbon atoms have replaced two boron atoms and two bridge hydrogens in the base of the pentagonal pyramid (Fig. 4). Consequently, this compound is named "dihydrocarborane-4". Recently,[30] some alkyl derivatives of $B_4C_2H_8$ have been reported.* It is very probable that other dihydrocarboranes will be prepared in the future.

Now that pure organoboron compounds can be synthesised and identified, methods for elemental analysis of boron and carbon are being developed.[31,32]

Zusammenfassung—Die Identifizierung vieler neuentdeckter Verbindungen, die nur die Elemente B, C und H enthalten, gelang mittels Massen-, Infrarot- und Kernresonanzspektroskopie in Verbindung mit Isotopensubstitution. Die Verbindungen können in zwei Klassen aufgeteilt werden: 1) organische Derivate der Borhydride und 2) Carborane (und ihre organischen Derivate). Beispiele von Verbindungen, die mit ausschließlich spektroskopischen Mitteln identifiziert wurden, werden angegeben.

Résumé—L'identification de nombreux composés nouvellement découverts, constitués seulement par les trois éléments B, C et H, a été réalisée par l'emploi des spectroscopies de masse, infrarouge, et de résonance magnétique nucléaire, en liaison avec la technique de substitution isotopique. Ces composés peuvent être classés en deux catégories générales: (1) les organo-dérivés des borohydrures et (2) les "carboranes" (et leurs dérivés organiques). On donne des exemples de composés identifiés par des méthodes purement spectroscopiques.

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* Attention is called to the fact that the structure of $B_4C_2H_8$ cited recently[30] was taken from the work of I. Shapiro and H G. Weiss without permission or acknowledgment of the senior investigator.

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POLAROGRAPHIC REDUCTION OF MANGANESE^{III} IN AN ALKALINE TARTRATE SOLUTION

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Summary—The formation of manganese^{III} complexes by the air oxidation of manganese^{II} in alkaline tartrate solution is confirmed by measurement of the direct current and the Kalousek polarograms. A distinct minimum is observed on the polarogram in the pH range from 10 to 13. The effects of pH, the concentration of sodium tartrate and surface-active substances on the polarogram are investigated, and the electrode processes of manganese^{III} in an alkaline tartrate solution are discussed

THE polarographic reduction of manganese^{II} has been extensively studied, but that of manganese^{III} has not received full investigation. Kolthoff and Watters[1] studied the reduction of the pyrophosphate complex of manganese^{III}, which was prepared by the preliminary oxidation of manganese^{II} in a pyrophosphate solution with excess lead dioxide. Novák, Kůta and Říha[2] studied the polarographic behaviour of manganese^{III} in a solution containing sodium chloride, sodium hydroxide and triethanolamine. Svátek, Roubal and Přibil[3] found a reversible wave for the manganese^{III} complex with pyrocatechol-3,5-disulphonate in an ammoniacal buffer and in sodium hydroxide solution. Verdier[4] reported the polarographic reduction of hexacyanomanganate$^{(III)}$, which was prepared by air oxidation of manganese^{II} in potassium cyanide solution. He[4] found, however, that in 2*M* potassium hydroxide solution containing sodium tartrate, manganese^{II} was oxidised to manganese^{IV} by atmospheric oxygen.

The present paper is concerned with a polarographic study of the manganese^{III} complex produced by the air oxidation of manganese^{II} in an alkaline tartrate solution. The oxidation state of the complex is discussed on the basis of the direct current and the Kalousek polarograms obtained. The minimum on the current-voltage curve is explained from the standpoint of the charges of the complex and the electrode. The deceleration and the acceleration of the electron-transfer process by the addition of surface-active ions are demonstrated.

EXPERIMENTAL

The manganese^{III} was prepared by air oxidation of manganese^{II} in an alkaline tartrate solution. The formation of manganese^{III} was confirmed by the polarographic method described later A 0 1*M* manganese^{II} solution was prepared by dissolving a known amount of manganese^{II} chloride tetrahydrate.

Direct current (d c.) polarograms were recorded by a Yanagimoto PB-4 pen-recording polarograph and a Yanagimoto Galvarecorder GR-103 with an automatic potential scanner. A Yanagimoto Galvarecorder Y-GR 2 with an automatic potential scanner was used to record alternating current (a.c.) polarograms. Kalousek polarograms[5] were obtained with the same circuit as previously described.[6,7] Current-time (i-t) curves were recorded using a Rikadenki ER-J 1 recorder with an RLDC-201 preamplifier. An electrolysis cell of a simple beaker type was used in all measurements. The dropping mercury electrode (DME) used had an m value of 2·16 mg/sec and a drop time t_d of 4 59 sec, being measured in 0 1*M* potassium chloride solution containing 0 005% of gelatin at 25°

and −0·5 V *vs* SCE at a 40 cm height of the mercury reservoir The potential of the DME was measured against a saturated calomel electrode (SCE), which was connected to the electrolytic solution through a Hume and Harris type salt bridge When a.c polarograms were measured, a platinum wire electrode of a large surface area was inserted in the electrolytic solution as the third electrode, which was terminated at the SCE through a 100-μF capacitor A Hitachi Model EHP-1 pH meter was used for measurement of the pH of the solution

All measurements were carried out in a thermostat of 25° ± 0·1°, and the dissolved oxygen in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution Precautions were taken against oxygen and light for manganese^{II} and manganese^{III}* solutions, respectively The d c and Kalousek polarograms given in this paper are corrected for the residual current.

RESULTS AND DISCUSSION

Manganese species in an alkaline tartrate solution

Polarograms of 1·2 mM of manganese obtained before and after the air oxidation in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·005% of gelatin are reproduced in Fig. 1. The polarogram of manganese^{II} (curve 1) is the same as that reported by Er-Kong and Vlček.[8] They consider that manganese^{II} exists in various forms of mono- and binuclear hydroxotartratomanganate$^{(II)}$, of which only the mononuclear complexes are reducible at the dropping mercury electrode. The polarogram obtained after the air oxidation (curve 2) shows a remarkable minimum, and does not coincide with the polarogram obtained by Verdier[4] in 2*M* potassium hydroxide solution containing sodium tartrate. The limiting currents of curve 2 measured at −1·55 V and −1·90 V were both proportional

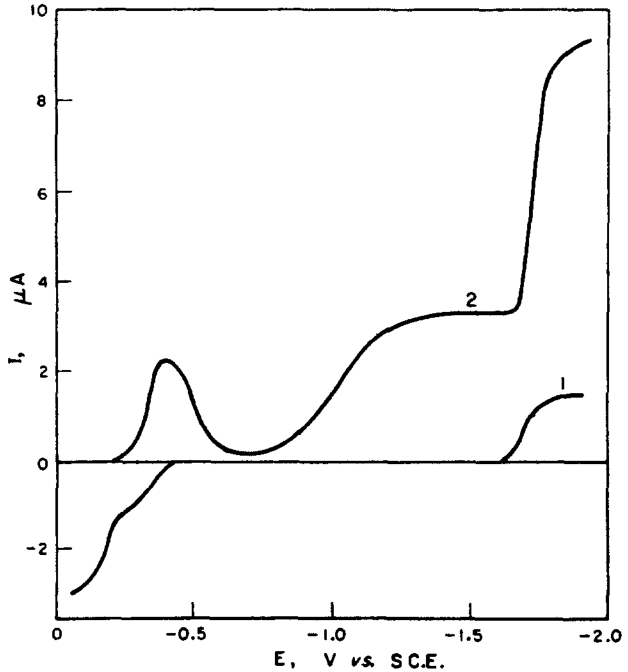

FIG 1 —Polarograms of 1·2 mM of manganese in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·005% of gelatin, obtained before (curve 1) and after (curve 2) the air oxidation.

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* Photochemical reduction of manganese^{III} in an alkaline tartrate solution is reported elsewhere.

to the concentration of manganese^{II} added, and the ratio of the latter to the former was found to be 2·96 after correction for the drop time. This means that the limiting current at −1·55 V is from the one-electron reduction of manganese^{III} to manganese^{II} because the second wave starting approximately at −1·6 V is a reduction wave of manganese^{II} to manganese^{0}.

The formation of manganese^{III} was also confirmed by the Kalousek polarograms recorded before and after the air oxidation. Curves 1 and 2 in Fig. 2 are the Kalousek polarograms which were recorded with an alkaline tartrate solution of manganese^{II} at —0·10 V and —0·30 V of E_2 potential.[6,7] The cathodic part of the polarograms is essentially the same as the polarogram obtained after the air oxidation. The Kalousek polarograms recorded after the air oxidation (curves 3 and 4 in Fig. 2) give anodic waves, which are similar to those observed with the alkaline tartrate solution of manganese^{II}. These observations suggest that the product obtained by the air oxidation is the same as that obtained by electro-oxidation. In addition, the Kalousek polarograms of the alkaline tartrate solution of manganese^{III} recorded at —0·42 V and —1·55 V of E_2 potential show that the reduction products are the same at both potentials and that the potential of the anodic wave agrees with that of the mononuclear manganese^{II} tartrate complexes.[8] This suggests that the manganese^{III}-tartrate complex obtained by the air oxidation is of a mononuclear type.

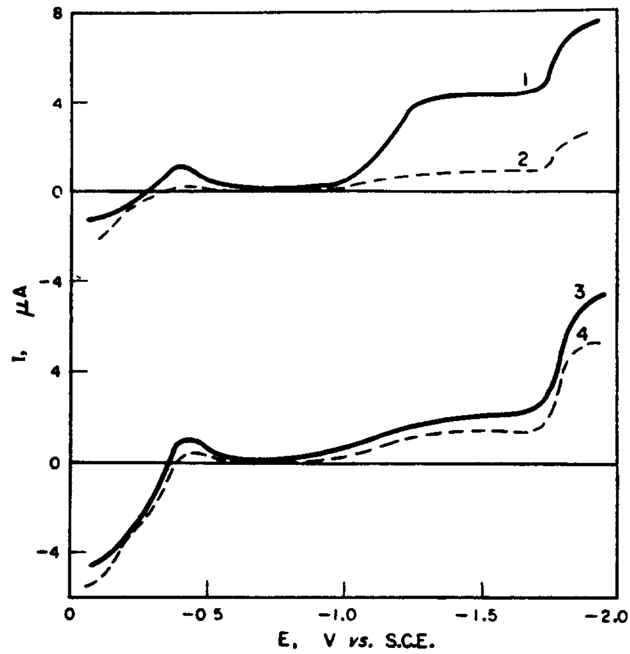

Fig. 2.—Kalousek polarograms of 1·2 mM of manganese^{II} (curves 1 and 2) and manganese^{III} (curves 3 and 4) in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and gelatin (0 005% for 1 and 2 and 0·001% for 3 and 4). E_2 potentials are:

(1) —0 10 V; (2) —0·30 V; (3) —0 42 V; (4) —1·55 V *vs.* SCE.

Effect of pH, tartrate concentration and potassium nitrate

A synoptical denotation of the wave is given in Fig. 3. The first round-shape wave is called the i_1' wave and the second drawn-out one the i_1 wave, because both are considered as being caused by the reduction of manganese^{III} to manganese^{II}. The average currents of both waves are represented with $\bar{i}_1'$ and $\bar{i}_1$, respectively.

The effect of pH on the polarogram of manganese^{III} in a tartrate solution is shown in Fig. 4. Because manganese^{II} was not readily oxidised by air at a pH less than 11, the pH of the solution was adjusted with perchloric acid after manganese^{II} is oxidised to manganese^{III} at pH 11·8. With decreasing pH, the minimum becomes less pronounced, the i_1' wave shifts to less negative potentials and $(\bar{i}_1')_l$ increases to reach the limiting value that is the same as $(\bar{i}_1)_l$, where $(\bar{i}_1')_l$ and $(\bar{i}_1)_l$ represent the limiting currents of the corresponding waves. At pH 9·1 a polarogram with no minimum is obtained (see curve 1), while in 0·1M sodium hydroxide the i_1' wave almost vanishes

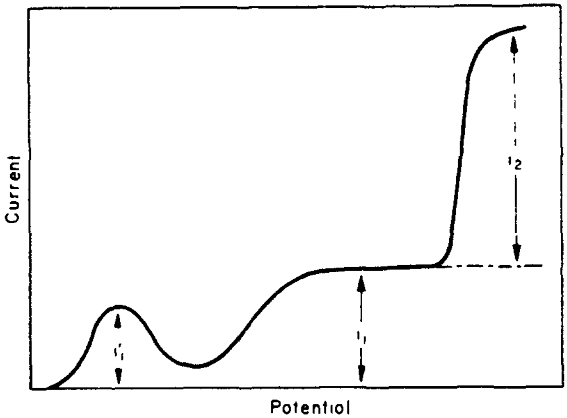

FIG. 3.—Synoptical denotation of the manganese^{III} wave in alkaline tartrate solution.

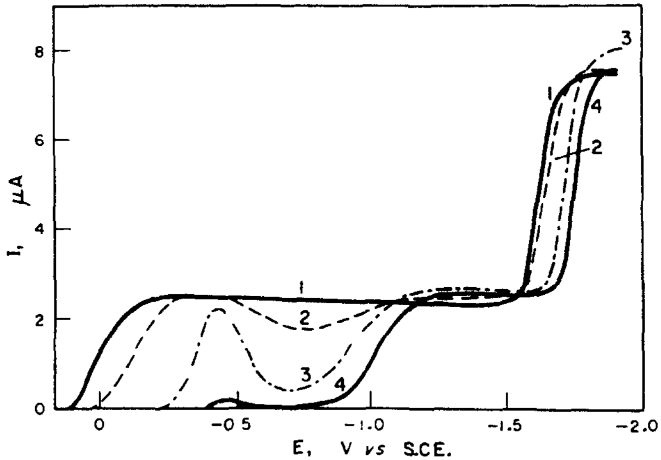

FIG. 4.—Polarograms of 1·0 mM of manganese^{III} at various pH in the solutions containing 0·25M sodium tartrate, 0·001% of gelatin and Britton-Robinson buffer (curves 1, 2 and 3) or 0·1M sodium hydroxide (curve 4)

(1) pH 9·1; (2) pH 10·5; (3) pH 11·8.

(curve 4). The decreasing pH also shifts the i_2 wave to less negative potentials. The shifts of the i_1' and the i_2 waves to more negative potentials with increasing pH indicate that hydrogen ions are taken up when the manganese^{III} and the manganese^{II} complexes are reduced to the corresponding lower oxidation states.

The effect of tartrate ion on the reduction wave was investigated by recording the polarograms in the presence of varied concentrations of sodium tartrate. With increasing concentrations of tartrate, the i_1' wave started at more negative potentials and the $\bar{i}_1'$ current decreased; the $\bar{i}_l/10$-potentials, which mean the potentials at $\bar{i} = \bar{i}_l/10$, were found to be $-0{\cdot}24$ V at $0{\cdot}10M$ and $-0{\cdot}35$ V at $0{\cdot}70M$ of tartrate, respectively. This suggests that tartrate ions are liberated when the manganese^{III} complex is reduced to the bivalent state. As for the i_1 wave, the potentials were not appreciably affected with the increase of tartrate concentration, but the limiting current was depressed to a great extent. The value of $(\bar{i}_1)_l/C$ measured at $-1{\cdot}55$ V *vs.* SCE varied from $2{\cdot}7_7$ μA/mM to $2{\cdot}2_5$ μA/mM, when the tartrate concentration was changed from $0{\cdot}25M$ to $0{\cdot}63M$. This decrease may be attributed to the increasing number of tartrate ions co-ordinating.

In Fig. 5 are given the polarograms which were obtained at various concentrations of tartrate but at a constant ionic strength, being adjusted with potassium nitrate The same decrease in the limiting current of the i_1 wave with increasing tartrate concentrations was observed. These polarograms in Fig. 5 present, however, not only the affect of tartrate but also the affect of potassium nitrate on the reduction wave. A separate experiment indicated that upon the addition of potassium nitrate, the i_1' wave was suppressed and the i_1 wave was shifted to less negative potentials The former seems to be from the presence of nitrate ions and the latter from potassium ions.

Effect of surface-active substances

By the addition of gelatin both the i_1' and the i_1 wave are depressed (Fig. 6). This agrees with the fact that gelatin adsorbs on the mercury surface in the wide range of potentials. On the other hand, the addition of thiocyanate ions, which adsorb mainly at the positive branch of the electrocapillary curve, depressed only the i_1' wave (Fig. 7). A most interesting effect of a surface-active substance was found when trimethyloctadecylammonium chloride, $(CH_3)_3(C_{18}H_{37})N^+Cl^-$, (denoted as TMOAC) was added to the solution. Fig. 8 presents the polarograms obtained at various concentrations of TMOAC. The addition of a small concentration of TMOAC depresses both the i_1' and the i_1 wave. At higher concentrations of TMOAC, however, the electron transfer at the i_1' wave is further decelerated but that at the i_1 wave is considerably accelerated. The dual (deceleration and acceleration) effect of surface active substance has been reported by Frumkin and coworkers,[9] who found that tetrapentylammonium ion, at its lower concentration, accelerates the reduction of tetrachloroplatinate$^{(II)}$ but, at its higher concentration, decelerates the reduction The dual effect of TMOAC on the reduction of manganese^{III} in an alkaline tartrate solution is seen also from the current-time curves during the life of a mercury drop measured at $-0{\cdot}82$ V *vs.* SCE (Fig. 9).

Electrode process of manganese^{III} in an alkaline tartrate solution

As mentioned above, the results obtained with the Kalousek polarograms suggest that the manganese^{III} species produced by the air oxidation in an alkaline tartrate

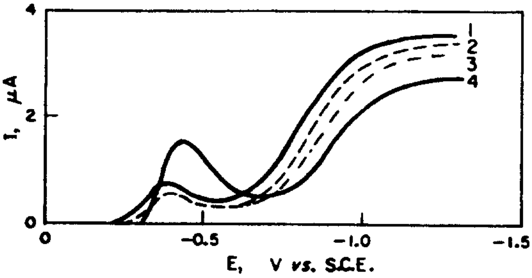

FIG. 5.—Polarograms of 1·2 mM of manganese^{III} in the solutions of pH 11·8 and ionic strength 2·0 (adjusted with potassium nitrate) containing Britton-Robinson Buffer, various concentrations of sodium tartrate and 0·001% of gelatin. Concentrations of sodium tartrate: (1) 0 125*M*; (2) 0·250*M*; (3) 0 375*M*; (4) 0 625*M*.

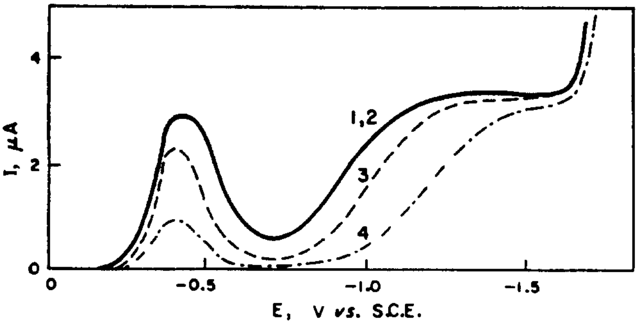

FIG. 6.—Effect of gelatin on the polarograms of 1·2 mM of manganese^{III} in the solutions of pH 11·8 containing Britton-Robinson buffer, 0 25*M* sodium tartrate. Concentrations of gelatin: (1) 0; (2) 0·001%; (3) 0 005%; (4) 0 01%.

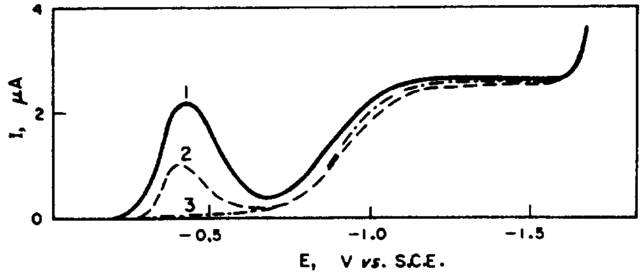

FIG. 7.—Effect of thiocyanate ions on the polarograms of 1·0 mM of manganese^{III} in the solutions of pH 11·8 containing Britton-Robinson buffer, 0·25*M* sodium tartrate and 0·001% of gelatin. Concentrations of thiocyanate: (1) 0; (2) 0·010*M*; (3) 0·030*M*.

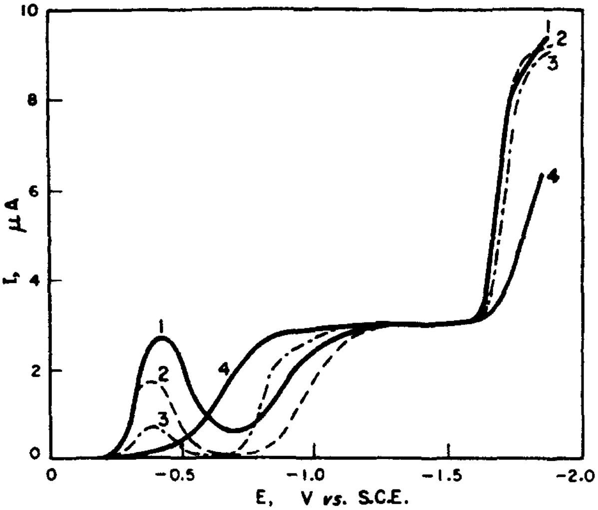

FIG. 8.—Polarograms of 1·2 mM of manganese^{III} in the solution of pH 11·8 containing Britton-Robinson buffer, 0 25*M* sodium tartrate in the absence (curve 1) and in the presence of 0 13 mM (2), 0 25 mM (3) and 1·2 mM (4) of trimethyloctadecylammonium chloride.

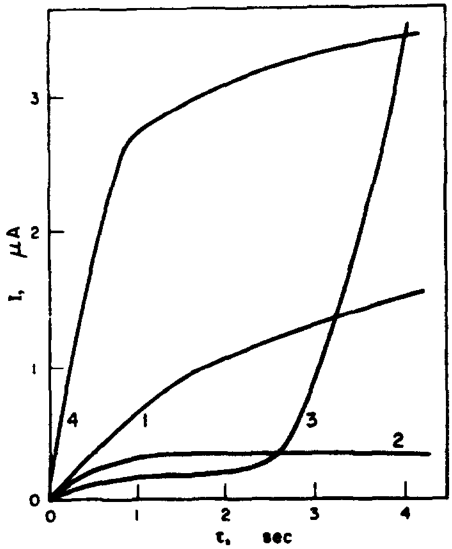

FIG. 9.—Current-time curves at −0·82 V vs. SCE obtained with the same solutions as given in Fig. 8.

solution is hydroxotartratomanganate(III) complex, $Mn(OH)_p(tar)_q^{\gamma-}$ (tar = tartrate), which is considered to be negatively charged in an alkaline solution.

The plot of log $\bar{i}/(\bar{i}_d - \bar{i})$ against E for the i_1' wave gives a straight line with a slope of approximately 80 mV, which is somewhat greater than expected for the reversible one-electron reduction. The i_1 wave, on the other hand, is drawn-out and of an irreversible type. The measurement of a.c. polarograms confirmed the degree of irreversibility of both i_1' and i_1 waves. The value of $i_p/n\bar{i}_d\sqrt{t_d}$[10] of the i_1' wave, where i_p means a peak current of a.c. polarogram, $\bar{i}_d$ the diffusion current of d c. polarogram, n the number of electrons involved in the electrode process and t_d the drop time, was calculated to be 25·4 $\mho A^{-1}$ $sec^{-1/2}$, which is about half of that for the reduction of zinc^{II} in 1*M* potassium nitrate solution, but approximately 4 times greater than that for the reduction of nickel^{II} in 0·1*M* potassium chloride solution. The i_1 wave, on the other hand, shows no peak on the a.c. polarograms.

The hydroxotartratomanganate(III) complex is reduced to the corresponding manganese^{II} complex. Because the complex is negatively charged, it can readily approach to the positively charged electrode surface and, consequently, the electrode process takes place with lower activation energy. The rate of electron transfer is of the magnitude of the quasi-reversible type, being estimated from the value of $i_p/n\bar{i}_d\sqrt{t_d}$ and the shape of the Kalousek polarogram. This electrode process is, however, easily hindered by the addition of a small amount of surface active substance that is specifically adsorbed in the positive branch of electrocapillary curve, such as thiocyanate ions, because the complex is not specially surface active, as was confirmed by the measurement of the electrocapillary curve.

This electrode process is decelerated by the decrease in positive charge and the increase in negative charge of the electrode. This causes a minimum on the current-potential curve as has been reported in the case of the reduction of many anions.[11] The minimum is not observed at lower pH, because of the decrease in negative charge of the manganese^{III} complex species.

In the negative branch of the electrocapillary curve, the electroreduction of the complex with higher activation energy takes place. This seems partly because of the electrostatic repulsion between the complex and the negatively charged electrode. The addition of cations that adsorb on the electrode surface neutralises the negative charge of the electrode or those cations act as bridging ions so that the activation energy is lessened and the electron transfer is accelerated.

Zusammenfassung—Die Bildung von Mangan(III)-Komplexen durch Luftoxydation von Mangan(II) in alkalischer Tartratlösung wurde durch Messung der Gleichstrom- und der Kalousek-Polarogramme bestätigt Ein deutliches Minimum erschien im pH-Bereich von 10 bis 13 auf dem Polarogramm Der Einfluß des pH, der Konzentration von Natriumtartrat und von oberflächenaktiven Stoffen auf das Polarogramm wurden untersucht und die Elektrodenprozesse von Mangan(III) in alkalischer Tartratlösung diskutiert

Résumé—La formation de complexes du manganèse(III) par oxydation à l'air du manganèse(II) en solution tartrique alcaline a été confirmee par la mesure du courant continu et les polarogrammes de Kalousek On a observé un minimum net sur le polarogramme, dans l'intervalle de pH 10–13 On a étudié les effets, sur le polarogramme, du pH, de la concentration du tartrate de sodium, et des substances tensioactives, on discute des processus à l'électrode du manganèse(III) en solution tartrique alcaline.

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A MODIFICATION OF THE EXPONENTIAL EXCHANGE LAW IN HETEROGENEOUS SYSTEMS

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Summary—The exponential exchange law for heterogeneous systems can be applied to isotope exchange between solid salts and their saturated solutions after allowance is made for the initial rapid exchange between the solution and the crystal surface. For a variety of salts it is possible to get information on the dynamic equilibrium between the surface and the interior of the crystals. Experimental results are presented for the chromates of silver, barium and lead. Silver chromate exchanges rapidly with silver ion, without showing significant exchange with chromate ion. Recrystallisation effects are evident in the chromates of barium and lead.

INTRODUCTION

THE exchange between fresh precipitates and saturated solutions has been the subject of study by Kolthoff and his associates since 1933.[1] The incorporation of radioisotope in the solid was attributed to recrystallisation of the solid, thus exposing continuously new surface. Most of this work preceded the formulation of the "exponential exchange law" by McKay in 1938.[2]

This law, as applied to heterogeneous systems, states that

$$Rt = -\frac{A \cdot B}{A + B} \ln (1 - F) \tag{1}$$

where R = moles of tagged material crossing the interface per time unit,
t = time,
A = moles of solid,
B = moles of tagged solute in solution,
F = fraction of exchange, which can be expressed in count rates of aliquots of the solution.

If the solution contains all the radioactivity initially,

$$F = \frac{S_0 - S_t}{S_0 - S_\infty}$$

in which S_0 = cpm at $t = 0$; S_t = cpm at $t = t$, and S_∞ = cpm at isotopic equilibrium throughout the system.

Experimental results show clearly that the exponential exchange law is not valid in exchange between an initially inactive solid and its saturated radioactive solution.

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* From Ph.D. dissertation, submitted by L. J. Parcell to the Graduate School of Arts, and Sciences, University of Virginia, June, 1963.

An example of the results of such an experiment is shown in Fig. 1, curve I A rapid initial increase, followed by a slower, but linear increase of $-\log(1-F)$ with time is shown.

Because the initial rapid exchange is caused by exchange with the surface, there is a simple method of separating the fast and slow exchanges mathematically. We studied the slow exchange process by application of a modification of the exponential exchange law. Apparent deviations from this law, as caused by the initial rapid surface exchange, are eliminated by this modification.

DISCUSSION

One essential requirement for conformity with the exponential exchange law of heterogeneous systems is a relatively rapid isotopic equilibrium in each phase compared to the rate-determining step in exchange at the interface. Generally the surface of crystals is considered to be part of the solid phase. However, in isotopic exchange it is necessary to treat the crystal surface and the solution as one single phase, and the interior of the crystals as the second phase. This approach is made because the rate-determining step in the slow exchange process is either between the surface and the interior of the crystals, or in the interior of the crystals, but certainly not between solution and surface.

The initial condition for the slow exchange process is ideally a solution in isotopic equilibrium with the surface, without any activity being present in the interior of the crystals. An approximation to this condition is obtained by extrapolation of the linear part of curve I in Fig. 1 to $t = 0$; the F value obtained by this extrapolation pertains to surface exchange only.

The slow exchange process starts with an initial activity in solution reduced by surface exchange from S_0 to $S_0{}^*$. The value of $S_0{}^*$ is obtained from $S_0{}^* = \dfrac{B}{M_s + B}$, in which B is the number of moles of tagged species in solution, and M_s is the number of moles of the same chemical species in the surface of the crystals. This modification of S_0 to $S_0{}^*$ is not dependent upon the mechanism of the secondary slow exchange process. The newly defined $S_0{}^*$ can be used to check the validity of the exponential exchange law for the slow secondary exchange. It is determined from the F value obtained by extrapolation of $-\log(1-F)$ to $t = 0$.

The exponential exchange law needs modification when it is applied to the slow exchange process after isotopic equilibrium is established between the solution and the surface. It takes the form

$$Rt = -\frac{(A - M_s)(B + M_s)}{A + B} \ln(1 - F^*) \qquad (2)$$

where A, B, R and t are as in equation (1), M_s = number of moles in the surface, and

$$F^* = \frac{S_0{}^* - S_t}{S_0{}^* - S_\infty}.$$

A plot of $-\log(1 - F^*)$ versus time is given in Fig. 1, curve II. For this example of exchange between solid silver chromate and its saturated solution containing tagged silver nitrate, a linear relationship is obtained. A small positive deviation from the origin on the time abscissa would be expected, because the slow exchange process cannot become significant until some exchange has occurred between the solution and the surface. However, the linear relationship is an indication of a rate-determining step in exchange between the surface and the interior of the crystals.

More indication of the validity of this form of the exchange law is obtained by changing variables which should not affect the chemical composition at the interfaces. The weights of identical crystals taken for an experiment can be varied. R should be directly proportional to the interfacial area, or to the weight of solid used. It is convenient to define K by $R = K \, . \, A$, because K is independent of the weight of solid used, and K is expressed in reciprocal time units. Because M_s is generally small compared with A, the following expression is obtained:

$$\mathrm{d}\frac{[-\ln(1 - F^*)]}{\mathrm{d}t} = K\frac{A + B}{B + M_s}. \tag{3}$$

The two criteria, a linear relationship between log $(1 - F^*)$ and time, and a value of K independent of the amount of solid used, can be applied to a variety of systems. Results of our studies show that the exchange between silver ion in solution and solid silver chromate conforms to equations (2) and (3) in all cases.

Deviations from this exchange law are evident in exchange between either solid lead chromate or barium chromate, and tagged chromate in their saturated solutions, because a linear relationship is not obtained The deviations do not necessarily show that there is no rate-determining step in exchange somewhere between the surface and the interior of the crystals. The requirements for conforming with equations (2) and (3) include:

(*a*) a relatively rapid equilibrium of isotopes in each of the two parts in which the system is separated;

(*b*) a constant interfacial area during the experiment. Recrystallisation generally decreases this area, and solutions should be used in which recrystallisation is kept to a minimum. Shaking may rupture crystals, causing increase of the surface area.

(*c*) no unidirectional recrystallisation. Some freshly prepared crystals (*e.g.*, lead chromate) may change to a more stable crystal lattice, or they may undergo a chemical change. A temporary heterogeneous isotopic distribution may result from such transitions.

Generally the number of moles of tagged species in solution is much smaller than the number of moles of solid, because the most accurate determinations of M_s are obtained when $B \cong M_s$. The value of S_∞ is much smaller than that of either S_0 or $S_0{}^*$ in our determinations. If S_∞ is ignored in calculation of F and of F^*, the following approximate values are obtained:

$$-\ln(1 - F) \cong -\ln\frac{S_t}{S_0} \quad \text{and} \quad -\ln(1 - F^*) \cong -\ln\frac{S_t}{S_0{}^*}.$$

The variable with time is S_t in both cases, and identical slopes are obtained for the linear part of curve I and curve II in Fig. 1. The modification of the exchange law causes a change in the relationship between the slope and K, without changing the slope significantly.

In any experiment with systems conforming to the modified exchange law, a value of the rate constant K can be found, giving the number of moles of tagged species crossing the interface per time unit per mole of solid present. More information on the actual mechanism can be obtained by determination of K at various temperatures, at different compositions of the saturated solution, and for changes of size and shape of crystals. The effect of some of these variables on the exchange between silver ion and silver chromate is shown under *Experimental.*

EXPERIMENTAL

Reagents

Radioactive silver 0·546 g of Analysed Reagent grade silver foil was irradiated in the 1-Mw reactor at the University of Virginia to give about 1 mcurie of ^{110m}Ag. The silver was dissolved in dilute nitric acid, and suitable portions of the solution were used for exchange studies. Excess of nitric acid was removed by evaporation under infrared radiation followed by heating at 110° for 1 hr. The residue was dissolved in distilled water

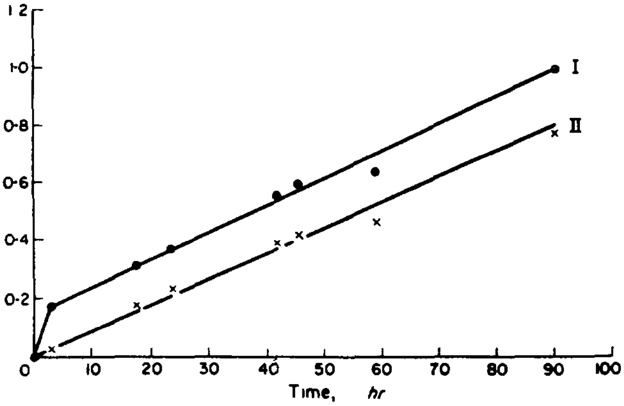


FIG. 1.—A typical exchange between solid silver chromate and tagged silver ion in 50% ethanol.

I. Ordinate is $-\log(1 - F)$
II: Ordinate is $-\log(1 - F^*)$

Radioactive chromium. ^{51}Cr in the form of chromate was obtained from Squibb in 50-μ curie amounts. Also 10 mcuries of $^{51}CrCl_3$ in HCl (Oak Ridge National Laboratories) was used. Chloride, which was present in the solutions from both sources, must be removed, because it would cause precipitates of silver chloride in silver ion-silver chromate exchange. This removal was done by addition of excess of 6N nitric acid and sufficient inactive potassium chromate to make a final solution of about $10^{-6}M$ chromate. Evaporation removes chloride as NOCl, and reduces chromate to chromic ion. Oxidation back to chromate was done by excess of hydrogen peroxide after adjustment of the pH to 10 with potassium hydroxide. After evapcration of this solution to remove hydrogen peroxide, the residue was dissolved in distilled water, and the pH was adjusted to 7·0 with 0·001M perchloric acid.

s-Diphenyl carbazide reagent for chromate contained 0·25 g of Eastman reagent (Cat 618) and 4 g of phthalic anhydride (Matheson Coleman and Bell, Cat 2619) in 100 ml of 95% ethanol.

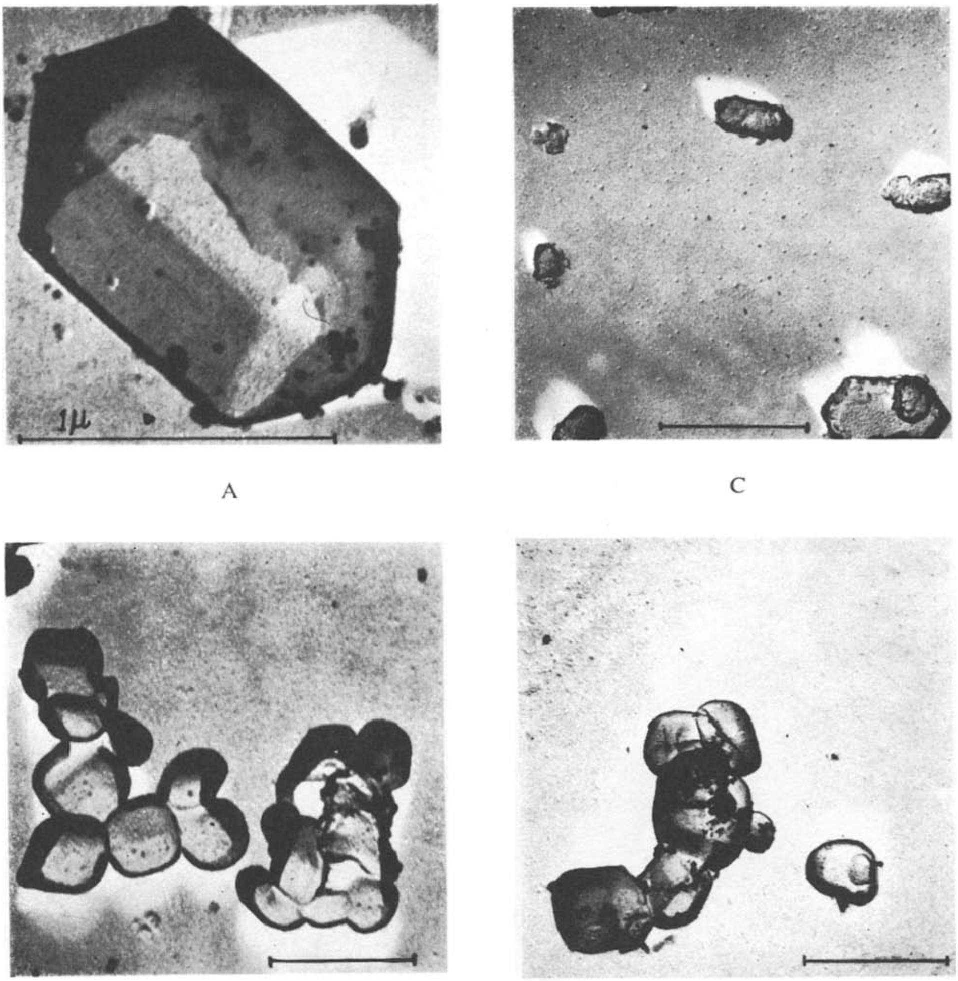
Silver nitrate and potassium nitrate: 0·100M stock solutions were prepared from Baker and Adamson AR-grade chemicals, and distilled water.

Barium chloride Baker and Adamson purified $BaCl_2 \cdot 2H_2O$ was used to prepare a 0·1M solution in distilled water.

Lead perchlorate. Baker's N.F. PbO was added slowly to 70% Baker and Adamson reagent-grade perchloric acid. The solution was filtered to remove traces of PbO_2, and was diluted to 2M. The pH was adjusted to 2·5 with dilute perchloric acid.

Acetate buffer 160 g of sodium acetate and 6·0 g of glacial acetic acid, both AR-grade were dissolved in 2 litres of distilled water.

Ethanol: Either Pharmco or USI ethanol was used in the experiments.



A C

B D

PLATE I.—Photomicrographs A B C D

Preparations of precipitates

In general, stock solutions of reagents were filtered through fine glass filters before use in precipitations Supersaturated mixtures were prepared by rapid mixing of equivalent solutions in a 400-ml polyethylene beaker A Sargent Cone-Drive Stirrer, with a glass impeller having two blades of 2-cm length each, was used at 300 rpm for mixing. After about 3 min most of the precipitate had formed, and the suspension was poured into 200-ml wide-mouth bottles, and was centrifuged for 5 min at 2000 rpm After decantation, the precipitate was washed twice with distilled water, then with inactive solution of the same composition as the exchange solution

Precipitates of silver chromate were prepared by rapid mixing of 200 ml of solutions of silver nitrate and of potassium chromate to give initial concentrations of silver chromate of 8 75 × $10^{-4}M$, and of 5·00 × $10^{-3}M$. The chromate solution contained 10 ml of acetate buffer.

Solid barium chromate was formed by mixing 0·005*M* solutions of barium chloride and of potassium chromate Lead chromate was formed in mixtures of 0·010*M* lead perchlorate and of 0 010*M* potassium chromate The pH of both solutions was adjusted to 1 8 before mixing

Exchange experiments

The precipitates were left in the 200-ml centrifuge bottles after the last washing The appropriate tagged solution was added (generally 100 ml), and the resulting suspension was kept agitated using a Burrell wrist-action shaker. The bottles were kept in a water bath at 25 ± 0 1°. At intervals the liquid and the solid phase were separated by centrifugation. Aliquots of 0·500 ml were taken from the solution for activity measurements. At the end of the experiment the crystals were filtered into fine sintered-glass crucibles, and their weight was determined after drying at 110° The chromate concentration in solutions containing silver nitrate was determined by the diphenylcarbazide method The absorbance at 540 mμ was compared with the absorbance of standard solutions of chromate The presence of silver ion did not affect the absorbance.

The counting of the aliquots was done in a scintillation well counter (Baird Atomic, Model 810) connected to a single channel analyser, which counted in the photopeak of the isotope The counting of ^{51}Cr samples was done at approximately the same time for each experiment in order to avoid decay corrections.

Because the surface area was poorly reproduced in duplicate experiments the values of *K* determined from the count rates were divided by the percentage of surface found by exchange *K* is expected to be proportional to the specific surface if the crystals are of identical shape, but of different size *K*/% surface gives a measure of the exchange per unit area of the surface.

RESULTS

Electron micrographs were made of carbon replicas of silver chromate crystals formed from stirred supersaturated solutions at various initial concentrations Typical results are presented for precipitates from 8·75 × $10^{-4}M$ Ag_2CrO_4 (micrograph A, Plate I), and from 5·00 × 10^{-3} *M* Ag_2CrO_4 (micrograph B, Plate I) The pyramid faces formed on crystals at the lower concentration are not visible on crystals from the higher concentration. Agglomeration is evident in the second micrograph.

Aging for three days in $10^{-4}M$ $AgNO_3$ in 50% ethanol gives an indication of surface changes on the large crystals, without causing change in the appearance of the agglomerates of small crystals. Micrograph C, Plate I, shows the effect of aging on crystals from 8·75 × $10^{-4}M$ Ag_2CrO_4, and micrograph D, Plate I, indicates little change of the agglomerates formed from 5·00 × $10^{-3}M$ Ag_2CrO_4.

Table I shows results obtained using precipitates formed under identical conditions. Nevertheless, surface exchange varied from 2·79% to 2·02%, and *K* from 2·14 × 10^{-3} to 1·52 × 10^{-3}/hr. However, *K*/% surface remains fairly constant, indicating little, if any, effect of the three-fold increase of the silver ion concentration in solution on the rate of exchange.

Table II shows the effect of increase of supersaturation in precipitate formation on exchange. The exchange surface and the exchange rate constant are smaller than

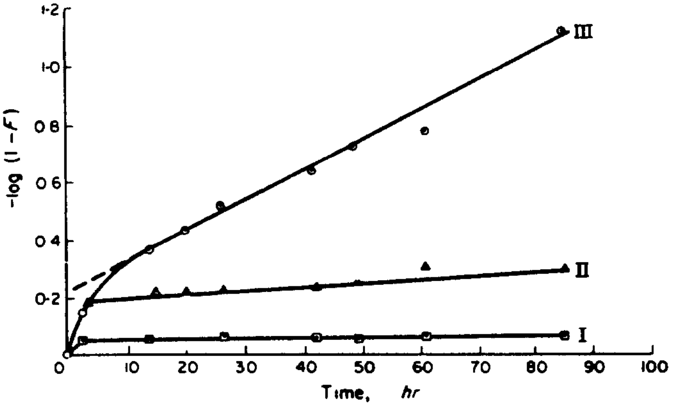


Fig 2.—Comparison of silver and chromate exchange.
I—1·00 × $10^{-4}M$ $K_2{}^{51}CrO_4$
II—8 77 × $10^{-6}M$ $^{51}CrO_4{}^{=}$ in 1·0 × $10^{-4}M$ $AgNO_3$
III—1·00 × $10^{-4}M$ $^{110m}Ag\ NO_3$
(Ag_2CrO_4 from solution 8 75 × $10^{-4}M$ in Ag_2CrO_4 initially.)

Table I.—Exchange between crystals from 8 75 × $10^{-4}M$ Ag_2CrO_4 and tagged Ag^+ in 50% ethanol.

100 ml of 1 0 × $10^{-4}M$ $AgNO_3$ A = 1·34 × 10^{-4} moles			100 ml of 3 0 × $10^{-4}M$ $AgNO_3$ A = 2 13 × 10^{-4} moles		
Time, *hr*	S_t	−log (1 − F)	Time, *hr*	S_t	−log (1 − F)
0	13,470	—	0	13,360	—
2·7	9,230	179	4·2	11,160	0·088
17 3	7,190	309	17·1	10,000	0 145
23 4	6,160	380	40 9	8,240	0 247
41 6	4,640	530	65 4	6,550	0 374
45 5	4,030	605	71 8	6,190	0 418
50·8	3,720	654	95·0	5,260	0 508
59 3	2,920	801	120·7	4,680	0·583
90 4	2,210	·992			

% surface = 2 79.
K = 2 14 × 10^{-3}/hr
K/% surface = 7 7 × 10^{-4}/hr.

% surface = 2 02.
K = 1 52 × 10^{-3}/hr.
K/% surface = 7·5 × 10^{-4}/hr.

Table II —Exchange between crystals from 5 0 × $10^{-3}M$ Ag_2CrO_4 and tagged Ag^+ in 50% ethanol

100 ml of 3 × $10^{-4}M$ $AgNO_3$ A = 35 9 × 10^{-4} moles			100 ml of 6 × $10^{-4}M$ $AgNO_3$ A = 35 3 × 10^{-4} moles		
Time, *hr*	S_t	−log (1 − F)	Time, *hr*	S_t	−log (1 − F)
0	10,890	—	0	12,130	—
3·0	4,250	416	5·0	6,310	289
21·7	3,530	495	21 0	5,080	378
28 0	3,320	526	52 1	4,400	·451
45·6	2,690	621	65 5	3,920	·503
50 5	2,680	623			
66 4	2,400	672			

% surface = 1 25
K = 2,14 × 10^{-4}/hr.
K/% surface = 1 7 × 10^{-4}/hr

% surface = 1 47.
K = 2 53 × 10^{-4}/hr.
K/% surface = 1 7 × 10^{-4}/hr

TABLE III.—COMPARISON OF SILVER AND CHROMATE EXCHANGE

100 ml of $10^{-4}M$ $AgNO_3$ in 50% ethanol tagged with $^{51}CrO_4^{2-}$ $A = 0{\cdot}60 \times 10^{-4}$ moles of Ag_2CrO_4 from 8 75 × $10^{-4}M$ Ag_2CrO_4			100 ml of 1 × $10^{-4}M$ $AgNO_3$ in 50% alcohol tagged with ^{110m}Ag $A = 0\ 73 \times 10^{-4}$ moles of Ag_2CrO_4 from 8·75 × $10^{-4}M$ Ag_2CrO_4		
Time, *hr*	S_t	$-\log(1 - F)$	Time, *hr*	S_t	$-\log(1 - F)$
0	15,920	—	0	6,570	—
2 7	10,440	·190	2 7	4,685	156
14 2	9,600	·222	14 2	3,090	362
20·0	9,560	·225	20 1	2,695	·433
26·2	9,460	·230	26·2	2,320	·511
41·8	9,310	·238	41·8	1,865	·632
49·1	8,880	·257	49·2	1,590	721
61 3	7,900	309	61 3	1,480	·762
85 5	8,130	·298	85 5	905	1·108
	% surface = ·85. $K = 4\ 7 \times 10^{-5}$.			% surface = 3.4. $K = 2{\cdot}7 \times 10^{-3}$.	

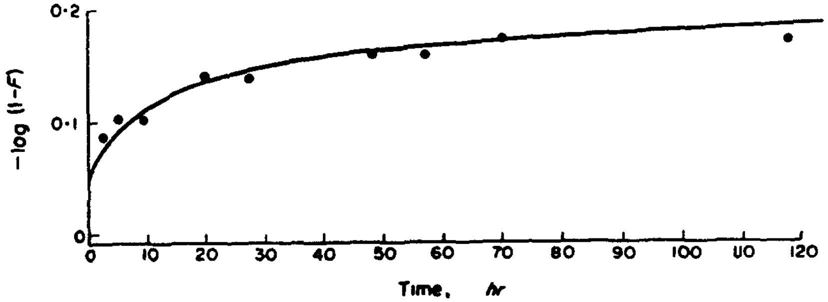


FIG. 3.—Exchange between solid $PbCrO_4$ and 1·00 × $10^{-4}M$ $K_2{}^{51}CrO_4$ in 50% ethanol. $A = 7{\cdot}44 \times 10^{-4}$ moles.

those found under the conditions in Table I. A two-fold increase of the silver ion concentration does not change the value of $K/\%$ surface.

Table III shows the results of exchange between portions of the same batch of precipitate of silver chromate and either $^{51}CrO_4^-$, or ^{110m}Ag ion in 50% ethanol. Surface exchange is only 0·85 mole%, and $K = 4{\cdot}7 \times 10^{-5}$/hr for chromate exchange in a saturated solution of silver chromate in $10^{-4}M$ silver nitrate. The exchange with silver ion gives 3·4 mole% of surface, and $K = 3{\cdot}3 \times 10^{-3}$/hr. Fig. 2 shows the difference in exchange rate, and it includes exchange in 1·00 × $10^{-4}M$ $K_2{}^{51}CrO_4$ (curve I). The unfavourable ratio of B/A prevents determination of K from the slope of curve I.

Our results indicate a ratio of eight readily exchangeable silver ions to one exchangeable chromate at the surface. Preliminary experiments with other precipitates gave a similar ratio.

Chromate exchange between solid lead chromate or barium chromate, and solutions tagged with chromate is illustrated in Figs. 3 and 4. The slopes of the curves change continuously, and therefore the modified exchange law cannot be applied to this exchange.

CONCLUSIONS

The modified exponential exchange law can be applied to exchange between solid silver chromate and solutions containing either tagged silver ion, or tagged chromate. The difference in the rate constant, *K*, between the exchange with silver ion and that with chromate is appreciable. Recrystallisation alone cannot account for the exchange mechanism. Moreover, recrystallisation would change the area of the interface, causing deviation from the exchange law. This process of recrystallisation may account mainly for the results obtained in exchange between $^{51}CrO_4^{2-}$ and solid lead or barium chromate.

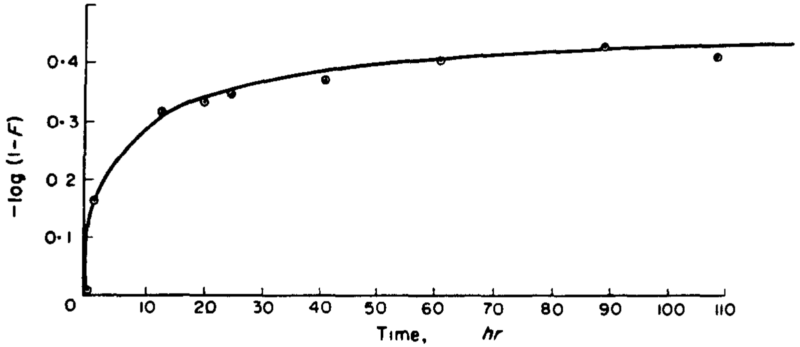


Fig. 4.—Exchange between solid $BaCrO_4$ and 1 00 × $10^{-4}M$ $K_2{}^{51}CrO_4$ in 50% ethanol A = 12 2 × 10^{-4} moles.

The difference between the exchange surface found in chromate and silver ion exchange with silver chromate cannot be explained before more extensive studies are completed. Possible causes include adsorbed silver salt during the preparation of the precipitate, and more surface layers with readily exchangeable silver than layers containing similar chromate ions.

Calculating *K*/% surface, in evaluation of the properties of precipitates, gives interesting results. According to the results in Tables I and II, the exchange rate per unit area is much smaller for the agglomerates of small particles than for the relatively large crystals. Rapid aging during the precipitation, causing agglomeration, could decrease the areas of faces on which exchange mainly takes place, possibly the pyramidal faces shown in electron micrograph A.

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Zusammenfassung—Das exponentielle Austauschgesetz für heterogene systeme kann auf den Isotopenaustausch zwischen festen Salzen und ihren gesättigten Lösungen angewandt werden, wenn man den anfänglichen schnellen Austausch zwischen Lösung und Kristalloberfläche berücksichtigt. Bei verschiedenen Salzen ist es möglich, Aufschluß über das dynamische Gleichgewicht zwischen Oberfläche und Innerem der Kristalle zu erhalten. Experimentelle Ergebnisse an den Chromaten von Silber, Barium und Blei werden angegeben. Silberchromat tauscht mit Silberionen rasch aus, mit Chromat nicht merklich. Bei Barium- und Bleichromat sind deutlich Rekristallisationseffekte zu beobachten.

Résumé—On peut appliquer la loi exponentielle d'échange des systèmes hétérogènes aux échanges isotopiques entre les sels solides et leurs solutions saturées, apres avoir apporte une correction pour l'échange initial rapide entre la solution et la surface du cristal. Pour des sels divers, il est possible d'obtenir des renseignements sur l'équilibre dynamique entre la surface et l'intérieur des cristaux. On présente des données expérimentales pour les chromates d'argent, de baryum et de plomb Le chromate d'argent montre un échange rapide avec l'ion argent, sans échange important avec l'ion chromate Les effets de la recristallisation sont evidents pour les chromates de baryum et de plomb

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REACTION OF IRON^{III} WITH HYDROXYAMINOACIDS

N,*N*-DIHYDROXYETHYLGLYCINEIRON^{III}

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Summary—The stoichiometry and equilibrium for the reaction of iron^{III} with *N*,*N*-dihydroxyethylglycine in aqueous medium has been investigated. Iron^{III} is shown to form only a 1:1 complex with the ligand; previous reports of a 2.3 complex are demonstrated to be erroneous and probably resulted from non-equilibrium titration measurements. Using a modified Bjerrum titration procedure, the equilibrium constant for the formation of the 1:1 complex at 25° has been determined to be $3 \cdot 8 \times 10^{-2}$ moles^2/litre^2. Attempts to differentiate between alternative structures for the complex are inconsequential, because the complex exists only in aqueous medium, where the ligand hydroxyl groups exchange rapidly with solvent water.

Previous studies in our laboratories[1,2] have investigated the use of *N*,*N*-dihydroxyethylglycine (DHEG) as a complexing agent to control the mechanism for hydrolysis of iron^{III} and permit the precipitation from aqueous solution of crystalline iron^{III} oxide as β-FeOOH. Because the role of the tetradentate DHEG ligand appears to be unique in facilitating the precipitation of the crystalline oxide, the stoichiometry and equilibrium for the reaction of DHEG with iron^{III} have been investigated in order to provide further information concerning the reactions involved.

In an aqueous solution of pH 2–4, iron^{III} reacts with DHEG to form the complex (I)

$$\mathrm{Fe^{+3} + HG + 2H_2O \rightarrow \underset{(I)}{Fe(OH)_2G} + 3H^+}. \qquad (1)$$

In this reaction DHEG is assumed to behave as a monoprotic acid HG, which coordinates in four positions about the iron^{III} ion. Formula (I) is identical with that proposed by Toren and Kolthoff[3] from polarographic studies of the reaction of iron^{II} and iron^{III} with DHEG. It conflicts with the earlier work by Martell and co-workers[4,5] who assumed DHEG to react as a triprotic acid H_3A, according to equation (2):

$$\mathrm{Fe^{+3} + H_3A + 2H_2O \rightarrow \underset{(II)}{Fe(H_2O)_2A} + 3H^+}, \qquad (2)$$

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where water fills the two co-ordination positions allotted to the hydroxyl ions in equation (1). Formulae (I) and (II) differ in that Martell *et al.* assumed the two hydroxyl groups in the co-ordinated ligand to be more acidic than water, whereas the conventional interpretation assumes the co-ordinated water to be the more acidic Because the iron^{III} complex is stable only in aqueous solution, where the ligand hydroxyl groups should exchange rapidly with the solvent, differentiation between the two structures would be trivial if Martell *et al.* had not reported the formation, above pH 8, of a second binuclear complex, $Fe_2A_3^{-3}$, which was not observed in the other studies [2,3]

The present work is a reinvestigation of the stoichiometry for the reaction between iron^{III} and DHEG, and the equilibrium constant for equation (1) has been determined The previous evidence[4] for the formation of the $Fe_2A_3^{-3}$ complex is demonstrated to be erroneous, and probably resulted from non-equilibrium titration measurements

EXPERIMENTAL

DHEG was purified by recrystallising twice from ethanol. Standard iron^{III} solutions were prepared by dissolving iron wire in hydrochloric acid and diluting to volume

Oxidation of aliquots of the iron solution was effected by treating with hydrogen peroxide and decomposing the excess hydrogen peroxide by boiling. The stability constant of the iron^{III}-DHEG complex was determined by titration at 25° (*vide infra*). Before titration, the acidity of the iron^{III} solution was reduced to pH 2·0 ± 0·05 by neutralisation with gaseous ammonia to prevent the excess acid from consuming an appreciable portion of the added base. The DHEG complexing agent was then added, and the solution was diluted to volume and titrated with standard sodium hydroxide solution Details have been described elsewhere [5]

NMR spectra were recorded using a Varian A-60 spectrometer.

RESULTS

Acidic solutions containing 0·001M iron^{III} and 0·0011M to 0·02M DHEG were titrated with standard base. The titration curves exhibit two end-point inflections. The first of these occurs when the ratio m, the number of moles of base added per mole of iron^{III} in solution, equals three. This end-point corresponds to the titration of the three equivalents of hydrogen ion liberated according to equation (1) or (2). Using a modified Bjerrum-type procedure, the equilibrium constant, K, for equation (1) may be calculated from the titration results, where

$$K = \frac{[Fe(OH)_2G][H^+]^3}{[Fe^{III}][HG]}. \qquad (3)$$

If n is the number of moles of complex formed per mole of total iron^{III}, for $n = 0·5$,

$$[Fe^{III}] = [Fe(OH)_2G],$$

and

$$K = [H]^{+3}/[HG]. \qquad (4)$$

In acid solution the concentrations of $[OH^-]$ and $(G^-]$ are negligibly small, and HG may be readily calculated as

$$[HG] = \frac{\{(3 - a)C_G - [H^+]\}K_1}{4[H^+] + 3K_1}, \qquad (5)$$

where a is the number of moles of base added per mole of total DHEG, K_1 is the first acid dissociation constant[3,4] of the protonated amino acid, H_2G^+, and C_G is the total concentration of DHEG in solution. Knowing [HG] as a function of the pH during the titration, n is given by

$$n = \frac{C_G - [HG]\{[H^+]/K_1 + 1\}}{C_{Fe}} \tag{6}$$

where C_{Fe} is the concentration of total iron^{III} in solution. Plotting $[H^+]$ and [HG] as a function of n, values corresponding to $n = 0·5$ permit the calculation of K in equation (4). Using this procedure, the pH of the solutions in the vicinity of $n \simeq 0·5$ remains sufficiently acidic (pH < 3·6) to prevent interference from the incipient precipitation of $Fe(OH)_3$.

TABLE I—DETERMINATION OF EQUILIBRIUM CONSTANT FOR $Fe(OH)_2G$.
(Ionic strength = 0·01 T = 25° $C_{Fe} = 1·00\ 10^{-3}M$)

C_G/C_{Fe}	$(pH)_{n=0·5}$	$10^3\ [HG]_{n=0·5}$	$10^8\ K$
1·1	3·55	0·490	4·58
1·1	3·60	0·492	3·21
2·0	3·54	1·26	1·90
2·0	3·55	1·17	1·91
5·0	3·34	3·61	2·64
5·0	3·36	3·74	2·23
10·0	3·10	8·43	5·82
10·0	3·10	6·21	8·21
			avg. = (3·8 ± 1·8)
			$pK = 7·4$

Table I indicates typical values for K calculated from titration results for various ratios of C_G/C_{Fe}. Our value of $pK = 7·4$ is in reasonable agreement with the equally precise value of 6·1 calculated from the polarographic data of Toren and Kolthoff[3] Their K_{III} is related to our K by

$$K = K_{III}K_w{}^2K_2,$$

in which K_w is the autoprotolysis constant for water and K_2 is the second ionisation constant for DHEG.[3,4]

The position of the second end-point inflection in the titration curves depends upon the concentration of excess DHEG in solution. For C_G/C_{Fe} ratios of 2, 5, 10 and 20, the end-point occurs when m equals 5, 8, 13 and 23, respectively. If three moles of base are required to titrate the acid liberated by the formation of the iron^{III}-DHEG complex according to equation (1) or (2), the remainder $(m - 3)$ represents the amount of base required to precipitate $Fe(OH)_3$ from the complex and to neutralise the excess DHEG in solution. These latter reactions may be represented by the general equation:

$$Fe(OH)_2G + (m - 4)HG + (m - 3)OH^- \rightarrow Fe(OH)_3 + (m - 3)G^- + (m - 4)H_2O. \tag{6}$$

As written, this reaction requires all of the iron^{III} in solution to be precipitated upon addition of $(m - 3)$ moles of base.

The amount of $Fe(OH)_3$ precipitated during the titrations was analysed gravimetrically by ignition to Fe_2O_3 and also by dissolving the hydrous oxide in acid and titrating with standard cerium^{IV} solution. Because the aggregation and precipitation of the colloidal iron^{III} hydroxide is very slow under these conditions, if solutions to which *m* moles of base had been added were allowed to settle for 1-3 days, quantitative precipitation of the iron was achieved in every case The ability to precipitate the iron under such conditions has been the basis for the procedure for the quantitative precipitation of crystalline iron^{III} oxide as β-FeOOH.[1]

DISCUSSION

The present studies have confirmed the stoichiometry of reaction (1) [or (2)] in which iron^{III} forms only a 1:1 complex with DHEG in acid medium They contrast sharply with those of Martell *et al.* (*loc. cit.*), who reported an unspecified partial precipitation of iron which led them to suggest a second binuclear complex $Fe_2A_3^{-3}$*. We conclude that the latter complex is not formed, for it is not thermodynamically stable, and iron^{III} is quantitatively precipitated under the experimental conditions

The propriety of formula (I) or (II) in solution cannot be determined. Intuitively, structure (I) is preferred, because the ligand hydroxyl groups should have approximately the same acidity as in ethanol, and should be considerably less acidic than water (K_3 and K_4 for DHEG are too small to be measured in aqueous medium) However, the relative acidities of $HOCH_2CH_2$— and H_2O when co-ordinated by iron^{III} have not been determined On the basis of polarisability and ligand-field strength, it is predicted that H_2O will dissociate to a considerably greater degree than will CH_3CH_2OH when co-ordinated by iron^{III}; and hydrolysed species such as $Fe(OH)^{-2}$ and $Fe(OH)_2^+$ are well known NMR spectra of solutions of DHEG in 99·5% D_2O show, in addition to the HOD singlet, two triplets and one singlet, each of relative area 2, which are characteristic of the three methylene groups in the ligand molecule The absence of a more detailed spectrum, including a triplet of relative area 1 at the proper chemical shift for the ethanolic —OH group, indicates that the ligand hydroxyl groups do exchange rapidly with the solvent water. Because the exchange is rapid, differentiation between structures (I) and (II) is inconsequential.

Zusammenfassung—Stochiometrie und Gleichgewicht der Reaktion von Eisen(III) mit N,N-dihydroxyathylglycin in wassrigem Medium wurden untersucht Es wird gezeigt dass Eisen(III) nur einen 1.1-Komplex bildet; fruhere Angaben uber einen 2 3-Komplex sind falsch und basierten wahrscheinlich auf Messungen ausserhalb des Gleichgewichts Mit einer modifizierten Titrationsmethode nach Bjerrum wurde eine Gleichgewichtskonstante von 3,8 10^{-8} mol^2/l^2 für die Bildung des 1 1-Komplexes bei 25°C erhalten. Strukturangaben für den Komplex sind nocht sinnvoll, da er nur in wassrigem Medium existiert, wo die als Liganden auftretenden Hydroxylgruppen rasch mit dem Lösungsmittel ausgetauscht werden

Résumé—La stoechiométrie et l'équilibre de la reaction du fer(III) avec l'acide N,N' dihydroxyéthyl amino-acétique en milieu aqueux ont été études Il est établi que le fer(III) forme seulement un complexe 1 1 avec le complexant; il est démontré que le complexe 2 3 décrit précédemment n'existe pas et résultait probablement de mesures faites avant que l'équilibre soit réalisé En utilisant une méthode de Bjerrum modifiée, la constante d'équilibre de formation du complexe 1 1 déterminée à 25°C est 3,80 . 10^{-8} $moles^2/l^2$. Les structures du

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* Martell *et al.*[4] do not report if approximately one-third of the total iron was precipitated as required by the stoichiometry of the reaction

complexe sont sans intérêt puisqu'il existe seulement en milieu aqueux où les liaisons entre les groupes hydroxyles s'échangent rapidement avec l'eau du solvant

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POTENTIOMETRIC STUDY OF THE COMPLEXES OF MERCURY^{I} WITH PYROPHOSPHATE, TRIPHOSPHATE AND TETRAPHOSPHATE

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Summary—The dimer of mercury^{I} forms stable complexes with polyphosphates The stabilities of these complexes decrease slightly as the chain length increases Because of the strong tendency of mercury^{I} to associate with hydroxide ions, the mixed complex species containing both polyphosphate and hydroxide ions were found to be the predominant species in slightly alkaline solutions. In polyphosphate solutions, polarographic waves of Hg^{I} and Hg^{II} are obtained at similar potentials, because the Hg^{II} reacts chemically with the mercury of the drop to form Hg^{I} complexes before the electrode reaction occurs Similar anodic waves are obtained in the presence or absence of mercury ions in solution because of the formation of mercury^{I} complexes. The tetraphosphate complexes which have not been studied before, and their over-all complexity constants in the presence of 1*M* KNO_3 and 0 15*M* guanidinium ion at 25°, are:

$Hg_2(P_4O_{13})^{4-}$, $10^{7.32}$, $Hg_2(P_4O_{13})_2^{10-}$, $10^{9\ 88}$,
$Hg_2(P_4O_{13})(OH)^{5-}$, $10^{15\ 26}$, $Hg_2(P_4O_{13})(OH)_2^{6-}$, $10^{22\ 45}$

INTRODUCTION

THE nature and stability of the various species formed by mercury are of considerable importance because of the unique application of mercury in polarography. The reversibility of a large number of mercury electrode reactions, and the possibility of forming either mercury^{I} or mercury^{II} species, enhance the importance of these studies.

Relatively few stable complexes of mercury^{I} have been prepared. In the presence of strong complexing agents, such as ethylenediamine[1] and ethylenediaminotetraacetate,[2] the mercury^{I} disproportionates to form the stable soluble mercury^{II} complex and free mercury as a black colloid. However, Yamane and Davidson[3] have shown that mercury^{I} forms stable complexes with pyrophosphate, triphosphate, oxalate, dimethylmalonate and succinate, and have determined their stability constants by means of potentiometric measurements using the mercury pool electrode. In the present study, a similar behaviour was established in tetraphosphate solutions, and the existence of mercury^{I} complexes in pyro- and triphosphate solutions was confirmed. By maintaining constant conditions, it was possible to establish trends in stability with increasing phosphate chain length.

Preliminary experiments were performed with the dropping mercury electrode, and electrode reversibility was established by the continuity of these waves across the

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* Abstracted from the thesis of R. A. Simonaitis submitted in partial fulfillment of the requirements for the Ph.D. degree, 1962, The Ohio State University.

zero-current axis. However, because of the requirement of very dilute mercury solutions to avoid precipitation in acidic solutions, the quiet mercury pool was used in the final potential measurements.

Previous studies of tetraphosphate and its acidic properties are described in an earlier paper.[4] Details of the theoretical approach to the interpretation of the potential values in the presence of several complexing species by Leden's method have also been described[5-7] The existence of the mixed hydroxide complexes and values for their complexity constants were obtained both by determinants and graphically by slope intercept plots.

Consider the equilibrium between a metal ion and several ligands involving only molecular complexes:

$$\mathrm{M + iA + jB + kC \rightleftarrows MA_iB_jC_k}$$

for which one can write the over-all complexity constant

$$\beta_{ijk} = [\mathrm{MA_iB_jC_k}]/[\mathrm{M}][\mathrm{A}]^i[\mathrm{B}]^j[\mathrm{C}]^k.$$

The corresponding equation and equilibrium constant for the stepwise addition of any one ligand, for example, C, are

$$\mathrm{MA_iB_jC_k + C \rightleftarrows MA_iB_jC_{k+1}}$$

$$K^{ijk}_{ijk+1} = [\mathrm{MA_iB_jC_{k+1}}]/[\mathrm{MA_iB_jC_k}][\mathrm{C}].$$

In this series of studies, A indicates H^+; B, the polyphosphate ion; and C, the hydroxide ion while i, j and k are small integers or zero. Ionic charges are omitted in general expressions. Brackets indicate concentrations, and parentheses indicate activities. For example, the over-all complexity constant for $Hg_2(P_4O_{13})(OH)^{5-}$ is indicated as follows

$$\beta_{011} = [\mathrm{Hg_2(P_4O_{13})(OH)^{5-}}]/[\mathrm{Hg_2}^{2+}][\mathrm{P_4O_{13}}^{6-}](\mathrm{OH})^-.$$

The stepwise constant for the addition of another OH^- ion to this species is

$$\mathrm{K}^{011}_{012} = [\mathrm{Hg_2(P_4O_{13})(OH)_2}^{6-}]/[\mathrm{Hg_2(P_4O_{13})(OH)^{5-}}](\mathrm{OH})^-.$$

As previously discussed, the simultaneous association of H^+ with the complexed polyphosphate and OH^- with the metal ion, if this should occur, cannot be detected, because this is equivalent to the addition of a molecule of water. Only the addition of one in excess causes a potential shift.

Mixed complexes containing hydroxide ions were found to be present throughout most of the pH range in which the mercury$^{\mathrm{I}}$ complexes were stable. As a result, the association of hydrogen ions with the complexed polyphosphate, which played an important role in the copper-polyphosphate systems, was generally not observed.

Leden's first function, F_0, has the general form

$$\mathrm{F_0} = \mathrm{antilog}\,\frac{E_{\mathrm{aq}} - E_{\mathrm{c}}}{S} = \sum_{i=O}^{i=N} \; \sum_{j=O}^{j=N'} \; \sum_{k=O}^{k=N''} \beta_{ijk}[\mathrm{A}]^i[\mathrm{B}]^j[\mathrm{C}]^k.$$

In this equation, E_{aq} is the spontaneous reversible electrode or half-wave potential of a particular concentration of aquo metal ion in a solution containing no complexing agent, while E_c is the corresponding potential of the same total concentration of a metal ion in the presence of a fixed excess concentration of ligands and at the same temperature. In order to maintain a constant ionic strength, both solutions should contain the same concentration of supporting electrolyte in large excess. The symbol

S indicates 2·303 RT/nF of the Nernst equation, and has the value 0·02958 for Hg_2^{2+} at 25°.

EXPERIMENTAL

The experimental procedure and methods for preparing the polyphosphates have already been described.[4,5,6] However, the experiments were all performed in the presence of 1M alkali metal ions In the tetraphosphate experiments, guanidinium ions were also present, because the ligand was purified by crystallisation in the form of the guanidinium salts Because alkali metal ions are known to form complexes with polyphosphates,[8,9] we have adopted the expedient followed by Yamane and Davidson of calculating the free ligand concentration on the basis of the experimentally determined apparent acidity constants after correcting for the concentration of ligand bound in the mercury complex. This is equivalent to ignoring the association of alkali metal ions with the free or complexed ligand, and is justified if the activity of the alkali metal ions and, consequently, the apparent acidity constants, are kept essentially constant. This phenomena is discussed in some detail at the end of the paper on copper triphosphate complexes [6] The last two acidity constants are indicated by the symbols K_N and K_{N-1}. For tetraphosphate, they have the form

$$K_6 = (H^+)[P_4O_{13}^{6-}]/[HP_4O_{13}^{5-}],$$

$$K_5 = (H^+)[HP_4O_{13}^{5-}]/[H_2P_4O_{13}^{4-}].$$

Following the procedure of Pugh,[10] a stock solution of mercury$^{\rm I}$ nitrate was prepared by shaking red mercury$^{\rm II}$ oxide, mercury and nitric acid until, after the addition of sodium chloride to precipitate mercury$^{\rm I}$, a filtered aliquot gave no test for mercury$^{\rm II}$ ion with H_2S. The stock solution was then standardised by titrating with a standard sodium chloride solution using 0·04% bromophenol blue as the indicator. In this paper, the concentration of mercury$^{\rm I}$ will be indicated in terms of the molar concentration of Hg_2^{2+} which is one-half that of the mercury$^{\rm I}$ atoms

Mercury$^{\rm II}$ nitrate was prepared by dissolving metallic mercury with freshly boiled concentrated nitric acid and diluting. The mercury$^{\rm II}$ nitrate solution was standardised against standard thiocyanate using ferric alum as the indicator, according to the method of Kolthoff and Sandell [11]

The most extensive preliminary polarographic experiments were performed in the presence and absence of pyrophosphates Just as was observed by Kolthoff and Miller,[12] the spontaneous potentials of similar concentrations of aquo mercury$^{\rm I}$ and aquo mercury$^{\rm II}$, namely 1 22 mM, were identical, but the diffusion coefficient of the latter was somewhat smaller. In the presence of $5 \times 10^{-2}M$ $Na_4P_2O_7$, 1M $NaNO_3$ and 0 0005% methyl red, the waves coincided even in the diffusion-current region Both waves were continuous across the zero-current axis, which proved that the electrode reaction was reversible The absence of any black colloidal mercury in the mercury$^{\rm I}$ solution indicated that a stable mercury$^{\rm I}$ complex was present Furthermore, a mercurous chloride precipitate was obtained upon the addition of excess chloride ion. A similar test of the mercury$^{\rm II}$ pyrophosphate solutions was negative After removing oxygen of the air by flushing with nitrogen, both solutions were shaken in the presence of an excess of free mercury The quantitative conversion of the mercury$^{\rm II}$ pyrophosphate complex to mercury$^{\rm I}$ complex, upon contact with free mercury, was shown by the previously described titration with standard NaCl

These experiments confirm the observation of Yamane and Davidson that both mercury$^{\rm I}$ and mercury$^{\rm II}$ form stable complexes However just as Kolthoff and Miller[12] observed for the aquo system, the mercury$^{\rm II}$ complex is chemically reduced to the mercury$^{\rm I}$ complex upon diffusing to the drop surface, so that, in both cases, it is the mercury$^{\rm I}$ complex which determines the electrode potential The diffusion currents for similar concentrations of the Hg^{2+} and Hg_2^{2+} coincide, so that their diffusion coefficients are similar. This probably results from the relatively large contribution of the complexed polyphosphate to the size of ions

The remainder of the study was made with mercury$^{\rm I}$ solutions. When the solution was made more acidic, the waves decreased in height and a precipitate was observed By reducing the concentration of mercury to the order of $10^{-5}M$, this complication was eliminated. The accuracy of measuring the spontaneous potential of the dropping electrode was greatly decreased because of the relatively large magnitude of the residual current, so that it was found expedient to replace the dropping mercury electrode with a quiet mercury pool Typical potential values for the mercury$^{\rm I}$ pyro-, tri- and tetraphosphate systems are given in Tables I, II and III, respectively. The absence of mercury$^{\rm II}$ in these solutions was established by the previously discussed qualitative tests.

The acidic limit was indicated by the failure of the electrode to undergo further change in potential. The alkaline limit, which was manifested by unsteady potentials, was ascribed by Yamane and Davidson to the formation of solid HgO The pH was varied without altering the total mercury$^{\rm I}$ and ligand concentrations, by mixing various portions of a solution which was acid-free with a similar solution which contained nitric acid. The experiments were performed as rapidly as possible after acidifying the solution, to minimise hydrolysis of the polyphosphates to lower phosphates. Fresh solutions were prepared after a few measurements. The extent of hydrolysis was readily shown by the phosphomolybdate test for orthophosphates.

TABLE I.—POTENTIAL VALUES FOR PYROPHOSPHATE-MERCURY[1] SYSTEM

Part A: $[Hg_2^{2+}]_t = 1{\cdot}22 \times 10^{-5}M$,
$[P_2O_7^{4-}]_t = 0{\cdot}05M$;
$[Na^+]_t = 1{\cdot}0M$;
$E_{aq} = 0{\cdot}3852$ v *vs* S.C.E.

Part B: like A, but $1M$ Na^+ replaced by $1M$ K^+, $E_{aq} = 0{\cdot}3753$ v.

pH	$E_{aq} - E_c$	$-\log[P_2O_7^{4-}]$	log F_1	log F_2	log F_{2a}	log F_{3a}
Part A						
9·62	0·3086	1·30	11·71	13·01	16·07	20·40
9·53	0·3035	1·30	11·55	12·85	15·99	20·40
9·16	0·2860	1·31	10·97	12·28	15·67	20·38
9·04	0·2822	1·31	10·84	12·15	15·60	20·40
8·58	0·2722	1·33	10·53	11·85	15·31	20·34
8·02	0·2640	1·41	10·33	11·72		
7·50	0·2539	1·59	10·17	11·74		
6·96	0·2332	1·94	9·82	11·71		
6·53	0·2125	2·32	9·48	11·67		
5·93	0·1819	2·97	9·12	11·67		
5·29	0·1482	3·85	8·86			
5·03	0·1349	4·27	8·83			
4·56	0·1098	5·12	8·83			
Av. limiting constant			8·83	11·72	15·07	20·40
Part B						
10·00	0·3223	1·41	12·20	13·71	16·28	20·08
9·59	0·3043	1·42	11·70	13·12	16·04	20·00
8·95	0·2863	1·45	11·12	12·56	15·85	
8·60	0·2802	1·49	10·96	12·44	15·87	
8·00	0·2652	1·66	10·72	12·26		
7·63	0·2539	1·86	10·49	12·27		
7·04	0·2276	2·33	10·02	12·27		
6·64	0·2075	2·72	9·73	12·27		
6·25	0·1891	3·16	9·55			
5·91	0·1721	3·59	9·40			
5·43	0·1481	4·30	9·30			
4·99	0·1288	5·06	9·41			
4·63	0·1132	5·74	9·56			
Av. limiting constant			9·25	12·27	15·85	20·05

RESULTS AND DISCUSSION

Using the symbol Pp to indicate the polyphosphate ion and omitting the complex ion charge for simplicity, the predominant species necessary to account for the potential shift as a function of pH and polyphosphate concentration were Hg_2Pp, Hg_2Pp_2, HgPpOH and $HgPp(OH)_2$. The corresponding Leden function F_0 is:

$$F_0 = \text{antilog}\,(E_{aq} - E_c)/S = 1 + \beta_{010}[Pp] + \beta_{020}[Pp]^2 + \beta_{011}[Pp](OH^-) + \beta_{012}[Pp](OH^-)^2$$

Subtracting unity, and dividing through by [Pp], yields the Leden function, F_1, thus

$$F_1 = (F_0 - 1)/[Pp] = \beta_{010} + \beta_{020}[Pp] + \beta_{011}(OH^-) + \beta_{012}(OH^-)^2.$$

The limiting constant value of F_1 at low values of [Pp] and (OH^-) or the F_1 intercept of a graph of F_1 versus [Pp] at low or constant values of (OH^-) is equal to β_{010}. In the

TABLE II.—POTENTIAL VALUES FOR TRIPHOSPHATE-MERCURY^{I} SYSTEM

Part A: $[Hg_2^{2+}]_t = 1·22 \times 10^{-5}M$;
$[P_3O_{10}^{5-}]_t = 0·05M$,
$[Na^+]_t = 1·0M$,
$E_{aq} = 0·3852$ v *vs.* S.C.E.

Part B: like A but 1*M* Na^+ replaced by 1*M* K^+, $E_{aq} = 0·3753$ v.

pH	$E_{aq} - E_c$	$-\log[P_3O_{10}^{5-}]$	log F_1	log F_2	log F_{2a}	log F_{3a}
Part A						
9·34	0·2791	1·31	10·74	12·05	15·40	20·05
9·03	0·2617	1·31	15·15	11·46	15·12	20·07
8·53	0·2330	1·32	9·19	10·51	14·65	20·07
8·07	0·2092	1·34	8·41	9·72	14·24	20·05
7·60	0·1927	1·40	7·91	9·22	13·95	20·04
7·32	0·1859	1·47	7·75	9·09	13·85	
6·73	0·1696	1·76	7·49	8·97	13·68	
6·38	0·1578	2·02	7·35	8·90		
6·03	0·1460	2·34	7·27	8·90		
5·73	0·1359	2·64	7·23	8·82		
5·53	0·1292	2·86	7·23			
5·28	0·1207	3·16	7·24			
Av. limiting constant			7·64	8·90	13·65	20·05
Part B						
9·99	0·3157	1·46	12·13	13·59	16·25	20·37
9·40	0·2877	1·46	11·18	12·64	15·78	20·37
9·01	0·2639	1·47	10·39	11·86	15·38	20·34
8·66	0·2440	1·48	9·72	11·28	15·08	20·31
8·35	0·2261	1·50	9·14	10·62	14·74	
8·09	0·2156	1·53	8·81	10·29	14·60	
7·69	0·2019	1·62	8·44	9·93	14·44	
7·28	0·1895	1·79	8·19	9·72	14·30	
7·04	0·1821	1·94	8·09	9·67	14·26	
6·60	0·1682	2·28	7·96	9·62	14·21	
Av. limiting constant			8·02	9·65	14·22	20·35

sodium pyrophosphate study, as shown in Table IA and summarised in the last line of Table IA, the limiting constant value of F_1 in the pH range 4·56–5·29 was $10^{8·83}$, corresponding to the complexity constant for the association of one pyrophosphate with Hg_2^{2+}. Thus:

$$Hg_2^{2+} + P_2O_7^{4-} \rightleftharpoons Hg_2(P_2O_7)^{2-},$$
$$\beta_{010} = [Hg_2(P_2O_7)^{2-}]/[Hg_2^{2+}][P_2O_7^{4-}] = 10^{8·83}.$$

In the presence of 1*M* potassium ions, a constant value was not obtained until the additional species $Hg(HP_2O_7^-)$ was assumed to be present. Solving simultaneous equations, assuming these two species to be present, yielded

$$\beta_{1\overset{*}{1}0} = [Hg_2HP_2O_7^-]/[Hg^{2+}][HP_2O_7^{3-}] = 10^{5·94}.$$

Because of the uncertainty of the values available for the more acidic solutions, these constants for species containing associated hydrogen ion cannot be regarded as reliable, so will not be reported,

The next Leden function obtained by subtracting β_{010} from F_1 and dividing by $[P_2O^4{}_7^-]$ was used to calculate β_{020}, thus:

$$F_2 = (F_1 - \beta_{010})/[P_2O_7^{4-}] = \beta_{020} + \beta_{011}(OH^-)/[P_2O_7^{4-}] + \beta_{012}(OH^-)^2/[P_2O_7^{4-}].$$

TABLE III —POTENTIAL VALUES FOR TETRAPHOSPHATE-MERCURY[1] SYSTEM

Part A: $[Hg_2^{2+}]_t = 1·22 \times 10^{-5}M$;
$[P_4O_{13}^{6-}]_t = 0·02491M$,
$[Na^+]_t = 1·0M$,
$E_{aq} = 0·3852$ v *vs.* S.C E

Part B: like A but 1*M* Na⁺ replaced by 1*M* K⁺, $E_{aq} = 0·3753$ v.

pH	$E_{aq} - E_c$	$-\log [P_4O_{13}^{6-}]$	$\log F_1$	$\log F_2$	$\log F_{2a}$	$\log F_{3a}$
Part A						
8·31	0·2863	1·62	11·29	12·91	16·98	22·63
8·14	0·2768	1·62	10·97	12·59	16·83	22·63
8·03	0·2706	1·63	10·77	12·40	16·74	22·64
7·63	0·2483	1·68	10·07	11·75	16·44	22·65
7·33	0·2315	1·74	9·56	11·30	16·22	22·60
7·22	0·2254	1·78	9·40	11·18	16·17	22·61
7·03	0·2170	1·85	9·18	11·03	16·14	22·72
6·71	0·1991	2·03	8·76	10·78	16·02	22·67
6·50	0·1874	2·18	8·51	10·68	15·97	22·65
6·37	0·1801	2·29	8·37	10·64	15·96	22·58
6·34	0·1779	2·31	8·32	10·61	15·93	
6·22	0·1723	2·42	8·24	10·64	15·97	
5·98	0·1578	2·66	7·99	10·61	15·94	
Part B						
8·61	0·2980	1·61	11·68	13·29	17·07	22·45
8·45	0·2885	1·61	11·36	12·97	16·91	22·45
8·35	0·2824	1·62	11·16	12·78	16·81	22·45
8·00	0·2612	1·63	10·45	12·08	16·45	22·42
7·64	0·2409	1·68	9·82	11·50	16·17	22·47
7·35	0·2245	1·74	9·32	11·06	15·94	22·48
7·00	0·2051	1·87	8·80	10·66	15·71	22·51
6·85	0·1983	1·94	8·64	10·56	15·67	22·60
6·68	0·1877	2·05	8·39	10·40	15·52	22·48
6·52	0·1790	2·16	8·21	10·31	15·43	22·41
6·30	0·1678	2·34	8·01	10·23	15·37	22·41
6·15	0·1600	2·48	7·89	10·23	15·35	22·46

From Table I, it is evident that, in the sodium pyrophosphate solution, F_2 has the constant value of $10^{11·72}$ from a pH of 8·32 to 5·73.

Thus

$$\beta_{020} = [Hg_2(P_2O_7)_2^{6-}]/[Hg_2^{2+}][P_2O_7^{4-}]^2 = 10^{11·72}.$$

Conclusive graphic evidence for the mixed hydroxide species was obtained by a graphic solution of the following Leden function:

$$F_{2a} = (F_2 - \beta_{020})[P_2O_7^{4-}]/(OH^-) = \beta_{011} + \beta_{012}(OH^-).$$

The limiting constant value of F_{2a} or the F_{2a} intercept of a graph in which F_{2a} is plotted versus (OH^-) is equal to β_{011} while the slope is equal to β_{012}. The following Leden functions constant value can be used to confirm β_{012}·

$$F_{3a} = (F_{2a} - \beta_{011})/(OH^-) = \beta_{012}$$

In all of the systems, pyro-, tri- and tetraphosphate, a region was found in which the plot of F_{2a} versus (OH^-) was linear and its intercept value agreed well with the constant value obtained for F_{3a} The F_{2a} graph was linear above a hydroxide concentration of $5 \times 10^{-6}M$ in pyrophosphate solutions. It was linear above a hydroxide concentration of $4 \times 10^{-5}M$ in the triphosphate solutions and it was linear above a hydroxide concentration of $2 \times 10^{-7}M$ in tetraphosphate solutions. These results constitute conclusive evidence for the existence of the mixed complexes of the type $Hg_2(Pp)(OH)$ and $Hg_2Pp(OH)_2$. For the pyrophosphate system in $1M$ $NaNO_3$:

$$\beta_{011} = [Hg_2(P_2O_7)(OH)^{3-}]/[Hg_2^{2+}][P_2O_7^{4-}](OH^-) = 10^{15\,07}$$

$$\beta_{012} = [Hg_2(P_2O_7)(OH)_2^{4-}]/[Hg_2^{2+}][P_2O_7^{4-}](OH^-)^2 = 10^{20\cdot40}.$$

TABLE IV —SUMMARY OF COMPLEXITY CONSTANTS FOR MERCURY^{I} POLYPHOSPHATE SYSTEM

Medium	pK_N	pK_{N-1}	β_{010}	β_{020}	β_{011}	β_{012}	K^{000}_{010}	K^{010}_{020}	K^{010}_{011}	K^{011}_{011}	K^{020}_{011}
					A-Pyrophosphate						
$1M$ K^+	7·89	5·66	9·25	12·27	15·85	20 05	9 25	3 02	5 20	4 20	3 58
$1M$ Na^+	7·48	5·40	8 83	11 72	15·07	20 40	8 83	2 89	5 33	4 34	3 35
$0\ 75M$ Na^+	8·00*	5·68*		12 38*	15 64*						3 26*
					B-Triphosphate						
$1M$ K^+	7·36	4·96	7·84	9 47	14 22	20 35	7 84	1 63	6 38	6 13	4 75
$1M$ Na^+	7 00	4 85	7·16	8 90	13 65	20 05	7 16	1 74	6 49	6 40	4 75
$0\ 75M$ Na^+	7·58*	5·29*		11 23*	15·00*						3 77*
					C-Tetraphosphate						
$1M$ K^+	6·92	5 22	7 32	9 88	15 26	22 45	7 32	2 56	7 94	7·19	5 38
$1M$ Na^+	6·52	4·97	6 98	9 42	15 91	22 64	6 98	2 44	8 93	6 73	6·49

* Results by Yamane and Davidson

A summary of the values obtained for all of the constants, both in the form of over-all constants and stepwise constants, is given in Table IV. These are the mean of all of the values obtained both by determinants considering all species and by slope intercept methods. The corresponding values obtained by Yamane and Davidson are also included. Our results confirm their important discovery of mercury^{I} polyphosphate complexes. The present study indicates the existence of additional species such as Hg(Pp) and the mixed hydroxide complex $HgPp(OH)_2$. Bringing this difference and the difference in experimental conditions into consideration, the quantitative agreement of the two studies is satisfactory. The difference in the values of our constants results in part from the difference in our experimentally determined acidity constants, pK_N and pK_{N-1}, shown in Table IV. Their experimental conditions of 27·4° and $0{\cdot}75M$ Na^+ are fairly similar to the 25° and $1{\cdot}0M$ Na^+ used in one phase of our study. In addition, the present study includes the Hg_2^{2+} tetraphosphate system.

Several interesting generalisations can be made. Just as was the case in the copper polyphosphate systems but not in the alkali polyphosphate systems, the stepwise constant for the addition of the first polyphosphate, as manifested by the value of K^{000}_{010}, decreases with increasing polyphosphate chain length, but the difference decreases from tri- to tetraphosphate. Of particular significance is the strong tendency of the polyphosphate complex to associate with additional hydroxide ions, as manifested by the magnitudes of K^{010}_{011} and K^{011}_{012}. As might be expected from the above observation, these constants increase in magnitude with increasing polyphosphate chain length. This observation is consistent with the observation by Bennett,[13] as well as Sillén and his coworkers,[14,15] who obtained values of the order of 10^9–10^{10} for the association of one hydroxide with the aquo Hg_2^{2+} ion. These can be compared to our values of $10^{7.94}$ and $10^{8.93}$ for the addition of one hydroxide to $Hg_2P_4O_{13}^{4-}$ in the presence of 1*M* KNO_3 and 1*M* $NaNO_3$, respectively.

Zusammenfassung—Das Dimere von Quecksilber(I) bildet stabile Komplexe mit Polyphosphaten Die Stabilität dieser Komplexe nimmt mit steigender Kettenlange schwach ab. Wegen der starken Tendenz von Quecksilber(I) zur Assoziation mit Hydroxylionen wurden in schwach alkalischen Losungen vorwiegend gemischte Komplexe mit Polyphosphat-und Hydroxylionen gefunden. In Polyphosphatlosungen findet man die polarographischen Wellen von Hg(I) und Hg(II) beim gleichen Potential, da Hg(II) mit dem Quecksilber des Tropfens vor der Elektrodenreaktion chemisch zu Hg(I)-Komplexen reagiert Ähnliche anodische Wellen findet man mit oder ohne Quecksilberionen in der Losung wegen der Bildung von Quecksilber(I)-Komplexen. Es wurden folgende bisher nicht untersuchte Tetraphosphatkomplexe mit ihren Gesamt-Komplexbildungskonstanten in Gegenwart von 1m KNO_3 und 0,15m Guanidiniumion bei 25°C gefunden· $Hg_2(P_4O_{13})^{4-}$ $10^{7,32}$, $Hg_2(P_4O_{13})_2^{10-}$: $10^{9,88}$; $Hg_2(P_4O_{13})(OH)^{5-}$ $10^{15,26}$, $Hg_2(P_4O_{13})(OH)_2^{6-}$ $10^{22,45}$

Résumé—Le dimère du mercure(I) forme des complexes stables avec les polyphosphates La stabilité de ces complexes décroît légèrement lorsque croît la longueur de la chaîne. Par suite de la forte tendance du mercure(I) à s'associer aux ions hydroxyle, on a trouvé que les types de complexes mixtes, contenant à la fois les ions polyphosphate et hydroxyle, sont ceux qui prédominent dans les solutions légèrement alcalines En solutions polyphosphoriques, les vagues polarographiques de Hg(I) et Hg(II) s'obtiennent à des potentiels similaires, parce que Hg(II) reagit chimiquement avec le mercure de la goutte en formant des complexes de Hg(I) avant que ne se produise la réaction à l'électrode On obtient des vagues anodiques semblables en présence ou en l'absence d'ions mercure dans la solution, par suite de la formation de complexes de mercure(I) Pour les complexes tétraphosphoriques qui n'ont pas été étudiés auparavant, les constantes globales de complexité en présence de KNO_3 1 M et d'ion guanidinium 0,15 M à 25° sont $Hg_2(P_4O_{13})^{4-}$, $10^{7,32}$; $Hg_2(P_4O_{13})_2^{10-}$, $10^{9,88}$; $Hg_2(P_4O_{13})(OH)^{5-}$, $10^{15,26}$, $Hg_2(P_4O_{13})(OH)_2^{6-}$, $10^{22,45}$.

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ANALYTICAL APPLICATIONS OF RADIOACTIVE VITAMIN B_{12}

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Summary—Radioactive vitamin B_{12} has been employed as an analytical tool, a biochemical tracer and as a diagnostic agent. Of the several labelled modifications reported, only those labelled with cobalt isotopes are useful at physiological dose levels. Because of the high specific activities of (1–200) $\mu c/\mu g$, detection sensitivities in the picagram region are realised with cobalt-labelled vitamin B_{12} Clinical applications including diagnostic tests for pernicious anaemia in humans, are in a sense analytical procedures, involving as they do measurements of vitamin B_{12} transport. Of more direct analytical character is the application of the isotope dilution method to pharmaceutical preparations, feed concentrates, sewage and fermentation products and crystalline cobalamins The stability of hydroxocobalamin in pH 4 2 stabilised aqueous solution has been demonstrated by this method The reverse isotope dilution method also has been very helpful in facilitating stability and degradation studies. The quantitative recovery of unchanged cyanocobalamin from cereals and from capsules containing biological concentrates has been demonstrated by this method. By contrast, the conversion of cyanocobalamin to hydroxocobalamin has been found to occur in the liver of dogs receiving labelled vitamin An extensive study of protective agents to stabilise vitamin B_{12} in solutions containing ascorbic acid has been performed by this reverse dilution procedure The sensitivity of the isotope dilution method has been greatly extended to physiological levels by the application of "saturation analysis," an extension of the binding power measurement applied to intrinsic factor concentrates and to animal tissues including serum or plasma

RADIOACTIVE vitamin B_{12}, in its several forms, has found wide use[1,2] as an analytical tool, as a diagnostic agent and as a biochemical tracer. Even the biological uses have been essentially analytical in nature, because they have involved quantitative determinations of the extent of vitamin adsorption by serum proteins or tissue, absorption or excretion by animals, including man, or stability and degree of conversion to related degradation products.

Vitamin B_{12} is one of a family[3,4] of related, highly coloured, corrinoid compounds called cobalamins or, by a more recent convention, cobamides. The cobalamins are corrin complexes of tervalent cobalt, *i.e.*, porphyrin-like with one bridge carbon atom missing. The best known of the cobalamins is the cyanide complex, cyanocobalamin, the structure of which is shown in Fig. 1, and which is customarily referred to as vitamin B_{12}. It is a neutral, undissociated, relatively stable molecule which can be converted to non-cyano cobalamins photochemically or by catalytic reduction. The major non-cyano analogue, hydroxocobalamin, is a weak base which is converted in the presence of acids into a positive aquocobalamin ion and the respective anion. All non-cyano forms are converted to cyanocobalamin by the addition of cyanide.

LABELLING

Vitamin B_{12} is produced microbiologically by a number of micro organisms incubated in appropriate nutrient media containing sufficient inorganic cobalt for maximal growth. This requires[5] about 2 ppm of cobalt. To produce radioactive cyanocobalamin, the fermentation is usually carried out in the presence of suitable radioactive precursors and, after a rather complicated isolation procedure, the pure crystalline radioactive vitamin is isolated. Radioisotopes which have been successfully incorporated in the cobalamin molecule in this manner are phosphorus-32, carbon-14 and the four long-lived cobalt isotopes. Carbon-14 is also readily introduced[6] as $C^{14}N$ to yield usable specific activities. This modification is, unfortunately, limited by the ease of exchange[7] of the cyanide group, which is in striking contrast to the exchange stability of the central cobalt atom.[8] Cyanocobalamin containing radioactive hydrogen has been prepared by prolonged contact with several curies of tritium gas. Cyanocobalamin containing radioactive cobalt is produced by fermentation in a nutrient medium containing a low concentration of $\lessdot$ 0·1 ppm of radioactive cobalt[9] to maintain a high specific activity of final product. Only radioactive cobalt yields labelled vitamin adequate for studies at physiological levels.

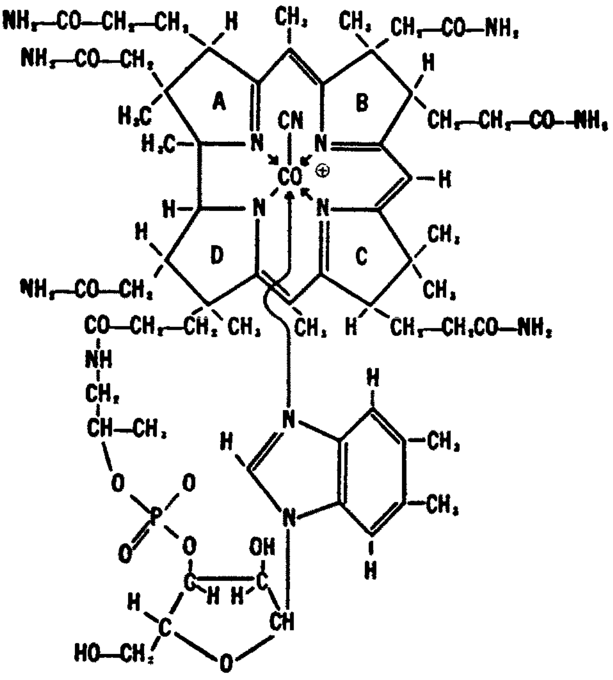

FIG. 1.—Structural formula of vitamin B_{12}.

Cobalt radioisotopes are by far the most useful nuclides with which to label cyanocobalamin. Their radiation properties are tabulated in Table I which lists the type (*i.e.*, beta ray, positron, gamma ray or K-capture X-ray), energy in MeV and frequency of emission of each radiation. Here, 100% signifies that a given ray or particle is emitted with each radioactive disintegration. Relative detection sensitivities will depend on the type of detection devices employed. Detectors, such as

TABLE I—EMISSION BY RADIOACTIVE COBALT ISOTOPES[a]

Cobalt isotope	Half-life	β^- or β^+		γ or K − X	
		MeV	%	*MeV*	%
^{60}Co	5.27y	0.31	100	1.17	100
				1.33	100
^{58}Co	71d	0.47	14.5	0.81	99.5
				0.0064	85.5
				0.51	29.0
^{57}Co	270d	—	—	0.0064	100
				0.123	93
				0.014	93
				0.137	7
^{56}Co	77d	1.50	18.1	0.845	100
				0.0064	81.9
				1.24	70.5
				0.51	36.2
				1.75	17.8
				2.60	15.9
				1.03	15.7
				3.25	12.3
				2.02	11.0

[a] Minor components omitted

Geiger-Muller and proportional counters, ionisation chambers and liquid scintillation devices, which measure particulate radiation efficiently are excellent for cobalt-56, -58 and -60 but least effective for cobalt-57. This order is reversed when gamma radiation is measured in solid scintillation counters. Thus, cobalt-57 is measured with greatest efficiency in a sodium iodide crystal and cobalt-58 least efficiently. In general, gamma scintillation counting is the most convenient means of determining these radioisotopes.

The characteristics of cyanocobalamin labelled with cobalt isotopes are tabulated in Table II, which shows first the cobalt content of the carrier-free (*i.e.*, 100% isotope) modifications of the vitamin, including the normal, non-radioactive form cobalt-59. This is followed by the maximum specific activities of such carrier-free forms of radioisotopic cobalt (mc/μg) and of the carrier-free labelled cyanocobalamin (in μc/μg) derived therefrom. The next two columns list the specific activities reported or readily available, and the ratios of radioactive cobalt atoms to total cobalt atoms in these preparations. Actually, cyanocobalamin-^{58}Co with specific activities up to 200 μc/μg may be obtained.[10] The last column lists estimated detection sensitivities (in picagrams) computed for a well-type scintillation counter, assuming a detection limit of ±3 cpm. Quantities of the order of picagrams of vitamin can be detected with the radioactive modifications listed, an order of magnitude not readily achieved by other analytical methods.

Vitamin B_{12}-^{57}Co would seem to be the isotopic modification of choice for biological and chemical purposes because of its many desirable properties which may be enumerated as follows:

1. Conveniently long half-life, with attendant flexibility in scheduling the biosynthesis of the radioactive vitamin, and greater shelf-life of the finished product.

2. Less intense gamma radiation, hence greater safety in handling, manufacture and storage of the vitamin.
3. Absence of particulate radiation, with resultant lower radiation exposure of tissue and greater safety for use of the labelled vitamin in humans and animals.
4. Lower self-irradiation exposures, therefore, greater stability of the radioactive vitamin.
5. High detection sensitivity in sodium iodide gamma scintillation phosphors.

TABLE II CHARACTERISTICS OF CYANOCOBALAMIN CONTAINING RADIOACTIVE COBALT ISOTOPES

	Cobalt in B_{12}, %	Specific activity carrier-free		Available specific activity B_{12}, μc/μg	Radioactive Co / Total Co	Detection sensitivity, pg
		Co, mc/μg	B_{12}, μc/μg			
^{60}Co	4.42	1.14	50	≃1.1	$\frac{1}{47}$	3.6
^{59}Co[a]	4.35	—	—	—	—	—
^{58}Co	4.27	32	1360	≃5	$\frac{1}{270}$	0.9
^{57}Co	4.20	8.5	357	10–30	$\frac{1}{12\text{–}35}$	0.07–0.2
^{56}Co	4.13	30	1250	≃5	$\frac{1}{240}$	0.45

[a] Stable cobalt.

For *in vitro* work, as is involved in conventional analytical procedures, cyanocobalamin-^{60}Co is perfectly satisfactory, even preferable, provided subdivision and concentration are such as to assure radiation stability. It has been shown that cyanocobalamin-^{60}Co with a specific activity of ≃1 μc/μg will deteriorate at a rate of ≃2% year because of self-irradiation when stored in the cold in concentrations of ≃1 μg/ml.[11,12] Even greater self-irradiation stability is exhibited by vitamin labelled with cobalt-57 and cobalt-58.[12]

CLINICAL APPLICATION

The earliest application of cobalt-labelled vitamin B_{12} led, fittingly, to simple and direct methods of diagnosis of pernicious anaemia, a disease for which vitamin B_{12} is a specific and life-saving treatment. Pernicious anaemia results essentially from the failure of the human stomach to secrete a substance called intrinsic factor. This factor is necessary for the oral absorption of vitamin B_{12}, which is of microbial origin and which is present in ingested food. Haematological diagnosis is a difficult and time-consuming procedure, depending as it does upon observations of the effect of doses of vitamin B_{12} on the blood picture and on changes therein. Radioactive vitamin B_{12}, however, permits a direct measurement of cyanocobalamin absorption[2] from observation of the (1) extent of faecal excretion, (2) extent of urinary excretion, (3) measurements of blood radioactivity, (4) external body scintillation counting over the liver area, and (5) by whole body counting. By these methods, the degree of oral absorption of vitamin B_{12}, and the effect of potent intrinsic factor preparations on oral absorption, are readily ascertained, and a judgement made as to whether absorption is normal or defective. By similar procedures the potency of intrinsic factor preparations employed for the treatment of pernicious anaemia can be evaluated, and the relative absorbability and retention of the several vitamin B_{12} analogues by animals and by man compared. These applications are based on measurements of the extent of vitamin transport from the gastro-intestinal tract, across the intestinal wall, into the blood stream and other tissue. The radioactive properties of the labelled vitamin make it possible to distinguish ingested vitamin in a medium which contains comparatively larger amounts of endogenous vitamin B_{12}.

Innumerable animal studies have revealed the pattern of distribution and excretion of vitamin B_{12} in animals and demonstrated the target organs and storage sites of the vitamin. A major storage site for the vitamin ingested by animals is the liver. The chief site of absorption from the gut appears to be the ileum, and the operation of an enterohepatic mechanism has been discovered. Turnover studies reveal the existence of several compartments or excretion forms of the vitamin.

ISOTOPE DILUTION ASSAYS

Radioactive vitamin B_{12} has been employed as an isotope dilution indicator to police the plant production of cyanocobalamin.[13] Assays[14,15,16] have been performed similarly of fermentation broths, sludge products, pharmaceutical preparations, oral grade solids and tissues, and crystalline vitamin B_{12}. In fact, the isotope dilution or "Radioisotope Tracer" method has been included in the U.S. Pharmacopoeia XV and the National Formulary XI as a standard cobalamin assay.[17]

The principle of the method and the conditions which must be satisfied for the proper application have been discussed elsewhere.[11] To a sample containing X μg of cyanocobalamin, one adds an amount Y μg of radioactive cyanocobalamin with a specific activity $S_0 = \dfrac{\text{A cpm}}{\text{Y}\ \mu\text{g}}$. Here, A cpm is the radioactivity of the tracer added in counts per minute on a suitable detection device. After treatment to ensure mixing of labelled and unlabelled vitamin, and isolation of a portion of the pure, or uniquely determined vitamin, one measures the radioactivity (B cpm) and quantity (Z μg) of a portion of the isolate. The specific activity of the isolate is obviously $S_f = \dfrac{B}{Z}$. The expressions by which X can be computed are

$$X = Y\left[\frac{S_0}{S_f} - 1\right] = Y\frac{S_0}{S_f} - Y = Z\frac{A}{B} - Y. \tag{1}$$

The ratio $\dfrac{A}{B}$ is the factor which corrects the quantity Z for inefficiency of isolation, and the term Y is subtracted from the total cyanocobalamin to correct for the quantity of radioactive indicator added initially. Specific activities of labelled vitamin are usually so high that the amount Y required for accurate radioactivity measurements is negligible compared to X. The above equations reduce accordingly to

$$X = Y\frac{S_0}{S_f} = Z\frac{A}{B}. \tag{2}$$

In the case of vitamin B_{12}, homogenisation of tracer with complex media, such as tissue, in which the vitamin may be retained within cellular matter and bound by biological components as proteins, is assured by treatment with acid nitrite, enzymes, and/or heat. Isolation is rather complicated, involving a variety of separation and purification procedures. A typical sequence of these steps applicable to the determination of total cobalamins in dog liver is enumerated below. Many modifications are permissible depending on the complexity of the matrix and the initial cobalamin content.

Isolation procedure for liver total cobalamins

1. Homogenise 200 g of tissue with $\simeq$350 ml of water, add radioactive vitamin B_{12} and mix[*], add $NaNO_2$ ($\simeq$5 mg/ml) and KCN ($\simeq$2 mg/ml)[†].
2. Adjust to pH 4 with glacial acetic acid; boil 1 hr with stirring (caution: in hood).
3. Zinc defaecation. Cool and add 40 g of $ZnSO_4$ and sufficient 20% NaOH to yield a pH of 7·8–8·0. Filter.
4. Extract with 10 ml of cresol CCl_4 (1·1), wash twice with 10 ml of H_2O
5. Dilute the cresol CCl_4 extract with 3 volumes of butanol CCl_4 (1·4); extract into 10 ml of water
6. Re-extract the aqueous phase with 5 ml of cresol:CCl_4 (1 1)
7. Repeat steps 5 and 6
8. Wash the cresol.CCl_4 extract four times with 10 ml of 5*N* H_2SO_4 and twice with 20 ml of pH 9 phosphate buffer (40 g of Na_2HPO_4/1.) containing a trace of cyanide (0·001*N*)
9. Repeat steps 5 and 6
10. Repeat step 5 extraction into 2 ml of H_2O.
11. Charge to chromatographic column (1 cm in diameter) containing (top to bottom) 2 g of alumina, 5 g of wet IRA 400 (OH cycle) and 5 g of wet IR120 (H cycle). Elute with water
12. Collect the aqueous eluate when a pink colour appears Total volume will be 5 ml Determine the cyanocobalamin content (Z) spectrophotometrically at 361 mμ and its associated radioactivity (B cpm)

This treatment is capable of eliminating "red pigments" resembling cobalamins in structure but devoid of comparable biological and clinical activity.[16]

Because the amount of cobalamin in the isolate is determined spectrophotometrically from absorbancies at 361 mμ, $\left(A_{1\,\mathrm{cm}}^{1\%} = 207\right)$ and the efficiency of isolation $\frac{B}{A}$ is 30–50%, one needs a bare minimum of 50 μg/sample to give a reasonably accurate absorbancy in the final 3–5 ml of resin column eluate usually recovered. Because so large a sample is required, other tissues, which contained $\leqslant$0·5 μg/g, have not been assayed by the isotope dilution method. Blood plasma or serum, for example, contains the order of 0·3 mμg of cobalamin/ml, which is completely out of reach of this procedure. Fortunately, another approach to be discussed below makes it possible to analyse even this tissue concentration by the radioactive indicator method.

Results of the isotope dilution assay of a feed concentrate are shown in Table III Two 100-g samples were analysed by a procedure modified from that described above for liver, by omission of the nitrate treatment and the initial introduction of an alcohol or water extraction procedure. The radioactive cyanocobalamin employed had a specific activity of $\simeq$ 60 μc/mg and the amount added was $\simeq$ 26 μg, which is not a negligible quantity, so that a correction for added tracer (Y) had to be applied. The average concentration was 2·6 μg/g or 1·2 mg/lb of concentrate which agreed

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[*] Remove $\simeq$2–4 g of homogenate as a standard to determine A cpm

[†] If only cyanocobalamin instead of total cobalamin is being sought, cyanide addition is omitted

TABLE III—ISOTOPE DILUTION ASSAY FOR VITAMIN B_{12}

Sample size, γ	100	100
Solvent	Water	Methanol
Amount vitamin B_{12}-^{60}Co (Y), μg	26	26
Vitamin B_{12} recovered (Z), μg	43	60
Recovered $\left(\frac{B}{A} \times 100\right)$, %	14 6	21·8
Vitamin B_{12} in sample (X)[a], μg	270	250

[a] $X = \frac{Z}{\left(\frac{B}{A}\right)} - Y$

with other, less convenient, biological assays, such as the chick growth assay employed at the time.

Crystalline cyanocobalamin and hydroxocobalamin preparations are also most reliably assayed by the dilution procedure which is specific for cobalamins. For cyanocobalamin and total cobalamin, a reproducibility of ±3% has been estimated. Hydroxocobalamin preparations can be analysed as a difference between total cobalamin content (cyanide addition in step 1) and cyanocobalamin content (no cyanide addition). Typical results of total cobalamin assays for a series of pharmaceutical preparations, fermentation products and crystalline cobalamins are listed in Table IV. Isotope dilution analyses of the two pharmaceutical products are not influenced by the addition of inert coloured materials which do, however, increase the

TABLE IV—ASSAY OF VITAMIN B_{12} PREPARATIONS BY ISOTOPE DILUTION

Sample		Labelled claim	Assay results[a]			
			ID assay	*L leichmannii* USP micro-biological assay	Spectro-photo-metric assay	Chick growth assay
Pharmaceutical products[16]	Cobalamin concentrate	950–1350 μg/g	1076	1117	—	—
	Same plus 200 μg red pigments	Same plus 200 μg/g	1067	1186	—	—
	Liver injection	50 μg/ml	51·8	53·7	—	—
	Same plus red pigments	Same plus 16 μg/ml	52·7	59·9	—	—
Animal protein factor[16]	Sewage product	—	1 6	1·7	—	1 1
	Fermentation products	13 5 mg/lb	11·6	13 5	8 0	—
		113 mg/lb	<0·3	77	11 6	<4
		6·0 mg/lb	6·3	8 2	4 2	—
		3 0 mg/lb	3·0	4·2	1·8	2·6
Crystalline -cobalamins	Cyanocobalamin	—	89 3%	—	87·2%	—
			89·7	—	91·2	—
			84 8	—	86·5	—
	Hydroxocobalamin	—	83 2	—	81·0	—
			78·7	—	81·2	—
			79 9	—	77·5	—

[a] Units the same as those listed under labelled claim.

L. leichmannii assay results. The analyses of vitamin B_{12} concentrates (*i.e.*, "animal protein factor") of fermentation origin emphasise the non specificity of microbial and spectrophotometric procedures as compared to the isotope dilution method, which is usually in good agreement with the chick-growth assay procedure. Agreement is also excellent for the crystalline cobalamin samples which contain 10–20% of volatiles.

The direct isotope dilution method has also been employed to demonstrate the thermal stability of hydroxocobalamin* in stabilised aqueous solution, buffered with acetate buffer and sodium chloride to pH 4·2 and containing $\simeq 1$ mg of hydroxocobalamin/ml. Extrapolation to room temperature of accelerated test data gathered at 40°, 75° and 121° indicated a half-life of 15–20 years, corresponding to a loss of $\not< 4\%$ of hydroxocobalamin/year.

REVERSE ISOTOPE DILUTION

The biochemist studying the mechanism of action or the degradation of a compound into metabolites frequently administers an isotopic modification and fractionates tissue or excreta into labelled components, the nature and quantity of which he seeks to ascertain. The chemist can apply the same technique to stability studies; and to facilitate recovery and assure identity at very low concentrations, he can add an excess of unlabelled modification as carrier before isolation. This is the reverse isotope dilution procedure; and in contrast to isotope dilution, it is not limited by the sensitivity of a spectrophotometric measurement but only by the detection sensitivity of the labelled cobalamin which, for cyanocobalamin containing radioactive cobalt, is in the picagram range. In the reverse isotope dilution assay method one adds the desired amount of the radioactive vitamin $B_{12}\left(X_0\,\mu g;\ A\text{ cpm};\ S_0 = \frac{A}{X_0}\right)$ to the matrix in question. This matrix might be simply an aqueous solution if thermal or radiochemical stability[11] of solutions is concerned or, as has been already reported, cereals or capsules containing biological concentrates.[11,18] Degradation studies in animals receiving labelled vitamin are also cases in point.

At any subsequent time of interest, a large excess (Y mg) of carrier cobalamin is added, and isolation undertaken with recovery of an isolate containing Z mg of cobalamin and B cpm $\left(i.e.,\ S_f = \frac{B}{Z}\right)$. The value of Z is again measured spectrophotometrically. If the actual amount of residual vitamin B_{12} is X μg, then one may say

$$X = Y\left[\frac{1}{\frac{S_0}{S_f} - 1}\right] \text{ or } X = Y\frac{S_f}{S_0} \text{ because } S_0 \gg S_f.$$

Accordingly, the percentage of cohalamin left is

$$\frac{X}{X_0} \times 100 = \left[\frac{Y}{Z} \times B\right] \times \frac{100}{A} \tag{3}$$

Here, $\frac{Y}{Z}$ is the spectrophotometric factor correcting for incomplete recovery of

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* Experiments performed by Miss Beate Feller and Messrs. J. Carr, E. J. Hanus and J. Kanora of these Laboratories.

B cpm, $\left[\frac{Y}{Z} \times B\right]$ is the actual radioactivity in cpm recovered with the X μg of cobalamin, and $\frac{X}{X_0} \times 100$ is the percentage of initial radioactivity (A) still recoverable as cobalamin. This method is independent of the presence of endogenous cobalamins.

An obvious use of this approach is for the establishment of the radiochemical purity and authenticity of a labelled compound. This is part of the armoury of methods which the radiochemist employs to prove the suitability of labelled materials. An application of more general analytical relevance is illustrated by the measurement of the radiochemical[11] stability of vitamin B_{12} in aqueous solution employing ^{60}Co-labelled vitamin. Thermal stability has also been investigated. A stabilisation study* of cyanocobalamin in the presence of ascorbic acid is reported in Table V.

TABLE V—STABILISATION OF VITAMIN B_{12} IN AQUEOUS SOLUTION CONTAINING ASCORBIC ACID (ROOM TEMPERATURE STORAGE)

Agent[b]		Composition[b]		B_{12} left, %			
No.	Concn., *mg/ml*	B_{12}, *μg/ml*	AA, *mg/ml*	0	2 months	6·5 months	10·5 months
IFC-1	2	0·25	12·5	—	—	85	87
IFC-1	6	0·83	12·5	96	92	97	—
IFC-2	0·6	0·25	12·5	—	—	80	—
IFC-2	2	0·83	12·5	98	85	80	—
IFC-3	2	0·83	12·5	98	64	52	—
IFC-3	10	0·83	12·5	107	80	106	—
IFC-6	2	0·83	12·5	97	86	75	—
IFC-6	10	0·83	12·5	98	87	94	—
IFC-7	2	0·83	12·5	99	95	63	—
IFC-7	10	0·83	12·5	100	81	71	—
IFC-8	2	0·83	12·5	94	88	43	—
IFC-8	10	0·83	12·5	101	87	92	—
Agar	5	0·25	12·5	—	—	70	—
Sorbitol	420	0·83	12·5	99	57	34	—
Bovine albumin	10	0·25	12·5	—	—	63	—
Liver fraction	8·2	0·25	12·5	—	—	68	—
Gelatin	2–10	1·14	11·5	—	8–5[a]	—	—
Cerulaplasmin	2–6	1·14	11·5	—	1–9[a]	—	—
Yeast nucleic acid	10	0·25	12·5	—	—	65	9
None	—	0·25	12·5	—	—	29	—

[a] ≃ 3 months.

[b] IF = intrinsic factor; AA = ascorbic acid.

Stock aqueous solutions were prepared from protective agent, ascorbic acid and cyanocobalamin-^{60}Co, and analyses by reverse isotope dilution performed initially and after ≃3, 6·5 and 10·5 months. Protective agents assayed included intrinsic factor concentrates, agar, sorbitol and proteins. Stabilisation was suspected in view of

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* Experiments performed by Messrs. H. T. Meriwether and P. E. Gethard of these Laboratories.

numerous reports of enhanced oral absorption of the vitamin ingested simultaneously with certain of these materials. Because clear solutions were involved, it was not necessary to apply that part of the isolation procedure designed to eliminate tissue components. Estimates based on spectral changes are uncertain because of the lack of knowledge of degradation products and their spectra. The dilution procedure is unequivocal in that pure cobalamin is isolated. It is also performed more expeditiously than a microbiological assay. Given the rapid degradation of vitamin B_{12} in the presence of ascorbic acid, it is seen from Table V that the vitamin is indeed much stabilised by several of the intrinsic factor preparations. Neither sorbitol nor the proteins were effective.

The fate of administered cyanocobalamin retained in animal tissue has also been studied by the reverse isotope dilution method. Thus, practically all of the radioactivity resident in the liver of dogs receiving 3·6 or 14·3 μg of vitamin B_{12}-^{60}Co by the intravenous route and examined 5–71 days after dosing, were found to be recoverable as a cobalamin.[19] The isolation procedure described above was applied to these liver specimens. This being the case, the resident cobalt-60 radioactivity could be assumed to represent vitamin B_{12}-^{60}Co, which could thus serve as a resident indicator for determining the vitamin B_{12} content of the liver specimens by the direct isotope dilution method. This was confirmed by direct isolation (without addition of carrier) of total cobalamin from 100 to 200-g samples of tissue and measuring its activity (B cpm) and quantity (Z) in the isolate. The value of the initial radioactivity (A cpm) was obtained by direct measurement of the tissue radioactivity. The cobalamin content of dog livers could then be calculated from equation (2). These values were confirmed simultaneously by the addition of high specific activity vitamin B_{12}-^{57}Co tracer prior to isolation. The actual isotope dilution analysis thus constituted a "double labelling" tracer experiment in which cobalt-60 and cobalt-57 were determined simultaneously in a gamma-ray scintillation spectrometer. Results are reported in Table VI which show that resident cobalt-60 radioactivity is recoverable quantitatively as a cobalamin, and the cobalamin could serve as an indigenous tracer for vitamin B_{12} because it yielded essentially the same values for the vitamin B_{12} content of dog liver as did exogenous vitamin B_{12}-^{57}Co.

Although retained as an intact cobalamin, the administered cyanocobalamin does

TABLE VI.—VITAMIN B_{12} CONTENT OF DOG LIVERS

Dog	Cobalamins, %	Cobalamin (μg/g) by isotope dilution	
		^{60}Co	^{57}Co
282	103; 100	0·10 0·06	0·08 0·07
274	98; 104	0·14	0·14
276	97; 98	—	—
328	95	0·28	0·24
320	95	—	—

undergo considerable conversion to the hydroxo analogue. This was shown by the reverse isotope dilution method employing the proteolytic enzyme papain instead of nitrous acid to liberate bound vitamin B_{12} from protein and other tissue components, and by using both cyanocobalamin and hydroxocobalamin as carriers. In this study,[20] 2·4 μg of oral vitamin B_{12}-^{57}Co and $\simeq 14$ μg of intravenous vitamin B_{12}-^{60}Co were administered in divided doses, and tissues examined 4 weeks after the last dose. It appears from Table VII that, regardless of the mode of administration,

TABLE VII.—REVERSE ISOTOPE DILUTION ASSAY OF DOG LIVERS (PAPAIN TREATMENT)

Dog	Carriers	Boiled, *min*	Recovered as			
			Cyanocobalamin, %		Hydroxocobalamin, %	
			^{57}Co	^{60}Co	^{57}Co	^{60}Co
1	Cyano + hydroxo	15[a]	6·7	7·4	101	108
		60[a]	19·7	21·4	66·6	66·4
2	Cyano	15	9·6	10·8	—	—
	Cyano	15	16·5	13·8	—	—
	Cyano + hydroxo	15	6·6	6·2	100	100
		60[a]	25·2	26·1	64·5	60·5
		60	17·7	17·1	70·4	69·2
		120	22·8	21·7	62·1	61·5
	Hydroxo	60	—	—	100	105

[a] These isolates were further purified by chromatography on paper, elution, solvent extraction and ion-exchange resins. Results were essentially the same as in the standard procedure.

most of the radioactivity was recoverable as hydroxocobalamin, and that only 7–25% was retained as intact cyanocobalamin. This is consistent with the observation that hydroxocobalamin predominates among the natural sources of vitamin B_{12} activity.

SATURATION ANALYSIS

The interaction between vitamin B_{12} and micro organisms, blood serum, intrinsic factor and other substances of biological importance has received intensive study because of the possible diagnostic significance and to gain an insight into the mechanism of action of the vitamin. This "binding power" for vitamin B_{12} has been employed, among other uses, as a qualitative indication of the potency of intrinsic factor (IF) preparations, and to guide the concentration and isolation of this biological material from animal intestinal sources.[21] The binding power (BP) is measured most easily if a radioactive vitamin is employed. In principle, one only needs to incubate suitable amounts of intrinsic factor concentrate (IFC) with an excess of labelled cyanocobalamin and, after a predetermined time, remove free vitamin by dialysis,[22] adsorption, chromatography or by electrophoresis. If the intrinsic factor is recovered quantitatively, as in the dialysis procedure where it remains in the dialysis sac employed, its radioactivity as measured by scintillation counting indicates the weight of vitamin B_{12} retained by the IF present, and the weight of vitamin/unit weight of binder (*i.e.*, BP) follows. Alternatively, the excess radioactive vitamin B_{12} removed by the inert adsorbent could be measured and the bound vitamin deduced by difference. A typical set of data[23] is illustrated in Table VIII, which shows the amount (mg) of a given intrinsic factor preparation added to 15 ml of solution containing a total of 624 mμg of cyanocobalamin-^{60}Co before dialysis, the percentage of vitamin retained by the intrinsic factor concentrate after incubation at room temperature for 1 hr and dialysis in Nojax casing against running tap water for 22 hr, and the ratio of the retained vitamin (mμg) to the weight (mg) of binder. Up to 0·928 mg of intrinsic factor concentrate, a constant average binding power of 675 mμg/mg is obtained because the binding capacity of the IFC is saturated. Beyond this point, which just corresponds to the retention of 100% of the labelled vitamin, the vitamin excess is exhausted and progressively lower B_{12}/IF ratios are obtained.

TABLE VIII—BINDING OF VITAMIN B_{12} BY INTRINSIC FACTOR CONCENTRATE (VITAMIN ADDED: 624 mμg)

Wt. IF, *mg*	B_{12} bound, %	BP, *mμg/mg*	Wt. IF, *mg*	B_{12} bound, %	BP, *mμg/mg*
0·055	5·7	650	0·764	84·0	686
0·218	23·1	660	0·819	89·3	681
0·328	35·2	669	0·874	94·2	672
0·437	48·4	689	0·928	99·5	669
0·546	56·8	650	1·09	99·6	570
0·655	73·7	701	1·64	97	370
0·710	79·5	699	2·18	97	280

At higher concentrations of vitamin, the percentage of total vitamin bound/given weight of IF would be lower because its binding power is fixed and its capacity already saturated. Clearly, therefore, the addition of extraneous vitamin B_{12} to the system represented in Table VIII would lower the percentage of vitamin B_{12} bound, and the radioactivity retained would be less than the figures shown in Table VIII. This, in effect, would constitute an isotope dilution assay without separation of the isotopic mixture for measurement. This would be valid if no extraneous components in the medium interfere with the binding of vitamin B_{12}; then the IF serves both to isolate pure or uniquely distinguished radioactive vitamin and to permit facile measurement of final specific activity. This approach to the measurement of small amounts of vitamin B_{12} was proposed[24] for the assay of urine and applied[25] to the measurement of the capacity of gastric juice to bind the vitamin. The adsorbent there was resting *L. leichmannii*[24] cells; the proposal was never actively pursued, presumably because of the difficulty of cultivating a cellular mass of uniform and reproducible binding capacity.

This principle* has since been applied to the micro estimation of fluoride[26] and, under the designation of "saturation analysis", to the analysis of biological media for insulin,[27] thyroxine[28] and recently, again vitamin B_{12}.[29,30,31] The vitamin B_{12} adsorbents utilised are, however, not micro organisms but hog intrinsic factor concentrate,[30]

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* A similar principle was employed[32] to determine the solubility of lead sulphate in aqueous solutions containing large excesses of sodium sulphate and in alcohol-water mixtures. The indicator utilised was the lead isotope ThB(^{212}Pb) and the adsorbent was lead sulphate of predetermined specific surface.

which is a proteinaceous material, or other binding protein as is supplied in a "standard" serum[31] or plasma[29] specimen. In all of these proposals, a specimen of urine, plasma or serum of unknown vitamin B_{12} content is heated to liberate its vitamin B_{12} burden, and incubated with a fixed amount of radioactive vitamin B_{12}-(^{57}Co or -^{60}Co) and a standardised vitamin B_{12} binder. After incubation for a suitable period, the sequestered radioactivity is determined either (1) by dialysis[29] to remove excess ("free") vitamin and measurement of residual ("bound") radioactivity, (2) by removal of free vitamin by adsorption on charcoal[31] and measurement of same, or (3) by removal of bound vitamin by precipitation of the IF-vitamin B_{12} complex by the Somogyi method,[30] and measurement of the free vitamin left in the filtrate. Because the quantity of the initial radioactive vitamin employed is known, one can always deduce the relative amounts of free and bound vitamin, and the ratios of these quantities, and from this measurement deduce the vitamin B_{12} content of the urine or plasma sample.

TABLE IX—COMPARISON OF VITAMIN B_{12} ASSAY METHODS

	Sample	Investigator[a]	Vitamin B_{12}, *mμg/ml*	
			Radiometric	Microbiological
Urine	Infectious hepatitis	G, S & M	0·25–1·6	0·10–1·2
Serum	Normals	B & E	0·33–0·84	0·27–1·2
Serum	Normals	R	0·10–0·33	—
Serum	Normals	B, S & M	0·50–0·60	—
Serum	Macrocytic anaemia	B & E	0·01–0·074	—
Serum	Macrocytic anaemia	R	0–0·072	—
Serum	Macrocytic anaemia (after treatment with vitamin B_{12})	G, S & M	1·0	1·2
Serum	Myeloid leukaemia	B & K	9·0	—
Serum	Myeloid leukaemia	G, S & M	2·5	3·5
Serum	Infectious hepatitis	G, S & M	2·5–4·0	2·0–4·8
Serum	Liver cirrhosis	G, S & M	1·5	1·6

[a] Grossowicz, Sulitzeanu and Merzbach; Barakat and Ekins; Rothenburg

It has been customary among investigators to construct a calibration curve relating exogenous crystalline vitamin B_{12} concentration (1) with free radioactive vitamin,[31] or (2) with the ratio of free to bound[29] radioactive vitamin or the inverse ratio,[30] and reading the vitamin B_{12} concentration of an unknown from such a calibration curve. A plot of Free/Bound radioactive vitamin *vs.* vitamin B_{12} concentration is perhaps most convenient because it is linear. The identification of saturation analysis as an isotope dilution procedure, where the adsorbent serves the dual function of isolation and facilitating the determination of final specific activity, was recognised by one group of investigators[29] whose expression for vitamin B_{12} concentration of an unknown is: $B_{12}\ \text{m}\mu\text{g/ml} = \frac{C_a}{V}\left[\frac{B}{C_r} - \frac{1}{S}\right]$, where V = sample volume; C_a = cpm added; C_r = cpm in aliquot dialysed; B = mμg of vitamin B_{12} interpolated from the linear calibration curve; and S = specific activity of the radioactive vitamin B_{12} in cpm/mμg. Rewriting with the notation employed above in an earlier section, we have $V \times B_{12} = X$; $C_a = A$ cpm, $S = S_0$; $B = Z$; and $C_r = B$ cpm, so that the preceding expression becomes $X = \frac{A}{B} Z - Y$, a standard isotope dilution equation.

This "saturation" variant of the isotope dilution method for vitamin B_{12} yields results in excellent agreement with those of microbiological assays for urine and serum, and has the advantages of being much more rapid and probably more reproducible. A comparison of both methods, and of the radiometric method as applied by its several protagonists, is shown in Table IX. This version of the isotope dilution method is significant as an extension of the vitamin B_{12} assay to physiological concentrations. Hitherto, one had been limited by the detection sensitivity of the spectrophotometric method to levels above approximately 50 μg/sample. This quantity is far beyond that which is readily available in samples of tissue and body fluids. The greatly increased detection sensitivity for vitamin B_{12} attainable with the adsorption method permits the analysis of extremely low levels of vitamin present in natural media, and opens up a whole area of applicability for the isotope dilution method.

Zusammenfassung—Radioaktives Vitamin B_{12} wurde als analytisches Hilfsmittel, als biochemischer Tracer und als diagnostisches Agens eingesetzt. Von den verschiedenen beschriebenen markierten Verbindungen sind nur die mit isotopem Kobalt markierten in physiologischen Dosierungen von Nutzen. Wegen der hohen spezifischen Aktivitäten von 1-200 μc/μg lassen sich Nachweisgrenzen im Picogrammbereich mit kobaltmarkiertem Vitamin B_{12} realisieren Klinische Anwendungen, wie diagnostische Tests auf perniciose Anamie beim Menschen, sind gewissermaßen analytische Vorgänge, die Messungen des Vitamin B_{12}-Transports erfordern. Von deutlicher analytischem Charakter ist die Anwendung der Isotopenverdunnungsmethode auf pharmazeutische Präparate, Nahrungskonzentrate, Abfall- und Gärungsprodukte und kristalline Cobalamine. Die Beständigkeit von Hydroxocobalamin in stabilisierter wäßriger Lösung bei p_H 4,2 wurde auf diese Weise gezeigt. Die umgekehrte Isotopenverdünnungsmethode war bei der Erleichterung von Stabilitäts- und Abbauuntersuchungen ebenfalls sehr nützlich. Auf diese Weise wurde die quantitative Gewinnung unveränderten Cyanocobalamins aus Getreide und aus biologische Konzentrate enthaltenden Kapseln gezeigt. Umgekehrt wurde Umwandlung von Cyanocobalamin zu Hydroxocobalamin in der Leber von mit markiertem Vitamin gefütterten Hunden gefunden. Eine umfangreiche Untersuchung uber Agentien zur Stabilisierung von Vitamin B_{12} in ascorbinsäurehaltigen Lösungen wurde mit Hilfe des umgekehrten Isotopenverdünnungsverfahrens durchgeführt. Die Empfindlichkeit der Isotopenverdunnungsmethode wurde in Richtung auf physiologische Mengen stark ausgedehnt durch Anwendung der "Sättigungsanalyse", eine Erweiterung der Messung der Bindungskraft, die auf "intrinsic factor-"Konzentrate und auf tierische Gewebe einschließlich Serum oder Plasma angewandt wurde.

Résumé—La vitamine B_{12} radioactive a été employee dans un but analytique, comme traceur biologique et comme agent de diagnostic Des différentes molécules marquées, seules celles marquées avec des isotopes du cobalt sont utiles au niveau des doses physiologiques A cause des hautes activités spécifiques de (1–200) μc/μg, la sensibilité de la détection dans la région du picagramme utilise de la vitamine B_{12} marquée au cobalt. Des applications cliniques, y compris les diagnostics de l'anémie pernicieuse chez l'homme, sont, en un sens, des moyens analytiques comprenant des mesures du transport de la vitamine B_{12} D'un caractère analytique plus direct est l'application

de la méthode de dilution isotopique aux préparations pharmaceutiques, concentrés alimentaires, produits de dégradation et de fermentation et aux cobaltamines cristallisées. On a montré par cette méthode la stabilité de l'hydroxocobaltamine en solution aqueuse tamponnée (pH = 4,2). La méthode de dilution isotopique en retour est aussi très utile pour faciliter les études de stabilité et de dégradation. On a montré par cette méthode que, dans les céréales et dans des capsules contenant des concentrés biologiques, on retrouvait la même quantité de cyanocobaltamine n'ayant subi aucune transformation. Au contraire, la cyanocobaltamine se transforme en hydroxocobaltamine dans le foie des chiens recevant de la vitamine marquée. Toujours par cette méthode on a peu effectuer une étude complète des agents protecteurs pour stabiliser la vitamine B_{12} dans des solutions contenant de l'acide ascorbique. La sensibilité de la dilution isotopique a été grandement accrue vers les niveaux physiologiques par l'application de "l'analyse de saturation", une extension de la mesure du pouvoir de liaison appliquée au facteur intrinsèque des concentrés et aux tissus animaux contenant du sérum ou du plasma.

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SOME PHYSICAL PROPERTIES OF HIGHLY PURIFIED BROMINE

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Summary—The electrical conductivity of very pure bromine is lower than that given in most of the earlier literature, and the surface tension is slightly higher. In the liquid range, these properties can be expressed by the equations $\log k = -11{\cdot}372 + 0{\cdot}0128t$ and $\gamma = 45{\cdot}5 - 0{\cdot}182t$, where k is in ohm^{-1} cm^{-1}, γ in dyne . cm^{-1} and t in °C. Data on the thermal conductivity of the liquid are given for the first time.

INTRODUCTION

AMONG the continuing interests of this laboratory is one involving the properties and applications of bromine and its compounds. Through the years, elemental bromine has become available commercially with ever-increasing purity, until the 99·98–99·99% products on the market today rival the especially purified materials used for properties measurements some generations ago. Much of the improvement in the commercial product derives from better methods of fractionation and other treatments to remove organic substances and chlorine, recognition of the need for eliminating moisture and acidity to minimise corrosion problems, and the development of improved analytical methods for detecting impurities. Infrared analysis, for example, can reveal the presence of a few ppm of moisture as well as of chloroform and other partially halogenated hydrocarbons. Wagner[19] has recently pointed out that pure bromine is transparent throughout the normal infrared region, a fact which had been known in the industry for quite a few years. The difficulty of removing the last traces of organic substances by permanganate or chromic acid oxidation had not been realised originally. Thermal oxidation processes have been found in this laboratory to be more effective. One such process has been described by Codell and Norwitz.[4]

With high-purity bromine available as a starting material, it appeared desirable to make new determinations of some of the physical properties of this element. The present paper deals with measurements of the electrical conductivity of liquid and solid bromine, and of the thermal conductivity and surface tension of liquid bromine.

I—ELECTRICAL CONDUCTIVITY

Previous determinations of the specific conductance of bromine have given results as shown in Table I (*cf.* Sharpe[18]).

The data are concordant in that they all indicate a very high resistance of bromine, but discrepancies are evident. It should be noted that Exner's value, reported in 1882, was necessarily obtained with equipment inferior to that available later, and that Moessen and Kraus in their work were concerned primarliy with bromine solutions rather than with a fundamental value for pure bromine. The conductivity of solid bromine has been reported by Rabinowitsch[14] as 8×10^{-12} at $-18\cdot5°$ and $4\cdot5 \times 10^{-11}$ at $-9°$.

TABLE I.—ELECTRICAL CONDUCTIVITY OF LIQUID BROMINE

Temp., °*C*	Spec. cond. (K), *mhos. cm*$^{-1}$	Reported by
-9*	$5\cdot14 \times 10^{-10}$	Rabinowitsch[14]
-6	$5\cdot50 \times 10^{-10}$	Rabinowitsch[14]
$-5\cdot5$	$7\cdot94 \times 10^{-14}$	Exner[5]
0	$8\cdot63 \times 10^{-14}$	Exner[5]
0	$9\cdot6 \times 10^{-10}$	Anderson[2]
0	$6\cdot32 \times 10^{-10}$	Rabinowitsch[14]
15·5	$8\cdot95 \times 10^{-10}$	Rabinowitsch[14]
17·2	$1\cdot21 \times 10^{-13}$	Exner[5]
18	$1\cdot6 \times 10^{-9}$	Finkelstein[7]
25	$1\cdot12 \times 10^{-9}$	Rabinowitsch[14]
25	1 to 6×10^{-10}	Moessen and Kraus[12]
38·5	$2\cdot5 \times 10^{-13}$	Exner[5]

* Supercooled

EXPERIMENTAL

Purification of bromine

A procedure combining that of Codell and Norwitz[4] with that of Hildenbrand, Kramer, MacDonald and Stull[8] was employed. High-purity commercial bromine was vapourised and passed with oxygen through a quartz tube at 900°. The condensed bromine was allowed to stand overnight with about 10% of its weight of previously fused caesium bromide (to remove chlorine), then was distilled. Traces of hydrochloric acid, hydrobromic acid, carbon dioxide and water were removed by repeated vacuum distillations back and forth through drying tubes containing alternate layers of ignited magnesium oxide and barium oxide, in a closed system. The product was finally distilled under its own vapour pressure into the evacuated and cooled conductivity cell. Although no freezing-point data were obtained, the purity should be slightly better than that of Hildenbrand *et al.* Their data had indicated an impurity content of less than 0·001 mole per cent, but the presence of 10–15 ppm of chloroform was subsequently found by infrared analysis.

Apparatus

The conductivity cell consisted of a Pyrex chamber of about 150-ml capacity, having near the centre two parallel square tungsten electrodes 2·6 cm on a side and a little less than 0·5 mm apart. Electrical leads were also of tungsten, brought in from opposite sides through Pyrex tubes. The cell constant as determined at audio frequency with 0·01*M* potassium chloride solution was $5\cdot92 \times 10^{-3}$.

Resistance was measured with a megohmmeter of a type similar to one described by Prinz,[13] loaned by V. J. Caldecourt. This had a feedback circuit yielding a linear current output proportional to the unknown resistance. The current was recorded by a Sargent MR recorder. The system was calibrated against a nominal 100*M*Ω resistor, which in turn had been standardised in a Wheatstone bridge circuit against precision resistors of smaller magnitude.

Temperatures above 10° were regulated to within 0·01° in a bath of the usual type. For lower temperatures it was necessary to add dry ice periodically for cooling, and the constancy during reading intervals was only to about 0·1°. Transformer oil was used as a bath liquid with suitable insulating properties.

Procedure

The leads from the electrodes were kept short-circuited except for the 0·5-min periods of measurement. After each recording the polarity of the leads was reversed to lessen polarisation effects. The period between recordings was at least 5 min. In each run the applied d.c. voltage was small, about 5 V. Because the resistance of the system was found to increase with time, indicating polarisation, an extrapolation to zero time was made and taken as the true value of the resistance. A typical run is illustrated in Fig. 1, showing the extrapolation. At least four runs were made at each temperature.

The conductivity of solid bromine was obtained in the same equipment after lowering the loaded cell into a dry ice-trichlorethylene bath at a rate of 5 mm/hr. The measurement and extrapolation were made in the same way as for the liquid.

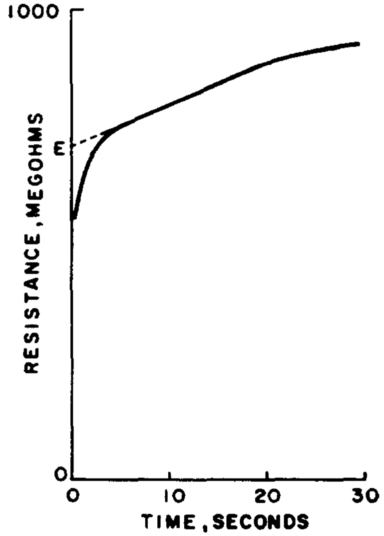

FIG. 1 —Change of resistance with time

RESULTS

Averaged values of the data obtained are presented in Table II. Generally, the individual runs at a given temperature yielded values agreeing within 3–5%. The conductances are estimated to be precise to 5% for the liquid and to 10% for the solid. The data are shown in a semi-log plot in Fig. 2. Over the linear range (liquid), the conductance can be represented by the equation:

$$\log k = -11{\cdot}372 + 0{\cdot}0128t$$

where k is in ohm^{-1}.cm^{-1}. and t is in °C.

TABLE II.—ELECTRICAL CONDUCTIVITY OF SOLID AND LIQUID BROMINE

Temp., °C	Resistance in cell, $M\Omega$	Spec. cond. (K), *mhos. cm*$^{-1}$
−20·0 (solid)	21,250	$2{\cdot}8 \times 10^{-13}$
−15·0	16,350	$3{\cdot}6 \times 10^{-13}$
−10·0	11,050	$5{\cdot}35 \times 10^{-13}$
−7·3	7,320	$8{\cdot}1 \times 10^{-13}$
−7·0 (liquid)	1,800	$3{\cdot}3 \times 10^{-12}$
−5·0	1,610	$3{\cdot}7 \times 10^{-12}$
0·0	1,390	$4{\cdot}25 \times 10^{-12}$
5·0	1,210	$4{\cdot}90 \times 10^{-12}$
10·0	992	$5{\cdot}97 \times 10^{-12}$
15·0	888	$6{\cdot}67 \times 10^{-12}$
20·0	753	$7{\cdot}86 \times 10^{-12}$
25·0	651	$9{\cdot}10 \times 10^{-12}$
30·0	586	$1{\cdot}01 \times 10^{-11}$
35·0	497	$1{\cdot}19 \times 10^{-11}$
40·0	439	$1{\cdot}35 \times 10^{-11}$
45·0	369	$1{\cdot}60 \times 10^{-11}$
50·0	321	$1{\cdot}84 \times 10^{-11}$

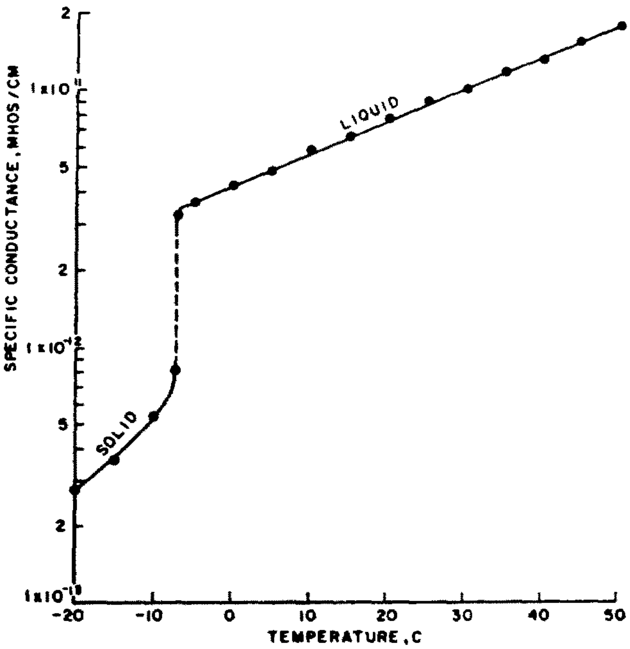

Fig. 2.—Electrical conductivity of bromine

DISCUSSION

Tungsten rather than platinum was chosen for the electrodes because of the observation that on prolonged contact with bromine, platinum became coated with a thin layer of a brownish-yellow substance which upon solution in water would yield a spot test for platinum.[2,6] Tungsten remained unchanged throughout the experiments, though considerably later after standing in moist air, the electrodes were found to have acquired an olive-green coating. The inertness of tungsten towards bromine was also evidenced by potentiometric measurements in a bromine-bromide system. A tungsten electrode exhibited a stable and reproducible potential, positive to that of a silver or magnesium electrode but identical with that of a tantalum electrode in the same system.

Ideally, the conductivity should be measured at audio frequency. However, with a resistance of about 1000 $M\Omega$ any small capacitance would short-circuit the input, making a.c. measurement exceedingly difficult. Therefore d.c. measurements were used here as well as in most of the work previously cited. Moessen and Kraus[12] used an a.c. method.

While polarisation still existed in our experiments, it was minimised by the use of a low d.c. voltage, brief recording time and short-circuiting between recordings. The reproducibility of the extrapolated values and their independence of the polarity of the electrodes indicate that polarisation had not caused any permanent changes in the system.

It is of interest to note the course of polarisation over longer recording periods, similar to what was found by Anderson.[2] Curve I of Fig. 3 was obtained after the electrodes had been shorted for a long time. The resistance slowly rose to a maximum, then tapered off. Curve II was obtained immediately after I and with the polarity changed. The resistance rapidly rose to a maximum A, dropped to a minimum B and finally rose again to a nearly level maximum C. Additional recordings after immediate changes of polarity were similar in shape to curve II, except that the resistances were shifted to lower values. Anderson's curves also showed a minimum in resistance (or rather a maximum in current in her paper), which was taken as the correct value. Separate similar experiments here showed that if our minimum had been considered the correct value according to Anderson, it would be within 10 to 20% of the extrapolated value E of Fig. 1. The extrapolated value was more reproducible, however, and hence was chosen as the one to be reported.

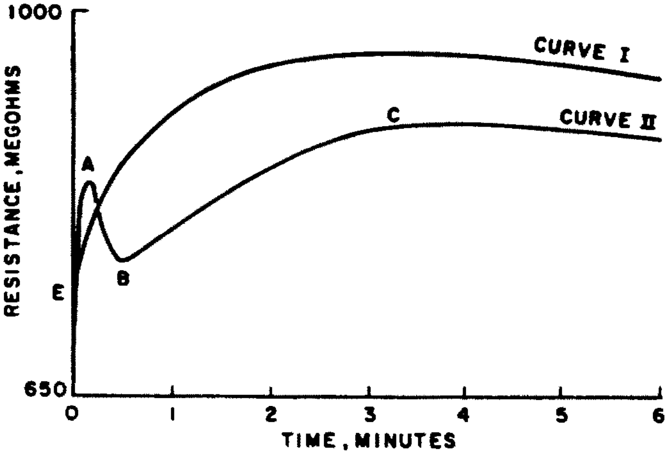

FIG 3.—Effect of polarisation Curve I—Resistance after prolonged shorting, Curve II—Resistance after passage of current and change of polarity.

Compared with the findings of other workers, except Exner, the present values are about two orders of magnitude smaller in specific conductance. This is attributed mainly to more complete removal of impurities, especially moisture, because a value more comparable with those of other workers ($1{\cdot}8 \times 10^{-10}$ at 25°) was observed in using high-quality commercial bromine without additional purification. Furthermore, the conductance of a purified sample continued to decrease with more passes through the purifying columns until about the tenth passage. On the other hand, Exner's values were about one order of magnitude smaller than ours. This may be fortuitous, in view of the fact that he used bromine without stated exclusion of moisture, in a cell of rather large cell constant (electrodes each 1·36 cm^2, 2 mm apart), which called for fairly large applied voltage. It is also of interest that Addenbrooke[1] in discussing Anderson's work, mentioned that he had earlier obtained a specific resistance of 10^{11} *megohms* for bromine. Clearly *ohms* was intended, judging from his data. Although he accepted Anderson's values, his own lies closer to ours (assuming it to be expressed in ohms).

The resistance curves of solid bromine during short recording periods with intermediate short-circuiting were similar in shape to those of the liquid. For longer recording time and intermediate switching of polarity the shapes of the curves were always like that of curve I in Fig. 3, showing that the effect of previous polarisation was negligible.

II—THERMAL CONDUCTIVITY

No previous data on the thermal conductivity of liquid bromine were located. It was decided to employ a hot wire method, the principle of which has been adequately discussed by Hutchinson.[9] Thanks are expressed to W. E. Hatton for assistance in applying this method.

EXPERIMENTAL

Apparatus

The cell was made up of a Pyrex tube, 2·79 mm o.d. and 1·57 mm i.d., housing a coil 5·5 cm in length and 0·092 mm in diameter made from tungsten wire 0·012 mm in diameter. Separate leads for current and potential measurement were connected at each end of the tungsten coil. The resistance of the coil in air was 146·809 Ω at 20°.

In the electrical circuit the following elements were connected in series, in a closed loop a bank of Edison cells with a total e.m.f. of 8 V, decade resistors ranging from 100 to 10,000 Ω to adjust the current level, a calibrated 100-Ω precision resistor with negligible temperature coefficient and the conductivity cell. A precision Rubicon potentiometer with a sensitive galvanometer was used to determine the potential across the cell to within 0·01 mV.

For temperature control a 4-litre beaker with a stirrer was placed in an ordinary constant temperature bath with an insulating cover. The temperature of water in the beaker could be kept constant to about 0·002°, as indicated by a Princo thermometer with divisions in 0·01°. For the measurement at 10°, ice-water was circulated through a coil in the outer bath. The conductivity cell was placed inside the beaker.

Reagents

Reagent-grade toluene and carbon tetrachloride were doubly distilled. By gas chromatography the toluene showed impurities totalling 0·46 area per cent. These consisted of two major impurities, probably paraffin hydrocarbons boiling near toluene, and three traces one of which was most likely benzene. This product should be similar to the analytical-reagent grade used by Challoner and Powell[8]

Procedure

The cell was dried by evacuation and was loaded in the same manner as the electrical cell, to avoid contact of bromine with the air. At each bath temperature a constant current was applied to the tungsten coil for 1 hr or longer. Potentials through the standard resistor and through the cell were measured at the end of the period. From these values the resistance of the tungsten coil at a definite power level could be calculated. The current was then changed and the determinations repeated. A plot of resistance against power resulted in a straight line, which also served as a check for internal consistency. With a series of bath temperatures, a series of such straight plots was obtained.

For each plot the extrapolated value of resistance at zero power level was the resistance of the coil at the bath temperature. When this resistance was plotted against the bath temperatures, the slope of the resulting straight line plot was equal to the temperature coefficient, α, of the coil.

Choosing a suitable value of power w from a resistance-power plot, its corresponding Δt_1 was obtained by reading ΔR from the plot and multiplying it by α. Δt_1 denoted the temperature difference between the wire and the bath. When a correction term Δt_2, representing the temperature drop across the Pyrex wall, was subtracted from Δt_1, the difference was Δt, the temperature drop across the thin shell of the sample liquid. The value of Δt_2 could be calculated from the dimensions of the cell by means of known formulae.[17]

The values of w and Δt are related by the equation:

$$w = kC\Delta t \tag{1}$$

where k is the thermal conductivity of the sample and C is the cell constant. The latter was determined by calibration experiments with toluene and carbon tetrachloride. For this purpose the data of Challoner and Powell[8] were used because of their apparently high precision (see below) and suitable spacing of temperatures.

RESULTS

Calibration data are listed in Table III and the averaged results obtained with pure bromine are shown in Table IV. The determinations on bromine presented no difficulty in the range from 20 to 50°, with results reproducible to 1 or 2%. Over-all accuracy is estimated at ±5%. The measurement at 10° showed larger scattering and its accuracy is estimated at ±10%. The data are plotted in Fig. 4.

TABLE III.—CALIBRATION OF THERMAL CONDUCTIVITY CELL

Standard	Temp., *°C*	Thermal conductivity[a]	Power (W), *watt*	Δt, *°C*	Cell constant, *cm*
Toluene	10	$3·36 \times 10^{-4}$	3×10^{-3}	0·1802	49·5
Toluene	20	$3·29 \times 10^{-4}$	3×10^{-3}	0·1935	47·1
Toluene	40	$3·15 \times 10^{-4}$	3×10^{-3}	0·1922	49·5
Toluene	50	$3·06 \times 10^{-4}$	3×10^{-3}	0·1961	50·0
					Average 49·0
Carbon tetrachloride	10	$2·58 \times 10^{-4}$	3×10^{-3}	0·2443	47·6
Carbon tetrachloride	20	$2·55 \times 10^{-4}$	3×10^{-3}	0·2372	49·6
Carbon tetrachloride	40	$2·48 \times 10^{-4}$	3×10^{-3}	0·2498	48·4
					Average 48·5

[a] Data of Challoner and Powell[3] expressed in cal cm^{-1}.sec^{-1}.deg^{-1}.

TABLE IV.—THERMAL CONDUCTIVITY OF LIQUID BROMINE (cell constant 49·0 cm, power 3×10^{-3} W)

Temp., *°C*	Δt, *°C*	Thermal conductivity, *cal cm^{-1} sec^{-1}.deg^{-1}*
10	0·2015	$3·04 \times 10^{-4}$
20	0·2051	$2·98 \times 10^{-4}$
25	0·2087	$2·93 \times 10^{-4}$
30	0·2106	$2·91 \times 10^{-4}$
40	0·2216	$2·76 \times 10^{-4}$
45	0·2303	$2·66 \times 10^{-4}$
50	0·2428	$2·52 \times 10^{-4}$

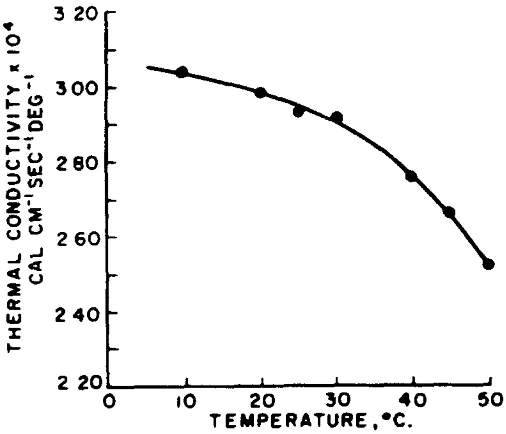

FIG. 4.—Thermal conductivity of bromine.

DISCUSSION

For work with bromine, it is a particular advantage of the hot wire method that the cell can be constructed of materials resistant to corrosion. However, the accuracy of the method is dependent upon calibration against a substance of known thermal conductivity. The thermal conductivity of toluene has been studied by many investigators, whose results have recently been examined statistically by Ziebland.[20] According to his conclusions, the values of Challoner and Powell are about 1·8% too high. If this is the case, our data for bromine are also too high. We have chosen to retain the higher values, particularly because a change would give poorer agreement for the cell constant as found with carbon tetrachloride.

The thermal conductivity of bromine around room temperature lies between those of toluene and carbon tetrachloride. The temperature coefficient is negative, as is also observed with many non-polar liquids, but it is not constant. The drop in thermal conductivity above 30° shown in Fig. 4 is not likely a result of experimental error. While the explanation is uncertain, it must be remembered that bromine is a liquid whose heat capacity, heat of vaporisation and boiling point are all quite low.

Over the range from 0 to 50°, the thermal conductivity of liquid bromine may be approximated by the expression $k = 3{\cdot}04 - 0{\cdot}004\,(t - 10) - 2{\cdot}0 \times 10^{-4}(t - 10)^2$.

III—SURFACE TENSION

A brief literature search failed to reveal any recent determinations of the surface tension of bromine. International Critical Tables[10] lists values which appear to have come almost entirely from unpublished work of W. D. Harkins and G. L. Clark, because the results in cited earlier references are either discordant or difficult to interpret. Mellor[11] gives an equation, based upon data by Ramsay and Aston,[15] which yields surface tension figures about 6% lower than those in International Critical Tables. In no case is there an indication that the bromine used was carefully purified. Both capillary rise and drop weight methods had been employed for the earlier measurements, the former was chosen for use in the present study.

EXPERIMENTAL

Apparatus

A cell was made from two sections of Pyrex tubing 9 inches long, the inside diameters being 2 inches in one case and 1·2 inches in the other. Two precision capillaries were positioned inside the narrower tube, affixed by glass rods to the tube walls. The larger tubes were connected side-by-side through very short sections of 3/8-inch glass tubing at each end, and the ends were sealed and flattened so that the cell would stand upright. An arm at the top of the smaller tube made a connection with the bromine purification train. The cell was placed in a constant temperature bath controllable within 0·01°.

Readings of the bromine levels were made with a Gaertner cathetometer, the vernier of which could be read to within 0·005 cm.

Reagents

Doubly-distilled reagent-grade benzene was used for calibration of the capillaries. Deionised water distilled from alkaline permanganate was employed for the same purpose.

Procedure

The cell was cleaned with a hot mixture of nitric and perchloric acids, rinsed with the above distilled water and thoroughly dried before calibration or connection with the bromine train. After filling and temperature adjustment, readings were taken of the liquid levels in both capillaries and in the wider arm of the cell. The cell was illuminated strongly from behind and no difficulty was encountered in reading the bottom of the bromine meniscus in the capillaries. In the wider tube, the meniscus was read at the lowest point through which transmitted light could be recognised. This was about 0·06 cm below the upper point of contact of liquid bromine with the cell wall.

Although readings were made on both capillaries, only those from one capillary were used in calculating the results. These were from the one which showed closest agreement between calibrations against benzene and water. The other capillary served as a check against any abnormality, such as the presence of a bubble

Density values used were extrapolated and rounded off from a set obtained on the purified bromine of Hildenbrand *et al.* by O L. Daniels of this laboratory. His data covered the range 15–30°, falling on a straight line. The gravitational constant was calculated as 980 5 by Helmert's equation. Surface tension data of Richards and Coombs[14] were used in calibrating the capillaries.

RESULTS

The radius of the capillary used for the calculations was taken as 0·005158 cm, this being the mean of the values from calibration against benzene and water. The value from benzene was only 0·1% larger than that from water.

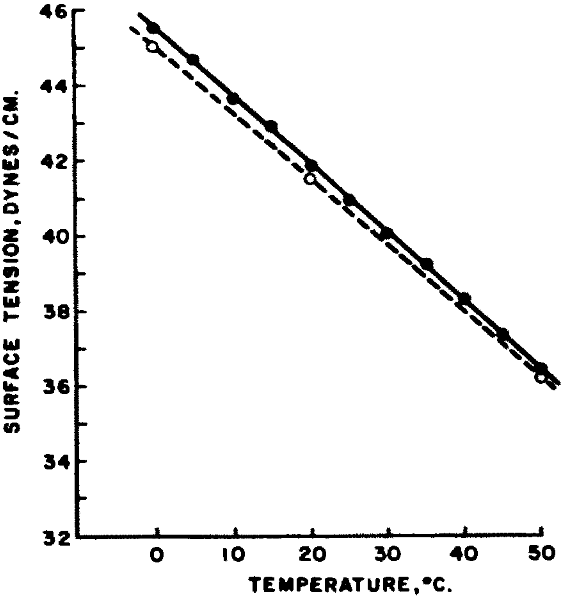

FIG. 5.—Surface tension of bromine: ●—present values, ○—I.C.T. data.

TABLE V—SURFACE TENSION OF LIQUID BROMINE

Temp., °C	Capillary rise, *cm*	Density, $g.ml^{-1}$	Surface tension, $dyne.cm^{-1}$
0	5 640	3 191	45·5
5	5 570	3 174	44·7
10	5·470	3·156	43·6
15	5·400	3 140	42·9
20	5 300	3·122	41·8
25	5·210	3·106	40·9
30	5·120	3·088	40·0
35	5·055	3·070	39·2
40	4·960	3·053	38·3
45	4·860	3 036	37·3
50	4 770	3·019	36·4

The surface tension data obtained with bromine are listed in Table V and plotted in Fig 5 along with those from the International Critical Tables. The equation representing the upper line is:

$$\gamma = 45{\cdot}5 - 0{\cdot}182t$$

where γ is in dyne.cm^{-1} and t is in °C.

DISCUSSION

The maximum error of the present results, based on possible errors in calibration, observed capillary rise and temperature, should not exceed 1·4% or 0·5 dyne.cm^{-1}. This compares favourably with the $\pm 0{\cdot}7$ dyne.cm^{-1} estimate given in the International Critical Tables, and the two sets of data are not separated by more than 0·5 dyne cm^{-1}. Actually, however, the consistency of each set suggests that the difference between the curves is a real one independent of small random measurement errors. This would point to the purity of the bromine as a possible major item in the discrepancy If such is the case, the difference in purity probably amounts to several tenths of 1 per cent. One experiment with high purity commercial bromine (impurity less than 0 05%) at 27·0° yielded a surface tension only 0·1 dyne.cm^{-1} below the upper curve Naturally this is within our experimental error. Nevertheless, it is apparent that the surface tension of bromine is not highly sensitive to the presence of trace impurities

Zusammenfassung—Die elektrische Leitfähigkeit von sehr reinem Brom ist niedriger als meist in der fruheren Literatur angegeben, und die Oberflachenspannung etwas hoher. Im flussigen Bereich konnen diese Eigenschaften beschrieben werden durch die Gleichungen $\log k = -11{,}372 + 0{,}0128t$ und $\gamma = 45{,}5 - 0{,}182t$, wo k in Ohm^{-1}.cm^{-1}, γ in dyn/cm und t in °C angegeben sind. Erstmals werden Angaben uber die Wärmeleitfahigkeit von flüssigem Brom gemacht

Résumé—La conductivité électrique du brome très pur est inférieure à celle donnée le plus souvant dans la littérature antérieure, et la tension superficielle est légèrement plus élevée Dans le domaine liquide, ces propriétés peuvent être exprimées par les équations $\log k = -11{,}372 + 0{,}0128t$ et $\alpha = 45{,}5 - 0{,}182t$, où k est exprimé en ohm^{-1} cm^{-1}, α en dyne cm^{-1} et t en °C. Pour la première fois, on fournit des données sur la conductivité thermique du liquide

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D_2O EFFECT ON $\Delta H\ddagger$ AND $\Delta S\ddagger$ IN THE IRON^{II}-IRON^{III} ELECTRON-EXCHANGE REACTION

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Summary—The equilibrium constant of the reaction $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ has been measured at 0·500 ionic strength at 5°, 15° and 25°. The ΔH and ΔS of this reaction are 9·32 ± 0.56 kcal mole^{-1} and 17·7 ± 2·0 cal. deg.$^{-1}$ mole^{-1}, respectively. The rates of the electron-exchange reactions $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ and $Fe^{2+} + {}^*FeOD^{2+} \rightarrow FeOD^{2+} + {}^*Fe^{2+}$ have been measured at 0·500 ionic strength at 5°, 15° and 25°. The enthalpy and entropy of the latter reaction are 11·5 ± 0·5 kcal mole^{-1} and −4·0 ± 1·8 cal. deg.$^{-1}$ mole^{-1}, respectively.

THE electron exchange-reactions (1) and (2) were studied by Silverman and

$$Fe^{2+} + {}^*Fe^{3+} \xrightarrow{k_0} Fe^{3-} + {}^*Fe^{2+} \quad (1)$$

$$Fe^{2+} + {}^*FeOH^{2+} \xrightarrow{k_H} FeOH^{2+} + {}^*Fe^{2+} \quad (2)$$

Dodson[1] in $H_2O + HClO_4 + NaClO_4$ media with the aid of ^{55}Fe tracer and an end-window Geiger tube to determine the radioactivity of the hydrous iron oxide precipitates obtained at various times throughout the course of the reaction. The energies and entropies of activation reported were 9·9 kcal.mole^{-1} and −25 cal. deg.$^{-1}$ mole^{-1} for reaction (1) and 7·4 kcal.mole^{-1} and −18 cal. deg.$^{-1}$ mole^{-1} for reaction (2).

Reactions (1) and (3) were studied by Hudis and Dodson[2] in

$$Fe^{2+} + {}^*FeOD^{2+} \xrightarrow{k_D} FeOD^{2+} + {}^*Fe^{2+} \quad (3)$$

~90% $D_2O + DClO_4 + NaClO_4$ media using essentially the same techniques. It was found that the rate constants in D_2O media were less than the rate constants of the corresponding reactions in H_2O media. At 7·1° the ratio of the rate constants of reaction (1) in H_2O and D_2O was approximately equal to 2 as was the ratio of the rate constants of reactions (2) and (3). It was not determined whether the substitution of D_2O for H_2O affected the enthalpy or entropy of activation or both The present-day availability of the isotopic tracer ^{59}Fe and of well-type scintillation counters allows more precise determinations of the rates of these reactions to be made. Hence, it was decided to determine the rates more precisely and to investigate the effect of D_2O on the enthalpies and entropies of activation.

The rate of the iron^{II}-iron^{III} exchange reaction in perchlorate media is given by[1,2]

$$R = \left\{\frac{k_{0,H} + k_H K_H/[H^+]}{1 + K_H/[H^+]}\right\} . [Fe^{II}][Fe^{III}] \quad (4)$$

$$= k_{ob} . [Fe^{II}][Fe^{III}] \quad (5)$$

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in which $k_{0,D}$, k_D, K_D and $[D^+]$ should be substituted for $k_{0,H}$, k_H, K_H and $[H^+]$, respectively, when the exchange occurs in D_2O media, K_H is the equilibrium constant of reaction (6) and K_D the corresponding equilibrium constant in

$$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+ \qquad (6)$$

D_2O. Hudis and Dodson[2] reported a determination of K_D at 21·6° and assumed that the enthalpy change for reaction (6) was approximately the same in D_2O as in H_2O but this was insufficient for our purpose. Hence, determinations of K_D at several temperatures are reported here.

EXPERIMENTAL

Reagents

D_2O (>99 8%). Obtained from Nichem Inc, Bethesda, U.S.A., and purified by distillation in an all-glass apparatus. D_2O used in an experiment was reclaimed and purified by vacuum distillation for further use. Anhydrous sodium carbonate and potassium permanganate were used, when necessary, to destroy acids and organic impurities before distillation. The D_2O content of the solvent was determined by measuring the specific gravity at 25°.[3] All D_2O solvent used had a D_2O content greater than 98 5%.

$DClO_4$· Prepared by passing a solution of $NaClO_4$ through a column of deuterated Dowex 50W-X-8 (50–100 mesh) cation-exchange resin. The deuterated form of the cation-exchange resin was obtained as follows Resin in the sodium form was dehydrated in vacuum at room temperature to eliminate most of the H_2O present, washed with a large amount of D_2O, placed in a 50-ml burette and converted to the deuterated form with a D_2SO_4 solution followed by pure D_2O. D_2SO_4 was prepared beforehand by dissolving anhydrous SO_3 in D_2O The $DClO_4$ solution obtained from ion exchange was distilled under reduced pressure several times to free it from small amounts of sulphate ion and organic impurities, the final distillate was found to be free from SO_4^{2-}. The concentration of acid in the final solution was determined by titration with a standard NaOH solution.

Crystalline $Fe(ClO_4)_3$ $6H_2O$ *and* $Fe(ClO_4)_2 \cdot 6H_2O$: Obtained from G. F. Smith Chemical Co, U.S.A., and dissolved in dilute $DClO_4$ solutions in D_2O in order to prepare the iron^{III} and iron^{II} perchlorate stock solutions used in the rate experiments, the amount of ordinary water introduced by the crystalline salts was negligible. The methods of standardising the iron concentrations and of preparing the iron^{III} perchlorate solution tagged with ^{59}Fe were entirely similar to those described in a previous paper[4] Care was taken to oxidise any trace of iron^{II} impurity to iron^{III} in preparing the iron^{III} perchlorate stock solution in D_2O to be used in the spectrophotometric determination of the hydrolysis constant of iron^{III} in D_2O by treating the salt with hot fuming $DClO_4$.[5] The total acid concentration, *i e.*, the sum $[DClO_4] + 3[Fe^{III}]$, was determined by potentiometric titration with a *standard NaOH solution. The concentration of iron^{III} was then determined spectrophotometrically*[6] and the $DClO_4$ concentration calculated It was established by adding known quantities of iron^{III} to known quantities of $HClO_4$ that each mole of iron^{III} added required three equivalents of base in the determination of the total acid concentration

Anhydrous $NaClO_4$, used to maintain a constant ionic strength, was prepared from $NaCO_3$ and $HClO_4$, recrystallising and drying at 130°.

Measurement of the acid dissociation constant of iron^{III} in D_2O

The methods used to determine the acid dissociation constant of iron^{III} in D_2O were essentially similar to those used by Siddall and Vosburgh.[7] A stock solution containing $5{\cdot}64 \times 10^{-4}M$ iron^{III} and $1\ 29 \times 10^{-1}M$ $DClO_4$ was diluted five-fold in making a set of sample solutions containing a constant concentration of iron^{III} and varying $DClO_4$ concentrations. All solutions were left to stand for a period of 2 weeks before spectrophotometric measurements were made. This was in excess of the necessary length of time[7] The aging period gives any polynuclear iron^{III} species, which may be present in the more concentrated stock solution, time to dissociate.

Transmittance measurements were made at 340 mμ by means of a Beckman DU spectrophotometer equipped with an insulated cell compartment thermostated on all six sides so as to control the temperature within ±0·1° A set of 10-cm corex cells with carefully measured cell characteristics was used and all absorbance values were corrected to correspond to hypothetical 10·00-cm cells with zero blank corrections

Measurement of isotope-exchange rate

The main modifications made on the method of Silverman and Dodson[1] for separation of the valence states and for determination of radioactivity in the iron^{II} portion have been described elsewhere.[4] However, further modifications were found to be necessary in the present study to reduce zero-time exchange. At a time t approximately 1 ml of reaction mixture was withdrawn and delivered by means of a pipette thermostatted at the temperature of the reaction into an ice-cold quenching solution stirred by a magnetic stirrer. An alcoholic solution of α,α'-dipyridyl was used as quenching solution to increase the solubility of tris-(α,α'-dipyridyl) iron^{II} perchlorate or precipitation of this salt gave incorrect results. Ice-cold Al^{3+}-carrier, ammonium acetate buffer and ammonium nitrate-aqueous ammonia buffer solutions were added successively at controlled intervals. Small fluctuations in the volume of sample withdrawn and in the drainage of the pipette resulted in small fluctuations of the iron^{II} concentration of the samples taken for radioactivity determination. To correct this source of error the absorbance of each radioactive iron^{II} solution at 520 mμ was compared with a standard iron^{II} solution and the radioactivity multiplied by an appropriate factor to take into account the change of iron^{II} concentration.

The reaction mixture was thermostatted to ±0·02° by means of an outer insulated bath controlled to ±1° and an inner bath controlled to ±0·02° by means of opposing heating and cooling devices

RESULTS

Determination of K_D *in* D_2O

If it is assumed that $[D^+] = [DClO_4] \gg [FeOD^{2+}]$ and that a wavelength can be found where $FeOD^{2+}$ is the main light absorbing species, then equation (7) is readily derived[7] for constant total $[Fe^{III}]$ and varying $[D^+]$.

$$\frac{1}{A} = a + b[D^+] \tag{7}$$

in which A = measured absorbance $\simeq \varepsilon_2 l[FeOD^{2+}]$, $a = 1/\varepsilon_2 l[Fe^{III}]$, $b = 1/K_D\, \varepsilon_2 l[Fe^{III}]$, ε_2 = molar extinction coefficient of $FeOD^{2+}$ and l = length of absorption cell. When A^{-1} was plotted versus $[D^+]$ an approximate value of K_D was obtained from the relation $K_D = a/b$. With this value of K_D, approximate values of $[Fe^{3+}]$, $[FeOD^{2+}]$, $[D^+] = [DClO_4] + [FeOD^{2+}]$ and the absorbance $\varepsilon_3 l[Fe^{3+}]$ from Fe^{3+} were calculated. Corrected absorbance values for $FeOD^{2-}$ and corrected $[D^+]$ values were now plotted to give new values of a and b in equation (7). Successive approximations were continued until the value of K_D remained constant; usually one or two cycles yielded constant K_D values. The corrected A and $[D^+]$ values used to obtain K_D are given in Table I and plotted in Fig. 1.

TABLE I.—DETERMINATION OF K_D IN $D_2O + DClO_4 + NaClO_4$ MEDIA

Temp., °C	$10^2[D^+]M$	A
25·2 ± 0·1	2·612	0·385
	4·618	0·248
	8·645	0·148
	12·68	0·104
15·0 ± 0·1	2·600	0·251
	4·609	0·154
	8·640	0·0866
	12·67	0·0616
5·0 ± 0·1	2·592	0·1587
	4·604	0·0945
	8·636	0·0518
	12·67	0·0362

{$[Fe^{III}] = 1{\cdot}128 \times 10^{-4}M$; $\mu = 0{\cdot}500$}

A weighted least squares[8] calculation of a and b in equation (7) was made; the results are given in Table II. The relative weight given to each point (x_i, y_i), where $x_i = [D^+]_i$ and $y_i = A_i^{-1}$, was taken to be equal to $(\Delta y_i)^{-2}$. The error, Δy_i, in the value of y_i was considerably larger than the corresponding error in x_i for most data points.

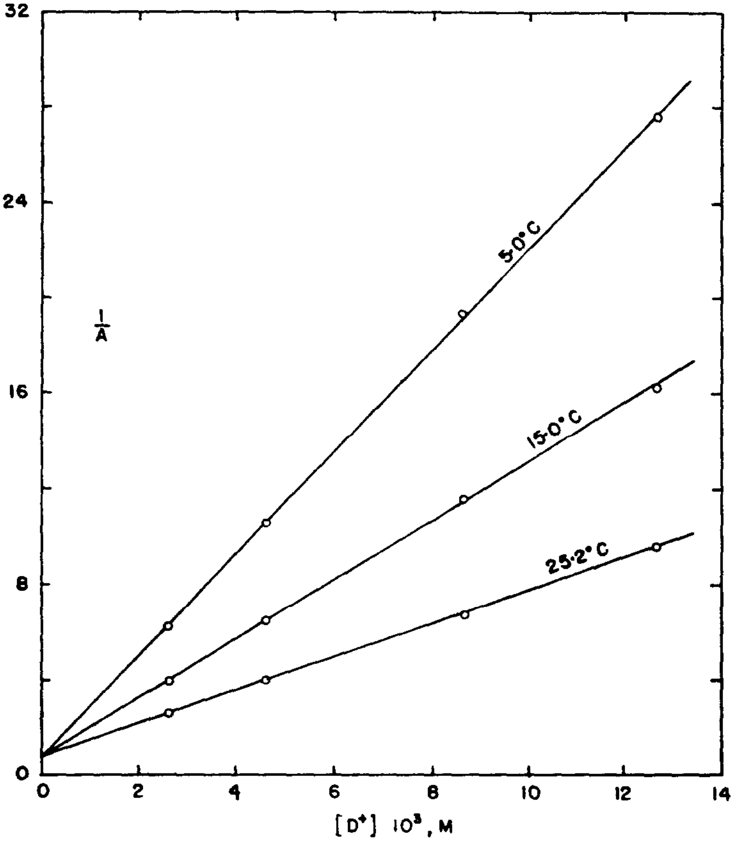

FIG 1—The inverse of the corrected absorbance for $FeOD^{2+}$ versus the deuterium ion concentration, $[D^+]$.

The error Δy_i was calculated from the relations

$$\Delta y_i = \Delta(A_i^{-1}) = \frac{d}{dT}\left(\frac{1}{A_i}\right)(\Delta T)$$

$$= \frac{1}{2{\cdot}303 A_i^2 T_i}(\Delta T) \qquad (8)$$

in which T_i is the percentage transmittance and ΔT is the error made in reading the percentage transmittance. ΔT was assumed to be constant over the scale used. A plot of log K_D versus $1/T$, shown in Fig. 4, gave the least squares values of ΔH and ΔS for reaction (6) in D_2O as 9·32 ± 0·56 kcal.mole^{-1} and 17·7 ± 2·0 cal. deg.$^{-1}$ mole^{-1}, respectively.

The values of ε_2 at 25°, 15° and 5° were 1130, 1140 and 1150 cm^{-1} M^{-1}, respectively. The corresponding extinction coefficient in H_2O[6] at 25° is 925 cm^{-1} M^{-1}.

TABLE II—WEIGHTED LEAST SQUARES CALCULATION OF *a*, *b* AND K_D

Temp., °*C*	a	b	10^3K_DM
25·2	0·787	0·697	1·129 ± 0·048
15·0	0·780	1·236	0·631 ± 0·034
5·0	0·768	2·134	0·360 ± 0·018

Exchange rate in H_2O

Because $\Delta H\ddagger$ and $\Delta S\ddagger$ have to be known rather precisely in order to determine the D_2O effect on each it was necessary to re-determine the rates of reactions (1) and (2) in H_2O. The results are given in Table III. The product D . k_{ob}, in which k_{ob} is defined by equations (4) and (5) and $D = 1 + K_H/[H^+]$, the denominator in the expression for k_{ob}, has been plotted versus $1/[H^+]$ in Fig. 2. Excellent precision was obtained. Milburn's semi-empirical expression,[9] equation (9), was used to calculate values of

TABLE III—RATE OF IRON^{II}–IRON^{III} EXCHANGE IN $H_2O + HClO_4 + NaClO_4$ MEDIA.[a]

Temp., °*C*[b]	$[H^+]M$	$10^4[Fe^{II}]M$	$10^4[Fe^{III}]M$	k_{ob}, *l. mole*$^{-1}$ *sec*$^{-1}$
5·00 ± 0·02	0·500	5·70	3·4	2·16
	0·250	3·17	3·4	3·20
	0·167	2·53	3·4	4·41
	0·125	2·16	14·5	5·51
	0·072	1·27	3·4	8·68
	0·050	1·27	3·4	12·05
15·00 ± 0·02	0·500	1·96	10·0	5·41
	0·250	1·35	10·0	9·19
	0·167	0·903	6·9	12·6
	0·125	0·753	10·4	15·8
	0·072	0·452	6·9	25·6
	0·050	0·301	6·9	36·2
25·00 ± 0·02	0·500	0·758	5·1	14·9
	0·250	0·442	5·1	26·0
	0·167	0·316	5·1	37·3
	0·125	0·253	5·1	47·5

[a] $\mu = 0·500$.

[b] The errors given in the temperatures are ranges; the standard deviation probably does not exceed ±0·01°.

$$\log K_H = \log K_H{}^{\circ} - \frac{4A\sqrt{\mu}}{1 + 2{\cdot}4\sqrt{\mu}} \qquad (9)$$

$\log K_H$ at $\mu = 0{\cdot}500$ and at each one of the temperatures 18°, 25° and 32°. A regression line, obtained from these values of $\log K_H$, is given in equation (10) and was used to obtain K_H at $\mu = 0{\cdot}500$ and at 5°, 15° and 25°.

$$\log K_H = 4{\cdot}531 - 2{\cdot}165 \times 10^3/T \qquad (10)$$

The errors of calculating $\log K_H$ by equation (10) were estimated[10] from equation (11), in which $Y = \log K_H$ calculated by equation (10), $X = 10^3/T$

$$\sigma(Y) = \sigma\left\{\frac{1}{n} + \frac{(X_i - \bar{X})^2}{\Sigma(X_i - \bar{X})^2}\right\}^{1/2} \qquad (11)$$

$X = \Sigma X_i/n$, n the number of (X_i, Y_i) sets used to obtain equation (10) and σ the standard error of $y_i = \log K_{H_i}$ calculated by equation (9) σ was estimated as the variance of Milburn's experimental values about expression (9).

A least squares treatment of the data shown in Fig. 2, together with the values of K_H calculated from equation (10) and the standard deviations of K_H calculated from equation (11), gave the rate constants and standard deviations listed in Table IV.

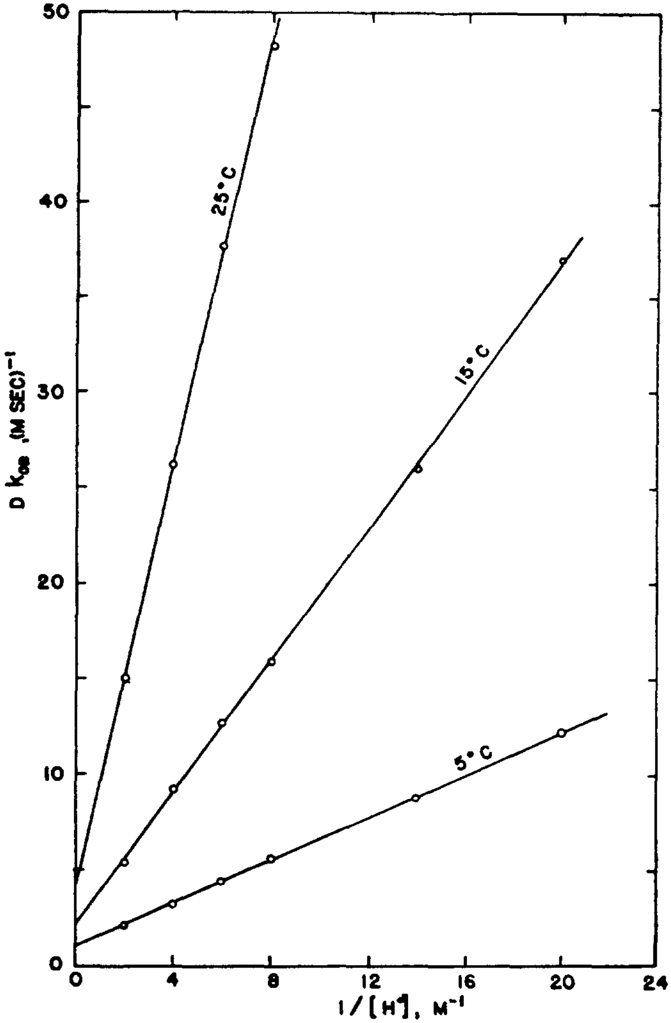

FIG. 2.—Dependence of observed rate constant on acid concentration in H_2O media.

A least squares plot of each log k versus 1/T gave $\Delta H_0^\ddagger = 10{\cdot}5 \pm 0{\cdot}85$ kcal. mole^{-1}, $\Delta S_0^\ddagger = -20{\cdot}6 \pm 3{\cdot}0$ cal. deg^{-1}. mole^{-1} for reaction (1) and $\Delta H_H^\ddagger = 8{\cdot}44 \pm 0{\cdot}47$ kcal.mole^{-1}, $\Delta S_H^\ddagger = -14{\cdot}4 \pm 1{\cdot}6$ cal. deg.$^{-1}$ mole^{-1} for reaction (2). The plot of log k_H versus 1/T is shown in Fig. 4. The values given by Silverman and Dodson[1] for these four quantities are in agreement with the values given here within the error of their measurements. The errors in $\Delta H_0^\ddagger$ and $\Delta S_0^\ddagger$ are still considerable because the steep slope of the D . k_{ob} versus $1/[H^+]$ plots at the higher temperatures gives rise to standard deviations of 8 to 10% in $k_{0,H}$ as may be seen in Table IV.

Exchange rate in D_2O

Exchange rate measurements made at three temperatures are given in Table V. Plots of D . k_{ob} are shown in Fig. 3. The intercepts, $k_{0,D}$, and slopes, $k_D . K_D$, of the straight lines in Fig. 3 are given in Table VI. The errors reported are least squares standard deviations. The values of k_D were obtained by dividing the slopes by the values of K_D obtained from regression equation (12). The standard deviation of each k_D was obtained from equation (13)

TABLE IV.—LEAST SQUARES VALUES OF THE RATE CONSTANTS IN H_2O

Temp., °C	$k_{0,H}$, *l. mole*$^{-1}$. *sec*$^{-1}$	$10^{-3}k_H$, *l. mole*$^{-1}$. *sec*$^{-1}$
5·0	1·04 ± 0·03	0·993 ± 0·043
15·0	2·09 ± 0·16	1·666 ± 0·039
25·0	4·00 ± 0·39	2·978 ± 0·089

$\mu = 0{\cdot}500.$

TABLE V.—RATE OF IRON^{II}-IRON^{III} EXCHANGE IN $D_2O + DClO_4 + NaClO_4$ MEDIA

Temp., °C	$[D^+]M$	$10^4[Fe^{II}]M$	$10^4[Fe^{III}]M$	k_{ob} l mole^{-1} sec.$^{-1}$
5·00 ± 0·02	0·500	12·63	1·9	0·936
	0·200	7·78	1·9	1·63
	0·125	5·83	1·9	2·36
	0·050	2·67	1·9	5·40
15·00 ± 0·02	0·500	3·72	1·9	2·94
	0·250	2·48	1·9	4·96
	0·167	2·48	1·9	6·95
	0·080	0·992	1·9	13·2
25·00 ± 0·02	0·500	1·83	3·3	8·10
	0·200	0·666	3·3	17·1
	0·150	0·500	3·3	23·6
	0·100	0·333	3·3	34·8

$\mu = 0{\cdot}500.$

TABLE VI.—LEAST SQUARES VALUES OF THE RATE CONSTANTS IN D_2O

t°C	$k_{0,D}$, *l mole*$^{-1}$. *sec*$^{-1}$	$k_D K_D$. *sec*$^{-1}$	$10^{-3}k_D$, *l. mole*$^{-1}$. *sec*$^{-1}$
5·0	0·400 ± 0·010	0·249 ± 0·003	0·699 ± 0·032
15·0	1·05 ± 0·06	0·975 ± 0·008	1·528 ± 0·045
25·0	1·0 ± 0·7	3·36 ± 0·10	3·04 ± 0·16

$\mu = 0{\cdot}500$

$$4{\cdot}576 \log K_D = 17{\cdot}72 - 9{\cdot}32 . (1/T) . 10^3 \tag{12}$$

$$\left[\frac{\sigma(k_D)}{k_D}\right]^2 = \left[\frac{\sigma(K_D)}{K_D}\right]^2 + \left[\frac{\sigma(k_D K_D)}{k_D K_D}\right]^2 \tag{13}$$

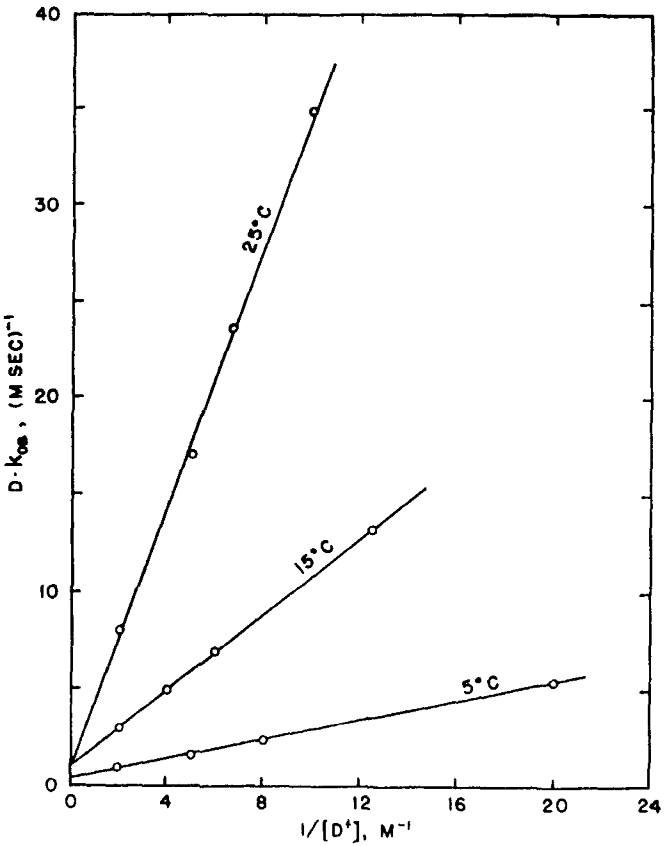

FIG. 3—Dependence of observed rate constant on acid concentration in D_2O media.

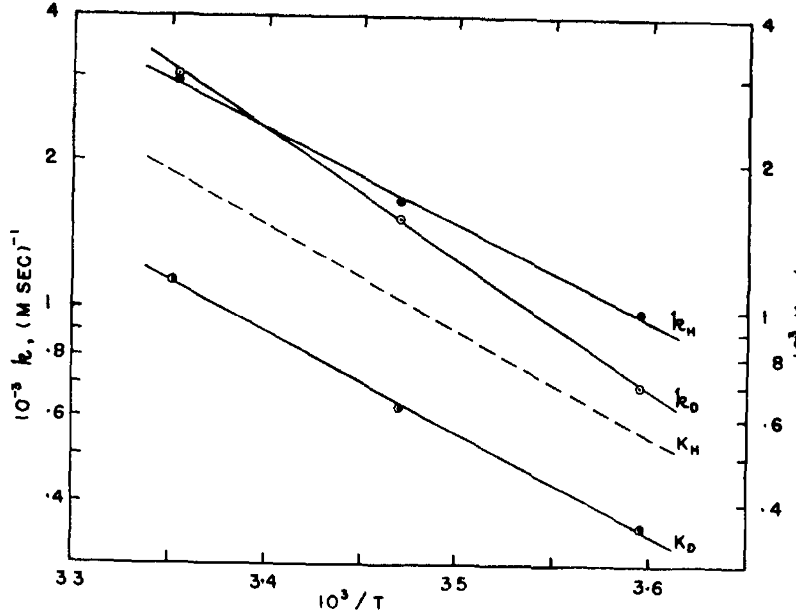

FIG 4—Equilibrium and rate constants plotted versus $(10^3/T)$. ⊙—k_D in D_2O, ●—k_H in H_2O, ◑—K_D in D_2O. The dashed line gives the calculated values of K_H in H_2O.

A least squares plot of log k_D versus 1/T shown in Fig. 4 gave the values $\Delta H_D^{\ddagger} = 11{\cdot}5 \pm 0{\cdot}5$ kcal.mole^{-1} and $\Delta S_D^{\ddagger} = -4{\cdot}0 \pm 1{\cdot}8$ cal. deg.$^{-1}$ mole^{-1} for reaction (3). The errors in $k_{0,D}$ do not make a similar plot for this rate constant worthwhile. Qualitatively it can be seen that the D_2O effect on reaction (1) is in agreement with the effect found by Hudis and Dodson [2]

DISCUSSION

The first acid dissociation constant of $Fe(H_2O)_6^{3+}$ was less in D_2O than in H_2O at the three temperatures and ionic strengths employed in this investigation. Thus at 21·6°, in particular, it was found that K_H/K_D is approximately equal to 1·7 instead of unity as reported by Hudis and Dodson.[2] Despite the fact that $K_H > K_D$, the enthalpy change in H_2O seems to be somewhat larger than in D_2O. However, the difference is small so that it is uncertain.

The differences between $\Delta H_H^{\ddagger}$ and $\Delta H_D^{\ddagger}$ and between $\Delta S_H^{\ddagger}$ and $\Delta S_D^{\ddagger}$ were much larger and seem to be outside of experimental error. The D_2O effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is much larger than that predicted by Marcus' equations[11] for an outer-sphere activated complex in which the inner co-ordination shells of the reactant complexes are not shared and in which the inner shell solvent is dielectrically saturated, whereas the solvent outside of the inner shell is dielectrically unsaturated. However, this result was to be expected in view of the small difference between the dielectric constants of H_2O and D_2O and the considerable effect of D_2O on the rate constants as has already been noted.[11] What is more important is the fact that D_2O seems to increase $\Delta H^{\ddagger}$ of the OH^--catalysed reaction more than it increases the $\Delta H^{\ddagger}$ of the Cl^--catalysed reaction[5] given in equation (14). The activation energy of the latter reaction in D_2O[5] was found to

$$Fe^{2+} + {}^*FeCl^{2+} \rightarrow FeCl^{2+} + {}^*Fe^{2+} \qquad (14)$$

be approximately 1·7 kcal. mole^{-1} greater than the activation energy in H_2O. However, the experimental error was sufficiently large so that this difference was not regarded as significant.[5] If the mechanism of the OH^--catalysed reaction is H-atom transfer as compared to either Cl-atom transfer or outer-sphere activated complex mechanisms for reaction (14), then it would be expected that the former reaction would show the larger increase in activation energy in D_2O.

Johnston and Rapp[12] have investigated the tunnelling effect in hydrogen atom transfer reactions of methyl radical with hydrocarbons and concluded that the tunnelling contribution was significant. The end groups in the activated complex $R_1 \cdots H \cdots R_2$ were considered to be so heavy that their contribution to tunnelling was negligible. These authors found that the ratio k_H/k_D increased with decreasing temperature more than the ratio would have increased if the ratio had been dominated only by the difference in the R—H and R—D bond energies in the reactants. Furthermore, a lower limit of 1·5 for the ratio k_H/k_D is given in the high temperature limit. In the present work it was found that the ratio k_H/k_D could be as small as unity. If hydrogen atom transfer, with its accompanying contribution from tunnelling, in the activated complex $[(H_2O)_5Fe^{II}(OH). \, .. \, H \, ... \, (OH)Fe^{III}(H_2O)_5]^{4+}$ is the most important mechanism for reactions (2) and (3), then it is apparent that isotope effects other than those considered by Johnston and Rapp must be contributing. Furthermore, if the dominant effect on the apparent $\Delta S^{\ddagger}$ in the D-for-H substitution comes from the mass effect on the tunnelling coefficient and if the tunnelling coefficient is assumed to be independent of temperature over the small temperature range used, then it is to be expected that the apparent $\Delta S^{\ddagger}$ would be larger for H_2O for D_2O. The opposite effect has been observed.

A possible explanation of the $\Delta S^{\ddagger}$ increase in D_2O is that water molecules are partially or wholly freed from some or all of the hydration shells when the activated complex is formed from the separated reactants This results in a positive contribution to $\Delta S^{\ddagger}$ even though the total $\Delta S^{\ddagger}$ for the activation reaction is negative. Because the entropy of 1 molecule of liquid water is approximately 1·5 cal. $deg.^{-1}$ $mole^{-1}$ greater for $D_2O(l)$ than for $H_2O(l)$,[13] each 1 mole of water wholly or partially freed in the activation reaction contributes towards a larger $\Delta S^{\ddagger}$ in D_2O than in H_2O. If an OH^--bridged activated complex is formed, at least one inner shell water molecule must be displaced from the hydrated $iron^{II}$ ion and perhaps other iron-ligand water distances appreciably lengthened in order to accommodate the penetration of $FeOH^{2+}$ with its attached water molecules into the first co-ordination shell of $iron^{II}$ However, the low activation energy of this electron-transfer reaction rather seriously limits the number of inner-shell water molecules which can be wholly or partially displaced. On the other hand, a hydrogen atom transfer does not require any of the inner-ligand water molecules to be wholly displaced.

Qualitatively, the increase of $\Delta H^{\ddagger}$ in D_2O is readily explained. If one assumes with Bigeleisen[14] that the 3 degrees of vibrational freedom of a water molecule essentially retain their identity in a ligand water molecule, then a hydrated metal ion such as $M(H_2O)_6^{+z}$ has 33 vibrational degrees of freedom associated with liberation and with vibration of the water molecules as rigid groups and 18 internal degrees of vibrational freedom inside the 6 ligand water molecules Each of these liberational and vibrational degrees of freedom has a smaller zero-point energy in $M(D_2O)_6^{+z}$ than in $M(H_2O)_6^{7+}$. If only a minor fraction[14] of this zero-point energy difference had to be absorbed in forming the activated complex the increase of 3 $kcal.mole^{-1}$ would be readily accounted for.

The D_2O effects reported in this paper, and which seem to be outside of experimental error, point up an obvious danger in measuring the D_2O effect on the rate constant alone without an accompanying investigation of the effect on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ The ratio k_H/k_D at room temperatures is very close to unity and had this ratio been measured at this temperature alone it would have been assumed that a D_2O effect was absent

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Zusammenfassung—Die Gleichgewichtskonstante der Reaktion $Fe^{3+} + D_2O \rightarrow FeOD^{2+} + D^+$ wurde bei der Ionenstärke 0,500 bei 5°, 15° und 25°C gemessen. Ferner wurden $\Delta H = 9{,}32 \pm 0{,}56$ kcal/mol und $\Delta S = 17{,}7 \pm 2{,}0$ cal/grad.mol gefunden. Die Geschwindigkeiten der Elektronenaustauschreaktionen $Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+}$ und $Fe^{2+} + {}^*FeOD^{2+} \rightarrow {}^*Fe^{2+} + FeOD^{2+}$ wurden bei der Ionenstarke 0,500 bei 5°, 15° und 25°C gemessen Aktivierungsenthalpie und -entropie der letzten Reaktion wurden zu $11{,}5 \pm 0{,}5$ kcal/mol und $-4{,}0 \pm 1{,}8$ cal/grad.mol gefunden.

Résumé—La constante d'équilibre de la réaction $Fe^{3+} + D_2O \rightleftharpoons FeOD^{+2} + D^+$ a éte mesurée à force ionique 0,500 et aux températures 5°, 15° et 25°C Les valeurs ΔH et ΔS de cette réaction sont respectivement 9,32 ± 0,56 kcal . mole^{-1} et 17,7 ± 2,0 cal . deg $^{-1}$ mole^{-1}. Les vitesses d'échange de l'électron dans les réactions $Fe^{2+} + {}^*Fe^{3+} \rightleftharpoons Fe^{3+} + {}^*Fe^{2+}$ et $Fe^{2+} + {}^*FeOD^{2+} \rightleftharpoons FeOD^{2+} + {}^*Fe^{2+}$ ont été mesurees à force ionique 0,500 et aux températures 5°, 15° et 25°C. L'enthalpie et l'entropie d'activation de cette dernière réaction sont respectivement 11,5 ± 0,5 kcal mole^{-1} et −4,0 ± 1,8 cal deg.$^{-1}$ mole^{-1}.

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LEAD-DITHIZONE EQUILIBRIA IN WATER-CARBON TETRACHLORIDE SYSTEMS*

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Summary—Equilibrium of the principal reactions involved in the extraction of lead dithizonate from aqueous solution with carbon tetrachloride (0) have been determined at $\mu = 0{\cdot}1$:

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0^2} = 5{\cdot}6 \pm 0{\cdot}3 \qquad (5{\cdot}8 \pm 0{\cdot}6 \text{ at } \mu = 0{\cdot}3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{soly. in } CCl_4}{\text{soly in } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^3$$

$$K_{diss} = \frac{[Pb^{2+}][HDz^-]^2}{[Pb(HDz)_2]} = 7 \times 10^{-16}$$

$$K_{sp} = [Pb^{2+}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{3-}]} = 5{\cdot}4 \times 10^5 \qquad \frac{[PbNO_3^-]}{[Pb^{2+}][NO_3^-]} = 0{\cdot}11$$

The pH range for extraction of >99% of lead under analytical conditions (citrate and cyanide present, low equilibrium concentration of dithizone) is 7·5–11·5 Cyanide in the concentrations likely to be used does not significantly decrease the extraction of lead. Above pH 10·85, >99% of the excess dithizone is extracted from the carbon tetrachloride phase into an equal volume of aqueous phase A pH of 10·8–10·9 is recommended for determination of lead with a carbon tetrachloride solution of dithizone A variation of *ca.* ~0·2 pH unit from this value causes little error

DITHIZONE is a valuable reagent both for the separation of lead and its spectrophotometric determination. Although dithizone extraction methods for lead with carbon tetrachloride or chloroform as solvent have now been worked out quite satisfactorily, they rest on an empirical basis. Therefore, it seemed desirable to study a little more closely than heretofore the equilibria existing in the system dithizone-water-carbon tetrachloride, with special reference to the factors bearing on the determination of lead.

EXPERIMENTAL

Reagents

Water. Conductivity water was run through a 20 × 500-mm column of Amberlite IR-120 ion-exchange resin. The content of heavy metals reacting with dithizone at pH 8, as determined spectrophotometrically, at 520 mμ was equivalent to 0·001 ppm of lead. No coloured substances were extracted by carbon tetrachloride. Water thus purified was lower in dithizone-reacting metals than water redistilled in Pyrex apparatus (0·014 ppm of lead)

Hydrochloric acid. A 7*M* solution obtained by isothermal distillation at room temperature (polyethylene beaker) contained heavy metals equivalent to 0·001 ppm of lead.

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* From the Ph.D. thesis of O. B. Mathre, University of Minnesota, 1956.

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Nitric acid A reagent-quality product contained 0·008 ppm of lead and was used without further purification after boiling out oxides of nitrogen.

Perchloric acid The 70% acid (reagent grade) available contained only *ca.* 0·001 ppm of lead. Because perchloric acid sometimes contains substances oxidising dithizone, the concentrated acid was diluted with water to 1*M* and shaken for 1 week with a saturated carbon tetrachloride solution of dithizone. The trace of dithizone was removed by extraction with carbon tetrachloride.

Aqueous ammonia A 9*M* solution obtained by isothermal distillation contained 0·001 ppm of lead. A 12*M* solution prepared by absorbing tank ammonia in water contained 0·0012 ppm of lead.

Sodium hydroxide Carbonate-free *ca* 0·15*M* sodium hydroxide solution was prepared by passing purified sodium perchlorate solution through a column of Amberlite IRA-410 resin in the hydroxide form and collecting under nitrogen. The heavy metal content of the solution was equivalent to 0·0008 ppm of lead.

Potassium cyanide A product free from sulphide and containing 0·008 ppm of heavy metals as lead was used without purification. (Some reagent-quality potassium cyanide contained so much sulphide that it could not be used in the dithizone determination of lead.)

Sodium perchlorate A slight excess of perchloric acid was added to sodium carbonate so as to give a solution *ca* 0·001*M* in acid. This was shaken for 2 days with dithizone in carbon tetrachloride to remove substances oxidising dithizone. The pH was adjusted to 8 and heavy metals were extracted with dithizone. A 6*M* sodium perchlorate solution contained 0·0045 ppm of heavy metals as lead.

Sodium citrate. After dithizone extraction at pH 8, a 0·5*M* solution contained 0·003 ppm of lead. *Sodium sulphite* (10%) and *sodium nitrate* (3*M*) solutions purified in like manner contained 0·0015 and 0·002 ppm of metals equivalent to lead.

Lead nitrate The salt was recrystallised several times from 0·01*M* nitric acid and vacuum-dried over potassium hydroxide after grinding to a powder. Determination of lead gravimetrically gave the theoretical value.

Dithizone Two g of Eastman dithizone were dissolved in 150 ml of reagent-quality chloroform, insoluble material was filtered off, and the filtrate was shaken with four 50-ml portions of dilute purified aqueous ammonia. A small amount of sulphur dioxide was passed into the combined aqueous extracts and an extraction was made with 25 ml of chloroform, which was discarded. Sulphur dioxide was passed into the aqueous solution until acidic and dithizone was extracted with four 30-ml portions of chloroform which had been washed with 1:100 aqueous ammonia just before use. The chloroform solution was filtered through a pledget of glass wool into a flask. An equal volume of carbon tetrachloride was added and nitrogen was bubbled through the solution at 40°. When the volume had been reduced to 50 ml, the liquid was cooled in ice and filtered through sintered glass. The solid dithizone as washed with a little carbon tetrachloride and vacuum-dried over potassium hydroxide for 2 weeks.

The dithizone content of the product was determined by photometric titration with silver. Ten-ml portions of *ca* $5 \times 10^{-5}M$ dithizone in carbon tetrachloride were shaken with 10-ml portions of 0·1*N* sulphuric acid containing varying amounts of silver (less than required for the stoichiometric ratio). A plot of the absorbance of the carbon tetrachloride at 620 mμ against the amount of silver gave a straight line whose intersection with the silver axis indicated the equivalence point. Two batches of dithizone gave the following replicate values (%) for active reagent:

99·9	100·1
99·8	99·8
100·2	99·8
99·8	100·2
100·1	

The molar absorptivities of dithizone in carbon tetrachloride (solutions prepared by weighing out solid dithizone) at 25°, based on an average of 8 absorbance measurements of $0{\cdot}25-1{\cdot}26 \times 10^{-4}M$ solutions (standard deviations *ca* 1%), were found to be

$$1{\cdot}90 \times 10^4 \text{ at } 450 \text{ m}\mu$$
$$4{\cdot}69 \times 10^4 \text{ at } 510 \text{ m}\mu$$
$$3{\cdot}17 \times 10^4 \text{ at } 620 \text{ m}\mu$$

and $\varepsilon_{620}/\varepsilon_{450} = 1{\cdot}67$. A Beckman DU spectrophotometer was used for these measurements. Weber and Vouk[1] report $\varepsilon_{450} = 2{\cdot}14 \times 10^4$, $\varepsilon_{620} = 3{\cdot}64 \times 10^4$ and $\varepsilon_{620}/\varepsilon_{450} = 1{\cdot}70$.

Lead dithizonate. The solid was prepared in two ways:

(1) A 0·01% solution of dithizone in chloroform was shaken with an ammoniacal cyanide solution containing 95% of the theoretical amount of lead required to react with the dithizone. The filtered chloroform phase was evaporated to small volume at 40° in the dark with a stream of purified

nitrogen. The suspension of lead dithizonate was cooled in ice and the microcrystalline lead dithizonate was collected on a sintered-glass filter. The product was vacuum dried over potassium hydroxide.

(2) Lead nitrate in 0·001*M* perchloric acid was added slowly to an aqueous ammonia-potassium cyanide-ammonium sulphide mixture of pH 10·5 which was $10^{-4}M$ in dithizone. The precipitated lead dithizonate was filtered off, washed with dilute aqueous ammonia, water, alcohol and chloroform, then vacuum-dried over potassium hydroxide.

Lead was determined in the products by precipitation as the chromate after destroying dithizone with perchloric acid. Dithizonate radical was determined spectrophotometrically after reverting a weighed amount of the solid by shaking the carbon tetrachloride solution with 0·1*M* hydrochloric acid. As a check on the gravimetric lead determination, a portion of the acid was analysed for lead spectrophotometrically with dithizone. The analytical figures shown in Table I were obtained.

TABLE I

	Pb, %	Dithizonate radical, %	Pb - dithizonate, %	% Dithizonate / % Pb
Preparation (1)	28·9 (grav.) 28·9 (grav.) 28·7	70·7	99·5	2·444
Preparation (2)	28·5 (grav.) 28·3 28·6	69·9 70·2	98·55	2·458
Theoretical	28·87	71·13	100·0	2·464

The solid lead dithizonate seems to be approximately 99% pure. If the remainder is water (which is not certain), its amount is not large enough to correspond to a hydrate.

The molar absorptivity of lead dithizonate in carbon tetrachloride at 520 mμ, the wavelength of maximum absorption, was determined by three methods, each average being based on 20 absorbance measurements (Table II). The standard deviation is a little less than 1%. The concentration of lead dithizonate ranged from 5×10^{-6} to $1·6 \times 10^{-5}M$; ε was independent of the concentration.

TABLE II.—MOLAR ABSORPTIVITY OF LEAD DITHIZONATE IN CARBON TETRACHLORIDE AT 520 mμ

Method	ϵ_{520}
(1) Known amounts of lead extracted with 0·005% dithizone from aqueous ammonia-cyanide-sulphite buffer of pH 10·8 into CCl_4	66,200 ± 500
(2) Solid lead dithizonate [Preparation (1)] dissolved in CCl_4 and absorbance measured. Lead dithizonate dissociated by shaking with dilute HCl and lead determined spectrophotometrically by mono colour dithizone method. These values were checked by determination of dithizone in original CCl_4 solution	66,300 ± 600
(3) Absorbance of CCl_4 solutions of solid lead dithizonate measured and lead determined by spectrophotometric titration with standard $AgNO_3$ solution	66,600 ± 500

The molar absorptivity-wavelength curve of lead dithizonate in carbon tetrachloride is reproduced in Fig. 1. Weber and Vouk[1] report $\epsilon_{620} = 7·29 \times 10^4$ and $\epsilon_{620} = 3·9 \times 10^3$ for lead dithizonate in carbon tetrachloride.

Carbon tetrachloride. The reagent-grade product was treated with a few drops of bromine, allowed to stand 2 weeks, shaken with 10% sodium hydroxide, refluxed for 4 hr with the same solution, washed free from alkali, refluxed with 10% aqueous hydroxylamine hydrochloride solution for 0·5 hr, washed with water, dried with Drierite and finally distilled from calcium oxide. The purified product was stored in a refrigerator.

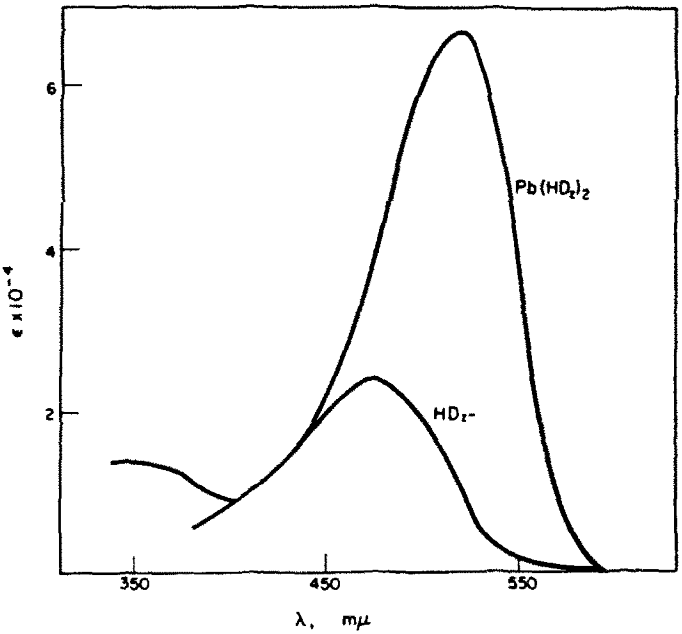

FIG. 1 —Molar absorptivity curves of lead dithizonate, $Pb(HDz)_2$, in carbon tetrachloride, and primary dithizonate ion, HDz^-, in 0·01M sodium hydroxide.

Dilute dithizone solutions prepared from carbon tetrachloride purified in this way show little decomposition in 1 week. For example, a $1{\cdot}29 \times 10^{-5}M$ dithizone solution kept in the dark at 23 ± 3° decreased in strength by about 1·5% after 1 week, as shown by the decrease in absorbance at 620 mμ (Table III).

TABLE III

Time, *days*	A_{450}	A_{510}	A_{620}
0	0·256	0·066	0·422
1	0·256	0·065	0·419
3	0·258	0·066	0·423
7	0·259	0·067	0·416

Used carbon tetrachloride was reclaimed by shaking with concentrated sulphuric acid, in portions one-tenth the volume of the carbon tetrachloride, until the acid remained colourless; washing with water and 1% sodium hydroxide; drying with Drierite and distilling from calcium oxide. Carbon tetrachloride reclaimed five times was used to prepare a $1{\cdot}99 \times 10^{-5}M$ dithizone solution, which after 10 days at room temperature in the dark gave a decrease of only *ca.* 1% in absorbance at 620 mμ.

Analytical-grade carbon tetrachloride which was not purified gives unstable dithizone solutions. "Analysed" carbon tetrachloride from two U.S. manufacturers gave *ca.* $5 \times 10^{-5}M$ dithizone solutions whose absorbance at 620 mμ decreased 14 and 41%, respectively after 10 days at room temperature in the dark.

EQUILIBRIA IN THE LEAD-DITHIZONE-WATER-CARBON TETRACHLORIDE SYSTEM

The equilibrium constant for the extraction reaction

$$Pb^{2+} + \underset{o}{2H_2Dz} \rightleftharpoons \underset{o}{Pb(HDz)_2} + 2H^+$$

(o = organic, *i.e.*, carbon tetrachloride, phase) is the *extraction constant* (at a specified ionic strength)

$$K_{ex} = \frac{[Pb(HDz)_2]_o(aH^+)^2}{[Pb^{2+}][H_2Dz]_o^2} \tag{1}$$

If the only lead species in the system are Pb^{2+} and $[Pb(HDz)_2]_o$, the *extraction coefficient*, the ratio of concentrations of lead in the organic and aqueous phases, is given by

$$E = \frac{[Pb(HDz)_2]_o}{[Pb^{2+}]} = K_{ex}\frac{[H_2Dz]_o^2}{(aH^+)^2} \tag{2}$$

In practice, other lead species will be present in the aqueous phase, so that

$$E = \frac{[Pb(HDz)_2]_o}{\Sigma[Pb]} \tag{3}$$

The equilibrium constants involving these species, relating their concentrations to $[Pb^{2+}]$, must then be known before E can be calculated as a function of $[H_2Dz]_o$ and aH^+. The possible presence of the following in the aqueous phase must be considered·

1. Hydroxo-lead species [$PbOH^+$, $Pb(OH)_2$, *etc.*],
2. Dithizone-lead species [$PbHDz^+$, $Pb(HDz)_2$],
3. Lead complexes with anions (cyanide, citrate, *etc.*).

The equilibrium constants for these species will be symbolised and defined as follows:

$$k_1 = \frac{[PbOH^+](aH^+)}{[Pb^{2+}]} \tag{4a}$$

$$k_2 = \frac{[Pb(OH)_2](aH^+)^2}{[Pb^{2+}]} \tag{4b}$$

$$k_3 = \frac{[HPbO_2^-](aH^+)}{[Pb^{2+}]} \tag{4c}$$

$$k_{d1} = \frac{[PbHDz^+]}{[Pb^{2+}][HDz^-]} \tag{4d}$$

$$k_{d2} = \frac{[Pb(HDz)_2]}{[Pb^{2+}][HDz^-]^2} \tag{4e}$$

$$k_{x1} = \frac{[PbX^+]}{[Pb^{2+}][X^-]} \tag{4f}$$

$$k_{x2} = \frac{[PbX_2]}{[Pb^{2+}][X^-]^2}, \text{ etc.} \tag{4g}$$

X represents a singly (or doubly) charged complexing anion. The values of the constants hold for a specified ionic strength.

The total concentration of lead in the aqueous phase is

$$\Sigma[\mathrm{Pb}] = [\mathrm{Pb}^{2+}] + [\mathrm{PbOH}^+] + \dots [\mathrm{PbHDz}^-] + \dots + [\mathrm{PbX}^+] + \dots$$

$$= [\mathrm{Pb}^{2+}] \times \left(1 + \frac{k_1}{aH^+} + \dots\ k_{d1}[\mathrm{HDz}^-] + \dots k_{x1}[\mathrm{X}^-] + \dots\right) \qquad (5)$$

and

$$[\mathrm{Pb}^{2+}] = \frac{\Sigma[\mathrm{Pb}]}{\left(1 + \frac{k_1}{aH^+} + \dots k_{d1}[\mathrm{HDz}^-] + \dots k_{x1}[\mathrm{X}^-] + \dots\right)} \qquad (6)$$

Substitution of (6) into (1) and rearrangement give

$$E = \frac{K_{ex}[\mathrm{H_2Dz}]_0^2}{(aH^+)^2\left\{1 + \frac{k_1}{aH^+} + \dots k_{d1}[\mathrm{HDz}^-] + \dots k_{x1}[\mathrm{X}^-] + \dots\right\}} \qquad (7)$$

or

$$E = \frac{K_{ex}[\mathrm{H_2Dz}]_0^2}{(aH^+)^2 + k_1(aH^+) + k_2 + \frac{k_3}{(aH^+)} + k_{d1}(aH^+)^2[\mathrm{HDz}^-] + \dots k_{x1}(aH^+)^2[\mathrm{X}^-] + \dots}$$

If O = original concentration of H_2Dz in carbon tetrachloride and phase volumes are equal: $[\mathrm{H_2Dz}]_0 = \frac{7 \times 10^8(aH^+)O}{1 + 7 \times 10^8(aH^+)}$. E should be independent of the lead concentration. It has been assumed that there is no polymerisation of any lead or dithizone species in either phase. Moreover, it has been assumed that no secondary lead dithizonate, PbDz, is formed. There is no experimental evidence to the contrary.

Except when otherwise noted, the constants reported in this paper refer to an ionic strength of 0·1*M* and a temperature of 25 ± 1°. The following values for the hydrolysis constants of lead ion, calculated to $\mu = 0{\cdot}1$, have been used:

$$k_1 = 3 \times 10^{-7}, \qquad k_2 = 3 \times 10^{-18}, \qquad k_3 = 7 \times 10^{-29}.$$

The values of k_1 and k_2 are based on the constants reported by Garrett *et al.*[2] and that of k_3 is derived from the dithizone extractability of lead in alkaline solutions as discussed later. The following activity coefficients have been used for $\mu = 0{\cdot}1$:

$$\gamma_{\mathrm{Pb}^{2+}} = 0{\cdot}37, \qquad \gamma_{\mathrm{PbOH}^+} = 0{\cdot}79, \qquad \gamma_{\mathrm{HPbO_2}^-} = 0{\cdot}80.$$

Solubility of lead dithizonate in carbon tetrachloride

As usually obtained, solid lead dithizonate has such a small particle size that it shows greater than normal solubility in carbon tetrachloride and even after shaking for 1 day its solubility is slightly greater than the true value. The recrystallisation of the small crystals of lead dithizonate proceeds more rapidly in the presence of an aqueous phase. Therefore, most of the solubility determinations were made by shaking solid lead dithizonate with deoxygenated carbon tetrachloride and an acidic or basic aqueous phase. As originally precipitated in most of these experiments, the lead dithizonate consisted of crystals 2–5 μ in length which grew to larger dimensions (crystal length up to 30 μ) on continued shaking. The rate of attainment of solubility

TABLE IV.—SOLUBILITY OF LEAD DITHIZONATE IN CARBON TETRACHLORIDE AT 25°

Expt. No.	Method	Shaking time, *min*	Solubility, $M \times 10^6$
1	10 mg of lead dithizonate [Preparation (2)] shaken with 150 ml of CCl_4.	1380	6·03
2	10 mg of lead dithizonate shaken with 100 ml of CCl_4 and 50 ml of aqueous ammonia-cyanide-sulphite buffer of pH 10·8.	240	5·55
3	Aqueous and solid phases of (2) shaken with 100 ml of fresh CCl_4.	75	5·65
4	50 ml of aqueous-cyanide-sulphite buffer (pH 10·8) containing 0·004 mmole of Pb and 0·009 mmole of H_2Dz shaken with 100 ml of CCl_4.	200	5·80
5	Aqueous and solid phases of (4) shaken with 100 ml of fresh CCl_4.	65	5·65
6	As in (4) except buffer of pH 9·3.	990	5·52
7	Aqueous and solid phases of (6) shaken with 100 ml of fresh CCl_4.	60	5·75
8	50 ml of 0·1*M* acetic acid-acetate buffer (pH 5·7) containing 0·004 mmole of Pb and 0·02 mmole of H_2Dz shaken with 100 ml of CCl_4.	75	5·65
9	Aqueous and solid phases of (8) shaken with 100 ml of fresh CCl_4.	45	5·70
10	50 ml of 0·1*M* acetic acid-acetate buffer (pH 4·3) containing 0·05 mmole of Pb and 0·05 mmole of dithizone shaken with 100 ml of CCl_4.	60	5·90
11	Aqueous and solid phases of (1) shaken with 100 ml of fresh CCl_4.	45	5·70
12	50 ml of 0·1*M* perchloric acid-perchlorate mixture (pH 3·05) containing 0·5 mmole of Pb and 0·05 mmole of dithizone shaken with 100 ml of CCl_4.	30	5·65
13	Aqueous and solid phases of (12) shaken with 100 ml of fresh carbon tetrachloride.	50	5·75
			Avg. 5·7 ± 0·1 (4·1 mg of $Pb(HDz)_2$ or 1·2 mg of Pb per litre)[a]

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[a] The first value, $6{\cdot}03 \times 10^{-6}$, has been omitted.

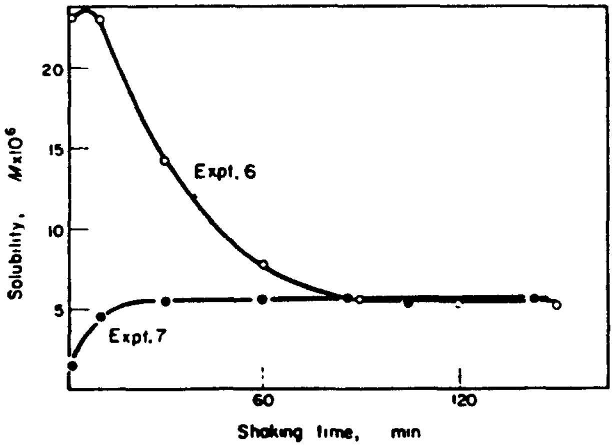

FIG 2.—Solubility of lead dithizonate in carbon tetrachloride (expts. No. 6 and 7, Table IV) at 25°.

equilibrium from supersaturation increases as the pH decreases. Within experimental error, the same solubilities were obtained by approaching equilibrium from supersaturation and undersaturation (Table IV). Fig. 2 illustrates the rate of attainment of equilibrium. Lead was determined spectrophotometrically as dithizonate at pH 10·8 after suitable dilution of the saturated solution.

Extraction constant of lead dithizonate

K_{ex} can be obtained from distribution determinations with aqueous solutions having a pH less than 4 so that the concentration of $PbOH^+$ can be neglected ($[PbOH^+]/[Pb^{2+}] < 0·01$ at $aH^+ = 10^{-4}$). The concentration of $Pb(HDz)_2$ in the aqueous phase can be disregarded under these conditions, and there is no indication that $PbHDz^-$ need be taken into account.

Carbon tetrachloride solutions of dithizone were shaken mechanically for 15 min with perchloric acid-sodium perchlorate solutions of lead at 25 ± 1°. The phases were separated by centrifugation. Dithizone was determined spectrophotometrically in the carbon tetrachloride phase by absorbance measurement at 620 mμ, corrected for $Pb(HDz)_2$. Lead was usually determined in both phases with dithizone at pH 10·8 in the presence of nitrate and cyanide according to the procedure described later. When E was <0·02, lead in the aqueous phase was obtained by difference. The pH of the aqueous phase was determined with a glass electrode (Beckman model G pH meter).

The average of 17 values of K_{ex}, over the pH range 1·5–4·0, is 5·6 ± 0·3 (*ca.* 5% relative standard deviation) (Table V). Least squares treatment of the data gives the same value (Fig. 3). Five determinations of K_{ex} at $\mu = 0·3$ yielded an average of 5·8 ± 0·6. The largest source of error in the measurements is probably the pH determination. A deviation of 0·01 in the pH leads to a deviation of about 5% in K_{ex}. Calculations from the lead-dithizone-carbon tetrachloride data of Babko and Pilipenko[3] give a K_{ex} of 8·9; the ionic strength and composition of their buffer solutions are not specified. Koroleff[4] found K_{ex} = 2·4 at pH 4·1–5·6 in acetate-containing solutions.

TABLE V.—EXTRACTION CONSTANT (K_{ex}) OF LEAD DITHIZONATE, WATER-CARBON TETRACHLORIDE ($\mu = 0·1$)

pH	$[Pb(HDz)_2]_0 \times 10^5$	$[Pb^{2+}] \times 10^4$	$[H_2Dz]_0 \times 10^4$	K_{ex}
1·50	0·503	9·85	93·6	5·8
1·92[a]	0·805	9·82	46·5	5·5
2·39	0·783	96·7	5·03	5·1
2·42	0·711	96·7	5·03	5·5
2·44	0·974	96·7	4·61	6·2
2·48	1·08	96·7	4·41	6·25
2·77[a]	1·14	30·2	4·54	5·4
2·80	1·67	71·5	3·23	5·6
2·82	0·98	14·0	5·22	5·9
2·89[a]	0·570	9·71	4·22	5·7
3·02	1·13	9·79	4·41	5·4
3·03	1·13	9·79	4·47	5·0
3·08	1·33	9·77	4·00	5·9
3·09	1·32	9·77	4·04	5·5
3·72	0·72	0·364	3·52	5·8
3·92[a]	1·05	1·10	1·58	5·5
3·99	0·401	0·080	3·08	5·5
				Avg. 5·6 ± 0·3

[a] CCl_4 phase initially $5 \times 10^{-4}M$ in lead dithizonate (in addition to dithizone)

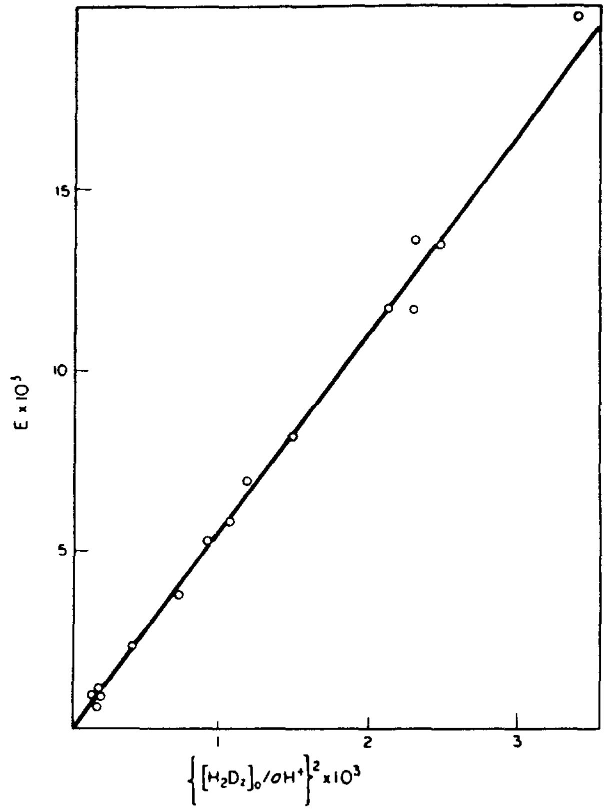

FIG 3.—Extraction coefficient of lead as a function of $\{[H_2Dz]_0/aH^+\}^2$ ($pK_{ex} = -0{\cdot}75$, $K_{ex} = 5{\cdot}6$).

Partition coefficient and water solubility of lead dithizonate

The partition coefficient $\frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = P$, was determined by obtaining the extraction coefficient of lead at pH 3·68–4·86 with the carbon tetrachloride phase saturated with dithizone and lead dithizonate.

Twenty-five ml portions of carbon tetrachloride saturated with dithizone (solid present) were shaken in a nitrogen atmosphere for 3 hr at 25 ± 1° with 200 ml of sodium perchlorate—perchloric acid solutions containing 0·65 ppm of lead ($\mu = 0{\cdot}1$). Lead was determined spectrophotometrically in both phases ($5{\cdot}7 \pm 0{\cdot}2 \times 10^{-6}M$ in carbon tetrachloride). A 10-cm absorption cell was used in determining the lead in the aqueous phase.

The lead species that must be considered in the aqueous phase are Pb^{2+}, $PbHDz^-$ and $Pb(HDz)_2$. From equation (7):

$$\frac{1}{E} = \frac{(aH^+)^2}{K_{ex}[H_2Gz]_0^2}(1 + k_{d1}[HDz^-]) + \frac{1}{P}$$

$\left(\text{because } k_{d2}(aH^+)^2[HDz^-]^2/K_{ex}[H_2Dz]_0^2 = \frac{1}{P}\right)$. If the term $\frac{(aH^+)^2k_{d1}[HDz^-]}{K_{ex}[H_2Dz]_0^2}$ can be neglected, a plot of $\frac{1}{E}$ against $\frac{(aH^+)^2}{[H_2Dz]_0^2}$ should give a straight line of slope K_{ex}. The data obtained seem to fulfill this condition (Fig. 4). The course of 10 of the 11 points can be represented quite well by a line which has a slope of 5·9 (theoretical 5·6). The intercept of the line is $\frac{1}{P} = 5{\cdot}0 \times 10^{-4}$, or $P = 2 \times 10^{3}$.

The value of k_{d1} has not been determined, but it is not likely to exceed 1×10^{7}. With this value of k_{d1} the slope of the plot of $\frac{1}{E}$ against $\frac{(aH^{-})^{2}}{[H_2Dz]_0^{2}}$ would be 4·85, which

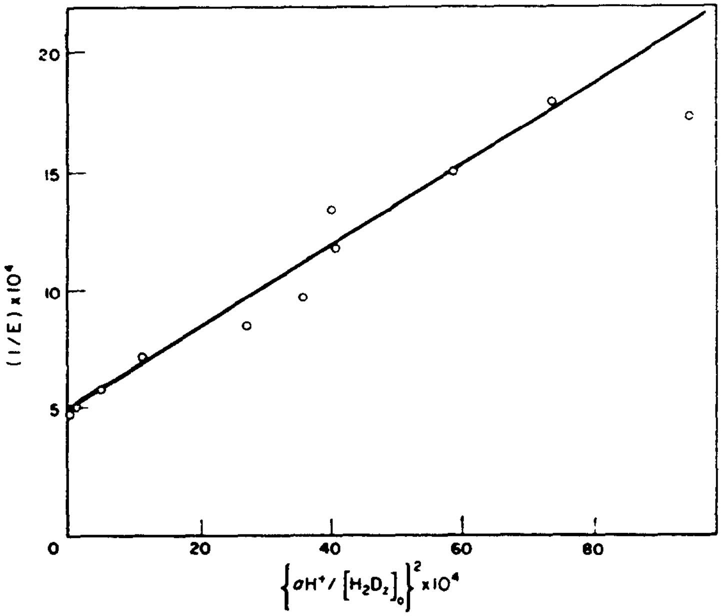

FIG. 4.—Reciprocal of extraction coefficient of lead dithizonate when carbon tetrachloride and aqueous phases are saturated with dithizone and lead dithizonate ($\mu = 0{\cdot}1$, 25°).

differs sufficiently from the slope of the experimental line to make the value implausible. But even if $k_{d1} = 1 \times 10^{7}$, an aqueous solution at pH 4·85 saturated with lead dithizonate and dithizone will be only *ca.* $1 \times 10^{-10}M$ in $PbHDz^{-}$ (and *ca.* $5 \times 10^{-11}M$ in lead ion) compared to *ca.* $3 \times 10^{-9}M$ in lead dithizonate. Thus P would be in error by about 5%, its true value then being $2{\cdot}1 \times 10^{3}$ instead of $2{\cdot}0 \times 10^{3}$ as based on the assumption that all other lead species than $Pb(HDz)_2$ are present in negligible concentrations in this solution. Because of the very low lead concentration in the aqueous phase, the spectrophotometric error in its determination is large, and P may be in error by *ca.* 25%.

From the solubility of lead dithizonate in carbon tetrachloride ($6 \times 10^{-6}M$), the calculated solubility in water (saturated with carbon tetrachloride) is $3 \times 10^{-9}M$.

The dissociation constant of lead dithizonate in water is given by the expression[5]

$$\frac{[Pb^{2+}][HDz^{-}]^{2}}{[Pb(HDz)_2]} = \frac{P_{Pb(HDz)_2}}{K_{ex}}\left(\frac{K_d}{P_d}\right)^{2} = \frac{2 \times 10^{3}}{5{\cdot}6} \times (1{\cdot}4 \times 10^{-9})^{2} = 7 \times 10^{-16}.$$

K_d and P_d are the primary ionisation constant and partition coefficient of dithizone. Because the solubility of lead dithizonate in water (saturated with carbon tetrachloride) is 3×10^{-9}, the solubility product constant of lead dithizonate in water is

$$[Pb^{2+}][HDz^-]^2 = 3 \times 10^{-9} \times 7 \times 10^{-16} = 2 = 10^{-24}.$$

Apparently the only other metal dithizonate whose dissociation constant and solubility product have been determined is primary copper^{II} dithizonate ($K_{diss} = 2 \times 10^{-23}$, $K_{sp} = 2 \times 10^{-31}$).[5] The great difference between the values of K_{ex} for lead and copper (10^{+10}) arises, as would be expected, from the much smaller dissociation constant of copper dithizonate. It may be noted that the solubility product constants of lead and copper dithizonates are much larger than those of the sulphides ($K_{sp\ PbS} = 10^{-27}$, $K_{sp\ CuS} = 10^{-41}$).

Extraction of lead from alkaline solutions

From weakly acidic and weakly basic aqueous solutions the extraction of lead is so complete with even a slight excess of dithizone that the distribution is hardly worth studying. Over a considerable pH range the extraction coefficient of lead is essentially equal to the partition coefficient of molecular lead dithizonate. If a $4 \times 10^{-5}M$ (0·001% w/v) dithizone solution in carbon tetrachloride is shaken with an equal volume of lead solution of such low concentration that the dithizone concentration is not significantly decreased by reaction with lead, the extraction coefficients may be calculated from equation (7), taking P as $2{\cdot}0 \times 10^3$ (Table VI).

TABLE VI

pH	E
6	$1{\cdot}4 \times 10^3$
7	$1{\cdot}9 \times 10^3$
8	$2{\cdot}0 \times 10^3$
9	$2{\cdot}0 \times 10^3$
10	$2{\cdot}0 \times 10^3$
11	$1{\cdot}7 \times 10^3$

From pH 7 to 10, E is essentially the same as P. Above pH 11, the extraction coefficient decreases rapidly because of the formation of biplumbite ion. Determination of the extraction coefficient in an alkaline solution allows the determination of the constant $[HPbO_2^-](aH^+)^3/[Pb^{2+}]$ and a check of equation (7) above pH ~11.

If lead species other than $HPbO_2^-$ can be neglected in the aqueous phase, the extraction coefficient of lead becomes

$$E = \frac{[Pb(HDz)_2]_0}{[HPbO_2^-]} = \frac{K_{ex}[H_2Dz]_0^2(aH^+)}{k_3}$$

$$= \frac{5{\cdot}6 \times (7 \times 10^8)^2[HDz^-]^2(aH^+)^3}{k_3} \text{ (because } [H_2Dz]_0 = 7 \times 10^8(aH^+)[HDz^-])$$

A plot of log E against log $\{(aH^+)^3[HDz^-]^2\}$ should give a straight line having the intercept log $\dfrac{2{\cdot}7 \times 10^{18}}{k_3}$.

Carbon tetrachloride solutions containing dithizone and lead dithizonate ($1{\cdot}5 \times 10^{-5}M$) were shaken under nitrogen with sodium hydroxide—sodium perchlorate solutions (from 0·01 to 0·009M sodium hydroxide, $\mu = 0{\cdot}1$) at 25 ± 1° for 5 min. The phases were separated by centrifugation and the concentration of HDz^- in the aqueous phase was determined by absorbance measurements at 475 mμ ($\varepsilon_{475} = 2{\cdot}40 \pm 0{\cdot}02 \times 10^4$). Lead was determined in the carbon tetrachloride phase by shaking with an aqueous ammonia-cyanide-sulphite mixture of pH 10·8 ($[HDz^-] = 10^{-4}M$) and measuring the absorbance at 520 mμ; it was determined similarly in an aliquot of the aqueous phase after acidifying to 0·16M with hydrochloric acid The pH was determined with an alkaline-range electrode. The values of aH^+ thus obtained agreed within 0·02 with the values calculated from the sodium hydroxide concentration and the activity coefficient $\gamma_{OH} = 0{\cdot}76$

From Table VII and Fig. 4, it is seen that the assumption of the presence of $HPbO_2^-$ as the only significant lead species in the pH range 11·9–12·8 is justified

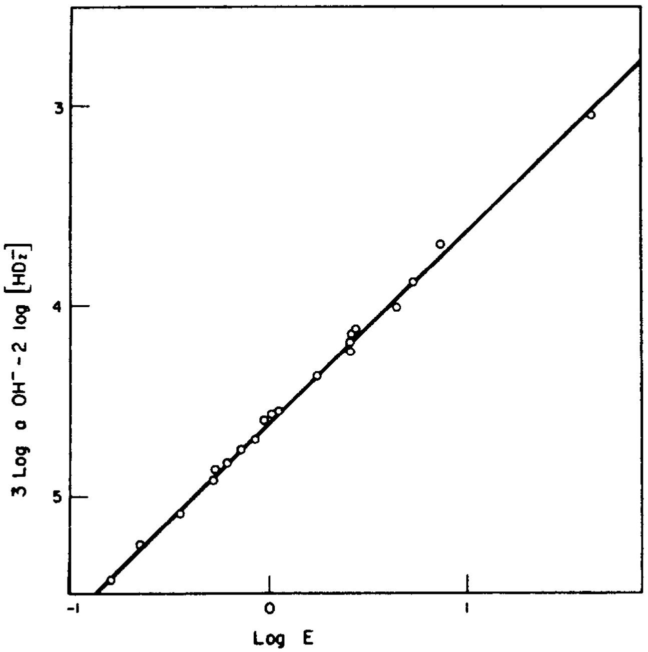

FIG. 5.—Extraction of lead dithizonate from basic solution (E as a function of aOH⁻ and [HDz⁻]).

TABLE VII.—EXTRACTION OF LEAD DITHIZONATE FROM ALKALINE SOLUTION

No. of detns.	pH	E	$K_{ex}\left(\frac{P_d}{K_d}\right)^2 \times \frac{1}{k_3} \times 10^{-46}$
6	11·88	2·68 – 44·5	4·2 ± 0·3
4	12·36	0·37 – 2·75	4·2 ± 0·4
5	12·58	0·29 – 2·9	4·2 ± 0·3
2	12·73	0·56 – 0·75	4·2
4	12·83	0·17 – 0·89	4·3 ± 0·1
Avg.		(0·17 – 44·5)	4·2 ± 0·3

The value of

$$k_3 = \frac{[\mathrm{HPbO_2^-}](\mathrm{aH^+})^3}{[\mathrm{Pb^{2+}}]}$$

derived from these distribution determinations is 7×10^{-29}. Because the factor 7×10^8 may be in error by *ca.* 7% (1:15), there may be an error of *ca.* 15% in k_3 from this source. The calculated value of $(\mathrm{aHPbO_2^-})(\mathrm{aH^+})^3/(\mathrm{aPb^{2+}})$ is $1{\cdot}5 \times 10^{-28}$, which agrees quite well with the value $1{\cdot}1 \times 10^{-28}$ of Garrett and coworkers.[2]

Extraction of lead dithizonate in the presence of cyanide and citrate

From equation (7), using the complex constant

$$\frac{[\mathrm{Pb(CN)_4^{2-}}]}{[\mathrm{Pb^{2+}}][\mathrm{CN^-}]^4} = 2 \times 10^{10}$$ (Kolthoff and Lingane[6])[*],

we calculate the following approximate values for the extraction coefficient of lead for systems in which the original carbon tetrachloride concentration of dithizone is 0·001% ($4 \times 10^{-5}M$) and 0·0001% ($4 \times 10^{-6}M$) and the phases are equal in volume, in the presence of cyanide (0·1M) and its absence (Table VIII).

TABLE VIII

pH	E			
	$4 \times 10^{-5}M$ $\mathrm{H_2Dz}$		$4 \times 10^{-6}M$ $\mathrm{H_2Dz}$	
	No $\mathrm{CN^-}$	0·1M $\mathrm{CN^-}$	No $\mathrm{CN^-}$	0·1M $\mathrm{CN^-}$
10	2×10^5	$1{\cdot}2 \times 10^5$	$1{\cdot}7 \times 10^3$	29
11	$1{\cdot}9 \times 10^5$	$1{\cdot}0 \times 10^5$	$2{\cdot}9 \times 10^3$	20
12	57	56	0·60	0·58

It has been assumed that the amount of lead present is so small that the dithizone concentration is not altered by reaction. Even at the relatively high concentration of 0·1M, cyanide should hardly affect the extractability of lead if the original dithizone concentration in the carbon tetrachloride is $4 \times 10^{-5}M$ and the phase volumes are the same or nearly so. However, if the original dithizone concentration is reduced ten-fold to $4 \times 10^{-6}M$ (equivalent to reaction of 90% of the dithizone in a $4 \times 10^{-5}M$ dithizone solution with lead), the effect of cyanide becomes marked.

The negligible effect of *ca.* 0·1M cyanide on the extraction of lead at pH 12 was verified experimentally. The distribution of lead between aqueous solutions, which were 0·01M in sodium hydroxide and 0·09M in potassium cyanide, and carbon tetrachloride-dithizone solutions (10^{-5}–$10^{-4}M$) was determined as described under the extraction of lead from alkaline solutions. The distribution was unaffected by the

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[*] The value of the constant, derived from the half-wave potential of lead in 1M potassium cyanide is approximate and tentative because of the question of the reversibility of the electro-reduction. It seems likely that the constant does not exceed 1×10^{11} (at $\mu = 0{\cdot}1$), for then, contrary to the experimental finding, cyanide would affect the extraction of lead at pH 12.

cyanide. Calculation of

$$\frac{K_{ex} \times (7 \times 10^8)^2}{k_3}\left(= \frac{[Pb(HDz)_2]_0}{[HPbO_2^-][HDz^-]^2(aH^+)^3}\right) \text{ gave the value } 4{\cdot}2 \times 10^{46},$$

the same as the average obtained in the absence of cyanide (Table VII). This agreement also indicates the absence of significant amounts of sulphide in the cyanide used.

The effect of citrate on the extraction of lead dithizonate up to a pH of approximately 8 is in accord with the formation of the complex ion PbCit.$^-$. Kety[7] has already shown that this ion forms in approximately neutral solution (pH 6·95–7·45) and his potentiometric data (corrected for incomplete dissociation of lead nitrate in his reference solution) give the value 1·7 × 10^{-6} for the constant $\{[Pb^{2+}][Cit^{3-}]\}/]PbCit^-]$. Below a pH of 7·5 the formation of this complex impedes the extraction of lead dithizonate (*cf.* Figs. 6 and 7) even when the concentration of dithizone is fairly high (0·001%) and the complex constant can thus be easily determined. Forty extraction coefficients determined in the pH range 4 to 6·8 lead to the value 1·85 × 10^{-6} for the dissociation constant (or 5·4 × 10^5 for $[PbCit^-]/\{[Pb^{2+}][Cit^{3-}]\}$) at $\mu = 0{\cdot}1$. The extractability of lead as a function of the citrate concentration was not studied systematically above pH 7·5, but it was observed that under analytical conditions the extraction of lead is as complete in the presence of citrate (0·01*M*) as in its absence (Figs. 6 and 7). There is considerable disagreement concerning the composition of the lead citrate complexes. According to Tikhonov,[10] $Pb(C_6H_5O_7)_2^{4-}$ is formed at pH 6–8 and $PbOH(C_6H_5O_7)^{2-}$ at pH 9–13. The formation of $Pb(C_6H_5O_7)_2^{4-}$ in approximately neutral solutions is not supported by the lead extraction data.

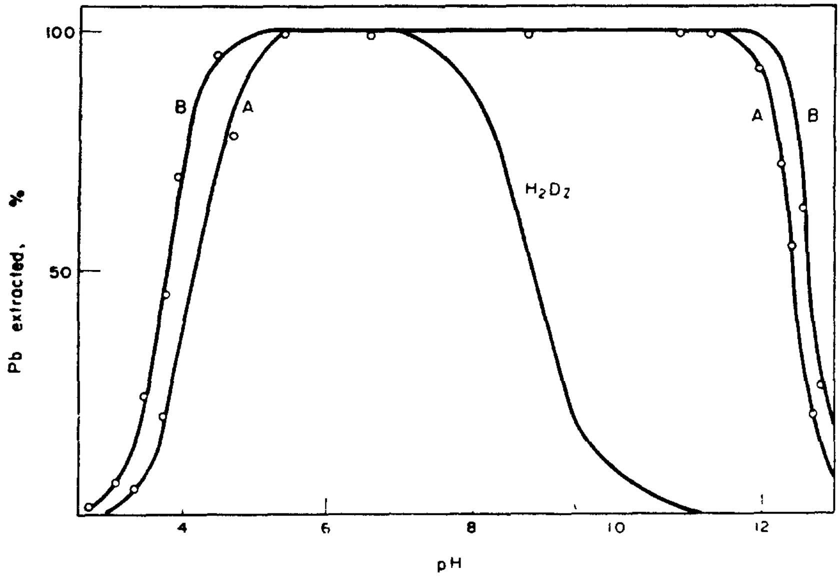

FIG 6 —Extraction of lead dithizonate and dithizone from sodium perchlorate solution The solid curves are the calculated curves for the extraction of lead (0 0625 mg in 25 ml aqueous solution, μ = 0 1) with 25 ml of 0 001% (w/v) dithizone in carbon tetrachloride (A), and with 25 ml of 0·002% (w/v) dithizone (B) The circles represent experimental values The extraction curve for dithizone ($_2$Dz) is calculated

Vouk and Weber[11] studied the extraction of lead dithizonate at pH 5–11 in the presence of citrate and cyanide with more dilute dithizone solutions than used in the present work. Decreasing extraction of lead from *ca.* 0·1*M* citrate solution was noted above a pH of about 8. (These authors obtained low and inconstant values for K_{ex} because they did not take into account the concentration of the lead citrate and cyanide complexes in the aqueous phase when formulating the expression for K_{ex}.)

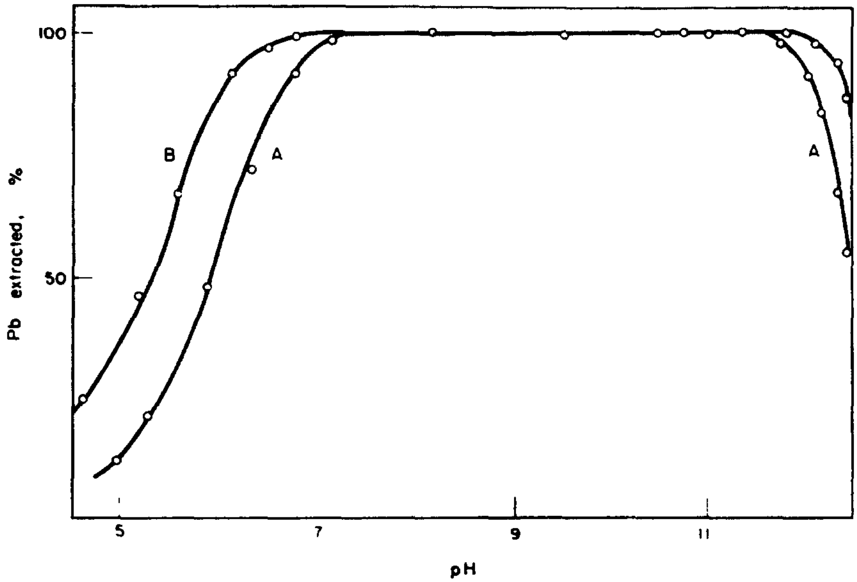

FIG. 7.—Extraction of lead dithizonate from sodium citrate-potassium cyanide solutions The solid curves are those calculated for the extraction of lead (0·0625 mg in 25 ml of aqueous solution, 0·01*M* in sodium citrate and 0·02*M* in potassium cyanide, $\mu = 0{\cdot}1$) with 25 ml of 0·001% (w/v) dithizone in carbon tetrachloride (A), and with 25 ml of 0·002% (w/v) dithizone (B). The circles represent experimental values

A few runs were made in the present work to test the effect of nitrate on the lead extraction. From 4 determinations of the extraction coefficient of lead at pH 3·0–3·5, with $[NO_3^-] = 0{\cdot}08$ and $\mu = 0{\cdot}1$, the average value 0·11 was obtained for $[Pb^{2+}] \times [NO_3^-]/[PbNO_3^+]$. Under analytical conditions the effect of nitrate is negligible.

ANALYTICAL CONSIDERATIONS

The spectrophotometric determination of trace amounts of lead usually involves two steps: first, the isolation and separation of lead by dithizone extraction from a basic citrate-cyanide solution, followed by the transfer of the lead to aqueous solution by shaking the carbon tetrachloride (or chloroform) phase with dilute acid; second, the determination proper, in which the aqueous phase is brought to a fixed, appropriate pH and lead is extracted with a standard dithizone solution and the absorbance of the organic phase is measured at a suitable wavelength. The final extraction is also made from a citrate-cyanide medium so that any small amounts of metals escaping separation in the first step will be inactivated. Sometimes sulphite is added to the aqueous solution to provide a reducing environment and lessen the possibility of oxidation of dithizone. Detailed directions for the procedure are available[12] and will not be repeated here We shall examine the effect of some factors in the procedure on the basis of the equilibria which have been discussed in a general way, beginning with the determination of lead after separation.

Determination of lead

The use of a carbon tetrachloride solution of dithizone allows spectrophotometric determination of lead by a mono colour method at a pH of approximately 11. At and near this pH, lead is virtually completely extracted into the carbon tetrachloride phase with a relatively slight excess of dithizone, whereas the latter is almost completely transferred to the aqueous phase. Other factors being the same, such a method for lead will be preferred to one in which some of the excess dithizone remains in the immiscible organic solvent, because the latter method will require a closer control of the pH and the concentration of the standard dithizone solution.

The theoretical extraction curves of lead—which are also the actual extraction curves—as a function of the pH are shown in Figs. 6 and 7, the former for a perchlorate solution, the latter for a citrate-cyanide solution. With equal volumes of aqueous and carbon tetrachloride phases initially containing, respectively, 2·5 ppm of lead ($1{\cdot}2 \times 10^{-5}M$) and 10 ppm (w/v) dithizone ($4 \times 10^{-5}M$), the calculated pH range for virtually complete (*ca.* 99%) lead extraction from $0{\cdot}01M$ sodium citrate —$0{\cdot}02M$ potassium cyanide is 7·5–11·5. The experimental and calculated values agree very well. The minimum pH for removal of 99% of the excess dithizone from the carbon tetrachloride phase is, from the relation

$$\frac{[\mathrm{HDz}^-]}{[\mathrm{H_2Dz}]_0} = \frac{1{\cdot}4 \times 10^{-9}}{\mathrm{aH}^+},$$

equal to 10·85. The pH range for a mono colour method with carbon tetrachloride as solvent is accordingly approximately 10·8–11·5. In practice one may aim for a pH of 10·8–10·9 to keep safely away from the sharp drop in extractability occurring above pH 11·5. The molar absorptivity of dithizone in carbon tetrachloride is only about 0·07 of that of lead dithizonate at 520 mμ, so that if a few per cent of the excess dithizone remains in the carbon tetrachloride little error results. The error incurred by a 0·2 unit departure from pH 10·8 can almost always be disregarded. Even if the standard curve is established at pH 10·6 and the determination is made at pH 11·0 with 0·001% dithizone, the error would be difficult to detect *ca.* 1% for 5 μg of lead and less for larger amounts of lead.

Because of the limited solubility of lead dithizonate in carbon tetrachloride, the amount of lead in the sample solution should preferably be such that the concentration of lead does not exceed 1·2 μg/ml in the carbon tetrachloride phase. Supersaturated solutions of twice, or even thrice, this concentration are, however, sufficiently stable to allow their use in the spectrophotometric lead determination. Because a carbon tetrachloride solution of lead dithizonate corresponding to 1 μg of lead/ml shows an absorbance of 0·32 at 520 mμ in a 1-cm cell, the concentration limit imposed by solubility does not limit the precision.

The accuracy attainable in the spectrophotometric determination of lead according to the recommended procedure[12] outlined is illustrated in Fig. 8. The accuracy of the reversion method (Irving and Butler[13]) is also represented. The two methods appear to be of comparable accuracy. By the use of a 10-cm cell (25 ml of carbon tetrachloride phase), 1 μg of lead can usually be determined to within 2%. With 5 μg of lead in 10 ml of carbon tetrachloride, the same accuracy is attainable in a 1-cm cell. By reducing the dithizone volume to 5 ml, similar accuracy should be attainable with 2–3 μg of lead

Carbon tetrachloride is superior to chloroform as a solvent in a mono colour method for lead, because the pH required to transfer 99% of the dithizone from chloroform into an equal volume of aqueous phase is *ca.* 12·5, which is in the range where biplumbite is formed to a considerable extent and *ca.* 10% of the lead is unextracted when a 0·001% dithizone solution is used.

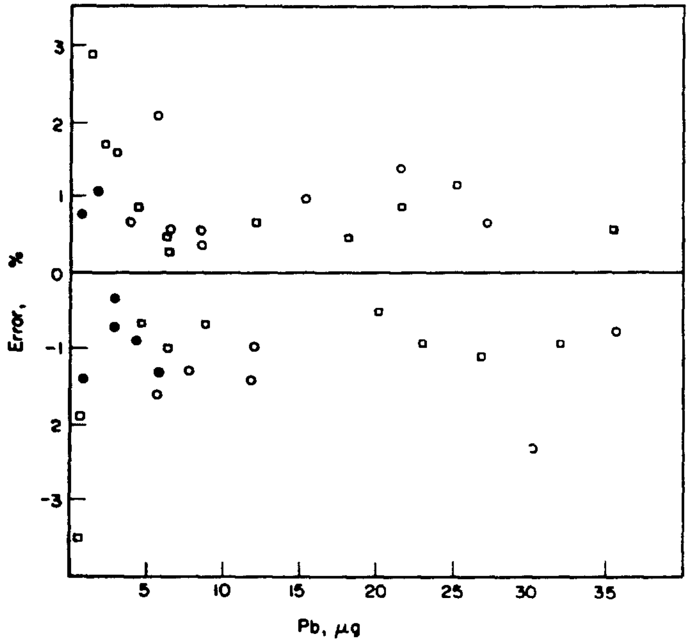

FIG. 8.—Accuracy of determination of lead by mono-colour dithizone method:
○—10 ml of aqueous phase, pH 10·8; 10 ml of 0·001 % dithizone in CCl_4; 1-cm cell, 520 mμ;
●—10 ml of aqueous phase, pH 10·8, 25 ml of 0·001 % dithizone in CCl_4; 10-cm cell, 520 mμ;
□—Reversion method: 10 of ml aqueous phase, pH 10·8; 25 ml of 0·001 % dithizone; reverted with 10 ml of 0·16*M* HNO_3; 1-cm cell (10-cm cell below 8 μg of Pb), 620 mμ.

Separation of lead

The separatory extraction with dithizone in carbon tetrachloride is usually carried out at pH 9–9·5 from an aqueous solution approximately 0·5*M* in citrate and 0·2*M* in cyanide. For a rough calculation of the lead extraction coefficient under these conditions we will use the equilibrium constants valid for an ionic strength of 0·1 and assume that $PbCit^-$ is the principal lead citrate species at pH 9. If the phases are equal in volume and the original concentration of dithizone in the carbon tetrachloride is 0·005% ($2 \times 10^{-4} M$), the extraction coefficient is

$$E = \frac{3{\cdot}8 \times 10^{-6}}{\underset{Pb^{2+}}{10^{-18}} + \underset{PbOH^{+}}{3 \times 10^{-16}} + \underset{Pb(OH)_2}{3 \times 10^{-18}} + \underset{HPbO_2^{-}}{7 \times 10^{-20}} + \underset{Pb(HDz)_2}{1{\cdot}9 \times 10^{-11}} + \underset{(PbCit^{-})}{3 \times 10^{-13}} + \underset{(PbCN)_4^{2-}}{8 \times 10^{-13}}}$$

$$= 1{\cdot}9 \quad 10^{3}$$

(The amount of lead present is taken to be so small that the concentration of dithizone is not significantly decreased.) The greater part of the lead in the aqueous phase is present as $Pb(HDz)_2$, so that the extraction coefficient is almost the same as the partition coefficient of lead dithizonate. Even when, as in practice, the volume of the carbon tetrachloride phase is 1/5–1/10 that of the aqueous phase, the recovery of lead should be satisfactory. Besides, a second extraction with a fresh portion of dithizone is always made so that there seems to be little likelihood of significant lead loss in the separation step, barring the formation of precipitates, such as calcium phosphate, which can carry down lead. A similar calculation for pH 10 gives $E = 1{\cdot}0 \times 10^{3}$, the lower value being from a smaller fraction of the cyanide being present as HCN at this pH. Because the dithizone extraction constants and the cyanide complex constants of a considerable number of metals are known, the extent of extraction of foreign metals from a cyanide medium can be calculated approximately when required.

The effect of sulphide, which appears to be a not uncommon impurity in alkali cyanides, on the extraction of lead cannot be precisely predicted because of incomplete knowledge of the Pb^{2+}—HS^{-}—S^{2-} system. However, on the assumption that Pb^{2+} is removed only as PbS, it can be demonstrated that very low concentrations of sulphide can have a serious effect on the dithizone extraction of lead. Taking K_{sp} of PbS as 10^{-27}, we obtain the following expression for the concentration of lead dithizonate in the carbon tetrachloride phase at pH 9 when solid lead sulphide is formed

$$[Pb(HDz)_2]_0 = \frac{(\Sigma[Pb] - \Sigma[S]) \pm \{(\Sigma[Pb]^{-} - \Sigma[S])^{2} + 4 \times 5{\cdot}6 \times 10^{-5}[H_2Dz]_0^{2}\}^{1/2}}{2}.$$

where $\Sigma[Pb] = [Pb(HDz)_2]_0 + ,q_{PbS}$ the latter term being the quantity of lead sulphide in moles obtained from 1 litre of aqueous lead solution, lead species in the aqueous phase being considered negligible in concentration compared to lead in the carbon tetrachloride phase; and $\Sigma[S] = [HS^{-}] + q_{PbS}$ (at pH 9, $[S^{=}] = 10^{-4}[HS^{-}]$). $\Sigma[Pb]$ and $\Sigma[S]$ are thus the initial molar concentrations of lead and sulphide (including HS^{-}) in the aqueous phase. The two phases are assumed to have the same volume. For example, if the initial dithizone concentration in carbon tetrachloride is $2{\cdot}0 \times 10^{-4} M$, $\Sigma[Pb] = 1{\cdot}0 \times 10^{-6} M$ and $\Sigma[S] = 6 \times 10^{-7}$ (corresponding to 19 μg ΣS per litre), $[Pb(HDz)_2]_0$ at pH 9 is calculated to be $8{\cdot}4 \times 10^{-7} M$ instead of $1{\cdot}0 \times 10^{-6}$ in the absence of sulphide. This illustration is given merely to show the possibility of serious interference by small amounts of sulphide. As long as the concentration of Pb^{2+} in the aqueous phase, in equilibrium with lead dithizonate in the carbon tetrachloride phase, is not great enough to cause the solubility product of lead sulphide to be exceeded, sulphide should have no effect on the extraction, provided other lead-sulphide species do not exist in the aqueous phase. But to assume that this is true would be naive.

Acknowledgment—We are grateful to the Proctor and Gamble Company for providing a summer fellowship for one of us (O B M) in 1955

Zusammenfassung—Die Gleichgewichtskonstanten der wichtigsten Reaktionen bei der Extraktion von Bleidithizonat aus waßriger Losung mit Tetrachlorkohlenstoff (0) wurden bei $\mu = 0.1$ gemessen

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{2+}][H_2Dz]_0^2} = 5{,}6 \pm 0{,}3 \quad (5{,}8 \pm 0\ 6 \text{ bei } \mu = 0{,}3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{Löslichkeit in } CCl_4}{\text{Loslichkeit in } H_2O} = \frac{6\ 10^{-6}}{3\ 10^{-9}} = 2\ 10^3$$

$$K_{diss} = \frac{[Pb^{2+}][HDz^-)^2}{[Pb(HDz)_2]} = 7\ 10^{-16}$$

$$K_{sp} = [Pb^{2+}][HDz^-]^2 = 2\ 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]} = 7\ 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{2+}][Cit^{2-}]} = 5{,}4\ 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{2+}][NO_3^-]} = 0{,}11$$

Der p_H-Bereich fur Extraktion von uber 99 % Blei unter analytischen Bedingungen (in Gegenwart von Citrat und Cyanid bei geringer Gleichgewichtskonzentration von Dithizon) ist 7,5–11,5 Cyanid in den üblichen Konzentrationen beeinträchtigt die Extraktion von Blei nicht wesentlich. Über p_H 10,85 werden uber 99 % des uberschussigen Dithizons von der organischen in das gleiche Volumen waßriger Phase extrahiert Ein p_H von 10,8–10,9 wird fur die Bestimmung von Blei mit einer Losung von Dithizon in Tetrachlorkohlenstoff empfohlen Anderung um etwa 0,2 p_H-Einheiten bringt keinen großen Fehler

Résumé—Les constantes d'équilibre des réactions principales mises en jeu dans l'extraction du dithizonate de plomb de solutions aqueuses parle tétrachlorure de carbone (0) ont été determinees à $\mu = 0{,}1$

$$K_{ex} = \frac{[Pb(HDz)_2]_0(aH^+)^2}{[Pb^{++}][H_2Dz_0^2]} = 5{,}6 \pm 0{,}3 \quad (5{,}8 \pm 0{,}6 \text{ à } \mu = 0{,}3)$$

$$P = \frac{[Pb(HDz)_2]_0}{[Pb(HDz)_2]} = \frac{\text{solubilité dans } CCl_4}{\text{solubilité dans } H_2O} = \frac{6 \times 10^{-6}}{3 \times 10^{-9}} = 2 \times 10^3$$

$$K_{diss} = \frac{[Pb^{++}][HDz^-]^2}{[Pb(HDz)_2]} = 7 \times 10^{-16}$$

$$K_{sp} = [Pb^{++}][HDz^-]^2 = 2 \times 10^{-24} \qquad \frac{[HPbO_2^-](aH^+)^3}{[Pb^{++}]} = 7 \times 10^{-29}$$

$$\frac{[PbCit^-]}{[Pb^{++}][Cit^{=}]} = 5{,}4 \times 10^5 \qquad \frac{[PbNO_3^+]}{[Pb^{++}][NO_3^-]} = 0{,}11$$

Le domaine de pH pour l'extraction de 99% du plomb dans des conditions analytiques (citrate et cyanure présents, faible concentration de dithizone à l'équilibre) est 7,5–11,5 Le cyanure aux concentrations où il a été utilisé ne diminue pas d'une manière importante l'extraction du plomb Au dessus de pH 10,85, 99% de la dithizone en excès est extraite du tétrachlorure de carbone par un égal volume d'eau. Un pH de 10,8–10,9 est recommandé pour la détermination du plomb avec une solution de dithizone dans le tétrachlorure de carbone. Une variation de 0,2 unité de pH de cette valeur ne cause qu'une légère erreur.

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THE ANODIC AMPEROMETRIC TITRATION OF LOW CONCENTRATIONS OF NITRITE WITH SULPHAMIC ACID OR CERIUM^{IV} ION*

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Summary—Nitrite at a concentration of approximately $6 \times 10^{-4}M$ in $0{\cdot}05M$ sulphuric acid can be titrated amperometrically at a rotating platinum micro-anode with sulphamic acid or cerium^{IV} ion Results with sulphamic acid are free from bias and have a standard deviation of about 1%. Titration with cerium^{IV} is less precise, giving results that are high or low according to the method used for end-point location, but is applicable to lower nitrite concentrations than is titration with sulphamic acid.

STOCK and BJORK[1] found that low concentrations of nitrite in acid media can be titrated amperometrically with potassium permanganate solution at a rotating platinum micro-anode. This titrant is not electroactive at potentials from $+1{\cdot}05$ to $+1{\cdot}10$ V with reference to a saturated calomel electrode (S.C.E.), but nitrite under these conditions yields an oxidation limiting current that is proportional to the concentration of nitrite.[2] A titration curve of "L" type is therefore obtained. The present work concerns the application of sulphamic acid and cerium^{IV} ion as alternatives to permanganate in the titration of nitrite by this method.

Hirozawa and Brasted[3] have demonstrated that amperometric titration with sodium nitrite solution at a dropping mercury cathode permits the determination of sulphamic acid in concentrations from 4×10^{-4} to $5 \times 10^{-3}M$. These workers used a hydrochloric acid-potassium chloride supporting solution that contained a low concentration of uranyl ion. In the presence of this ion, nitrite gives a well-defined reduction wave; the limiting current measured at a potential of $-1{\cdot}2$ V *vs.* S.C.E. is proportional to the concentration of nitrite. Sulphamic acid is not reduced under these conditions, so that the titration curve is of "reversed-L" form.

Kolthoff, Harris, and Matsuyama[4] discovered that the simultaneous reduction of uranyl ion catalyses the reduction of nitrate ion at a dropping mercury electrode. Keilin and Otvos[5] found that nitrite in acid solution yields the same reduction wave as nitrate in the presence of uranyl ion. Any appreciable concentration of nitrate that is introduced into the supporting solution used for the amperometric titration of sulphamic acid by Hirozawa and Brasted's method therefore gives a high background current and hence poor end-point discrimination. Hirozawa and Brasted found that the presence of nitrate in the titrant solution gives a positive slope to the pre-equivalence portion of the titration curve and causes low results. The error is tolerable only if the nitrate : nitrite molar ratio does not exceed 2 : 100. Interference is, of course, caused by phosphate and other substances that precipitate uranyl

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* Taken largely from the thesis submitted by Robert Gesler Bjork in partial fulfilment of the requirements for the M.S. degree.

ion. Because the presence of uranyl ion is not required when changes in the concentration of nitrite are measured in terms of its *oxidation* limiting current, it should be possible to perform nitrite-sulphamic acid titrations at a rotating platinum anode without interference by nitrate or phosphate.

EXPERIMENTAL

Apparatus

Amperometric titration assembly Titrations were performed in a 100-ml tall-form beaker. This was closed with a cover that carried the nitrogen dispersal tube and the junction tube that accommodated the salt bridge of a large saturated calomel electrode. Holes in the cover were provided for the insertion of the rotating platinum electrode and the jet of the Gilmont 1-ml microburette; these holes were large enough to allow free escape of nitrogen. Except when current readings were taken, the solution in the beaker was stirred at a steady rate of about 200 rpm by means of a small glass-covered magnetic stirrer bar.

Rotated at 600 rpm by a Sargent Synchronous Rotator, the platinum wire micro electrode gave an average current of 14·8 μA in $2 \times 10^{-4}M$ nitrite in deoxygenated 0·05M sulphuric acid, when maintained at a potential of +1·05 V *vs.* S.C.E. The actual sensitivity was poorly reproducible and sensitive to electrode pretreatment However, changes in sensitivity that occurred from run to run did not affect the linearity of the current-to-nitrite concentration relationship within a given run The electrical equipment was similar to that used previously,[6] a shunt-equipped Cambridge Spot galvanometer of maximum sensitivity 170 mm per μA was used to measure the current.

Reagents

Sodium nitrite solution: Prepare an approximately 0·1M solution and standardise against permanganate solution by thiosulphate titration of iodine liberated by the excess of permanganate.[7] This method was used to permit the direct comparison of the results of the present work with those obtained in the amperometric titration of nitrite with permanganate.[1]

Standard (approximately 0·1M*) sulphamic acid solution:* Prepare by the direct weighing of the recrystallised and dried analytical-grade reagent.[8]

Cerium^{IV} *ammonium sulphate solution*· Prepare an approximately 0·1M solution in 3% (v/v) sulphuric acid and standardise against arsenious oxide [8]

Osmium catalyst solution Prepare approximately 0·01M osmium tetroxide in 0·05M sulphuric acid.

Anodic voltammetry of sulphamic acid

The current-voltage curve of $1 \times 10^{-3}M$ sulphamic acid in 0·05M sulphuric acid at a rotating platinum anode was found to be essentially the same as that of 0·05M sulphuric acid alone.

Pretreatment of the platinum electrode

Store the platinum electrode in approximately 10M nitric acid. Before use, rotate in deoxygenated 0·1M perchloric acid and maintain at zero potential (*i.e.*, short-circuit to the S.C.E.) until the current becomes very small [9] Rinse well and prepolarise for 10 min at the chosen potential in a solution of composition similar to that to be titrated

Titration of nitrite with sulphamic acid

Place 50 ml of 0·05M sulphuric acid in the titration apparatus and deoxygenate with a stream of nitrogen, this step improves the precision of the titration. Stop the gas stream and introduce the nitrite solution from a microburette until the concentration is about $5 \times 10^{-4}M$. Titrate immediately with small increments of 0·1M sulphamic acid at a potential of +1·05 V *vs.* S.C.E. (or at +1·10 V if the nitrite concentration is greater than about $6 \times 10^{-4}M$). Take current readings 15–20 sec after each titrant addition Temporarily increase the interval to about 40 sec when near the end-point

Titration of nitrite with cerium^{IV} *ion*

Proceed as described for the titration with sulphamic acid, but add 3 drops of osmium catalyst before titrating with 0·1M cerium^{IV} solution

RESULTS AND DISCUSSION

Titration with sulphamic acid

Well-defined linear L-shaped titration curves were obtained at nitrite concentrations that were not less than $6 \times 10^{-4}M$. The descending arm of the curve became very slightly bowed when the nitrite concentration was lowered to 4 × $10^{-4}M$. This malformation increased as the initial nitrite concentration was lowered further, and became excessive when the titration of 1 × $10^{-4}M$ of nitrite was attempted. Results for sets of six replicate titrations of nitrite are given in Table I. In the concentration range 6 × 10^{-4} to 1 × $10^{-3}M$ of nitrite, the standard deviations are a little larger than those obtained with permanganate as the titrant.[1] Permanganate, but not sulphamic acid, can be used to titrate nitrite at a concentration as small as 5 × $10^{-5}M$. These effects are almost certainly caused by differing speeds of reaction; the titration of a given concentration of nitrite can be performed considerably more rapidly with permanganate than with sulphamic acid.

TABLE I.—TITRATION WITH 0·0995*M* SULPHAMIC ACID

Nitrite in 50 ml of 0·05*M* sulphuric acid Six titrations at each concentration of nitrite.

Nitrite concn., × 10^4M	Potential, *V*	Average error, %	Standard deviation, %
10·00	+1·10	0·0	0·9
8·00	+1·10	0·0	1·0
6·00	+1·05	0·0	0·9
4·00	+1·05	−2·5	2·4

Low results, obtained when permanganate is the titrant and attributed to the instability of nitrite in acid solution,[1] were generally absent in titrations with sulphamic acid. The absence of bias in most of the results given in Table I probably arises from the fortunate compensation of the negative error through loss of nitrous acid by positive errors arising from the non-stoichiometry of the reaction

$$HNO_2 + H_2NSO_3H \rightarrow H_2SO_4 + N_2 + H_2O$$

and the effects of the oxides of nitrogen that are produced in side reactions.[10]

The titration of 1 × $10^{-3}M$ nitrite in 0·05*M* sulphuric acid-0·1*M* potassium nitrate or 0·05*M* sulphuric acid-0·1*M* phosphoric acid gave results that were within one standard deviation of those given in Table I. There is thus no evidence of interference by massive amounts of nitrate or phosphate ion.

Titration with cerium^{IV} ion

The titrations were all performed at a potential of +1·05 V *vs.* S.C.E. The results exhibited somewhat larger standard deviations than those obtained in the titration of nitrite with permanganate or sulphamic acid. As indicated in Fig. 1, the excess titrant line (which is horizontal in titrations with permanganate or sulphamic acid) has a definite negative slope. An inspection of the current-voltage curves at a rotating platinum electrode of the cerium^{IV}–cerium^{III} couple in sulphuric acid medium[11] suggests this type of behaviour. Positive errors were obtained when the end-point was located by the usual extrapolation of the linear portions of the branches of the titration curve (construction A). An alternative method of location (construction B) shown in Fig. 1 is to produce the descending branch of the titration curve to cut the residual current line (*i.e.*, the horizontal line drawn through the current reading

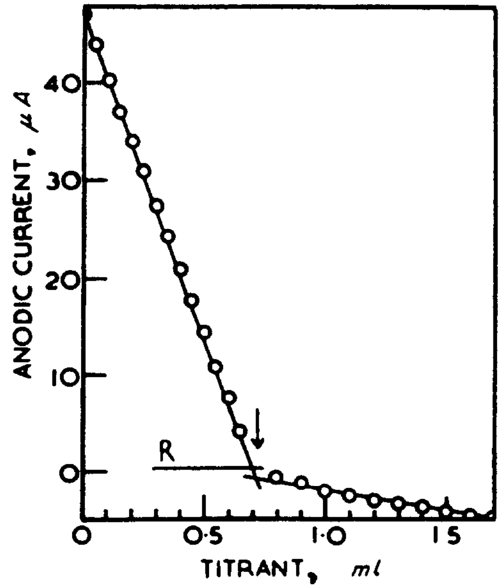

FIG 1 —Titration of 50 ml of 6 00 × $10^{-4}M$ nitrite with 0 0820M cerium^{IV}
The arrow indicates the stoichiometric end-point
R is the residual current line

TABLE II —TITRATION WITH 0·820M CERIUM^{IV}

Nitrite in 50 ml of 0 05M sulphuric acid Applied potential, +1 05 V *vs* S C.E. Six titrations at each concentration of nitrite

Nitrite concn, × 10^5M	Construction A		Construction B	
	Average error, %	Standard deviation, %	Average error, %	Standard deviation, %
60 0	−1 4	1 4	−1 9	2 4
40 0	−0 2	0 8	−2 6	3·1
20 0	+2 9	2 6	−2 5	3·0
10 00	−0 8	5 2	−3 3	2·4
8·00	−2 6	2 5	−0 9	1·9
6 00	−5 5	2 4	−0 4	2·7
4 00	−5 7	5 0	−5 2	4 1

obtained in the absence of both nitrite and titrant). The two constructions give results that are comparable in over-all precision and accuracy (Table II). However, neither set of results is free from bias; the over-all average errors for 42 titrations of nitrite in the concentration range 4 × 10^{-5} to 6 × $10^{-4}M$ were +2·7 and −2·4% for constructions A and B, respectively.

From the practical point of view, the negative bias of the results obtained by use of construction B is in line with the known instability of nitrite in acid solution. Readings beyond the end-point are not utilised, so that the determination is expedited. However, the residual current must be frequently checked.

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Zusammenfassung—Nitrit kann in einer Konzentration um 6 10^{-4} m in 0,05 m Schwefelsäure amperometrisch an einer rotierenden Platinmikroanode mit Amidosulfonsaure oder Cer(IV) titriert werden. Die Ergebnisse mit Amidosulfonsaure sind frei von systematischen Abweichungen und haben eine Standardabweichung von etwa 1% Die Titration mit Cer(IV) ist weniger genau, gibt je nach der Endpunktsbestimmung zu hohe oder zu niedrige Ergebnisse, aber sie ist bei niedrigeren Nitritkonzentrationen anwendbar als die Titration mit Amidosulfonsaure.

Résumé—On peut titrer ampérométriquement les nitrites, à une concentration d'environ 6 × 10^{-4} M, en acide sulfurique 0,05 M, avec l'acide sulfamique ou l'ion cérium (IV), au moyen d'une microanode rotative en platine. Les résultats obtenus avec l'acide sulfamique sont exempts de divergences, et présentent un écart type d'environ 1%. Le dosage au cérium (IV) est moins précis, et donne des résultats trop élevés ou trop faibles selon la méthode employée pour déterminer le point final, mais il est applicable à des concentrations en nitrite inférieures à celles qu'autorise le dosage à l'acide sulfamique

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EFFECTS OF ADSORBED FILMS OF CAMPHOR AND THYMOL ON KINETICS OF THE TITANIUM^{IV}–TITANIUM^{III} ELECTRODE REACTION

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Summary—The effect of contamination of a mercury surface by camphor and thymol on the standard rate constant of the titanium^{IV}–titanium^{III} half reaction in 1*M* tartaric acid has been determined by means of voltage-step and impedance methods. Complications arising from specific adsorption of the electronegative species proved more disturbing to the impedance method than to the voltage-step method. A linear decrease of rate constant with surface coverage is indicated.

IT has long been known that adsorption of many surface active substances can affect an electrochemical reaction. The various important features of this problem have already been reviewed by several authors.[1-4] In this work the effect of camphor and thymol, substances of different surface active characteristics, on the Ti^{IV}/Ti^{III} redox reaction has been investigated by measuring the standard rate constants of the reaction in the presence of these surfactants. It was desired to compare the voltage-step method with the impedance method to obtain the rate constant of the reaction.

The electroactive species employed were chosen so that the redox potential of the couple was located as close to the electro-capillary maximum (e.c.m.) potential as possible. No surface-active anion was included in the supporting electrolyte. In such circumstances perturbation of the double layer charge can be neglected. The potential of maximum adsorption can generally be expected to be located close to the e.c.m. potential of the system. However, such a condition has not been fully satisfied by the systems employed. Hence, the electrode coverage was calculated from differential and integral capacity and used for the interpretation of the observations.

EXPERIMENTAL

Apparatus

Cell· The cell was essentially a 100-ml lipless beaker with a rubber stopper which had been bored with a variety of holes to admit a dropping mercury electrode, a stirring rod, a gas disperser, a porous Vycor tube and a glass-frit tube. The cell solution was electrically connected to the S.C.E through an agar bridge inserted into a glass-frit tube.

Dropping mercury electrode (*d.m.e.*): Because it was essential for the voltage-step method to keep the total resistance of the cell circuit as low as possible, a low resistance d.m.e. was employed A piece of glass tubing was sealed to 0·04-mm i.d. marine barometer tubing, then drawn out and cut to give a fine tip at one end. Contact was made through a platinum wire sealed into a portion of large bore. The electrical resistance of this type of electrode was in the range of 1·0 to 1 5 Ω.

A sufficiently long life of each mercury drop and small "m" value as well as a fine tipped capillary[5]

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were required to allow the impedance measurements to be carried out satisfactorily A capillary tube with a pointed tip to meet these requirements was made by stretching under heat an ordinary commercial polarographic capillary and cutting so as to provide a sharp end The "m" value was $1{\cdot}880 \times 10^{-4}$ g/sec at the mercury head of 70 cm, and the drop life was long enough for the experimental use.

Voltage-step apparatus: The electrical circuit and apparatus were quite similar to those of Laitinen and Roe.[6,7] A voltage divider, a three-way mercury relay switch and an oscilloscopic recording divider were essential parts of the whole assembly

Impedance Bridge: The assembly used for the a.c. impedance-bridge method consisted of an oscillator, a variable resistance and capacitance, a potentiometer, a mechanical drop-detacher controlled by a timing device, a cathode-ray oscilloscope and a cell containing the solution in question. The entire setup of the assembly, except the cell, has been exhaustively described [8]

Solutions

All aqueous stock solutions were prepared by dissolving reagent-grade materials, with or without further purification, in distilled water.

H_2SO_4 (1 00*M*) *and* NaOH (2 00*M*). Slightly more concentrated solutions were prepared by dissolving reagent-grade materials in water. These solutions were diluted with water until they gave the required values of concentration in the titration with standard alkali and acid solutions, respectively.

Titanium^{IV} (0·0500*M*): A weighed amount of titanium dioxide was converted into soluble sulphate by fusion with $KHSO_4$, and was dissolved in dilute H_2SO_4. Titanium was precipitated with NaOH, and then redissolved in dilute H_2SO_4. The procedure was repeated, and the final precipitate was dissolved in 1·00*M* H_2SO_4 to make up the required volume.

Tartaric Acid (2*M*). *d*-Tartaric acid was purified by repeated recrystallisation from water A weighed amount was dissolved in water.

Camphor (0·1*M*): *d*-Camphor was dissolved nearly to saturation in methanol and crystallised out by adding an equal volume of water. The procedure was repeated. Camphor thus treated was submitted to further purification by sublimation under reduced pressure

A weighed amount of purified camphor was dissolved in methanol and then water was added dropwise from a burette until the volume of water added was equal to that of methanol The solution was made up to volume with a 1:1 mixture of methanol and water.

Thymol (0·1*M*): A weighed amount of thymol, which had been purified by two-fold distillation under reduced pressure, was dissolved in a mixture of methanol and water (1 · 1), and the solution was left standing overnight until it became clear.

Mercury: Mercury was purified by distillation under reduced pressure

Ti^{IV}–Ti^{III} *mixed solution* An equimolar mixture of Ti^{IV} and Ti^{III}, 10 mM in total concentration, was extensively used for the rate determinations. A solution 10 mM in Ti^{IV}, 1*M* in *d*-tartaric acid and 0·2*M* in sodium sulphate was prepared by mixing the stock solutions. A mixture of Ti^{IV} and Ti^{III} was made just before use by electrolysing the Ti^{IV} solution, with constant stirring, at a constant current of about 10 mA between a mercury-pool cathode and a platinum-wire anode inserted into a porous Vycor tube. The solution had been completely deaerated by passing nitrogen, and a thick nitrogen blanket was maintained over the solution during the electrolysis. Under such conditions electrolysis proceeded without an appreciable amount of evolution of hydrogen gas. The concentration ratio of Ti^{IV} to Ti^{III} was determined polarographically. Characteristics of the Ti^{IV} solution were as follows: pH = $1{\cdot}6_5$, $E_{1/2} = -0{\cdot}64$ V *vs.* saturated calomel electrode (S.C E), and the diffusion current constant,

$$I = \frac{i_d}{Cm^{2/3}t^{1/6}} = 1{\cdot}34.$$

Blank solution: A solution 1*M* in *d*-tartaric acid and 0·2*M* in sodium sulphate was prepared from stock solutions for the differential capacity measurement. The pH of the solution was $1{\cdot}5_8$.

Special care was taken in introducing thymol and camphor into the cell solution because of their low solubility and high volatility. Injection of a 0 1*M* 50% methanol solution of surfactant with a microlitre syringe pipette was satisfactorily used for this purpose.

Measurement procedure

A. *Voltage-Step Method:* Each time 60 ml of the Ti^{IV}–Ti^{III} solution were used It was important to keep a thick nitrogen blanket over the solution in the course of the measurement [5] A voltage step, usually about 5·5 mV, was applied between the mercury pool and the d.m e. through a three-way mercury relay switch. Because the faradaic current to be determined was quite low, a Tektronix 532 oscilloscope, equipped with an E-type high gain a.c. differential preamplifier, was used for obtaining the current-time relation The trace photographed on Polaroid-3000 film was reproducible. Sweep rates of 20–50 μsec. cm^{-1} were chosen because the current of interest was expected to be displayed for less than 500 μsec The faradaic current was obtained by simply subtracting the charging current from the observed current, the former being given by the equation $i_{ch} = V/R_T \times \exp(-t/R_TC_{dl})$, where V, R_T and C_{dl} are the voltage, the total resistance and the double layer capacity, respectively. The total resistance thus obtained was not as reproducible as other quantities, especially in the presence of high concentration of a surfactant, because of the rather large rise time of the preamplifier. Therefore R_T and C_{dl} were determined by means of an a.c. impedance bridge at 1,000 cycles. The resistance was varied from 53 to 56 Ω, corresponding to the change of distance between the electrodes, 2 5 to 5 5 mm. The time between the instant at which the preceding droplet fell from the capillary and the instant at which the voltage step was applied was measured with a 1/100-second electric stop-clock. It was usually 8–10 sec. The area of a drop was calculated assuming its sphericity. There was no perceptible difference in the rate constant between 8 and 10 sec. The equations (2) and (7) of Vielstich and Delahay[11] were used to determine the kinetic parameters of the reaction from the faradaic current at zero time, $i_{t=0}$. Although the maximum of the faradaic current was taken as $i_{t=0}$ instead of estimating an "effective zero time,"[6,7] no appreciable error could be introduced by this procedure, because the slope of the i *vs.* $t^{1/2}$ plot was very small, as expected.

B. *Impedance method. Blank solution.* All the electronic instruments were warmed up for more than 20 min before use A single frequency of 1,000 cps was employed for the measurement of differential capacity throughout the range of polarisation potential from +0 2 to −1·4 V (*vs.* S.C E), while frequencies 200–500 cps. were employed at the certain potentials which corresponded to the equilibrium potential of the titanium couple Because the detailed description of the operation has been provided by Sherman[9] a brief comment will suffice here

As differential capacity data are needed after exactly 8 0 sec of the growth of a mercury drop, the timing device was so adjusted that the mechanical drop-detacher was operated at exactly 9 0-sec intervals. At the same time, the horizontal stretch of the image on the oscilloscopic screen was extended to 9·0 divisions. This resulted in a scanning rate of 1·0 division per sec on the screen. When the impedance of the electrode was balanced at 8 0 sec of drop-life, the vertical amplitude of the image on the screen was reduced to a point only at the eighth division line.

Reactants. An identical procedure was employed in determining the impedance of the electrode as was previously described for the blank solution. However, in the presence of the redox couple the dropping mercury cathode was maintained at a constant potential by means of a polarisation unit[8–10] Only the results obtained at the lower frequencies were analysed because of their better reliability.

RESULTS AND DISCUSSION

Determination of surface coverage

It is first necessary to consider the evaluation of differential double-layer capacity measurements in terms of the surface concentration of adsorbate. If the potential of the redox couple, the electrocapillary maximum, and the potential of maximum adsorption of surfactant were all coincident, the fractional coverage could be calculated from the equation

$$\theta = (C_1 - C)/(C_1 - C_2)$$

where C, C_2 and C_1 are, respectively, the corresponding differential capacities of the partially covered surface, the fully covered surface and the bare surface. From Figs. 1 and 2 the potentials of maximum adsorption of camphor and thymol have been estimated as −0·70 V and −0·55 V, respectively, whereas the redox potential of the Ti couple, at which the coverage has to be estimated, is located at −0·63 V *vs.* S.C.E. It should be better in such circumstances to make use of the integral capacity or the charge density instead of the differential capacity for the calculation of θ. Recently, Breiter and Delahay[12] reported that Frumkin's expression[13] for θ in terms of the charge density gave a good agreement with the thermodynamic surface excess over the entire range of potential including the potential of desorption. Thus, the two kinds of covered fraction were calculated, one from the integral capacity, denoted by θ, and the other from the differential capacity θ'; these are illustrated in Figs. 3a and 3b, and are tabulated in Table I. Integration of the differential capacity was

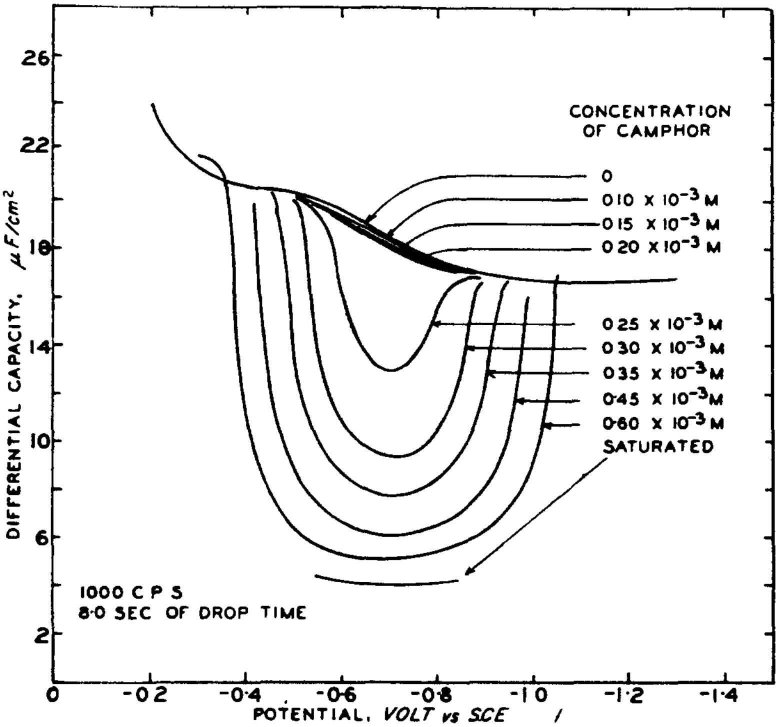

FIG 1 —Differential capacity in the presence of camphor.

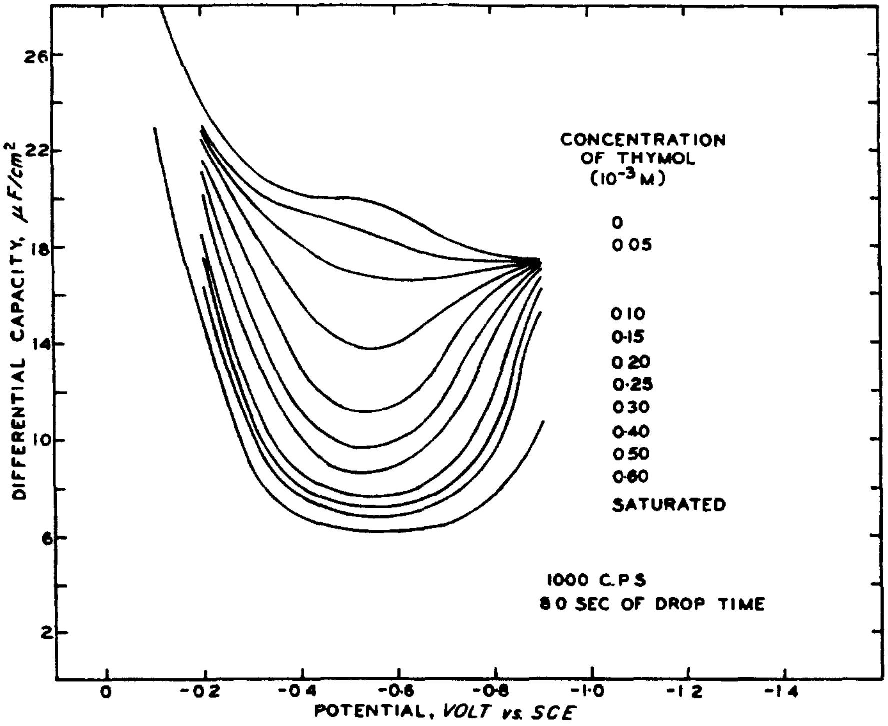

FIG 2.—Differential capacity in the presence of thymol

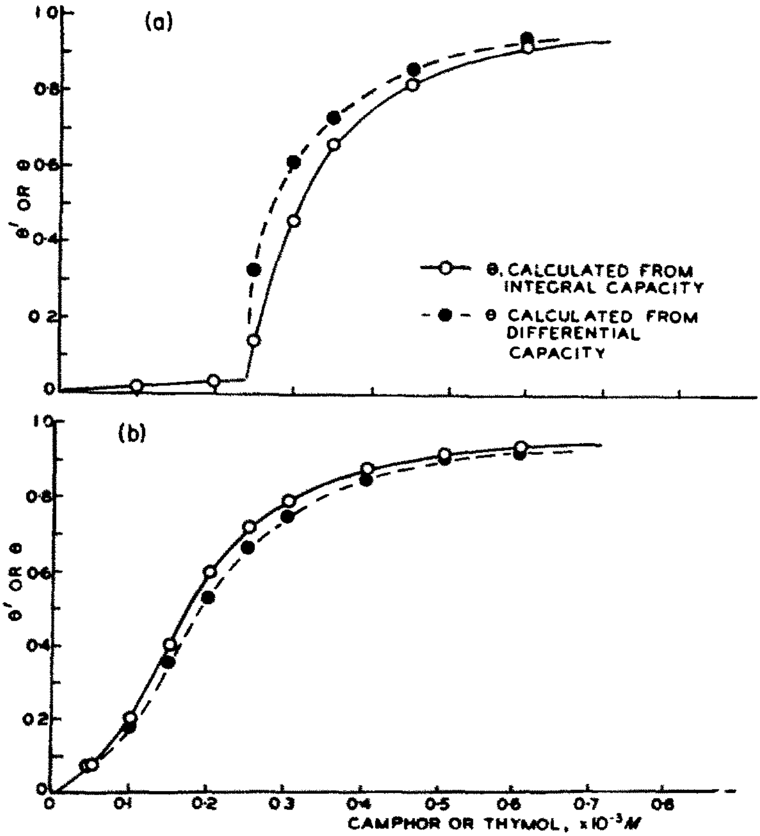

FIG. 3a.—Surface coverage *vs.* concentration of camphor.
FIG. 3b.—Surface coverage *vs.* concentration of thymol

TABLE I.—DOUBLE LAYER CAPACITY AND SURFACE COVERAGE AS A FUNCTION OF CONCENTRATION OF SURFACTANT AT −0·64 V *vs.* S C E.
C, differential capacity; *K*, integral capacity;
θ', coverage calculated from differential capacity;
θ, coverage calculated from integral capacity.

	Camphor				Thymol			
Conc., *mM*	*C* µF. cm^{-2}	*θ'*	*K* µF. cm^{-2}	*θ*	*C* µF cm^{-2}	*θ'*	*K* µF. cm^{-2}	*θ*
0·00	19·0	0·00	19·7	0·00	19·0	0·00	19·5	0·00
0·05	—	—	—	—	18·1	0·07	18·4	0·08
0·10	18·8	0·01	19·5	0·01	16·7	0·18	16·7	$0·20_5$
0·15	18·7	0·02	19·4	0·02	14·5	0·36	14·0	0·41
0·20	18·5	0·03	19·3	0·03	12·2	0·54	11·5	0·60
0·25	14·1	0·33	17·6	0·14	10·4	$0·67_5$	9·9	0·72
0·30	9·9	0·61	14·3	0·46	$9·3_5$	0·76	$8·8_5$	0·80
0·35	$8·1_5$	0·73	9·4	0·66	—	—	—	—
0·40	—	—	—	—	8·0	$0·86_5$	$7·6_5$	0·89
0·45	6·2	0·86	7·0	0·82	—	—	—	—
0·50	—	—	—	—	7·5	0·91	7·2	0·92
0·60	5·1	$0·93_5$	5·4	0·92	7·1	0·94	6·8	0·95
Sat.	4·2	1·00	4·2	1·00	6·2	1·00	6·2	1·00

performed graphically between the redox potential and the e.c.m. potential of the blank solution. The latter was estimated as —0·52 V from the potential dependence of the drop time. The differential capacity at 1,000 cycles was used for the integration because the frequency dispersion of the capacity at —0·64 V over the range 200–5,000 cycles was less than 3% with all of the concentrations of the surfactant solution. In Fig. 4, the differential capacity has been plotted against the coverage calculated from the integral capacity. It can be seen that the error caused by using differential capacity calculations is not much in the case of thymol, as expected.

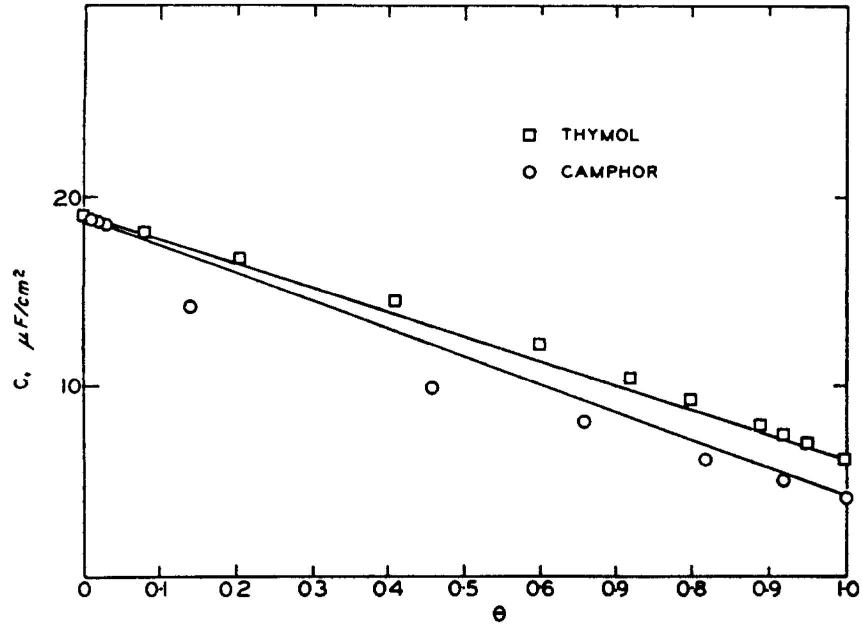

Fig. 4.—Differential capacity *vs.* coverage calculated from integral capacity.

At camphor concentrations less than 0·35 mM, the measured double layer capacity per unit of electrode area decreased slightly during drop growth. The maximum rate of decrease at —0·64 V was observed at a concentration of 0·25 mM, where the value decreased from 16·0 μF. cm^{-2} at 2-sec drop age to 14·0 μF. cm^{-2} at 8-sec drop age. This indicates that adsorption equilibrium had not quite been attained during growth.

Determination of rate constants by voltage-step method

In the absence of surfactant, the Ti^{IV}/Ti^{III} couple had the following kinetic parameters: the standard rate constant $k = 1{\cdot}7_2 \pm 0{\cdot}05 \times 10^{-3}$ cm. sec^{-1} at $0{\cdot}63_5$ V *vs.* S.C.E. and the cathodic transfer coefficient $\alpha = 0{\cdot}48$. The number of electrons transferred at the rate-determining step has been assumed as unity. In Figs. 3, 5 and 6, the rate constant and the differential double-layer capacity at the redox potential have been plotted against the concentration of the surfactant. The effect of the adsorption on the rate constant appears quite similar to that on the capacity.

Figs 7 and 8 show a relationship between the rate constant and the coverage θ. A few points plotted against θ are also included in these figures for comparison.

Taking various complications and difficulties associated with those determinations

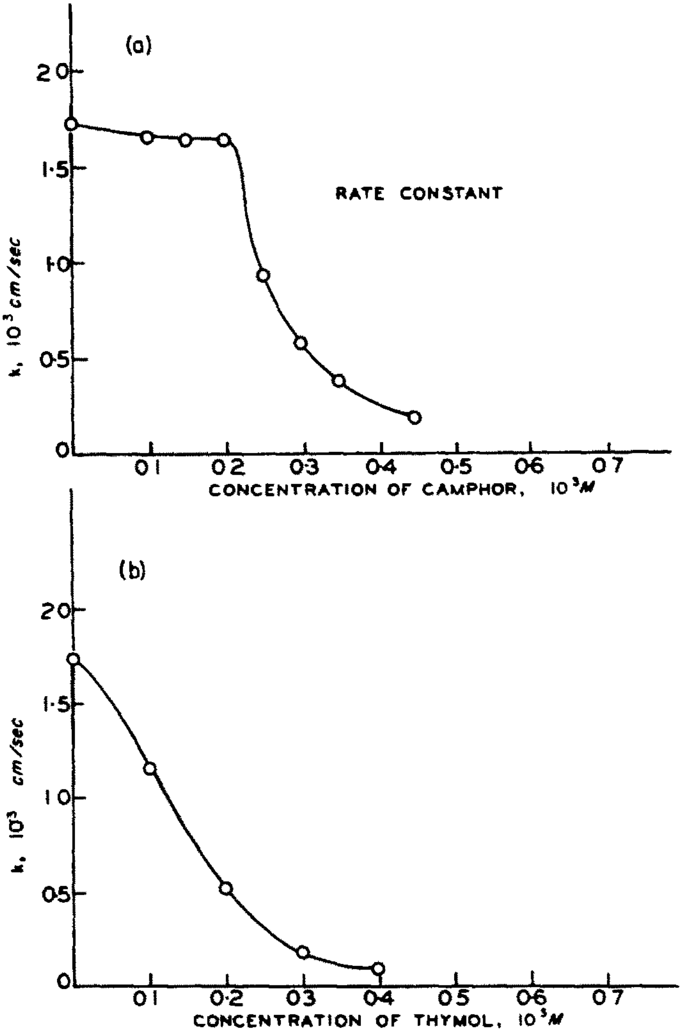

FIG 5a —Differential capacity *vs.* concentration of surfactant (camphor) at 0 64 V.
FIG 5b.—Rate constant *vs.* concentration of surfactant (camphor).

into account, the change of the rate constant can be considered as linear with respect to θ in both cases. Thus, $k = k_1(1 - \theta) + k_2\theta$, where k_1 and k_2 are the rate constants of bare and of fully covered surface, respectively, the latter being estimated with thymol as less than 10^{-9} cm. sec^{-1} from d.c. current measurements.

Determination of rate constants by impedance method

The faradaic impedance at an electrode-solution interface of an electrochemical reaction can be represented by a series combination of a capacitance, C_F, and a resistance, R. In the case where the concentration of the oxidised form is equalised to that of the reduced form, the two components of the impedance are expressed by the equations[14-17]

$$R_F = \frac{RT}{n^2F^2AC}\left[\frac{1}{k_s} + \left(\frac{2}{\omega D}\right)^{1/2}\right] \quad (1)$$

and

$$\frac{1}{\omega C_F} = \frac{RT}{n^2F^2AC}\left(\frac{2}{\omega D}\right)^{1/2} \tag{2}$$

where k_s is the heterogeneous rate constant of the reaction, ω is the angular frequency of a.c. employed, C and D are the concentration and the diffusion coefficient, respectively, of the ion, and A is the area of the electrode surface. R, T, F and n have the usual significance.

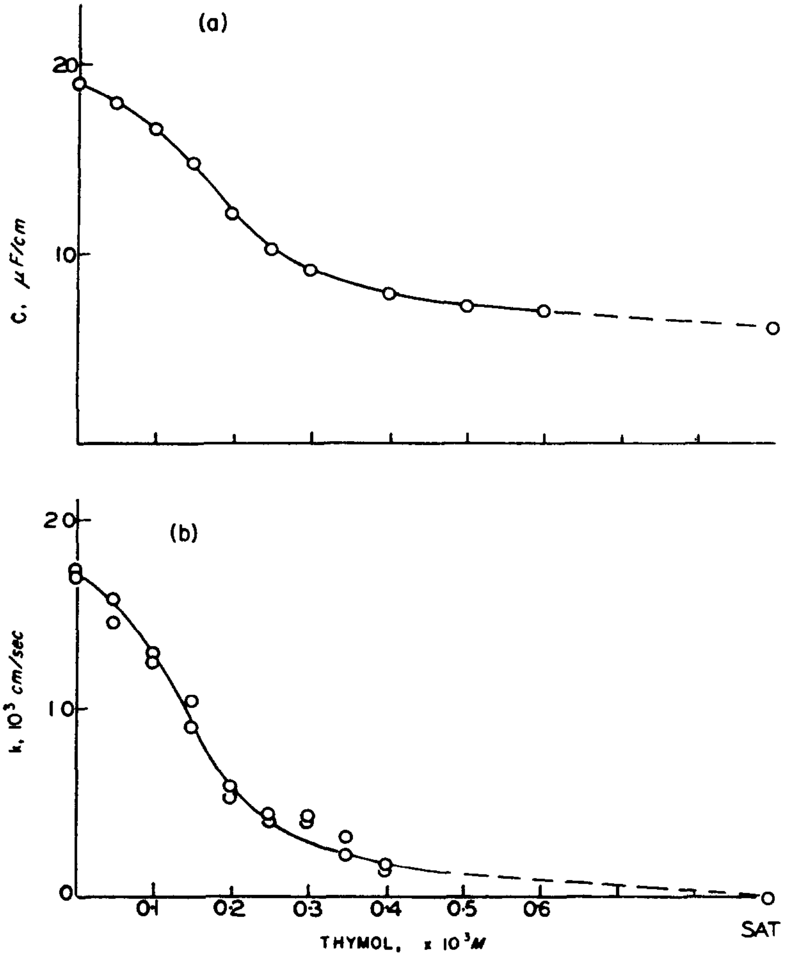

FIG. 6a.—Differential capacity at 0·64 V *vs.* concentration of surfactant (thymol).
FIG. 6b.—Rate constant *vs.* concentration of surfactant (thymol)

Observation of equations (1) and (2) shows that a plot of the faradaic reactance, $1/\omega C_F$ against $\omega^{-1/2}$ should lie on a straight line which extrapolates to the origin; and that a corresponding plot of the faradaic resistance, R_F, should lie on another straight line which is parallel to the reactance line. The rate constant, k_s, can be calculated from the vertical distance between the two lines.

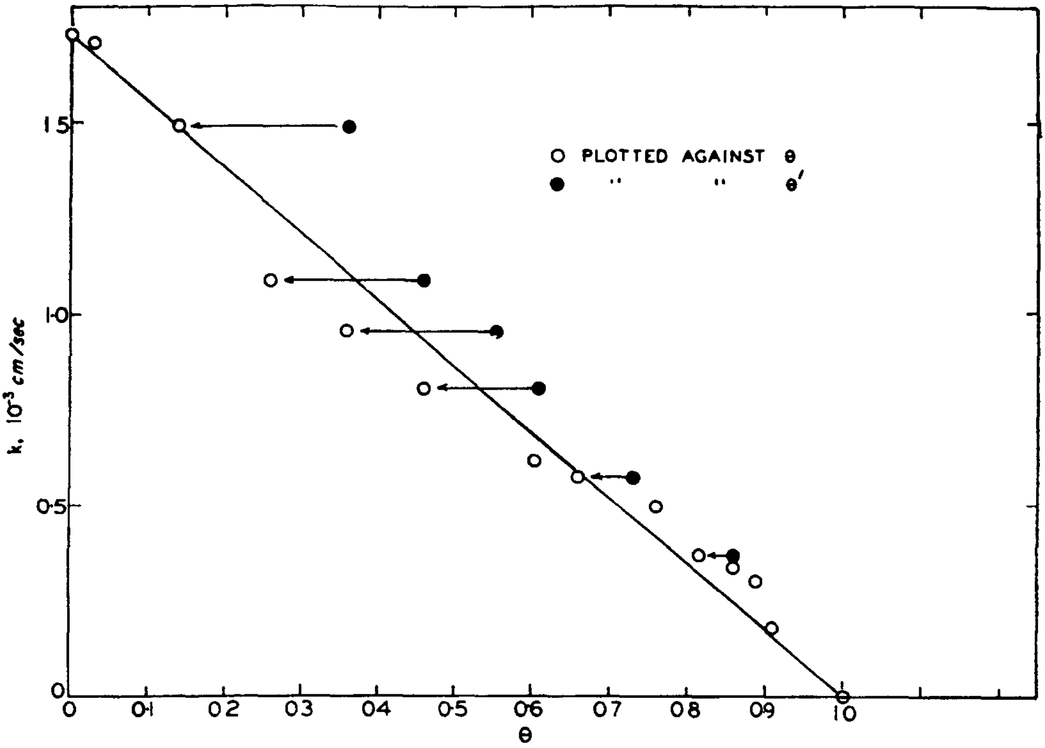

FIG 7.—Rate constant *vs.* surface coverage (camphor)

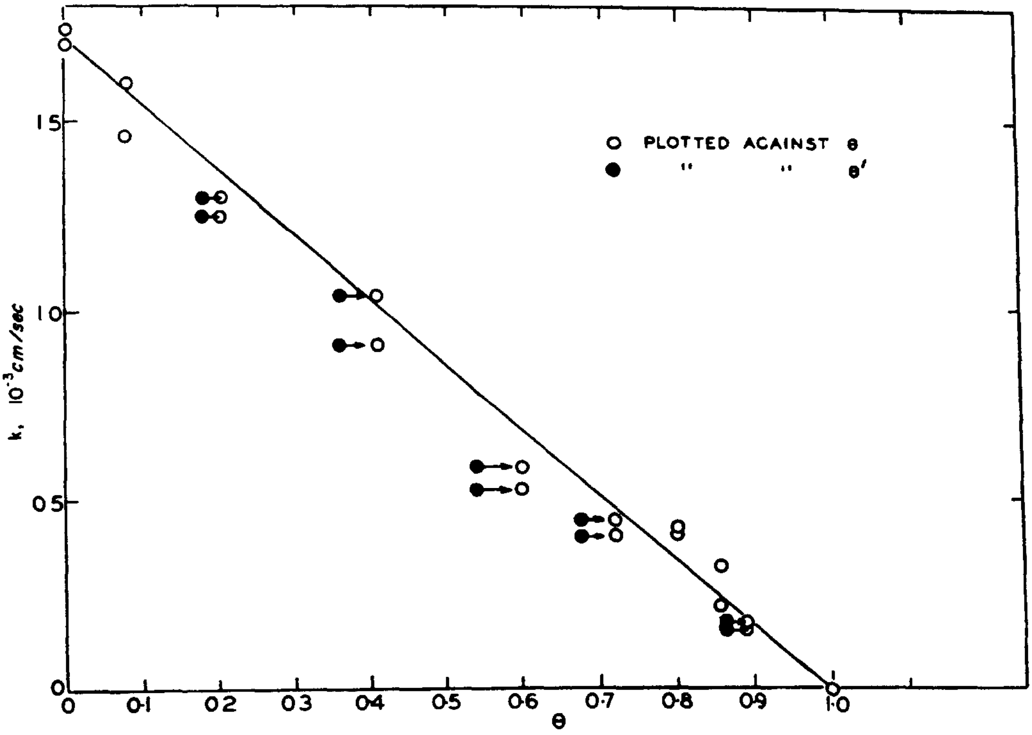

FIG 8.—Rate constant *vs.* surface coverage (thymol).

First, the over-all impedance across the solution and the solution-mercury interface, in the presence of the titanium couple, was assumed to be represented by the equivalent circuit as shown in Fig 9.[5 14–18] Calculation for the faradaic resistance and reactance can be performed by either the numerical[18] or vector diagram[14] method

Values of R_s, the ohmic resistance of solution, and C_{dl}, the capacity of double layer, were supplied by the experiment for differential capacity, which had been determined with a.c. of 1,000 cps applied to the blank solution.

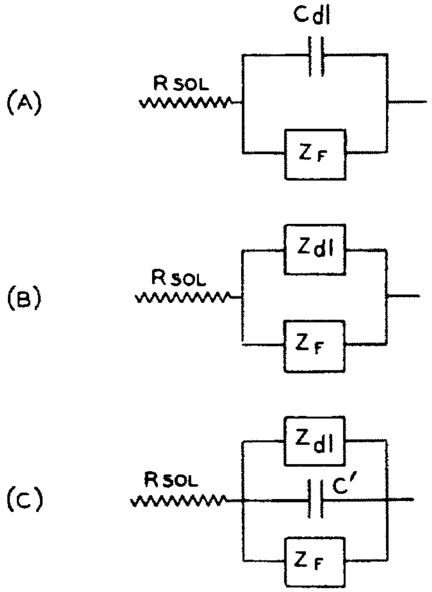

FIG 9.—Equivalent circuits of electrode impedance

The calculated values of the faradaic resistance, R_F, and the faradaic reactance, $1/\omega C_F$, were plotted against $\omega^{-1/2}$. The plots never lay on two parallel straight lines as postulated by equations (1) and (2). Instead two curved lines were obtained, and the vertical distance between these lines decreased with an increase of frequency. This was a trend common to all the results.

The blank solution was carefully re-examined to determine whether the equivalent circuit shown in Fig. 9A is consistent with the actual case. The results obtained by employing various frequencies revealed that the matched values of resistance increased at lower frequencies, especially in the higher concentration range of surfactants, while the values of capacitance remained almost constant regardless of frequency. The observed values of resistance in the blank solution were extrapolated to infinite frequency to obtain the resistance of the solution, R_{sol}. Then each resistance subtracted by R_{sol} can be considered as the resistance of the double layer. When the surfactants were either absent or in small concentrations, the resistance of the double layer was so small that it could reasonably be ignored in the calculations. But when the concentration of the surfactants were relatively large, the contribution of the resistance reached at most 2% of the corresponding reactance in magnitude and was no longer negligible.

A. *Double layer as a complex impedence* To represent the double layer in the presence of adsorbed material Grahame[5] proposed an equivalent circuit consisting of a capacitance in series with a parallel combination of capacitance and resistance. The experimental values of capacitance, C_s, and resistance, R_s, represented as a series combination, are given for several concentrations of thymol in Table II. The resistance represents the excess over the solution resistance (330 Ω) extrapolated to infinite frequency, the same value being observed in the absence or presence of surfactant Because the capacitance, C_s, remains almost constant with frequency while the excess resistance, R_s, is strongly dependent on frequency, it is qualitatively apparent that the Grahame equivalent circuit must consist of a relatively small capacitance, C_T, in series with a parallel combination of a relatively large capacitance C_3, and a large resistance, R_3. By trial and error, the components C_T, C_3 and R_3 were chosen to give the representation of R_s and C_s, as shown in Table II. The effect of increasing thymol concentration is to decrease C_T, the "pure" capacitance, more rapidly than C_3, the frequency-dependent capacitance. The parallel resistance R_3 goes through a minimum at an intermediate thymol concentration (0·4 × $10^{-3}M$), corresponding to a maximum in the observed series resistance R_s. The reason for this behaviour is not clear, but it leads to complications in subtracting the double-layer admittance in calculating the rate constant of the electrode process.

TABLE II—COMPONENTS OF THE DOUBLE-LAYER IMPEDANCE

Conc of thymol, $10^{-3}M$		cps.	R_s, Ω		C_s, μF	
			obs	calc	obs	calc
0·2	C_T = 0·15 μF C_3 = 1·6 μF R_3 = 1·9 K	200	90	120	0·136	0·138
		400	40	32	0·136	0·137
		600	18	15	0·137	0·137
		1000	14	6	0·137	0·137
0·4	C_T = 0·10 C_3 = 1·3 R_3 = 1·25	200	180	240	0·092	0·094
		400	65	70	0·093	0·093
		600	40	35	0·094	0·093
		1000	20	14	0·094	0·093
0·6	C_T = 0·09 C_3 = 1·2 R_3 = 2·0	200	120	175	0·083	0·084
		400	54	54	0·084	0·084
		600	25	25	0·085	0·084
		1000	18	10	0·085	0·084

Faradaic resistance and reactance were calculated by the vector-diagram method, using the complex admittance, in place of mere capacitive admittance of the double layer. The calculated values, however, gave only small increases to the plots for both components. Hence, the resulting curves were not remarkably improved.

B. *Introducing an additional capacitance*: Assuming that the double layer capacity might change its magnitude between the blank solution and the solution containing titanium, an equivalent circuit was considered which included an additional capacity parallel to the impedance of double layer (C in Fig. 9).

The magnitude of the capacitance was empirically chosen so that the resistive and the reactive components of the faradaic impedance were as close to those postulated by equations (1) and (2) as possible. The vector-diagram method was adopted for the calculation.

By choosing a suitable capacitance, both the resistance and the reactance lines became almost straight and parallel to each other, and the latter lines could be extrapolated to the origin. The values of the additional capacitance are tabulated in Tables III and IV, where they are also compared with the differential capacity measured at 1,000 cps. The improvement is marked by thus introducing an additional capacitance.

TABLE III—EFFECT OF CAMPHOR

Concentration of camphor, $10^{-3}M$	C', Capacity subtracted		Slope, $10^{2}\ \Omega\ sec^{-1/2}$	D(apparent), $10^{-6}\ cm^{2}\ sec^{-1}$	k_s, $10^{-3}\ cm\ sec^{-1}$
	$\mu F/cm.^2$	% to C_{dl} at 1000 cps			
0	2·50	13·1	7	1	1·7$_3$
0·10	1·88	9·9	10	0·5	1·6$_6$
0·15	1·66	8·8	11	0·4	1·6$_5$
0·20	1·63	8·7	12	0·3	1·6$_5$
0·25	0	0	15	0·2	0·9$_4$
0·30	0·29	2·9	48	0·02	0·5$_9$
0·35	0·43	5·3	70	0·01	0·3$_9$
0·45	0·29	4·6	125	0·003	0·2$_0$

TABLE IV—EFFECT OF THYMOL

Concentration of thymol, $10^{-3}M$	C', Capacity subtracted		Slope, $10^{2}\ \Omega\ sec^{-1/2}$	D(apparent), $10^{-6}\ cm^{2}\ sec^{-1}$	k_s, $10^{-3}\ cm.\ sec^{-1}$
	$\mu F/cm^2$	% to C^{dl} at 1000 cps			
0	2·47	12·9	8	0·5	1·7$_4$
0·10	3·26	19·6	12	0·2	1·1$_6$
0·20	2·47	20·1	38	0·02	0·5$_2$
0·30	1·68	16·8	100	0·002	0·1$_8$
0·40	1·13	13·6	650	(8×10^{-5})	0·0$_9$

The effect of this additional admittance may be interpreted as a rapid electron exchange between the adsorbed reactants and the electrode, such as that postulated by Laitinen and Randles[18] for a cobalt^{III}/cobalt^{II} system.

C. *Reaction rate*: Estimated values of R_F and $1/\omega C_F$ for various concentrations of the surfactants, camphor and thymol, were plotted against $\omega^{-1/2}$. Fig. 10, which is an example of the plots, illustrates the variation of both R_F and $1/\omega C_F$ with the increasing concentration of camphor.

Rough estimation of the apparent diffusion coefficient of the titanium ion is possible from the slopes of each pair of corresponding lines. Values of slopes and, hence, the diffusion coefficient are shown in Tables III and IV in the presence of camphor and thymol, respectively. The large decrease of apparent diffusion coefficient observed at high surface coverages cannot be attributed to a change of diffusion rate in solution because the polarographic diffusion current is not appreciably affected even by high concentrations of camphor or thymol. It might be regarded, however, as evidence for a slow penetration step of a nearly saturated surface layer. Further experimental work on this point is desirable.

Vertical distances between corresponding resistance and reactance lines permit

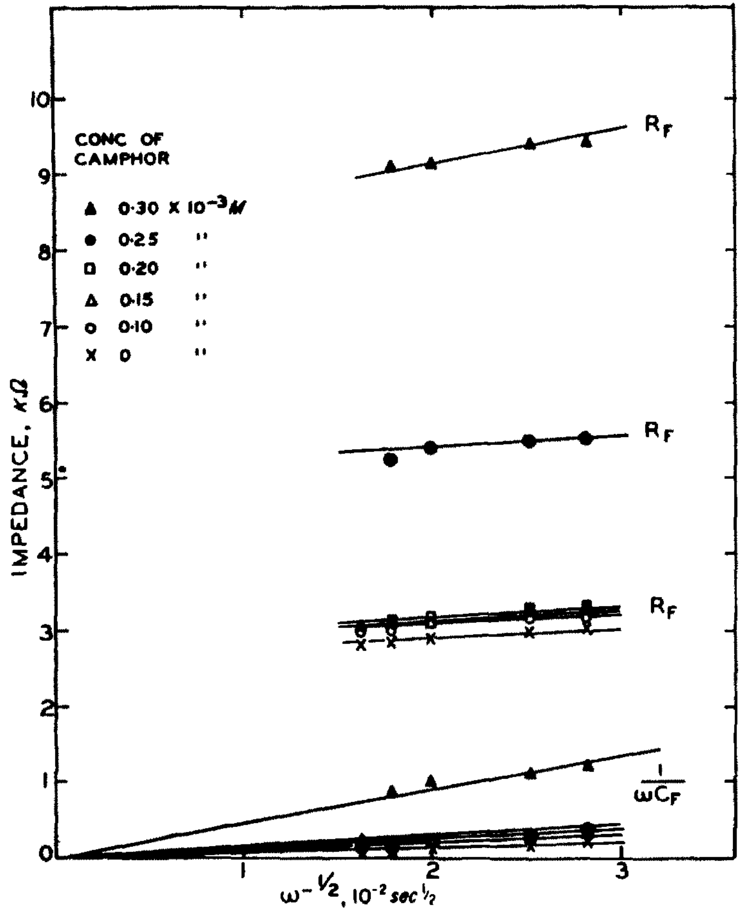

FIG. 10a.—Faradaic resistance, R_F and reactance, $1/\omega C_F$, in the presence of camphor.

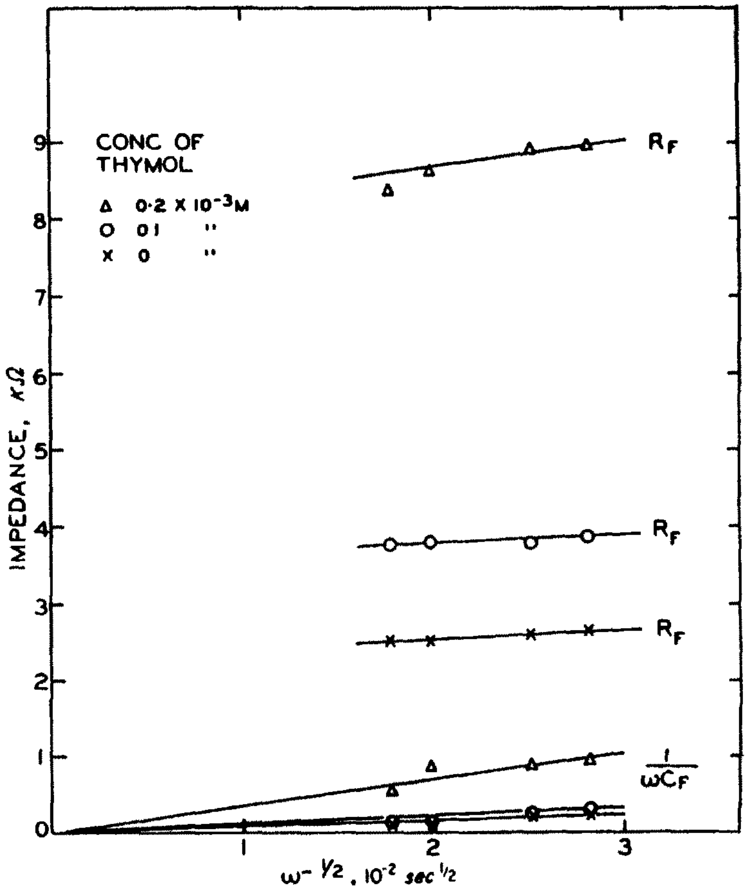

FIG 10b.—Faradaic resistance, R_F and reactance, $1/\omega C_F$, in the presence of thymol.

the reaction rate constants to be calculated, the values also being tabulated Experiments had been extended to the saturating concentrations of camphor and thymol, but the extremely small values of capacitance gave rise to intolerable errors in calculation; therefore, these results have been neglected here

The observed value of the rate constant, 1·7 × 10^{-3} cm sec^{-1}, in the absence of surfactants is in good agreement with that obtained by the voltage-step method This is smaller than either 9 × 10^{-3} by Randles and Somerton[20] or 5 or 3·5 × 10^{-3} by Delahay and Trachtenberg[21] obtained by the impedance method. Because the experimental condition of the former was not described and the latter was obtained in a solution containing sodium chloride, an exact comparison is difficult to make.

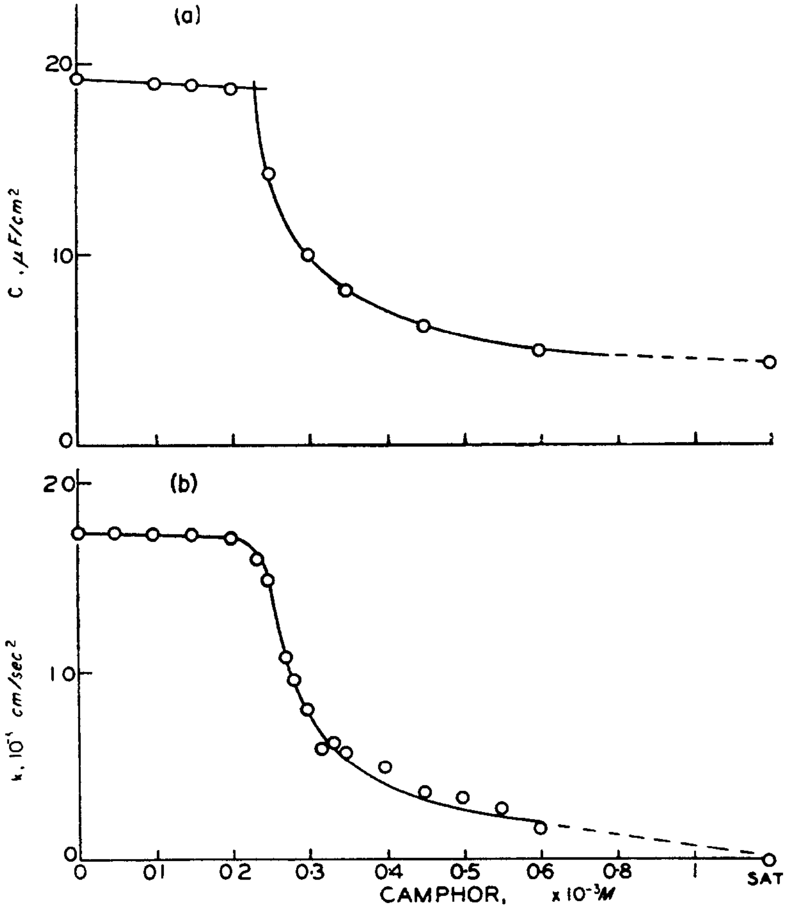

FIG. 11a — Effect of camphor on electrode reaction of Ti
FIG 11b — Effect of thymol on electrode reaction of Ti

The rate constant decreases rapidly in the presence of thymol, and is reduced to one-tenth of the original value at the concentration of thymol 0·3 × $10^{-3}M$. On the other hand, camphor exerts almost no inhibiting effect up to 0·2 × $10^{-3}M$, then exerts a serious effect, the rate constant being about one-tenth of the original value at 0·45 × $10^{-3}M$. These effects on the rate constant are shown in Fig. 11.

Comparison of voltage-step and impedance methods

For a simple electrode reaction, the voltage-step and impedance methods may be said to be equivalent, but for the determination of rate constants greater than 10^{-2} cm. sec^{-1} the impedance method is usually more accurate.[22]

In the present case, however, the voltage-step method has advantages which led to more reliable values for rate constants in the presence of adsorbed organic materials. The essential difficulty in interpreting impedance results arises from complications in subtracting out the admittance of the blank. First, the frequency dependence of resistance and capacitance observed in the presence of an adsorbed layer means that the double layer can no longer be represented as a simple capacitance but a capacitance shunted by a resistance, as has previously been shown by Grahame.[5] In the present investigation, it has been shown that this is a relatively minor complication, but undoubtedly it leads to additional scatter in the calculated rate constants. Second, the abnormally great Warburg impedance observed in the presence of adsorbed materials especially at high surface coverages needs further study. The uncertainty from this correction appears to be more serious, and would probably be encountered whenever adsorbed phases are present. Third, a specific effect encountered in the present problem is that of adsorption of electroactive species. Although this effect may not always be observed, it has led in the present case to further uncertainties in the rate constant calculated from impedance values.

In the voltage-step method, the total period of time during which a current was recorded was usually less than 300 μsec. Thus, all observations in this study would correspond to bridge measurements at high frequencies (several kilocycles per sec). The frequency dispersion of double-layer capacity becomes unimportant at high frequencies. Moreover, the abnormal Warburg admittance becomes relatively less important at high frequencies because it approaches zero at infinite frequency. Finally, the effect of adsorbed electroactive species appears as an abnormally large double-layer capacitance, which is subtracted out automatically in the extrapolation procedure. This latter statement is true only if the adsorbed species undergo sufficiently rapid electron exchange that their effect can be represented by a pure capacitance. A slow electron exchange of adsorbed species would give rise to a capacitance in series with a resistance, which would result in an increased time constant for the reduction process as compared with the charging process.

CONCLUSIONS

The adsorption of camphor and thymol on a dropping mercury electrode was determined from capacitance measurements. A comparison was made of the electrode coverage as calculated from differential and integral double-layer capacity, and the magnitude of the error caused by using differential capacity calculations was estimated.

The standard rate constant for the titanium^{IV}-titanium^{III} couple in 1*M* tartaric acid, 0·2*M* sodium sulphate was determined in the absence of surfactant. The voltage-step method gave a value of $1{\cdot}72 \times 10^{-3}$ cm. sec^{-1}, and the impedance method gave 1·73 and $1{\cdot}74 \times 10^{-3}$ cm. sec^{-1}.

The voltage-step method proved simpler than the impedance method in the presence of surfactant. To interpret the impedance method, it was necessary to introduce an empirical correction in the form of an additional capacitative admittance in parallel with the usual Warburg admittance. This correction arises from specific adsorption of electroactive species.

The rate constants calculated from voltage-step measurements were more reliable than those from impedance values, and showed approximately linear dependance on surface coverage, for both thymol and camphor.

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Zusammenfassung—Es ist mit Hilfe der Spannungsstufen- und Impedanzmethoden untersucht worden, wie Kampfer- und Thymolverunreinigungen an einer Quecksilberoberfläche die Geschwindigkeitskonstante der TiIV/TiIII Redoxreaktion in 1 M Weinsäure beeinflussen. Eine spezifische Adsorption der elektronegativen Bestandteile erwies sich als Nachteil mehr bei der Impedanzmethode als bei der Spannungsstufenmethode Die Geschwindigkeitskonstante scheint mit Oberflächenbedeckung linear abzunehmen.

Résumé—On a déterminé l'effet de la contamination d'une surface de mercure par le camphre et le thymol sur la constante de vitesse normale de demi-réaction du système titane(IV)–titane(III) en acide tartrique 1 M, au moyen des méthodes par incrément de potentiel et d'impédance Les complications dues à l'adsorption spécifique des espèces électroactives sont plus perturbatrices avec la méthode d'impédance qu'avec la méthode par incrément de potentiel. On indique une décroissance linéaire de la constante de vitesse avec l'étendue de la surface

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CHRONOPOTENTIOMETRIC STUDY OF THALLIUM[1] ION IN GLACIAL ACETIC ACID†

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Summary—The thallous ion-thallium amalgam system has been studied chronopotentiometrically in glacial acetic acid (HAc) as a solvent, using 0·25*M* ammonium acetate as supporting electrolyte The transition time relationships between the cathodic transition time and the first anodic transition time on current reversal were verified. Analogous studies were carried out at the thallium amalgam electrode, determining the anodic transition time and the cathodic transition time on current reversal. The predicted potential-time relationships for the above-mentioned chronopotentiometric processes were verified, and it was established that the thallous acetate-thallium amalgam couple is reversible with the formal potential of 0 347 ± 0·005 V *vs.* the saturated aqueous calomel electrode. The diffusion coefficients of thallous ion and thallium in mercury were found to be identical, 4 3 × 10^{-6} cm^2. sec^{-1}.

INTRODUCTION

VARIOUS investigators[1–17] have obtained solutions for a number of simple and complex problems arising in chronopotentiometry. The present work is concerned with the verification of the predicted relationships between concentration and transition time, and between potential and time, for the thallous acetate—thallium amalgam couple, using 0·25*M* ammonium acetate supporting electrolyte in acetic acid (HAc) as solvent. Studies reported below include the reduction of thallous acetate into a mercury pool or thallium amalgam, followed by current reversal at the first cathodic transition time; and oxidation of thallium from thallium amalgam followed by current reversal at the first anodic transition time.

Table I summarises the surface concentrations of thallous ion, C_O^s, and thallium amalgam, C_R^s, which will result at time, t, after the start of reduction before the first cathodic transition time, τ_c, and between the first cathodic transition time and the subsequent anodic transition time, τ_a', on current reversal at $t = \tau_c$,[12]

where $$\tau_c = \frac{n\mathscr{F}(\pi D_O)^{\frac{1}{2}}}{2i_0} C_O^{\circ},$$

D_O and C_O° represent the diffusion coefficients and bulk concentrations of the oxidised species, respectively, i_0 is the absolute value of constant current density, and τ_a' is the time lapse between the cathodic transition time and the anodic transition time. Analogous relations are given for the case where the initial process is an oxidation, resulting first in an anodic transition time, τ_a,

where $$\tau_a = \frac{n\mathscr{F}(\pi D_R)^{\frac{1}{2}}}{2i_0} C_R^{\circ},$$

followed by cathodic transition time, τ_c', on current reversal at $t = \tau_a$.[12]

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TABLE I —SURFACE CONCENTRATIONS DURING CONSTANT CURRENT ELECTROLYSIS FOLLOWED BY CURRENT REVERSAL AT FIRST TRANSITION TIME†[12]

Initial Process	Before first transition time		Between first and second transition times	
	C_O^s	C_R^s	C_O^s	C_R^s
Reduction	$k_O\{\tau_c^{1/2} - t^{1/2}\}$ $(t \le \tau_c)$	$k_R\{\tau_a^{1/2} + t^{1/2}\}$ $(t \le \tau_c)$	$k_O\{\tau_c^{1/2} + 2(t - \tau_c)^{1/2} - t^{1/2}\}$ $(\tau_c < t \le \tau_c + \tau_a')$	$k_R\{\tau_a^{1/2} - 2(t - \tau_c)^{1/2} - t^{1/2}\}$ $(\tau_c < t \le \tau_c + \tau_a')$
Oxidation	$k_O\{\tau_c^{1/2} + t^{1/2}\}$ $(t \le \tau_a)$	$k_R\{\tau_a^{1/2} - t^{1/2}\}$ $(t \le \tau_a)$	$k_O\{\tau_c^{1/2} - 2(t - \tau_a)^{1/2} + t^{1/2}\}$ $(\tau_a < t \le \tau_a + \tau_c')$	$k_R\{\tau_a^{1/2} + 2(t - \tau_a)^{1/2} - t^{1/2}\}$ $(\tau_a < t \le \tau_a + \tau_c')$

† For the reduction (or oxidation) of one soluble species to another where

$$k_O = \frac{2i_0}{n\mathscr{F}(\pi D_O)^{1/2}}$$

$$k_R = \frac{2i_0}{n\mathscr{F}(\pi D_R)^{1/2}} \text{ and } i_0 = \text{absolute value of current density}$$

If the first electrode process is a reduction, the relationship between the first cathodic transition and the anodic transition time occurring on current reversal is

$$[\tau_c + \tau_a']^{1/2} + \tau_a^{1/2} = 2[\tau_a']^{1/2}, \tag{1}$$

while if the initial process is an oxidation, the analogous relation is

$$[\tau_a + \tau_c']^{1/2} + \tau_c^{1/2} = 2[\tau_c']^{1/2}. \tag{2}$$

The potential-time curves for the reversible electrode process are obtained by substituting the surface concentrations given in Table I into equation (3a)

$$E = E^* + \frac{RT}{n\mathscr{F}} \ln \frac{C_O^s D_O^{1/2}}{C_R^s D_R^{1/2}}, \tag{3a}$$

where E^* is the observed potential when $C_O^s D_O^{1/2} = C_R^s D_O^{1/2}$. In the case under consideration, E^* is identical with the polarographic half-wave potential and the chronopotentiometric quarter-wave potential, *i.e.*,

$$E^* = E^\circ + \frac{RT}{n\mathscr{F}} \ln \frac{f_O D_R^{1/2}}{f_R D_O^{1/2}}, \tag{3b}$$

where E° is the standard potential for Ox. + $n\varepsilon$ = Red. and f represents the activity coefficient of the species indicated in the subscript. We call E^* the "characteristic potential". This characteristic potential occurs at a time, t^*, the "characteristic time". Relationships for the various cases are given in Table II. If the first electrode process

TABLE II —CHARACTERISTIC TIMES, t^*

Initial process	Before first transition time	Between first and second transition times
Reduction	$0.5(\tau_c^{1/2} - \tau_a^{1/2}) = t^{*1/2}$ observed only if $\tau_c > \tau_a$	$4(t^* - \tau_c)^{1/2} - 2(t^*)^{1/2} = \tau_a^{1/2} - \tau_c^{1/2}$ always observed
Oxidation	$0.5(\tau_a^{1/2} - \tau_c^{1/2}) = t^{*1/2}$ observed only if $\tau_a > \tau_c$	$4(t^* - \tau_a)^{1/2} - 2(t^*)^{1/2} = \tau_c^{1/2} - \tau_a^{1/2}$ always observed

is a reduction and $C_R'' = 0$, then $\tau_a = 0$ and the first current reversal relationship given in Table II reduces to a result previously obtained by Berzins and Delahay.[3]

EXPERIMENTAL

Apparatus

The constant current source high impedance amplifier and recorders used in this study are described elsewhere.[12] The chronopotentiometric cell used was similar to that used by Delahay[13] with the following differences. (1) The plug was machined from Teflon instead of from Lucite. (2) The entire cell body was jacketed with water and maintained at 25 ± 0·2 by circulating water from a thermostat. (3) The Lugen capillary was sealed through the side of the cell to fix the position of the tip of the salt bridge with respect to the mercury pool. The diameter of the hole in the Teflon plug was 1·630 cm. and exactly the same volume of mercury was delivered to the plug in all the experiments to ensure a constant distance between the tip of the salt bridge and the mercury surface. The effective electrode area was determined by a procedure which will be reported elsewhere.

Reagents

Reagent-grade chemicals were used in all cases.

Glacial acetic acid was purified by boiling with anhydrous chromic oxide, followed by azeotropic distillation with excess benzene to remove water, in turn followed by careful fractionation.

0·25*M Ammonium acetate*. Reagent-grade ammonium acetate was dissolved in the purified HAc. The water content of the supporting electrolyte used was found to be 0·1% by Karl Fischer titration.

Thallium amalgams were prepared *in situ* in the chronopotentiometric cell by constant-current electrolysis at the mercury cathode of stirred, deaerated solutions of thallous acetate in 0·25*M* ammonium acetate in HAc. The current densities chosen were such that the potential of the mercury cathode insured 100% current efficiency for the reduction of thallous ion. The concentration of the amalgams was calculated from the number of coulombs used in the electrolysis and the known volume of the mercury cathode.

Thallium acetate. A standard thallium acetate solution was prepared by solution of an appropriate amount of thallium formate in water followed by precipitation with sodium carbonate. The resulting carbonate was recrystallised several times from water, washed and dried. A weighed amount of this carbonate was dissolved in the ammonium acetate supporting electrolyte. The amount of water formed in this process is negligible compared with the total amount of water in the electrolyte.

All potentials were measured against the saturated aqueous calomel electrode. An intermediate salt bridge containing the acetic acid supporting electrolyte present in the chronopotentiometric cell was placed between aqueous calomel electrode and the Lugen capillary.

RESULTS AND DISCUSSION

The reaction

$$\mathrm{Tl^{(I)}} + \varepsilon + \mathrm{Hg} \rightleftharpoons \mathrm{Tl(Hg)} \tag{4}$$

was studied in 0·25*M* ammonium acetate in HAc in order to verify the relations given in Tables I and II. In such a mixture of reduced and oxidised forms, two transition time constants, J_O and J_R, may be defined in terms of relationships given in Table I. The transition time constant for the oxidised form is given by

$$J_O = \frac{i_0\tau_c^{\frac{1}{2}}}{C_O^{\circ}} = \frac{-i_0[(\tau_a + \tau_c')^{\frac{1}{2}} - 2(\tau_c')^{\frac{1}{2}}]}{C_O^{\circ}} = \frac{n\mathscr{F}(\pi D_O)^{\frac{1}{2}}}{2} \tag{5a}$$

in the case where the first electrochemical process is a reduction.

If the current is reversed at the first transition time, the transition time constant for the reduced form is given by

$$J_R = \frac{i_0\tau_a^{\frac{1}{2}}}{C_R^{\circ}} = \frac{-i_0[\tau_c + \tau_a')^{\frac{1}{2}} - 2(\tau_a')^{\frac{1}{2}}]}{C_R^{\circ}} = \frac{n\mathscr{F}(\pi D_R)^{\frac{1}{2}}}{2} \tag{5b}$$

when the initial process is an oxidation and the current is reversed at the first transition time.

TABLE III —CHRONOPOTENTIOMETRY OF THALLOUS ION–THALLIUM AMALGAM IN HAc

Initial process	$C^{0(b)}_{Tl^+}$ mM	$C^{0(b)}_{Tl(Hg)}$, mM	$J'^{(a)}_{Tl^+}$ $\frac{\mu A\ sec^{\frac{1}{2}}}{cm^2 mM}$	$J^{(a)}_{Tl(Hg)}$ $\frac{\mu A\ sec^{\frac{1}{2}}}{cm^2 mM}$	Exptl value of $2·303 \frac{RT}{n\mathcal{F}}$ Before first transition time v	Exptl value of $2·303 \frac{RT}{n\mathcal{F}}$ After current reversal, v	E^*, v	Number of determinations
Reduction	3·19	0·0	185 ± 3·0%	—	0·064 ± 0·002	0·060 ± 0·002	0·346 ± 0·002	24
Reduction	4·25	0·0	177 ± 2·3%	—	0·061 ± 0·001	0·058 ± 0·002	0·349 ± 0·002	26
Reduction	3·34	2·12	—	157 ± 10·6%	0·064 ± 0·005	0·070 ± 0·005	0·345 ± 0·002	16
Oxidation	3·34	2·12	177 ± 2·4%	181 ± 10·0%	0·065 ± 0·007	0·061 ± 0·003	0·343 ± 0·001	14
Oxidation	3·27	2·82	—	231 ± 9·2%	0·061 ± 0·001	0·071 ± 0·006	0·354 ± 0·002	4
Average			180 ± 2·1%	190 ± 14·7%	0·063 ± 0·003	0·064 ± 0·005	0·347 ± 0·005	

(a) See equations (5a) and (5b) for definition.

(b) C^0 = bulk concentration.

The results obtained with several HAc solutions containing thallous acetate at mercury and at thallium-amalgam electrodes are summarized in Table III. The values of J_{Tl^+} for the initial cathodic experiments at an amalgam electrode are omitted, because the concentration of the HAc solution, after preparation of the amalgam, was determined from the cathodic transition times and the value of J_{Tl^+} found for experiments at a mercury electrode. Current densities varied from 154 μA. cm^{-2} to 2050 μA. cm^{-2}. As is seen in Table III, the agreement between the various J values is good, and verifies the relationships between the different transition times. Also summarised in Table III are the slopes of E *vs.* log $\dfrac{C^s_{\mathrm{Tl}^+}}{C^s_{\mathrm{Tl(Hg)}}}$ where the appropriate surface concentrations given in Table I have been substituted. The slopes indicate that reaction (4) occurs reversibly in a supporting electrolyte of 0·25M ammonium acetate in HAc

The characteristic potentials listed in Table III are corrected for the ohmic potential drop contribution which cannot be avoided in this high-resistance supporting electrolyte. The observed characteristic potential, $(E^*)_{\mathrm{obs}}$, is related to the actual characteristic potential by

$$(E^*)_{\mathrm{obs}} = E^* - iR \tag{6}$$

where R is the effective resistance between the tip of the Lugen capillary and the mercury pool. The actual characteristic potentials listed in Table III were obtained by plotting the observed characteristic potential *vs.* the current used in the particular electrolysis and extrapolating to zero current. The agreement found between the characteristic potentials is excellent, and verifies the validity of the theoretical relationship pertaining to these different situations.

In addition, potentiometric measurements (at zero current) indicate that the value of formal potential for reaction (4) is $-0{\cdot}353$ v. Because ion-pair formation must be extensive, this potential value merely represents the e.m.f. at which the ratio of the analytical concentration of thallous acetate to the thallium amalgam concentration is 1. We also find that the diffusion coefficient of thallous ion in HAc solutions of 0 25M ammonium acetate (4 3 $\times$ 10^{-6} cm^2. sec^{-1}) equals that of thallium amalgam, therefore the observed formal potential should correspond exactly to E^*. Within the experimental error this result is found, further supporting the above conclusions

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Zusammenfassung—Das System Thallium(I)-Thalliumamalgam wurde chronopotentiometrisch in Eisessig als Losungsmittel mit 0,25m Ammonacetat als Leitsalz untersucht Die Beziehungen zwischen kathodischer Transitionszeit und erster anodischer Transitionszeit bei Stromumkehr wurden verifiziert Analoge Untersuchungen wurden an der Thalliumamalgam-elektrode durchgeführt, wobei die anodische und die kathodische Transitionszeit bei Stromumkehr bestimmt wurden Die vorausgesagten Potential-Zeit-Beziehungen fur die erwahnten chronopotentiometrischen Prozesse wurden bestatigt und es wurde festgestellt, daß das System Thalliumacetat/Thallium-amalgam reversibel ist mit einem formalen Potential von 0,347 ± 0,005 Volt gegen die gesättigte wäßrige Kalomelelektrode Die Diffusionskoeffizienten von Thallium(I) und Thallium in Quecksilber sind gleich und betragen 4,3 10^{-6} cm^2/sec.

Résume—On a etudie chronopotentiometriquement le systeme ion thalleux-amalgame de thallium en acide acetique glacial (HAc) comme solvant, avec de l'acetate d'ammonium 0,25 M comme electrolyte support On a vérifié les rapports des temps de transition, entre le temps de transition cathodique et le premier temps de transition anodique, lors de l'inversion du courant On a effectue des etudes analogues à l'électrode en amalgame de thallium determinant les temps de transition anodique et cathodique lors de l'inversion du courant Les relations potentiel-temps prévues pour les techniques chronopotentiometriques ci-dessus ont ete vérifiees et on a etabli que le couple acétate thalleux-amalgame de thallium est reversible, avec le potentiel defini de 0,347 ± 0,005 volt par comparaison a l'electrode au calomel aqueux saturé On a trouvé que les coefficients de diffusion des ions thalleux et du thallium dans le mercure sont identiques, 4,3 10^{-6} cm^2 sec

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RADIOCHEMICAL DETERMINATION OF STRONTIUM-89 AND -90 IN URANIUM MINERALS AND SALTS

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Summary—A combination of low-level counting technique and large-scale analytical operation has been employed to determine extremely small quantities of strontium-89 and -90 in uranium ores and salts Strontium carrier is added to a kilogram quantity of the samples of non-irradiated uranium ore and salt, exhaustively purified, and counted The levels of radiostrontium found are of the order of 10^{-4} disintegrations $sec^{-1}.g^{-1}$ of uranium in the sample. These strontium isotopes are formed in non-irradiated uranium salts and ores predominantly by the spontaneous fission of uranium, but neutron-induced fission of uranium-235 also appears to occur in the latter

INTRODUCTION

THE existence of extremely small activities of natural fission-produced strontium-89 and -90 in pitchblende was first reported by Kuroda and Edwards[1] about a decade ago. Determination of these strontium isotopes in uranium ore is tedious and requires a large-scale chemical operation, which looks somewhat like a miniature version of Mme. Curie's experiment of the isolation of radium from pitchblende.

In connection with a study on the process of natural fission, currently being carried out in this laboratory, it was necessary to measure the levels of strontium-90 in pitchblende and in various uranium-bearing materials. The purpose of the experiment was to see if the amount of strontium-90 found in pitchblende agrees with the calculated amount from the known spontaneous fission half-life ($8 \cdot 0 \times 10^{15}$ years) of uranium-238, or if there is an excess of strontium-90 from the contribution by neutron-induced fission of uranium-235. The contribution from the latter process would imply that a nuclear chain reaction occurs in nature, *i.e.*, some of the neutrons produced by the uranium-238 spontaneous fission are absorbed by the uranium-235 atoms and produce additional fission neutrons.

The existence of such a nuclear chain-reacting system in nature has been demonstrated mass-spectrometrically.[2,3] The mass-spectrometric measurements deal, however, with the stable isotopes of krypton and xenon, and hence reveal the cumulative effects of the nuclear chain reaction throughout the life-time of the uranium ores.

Measurements of the levels of strontium-90 in pitchblende would tell us something about the extent to which the nuclear chain reaction is occurring "today" in the uranium ore Knowing this, one may be able to compute the total number of uranium atoms which have participated in the nuclear chain reaction during the entire history of the earth.

The recent discovery that the earth's atmosphere appears to contain an excess of "fission-produced" xenon isotopes relative to the xenon extracted from meteorites can be explained from either (*a*) the contribution from the extinct transuranium element, such as plutonium-244 (half life· 7·6 × 10^7 years),[4,5] or (*b*) the natural uranium chain reaction which occurred during the geological history of the earth.[6–9]

No attempt will be made in this paper to discuss fully the nuclear and geo-cosmochemical aspects of the process of natural fission However, mention will be made here that pitchblende and other uranium ores are expected to contain similar activities of natural fission-produced technetium and promethium isotopes. These so-called "missing" elements can be also isolated from uranium ores by a large-scale chemical operation Measurements of the levels of technetium and promethium activities in pitchblende are currently being continued in this laboratory [10–15]

The present paper describes some of the analytical and radiochemical problems encountered in the separation and determination of the extremely small quantities of strontium-89 and -90 in kilogram-quantities of uranium ores. It has been our experience that the strontium fraction of pitchblende can be very easily lost during the chemical operation, even when a fairly large quantity of strontium carrier is added to the pitchblende sample. A failure in the recovery of the strontium fraction meant a loss of kilogram quantity of pitchblende, as well as a loss of "face" to the investigators involved in the operation. In fact, the experiment of Kuroda and Edwards[1] has never been successfully repeated in this laboratory and elsewhere until the new analytical scheme described in this paper was developed

EXPERIMENTAL

Materials

A large quantity of African pitchblende and a sample of depleted uranium with the isotopic composition of 99 98 % ^{238}U and 0·011 % ^{235}U were made available to us for this study by Dr H M Roth of the Research and Development Division, U.S. Atomic Energy Commission, Oak Ridge, Tennessee, U S.A.

All reagents used in this work were of the highest purity obtainable, usually Reagent ACS purity

Counting equipment

A CE14 Tracerlab Low-Background Beta Counter was used to count the strontium fractions isolated from pitchblende and depleted uranium.

Chemical procedure

A flow sheet of the chemical operations is shown in Fig. 1. The final adoption of the analytical scheme shown in Fig 1 was based on the knowledge gained from the preliminary experiments on the behaviour of strontium as described in the latter part of this report.

In the case of the determination of radiostrontium in depleted uranium salt, the sample was converted to $UO_2(NO_3)_2$ $6H_2O$, 200 mg of strontium carrier were added, and this was first treated with 80% nitric acid The strontium nitrate found in the precipitate was then exhaustively purified and counted.

RESULTS AND DISCUSSION

The final strontium carbonate precipitate recovered from 2·6 kg of pitchblende weighed 124 mg and showed an activity of about 300 cpm. This activity was found to be mostly from the decay products of radium. The sample was dissolved in dilute nitric acid and was repurified, starting with the ion-exchange separation step of the flow sheet shown in Fig. 1.

The purified strontium carbonate precipitate weighed 114 mg and had a weak beta activity shown as Curve I in Fig 2. The growth-decay curve observed indicated the presence of 50-day ^{89}Sr and the growth of 64·5-hour ^{90}Y from 28-year ^{90}Sr.

To calculate the radiostrontium content of the pitchblende, the chemical yield has

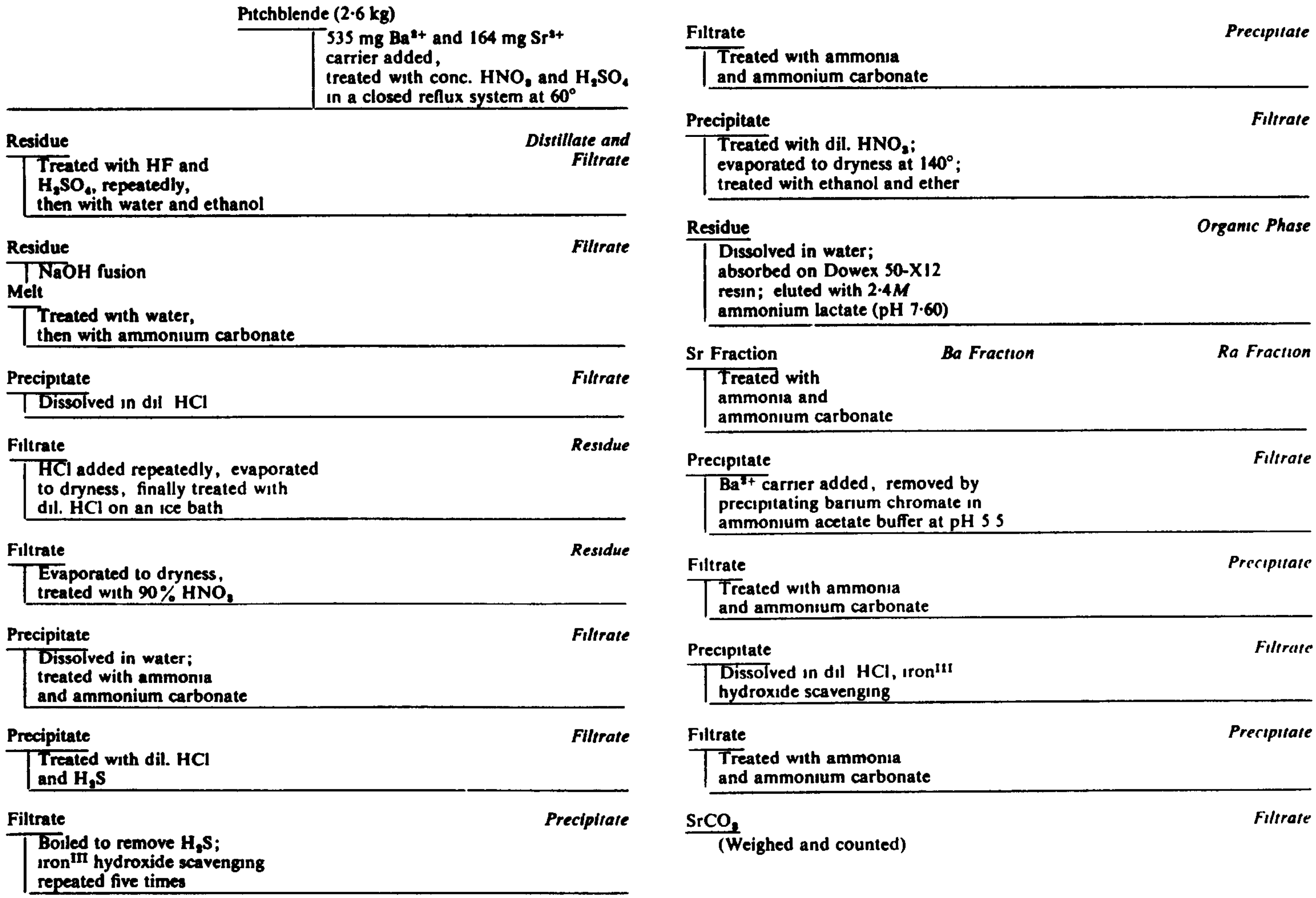

FIG. 1.—Flow diagram for the determination of strontium-90 in pitchblende.

to be accurately known. If *a* mg of strontium carrier were added and *b* mg were recovered, the chemical yield, *y*, is

$$y = \frac{b}{a - x} \; 100\% \qquad (1)$$

where x is the amount of strontium originally present in the sample

Attempts to determine x in the African pitchblende have all failed and we are currently of the opinion that $x \ll a$ Thus, if one neglects x, the chemical yield in this case is calculated to be 42%, which is the highest chemical yield so far attained

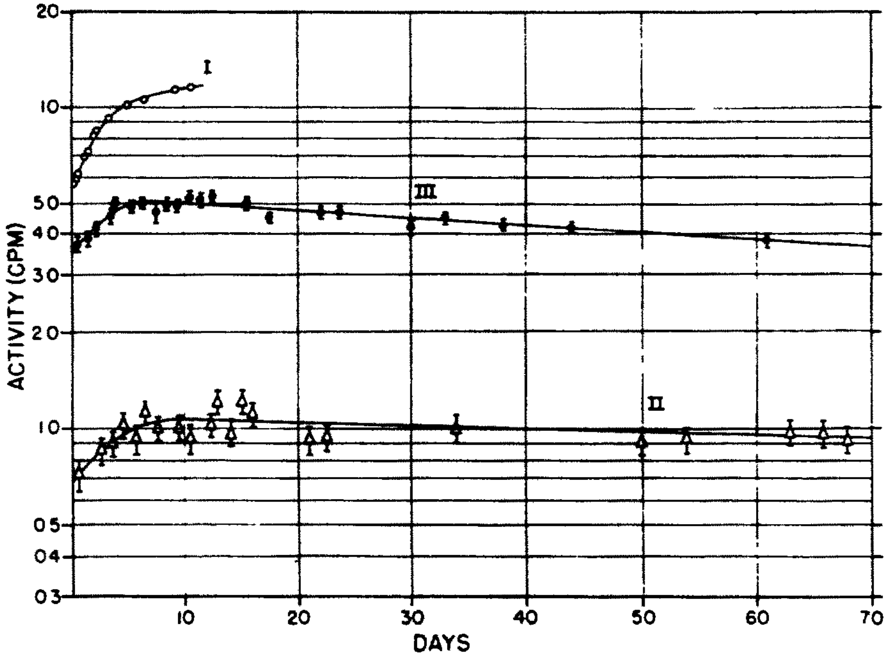

FIG 2.—Radioactivity of the strontium fractions isolated from pitchblende and depleted uranium.

I—2,600 g of pitchblende; chemical yield: 42%.
II—3,750 g of pitchblende; chemical yield 5%,
III—2,052 g of ^{238}UO$_3$; chemical yield 39%.

Numerous attempts made to recover strontium from acid-soluble fractions of the African pitchblende have all failed. The chemical yields were generally 5% or less in all such analytical schemes.

For example, strontium carrier (141 mg) was added to 3,750 g of the pitchblende, the whole being dissolved in dilute nitric acid; and, after the nitric acid was distilled off, the bulk of uranium was extracted with ether. The strontium carrier was recovered from the residue, after a lengthy chemical operation, with a chemical yield of only 5%. The counting data for the strontium fraction obtained in this experiment are shown in Fig. 2 as Curve II.

An attempt to separate the strontium fraction from 200 g of the pitchblende together with 150 mg of added barium carrier gave a chemical yield of only 3·7%. A chemical yield of 0% was obtained in many similar experiments.

All of these results suggest that the strontium is probably precipitated as the sulphate in the initial stage of the sample treatment, and hence it is almost impossible to recover the strontium fraction without the process of fusion.

The recovery of the strontium fraction from uranium salt is somewhat easier, in that the fusion step is not required. $^{238}UO_3$(2,052 g) was converted to

$$UO_2(NO_3)_2.6H_2O(2{,}945\ g)$$

and was treated with 40 litres of 80% nitric acid, after the addition of 200 mg of strontium carrier. The precipitate, which contained calcium, strontium, barium and radium, was converted to the carbonates. The carbonate precipitate was dissolved in dilute hydrochloric acid, and the iron^{III} hydroxide scavenging process was repeated three times. The purified carbonate precipitate was treated with nitric acid and evaporated to dryness. The strontium fraction was further purified according to an analytical scheme similar to that given in Fig. 1. The strontium was finally precipitated as the carbonate, filtered, dried and weighed. The chemical yield was 39%. The counting data are shown in Fig. 2 as Curve III.

TABLE I—RADIOSTRONTIUM CONTENTS OF THE AFRICAN PITCHBLENDE AND DEPLETED URANIUM

Sample	Chemical yield, %	10^{-4} × Disintegrations. sec^{-1}. g^{-1} of uranium in the sample[b]	
		^{89}Sr	^{90}Sr
I. African pitchblende (2,600 g)[c]	42	3·5 ± 0·3	5·8 ± 0·5
II. African pitchblende (3,750 g)[d]	5·0	——[a]	3 ± 2
III Depleted uranium (2,052 g) as $^{238}UO_3$[d]	39	2·8 ± 0·2	1·1 ± 0·1

[a] Measurement was impossible because about 200 days have elapsed since the initial separation of strontium from pitchblende.

[b] The errors reported here originate from uncertainty in analyzing the decay-growth curves.

[c] Sample I treated by fusion procedure.

[d] Samples II and III treated by acid-extraction procedure.

Precise determinations of the low-level activities of strontium-89 and -90 require at least a few months of careful counting, and hence only preliminary results can be reported here. Table I summarises the results obtained so far.

The results indicate that the strontium-89 and -90 are formed predominantly by the spontaneous fission of uranium-238. The equilibrium activity of the spontaneous fission-produced strontium-90 in uranium-bearing materials is calculated to be

$$\begin{aligned} N^{90}\lambda_{90} &= N^{238}\lambda_{238f} \,.\, Y^{90} \\ &= \frac{6{\cdot}02 \times 10^{23}}{238} \cdot \frac{\ln 2}{(8{\cdot}0 \times 10^{15})(3{\cdot}16 \times 10^{7})} \cdot (0{\cdot}05) \qquad (2) \\ &= 3{\cdot}5 \times 10^{-4} \text{ (disintegrations. sec}^{-1}\text{. g}^{-1}\text{ of uranium),} \end{aligned}$$

where N^{90} and N^{238} are the number of atoms of strontium-90 and uranium-238, respectively, λ_{90} is the decay constant of strontium-90, λ_{238f} is the spontaneous fission decay constant of uranium-238, and Y^{90} is the yield of mass 90 chain (tentatively assumed to be 5% in the above calculation).

The amount of strontium-90 in pitchblende appears to be considerably higher than the value calculated above, probably because of the contribution from the neutron-induced fission of uranium-235.

On the other hand, the level of strontium-90 in non-irradiated depleted uranium is much lower than that in uranium ore. This is most likely because the half-life of strontium-90 is greater than the "age" or the time elapsed since the preparation of the uranium salt. The results thus indicate that the secular equilibrium between strontium-90 and uranium is not yet established in the uranium salt. The following relationship should hold between the strontium-90/uranium-238 ratio and the "age" of the uranium salt:

$$N^{90}\lambda_{90} = N^{238}\lambda_{238f} \, . \, Y^{90} \, . \, (1 - e^{-\lambda_{90}t}) \tag{3}$$

where t is the "age" of the uranium salt. Thus it appears that the uranium salts can be dated from the observed strontium-90/uranium-238 ratios.

It is interesting to compare the activities of strontium-90 and radium in pitchblende. Because radium is expected to be also in secular equilibrium with uranium in pitchblende,

$$\frac{\text{Strontium-90 activity}}{\text{Radium-226 activity}} = \frac{\lambda_{238f}}{\lambda_{238\alpha}} \, . \, Y^{90}, \tag{4}$$

where $\lambda_{238\alpha}$ is the alpha-decay constant of uranium-238.

Equation (4) yields a value of 28 mμc of strontium-90 per g of radium in pitchblende. This calculation shows that Mme. Curie must have handled quite a considerable activity of strontium-90 (in fact, roughly 60,000 disintegrations per min of strontium-90 per g of radium isolated from pitchblende!) during her experiments. This activity would have been well within the limit of detection of the electroscope used in those days. It is perhaps fortunate, though, that man did not discover the process of nuclear fission almost a half century earlier!

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Zusammenfassung—Durch Zählen bei niedrigen Zählraten und analytische Verarbeitung großer Mengen wurden extrem geringe Mengen von Strontium-89 und -90 in Uranerzen und -salzen bestimmt. Strontiumträger wurde zu Kilogramm-Mengen nicht bestrahlten Uranerzes bzw. -salzes gegeben, erschopfend gereinigt und gezählt. Der Anteil von Radiostrontium lag in der Größenordnung von 10^{-4} Zerfällen pro Sekunde und Gramm U in der Probe. Diese Strontiumisotope werden in nicht bestrahlten Uransalzen und -erzen vorwiegend durch spontane Spaltung von Uran gebildet, in den Erzen scheint aber auch neutroneninduzierte Spaltung von Uran-235 vorzukommen.

Résumé—Une technique de comptage à bas niveau a été combinée à une opération analytique à grande échelle pour déterminer des quantités extrêmement faibles de strontium-89 et -90 contenues dans les minerais et les sels d'uranium. On a ajouté du strontium comme porteur à un échantillon d'un kilogramme de minerai et de sel d'uranium non irradié, parfaitement purifié et compté Les niveaux du strontium radioactif étaient de l'ordre de 10^{-4} désintégration par seconde et par gramme d'uranium dans l'échantillon Ces isotopes du strontium dans les sels et les minerais d'uranium non irradiés proviennent principalement de la fission naturelle de l'uranium, mais la fission induite par les neutrons de l'uranium-235 semble aussi se produire

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THE DETERMINATION OF THE OXIDATION STATES OF TRACER URANIUM, NEPTUNIUM AND PLUTONIUM IN AQUEOUS MEDIA

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Summary—This report describes the development, testing and application of a chemical procedure for determining the distributions of uranium, neptunium and plutonium among their respective oxidation states in various aqueous media at tracer concentrations. The separations achieved are of the order of 95% clean. Results are presented which show the per cent extraction of uranium, neptunium and plutonium oxidation states by $0{\cdot}4M$ 2-thenoyltrifluoracetone at various values of pH, and per cent carried by lanthanum fluoride from distilled water and sea water under various conditions. Radiochemical analysis of the separated fractions can then be used to determine the required oxidation state distributions.

INTRODUCTION

Uranium, neptunium and plutonium oxidation state determinations become increasingly important as the utilisation of nuclear power expands, the study of radioactive fallout progresses, and plans are made to test peaceful applications of nuclear explosions. Published material provides much useful information, but some of this is conflicting, and additional data are required to permit reliable measurements of oxidation state distributions. This report describes the development and testing of a method for determining the distribution of tracer concentrations of uranium, neptunium and plutonium among their respective oxidation states in aqueous media. Some areas of application are as follows.

The contribution of uranium-237 and neptunium-239 to the gross activity after a nuclear detonation may be appreciable for a period of ten half lives for each radionuclide.[1] Nuclear detonations in sea water will cause significant quantities of these radionuclides to be present in the aqueous phase of the debris.[2] Nuclear reactor accidents at sea or in the air above are more recent potential sources of sea water contamination by these nuclides as well as by plutonium-239. The biological fate of such contaminants would be expected to depend upon their oxidation states.

The chemical behaviour of uranium, neptunium and plutonium in the process of concentrating, isolating and purifying these elements from aqueous solutions will depend upon their oxidation states. It is therefore important to have means of verifying predicted species.

The development of an oxidation state separation scheme at the tracer level is beset with certain inherent difficulties. The only observable properties of a tracer which give evidence of the oxidation state arise from its chemical behaviour, which in most instances closely resembles the chemical behaviour of the element at macro concentrations. However, the importance of such effects as radiocolloid formation, adsorption on container walls, and oxidation state perturbation by small amounts of impurities becomes greatly magnified at tracer levels, and modifies the properties observed. Two other peculiarities of tracer behaviour are particularly appropriate. The first involves the kinetics of homogeneous bimolecular reactions when both reactants are present at tracer concentrations. Such reactions include the disproportionation of tracer uranium^{V}, neptunium^{V}, plutonium^{IV}, and the corresponding reproportionation reactions. In the absence of surface catalysis, such reactions will be exceedingly slow. The second is concerned with the solubility and carrying of neptunium^{V}. According to Katz and Seaborg[3] macroscopic neptunium^{V} fluoride is soluble, but according to Hyde[4] the tracer is carried on lanthanum fluoride precipitates. As a result of situations like these the investigator must be continually on guard against begging the question.

The recognised oxidation states of uranium, neptunium and plutonium in aqueous solution are summarised in Table I.

Table I.—Oxidation states of uranium, neptunium, plutonium in aqueous solution

Oxidation state	Uranium	Neptunium	Plutonium
III	Oxidised by water to uranium^{IV}	Rapidly oxidised by dissolved oxygen	Stable
IV	Stable	Stable	Stable
V	Disproportionates to uranium^{IV} and uranium^{VI}	Stable	Thermodynamically unstable
VI	Stable	Stable	Stable

It is well known that 2-thenoyltrifluoracetone (TTA) in benzene is a good extracting agent for actinide elements in the +4 oxidation state at low pH values[3,5] and that lanthanum fluoride carries all oxidation states of the actinides except the +6 state.[4] It was therefore decided to use a combination of these methods as the basis for a determination scheme. Although at low concentrations plutonium^{V} is fairly stable in the pH range 2 to 7,[6] its behaviour during extraction has not been previously determined. Marklen and McKay[7] have assumed that it is not extracted by TTA and Connick[8] has concluded that it is carried on a lanthanum fluoride precipitate.

EXPERIMENTAL

Tracers

Uranium-237 was produced by irradiating enriched uranium-236 oxide with thermal neutrons in the MTR at Arco, Idaho.

Neptunium-239 was produced by irradiating depleted uranium-238 metal with thermal neutrons.

Plutonium-237 was produced by bombarding enriched uranium-235 with 30 MeV alpha particles in the University of California 60-inch cyclotron.

In each case the target material was dissolved in hydrochloric acid and purified by ion exchange.[9,10] The radiochemical purity was established by gamma-ray spectrometry and by decay measurements during the course of experimental work.

Reagents

2-*Thenoyltrifluoracetone*, obtained from the Peninsular Chemical Research, Inc., Gainesville, Florida was used without further purification. Otherwise, natural sea water and reagent-grade chemicals were used throughout.

Preparation of stock solutions

Uranium^{IV} was prepared by passing uranium-237 tracer solution containing 2 mg of normal uranium in 4M hydrochloric acid through a 0·4-cm × 10-cm lead reductor column.[11]

Uranium^{VI}, *neptunium*^{VI} and *plutonium*^{VI} were all prepared by evaporating the tracer to dryness with nitric acid and taking up the residue with 0·05M perchloric acid and 0·005N potassium dichromate.

Neptunium^{IV} tracer was prepared by evaporating the neptunium tracer solution to dryness and dissolving with a warm solution of 0·5M hydrochloric acid, 0·1M potassium iodide and 0·1M hydrazine hydrochloride. Attempts to prepare neptunium^{IV} quantitatively with potassium iodide or hydroxylamine or both, and by back-extraction from 2-thenoyltrifluoracetone with 8M hydrochloric acid did not produce solutions with the expected properties.

Plutonium^{III} was prepared by evaporating the tracer to dryness and dissolving the residue in 0·6M hydrochloric acid and hydroxylamine solution.

Plutonium^{IV} tracer was prepared by evaporating the solution to dryness with hydroxylamine and dissolving the residue in a dilute nitric acid and sodium nitrite solution.

Extraction procedure

A 10-ml portion of the aqueous solution was adjusted to the appropriate pH with hydrochloric acid or ammonium acetate and "spiked" with a μlitre portion of tracer solution in a given oxidation state. An equal volume of 0·4M 2-thenoyltrifluoroacetone in benzene was added and the total solution was shaken for approximately 10 min. The phases were separated and a 4-ml aliquot of each phase was pipetted into a glass tube and counted in a well crystal scintillation counter.

Precipitation procedure

A 25-ml portion of solution was "spiked" with a μlitre portion of tracer solution in a given oxidation state, followed by the addition of 2·5 mg of lanthanum carrier and 1 ml of hydrofluoric acid. The solution was stirred for 2 min and centrifuged. The supernatant solution was decanted and the precipitate dissolved, without washing, in a mixture of 1 ml of saturated boric and 1 ml of concentrated hydrochloric acid. The volume was adjusted to equal that of the supernatant solution and gamma-ray assay was performed on both portions.

RESULTS

The results in Table II show that the extraction of uranium^{VI} increases with an increase in the pH from 0·4 to 4·2. Uranium^{IV} is extracted. The extraction of the hexavalent form could be the result of the increase in the effective ligand concentration with the increase in pH on the addition of dilute aqueous ammonia

TABLE II.—PER CENT EXTRACTION OF U^{IV} AND U^{VI} BY 0·4M TTA *vs.* pH IN THE ABSENCE OF ACETATE IONS

pH	U^{IV}	U^{VI}
0·4	94·5	1·1
1·7	—	73·6
2·3	—	96·9
3·1	—	99·3
4·2	98·5	99·5

Table III shows the effect of acetate concentration upon the extraction of uranium^{IV} and uranium^{VI} at pH 4·2. The extraction of uranium^{VI} decreases with an increase in the molarity of the ammonium acetate whereas uranium^{IV} is extracted at all molarities. It would take approximately 11M ammonium acetate to complex almost all of the hexavalent state in order to prevent its extraction by TTA.

The per cent extraction of the oxidation states of uranium, neptunium and plutonium from distilled water and sea water at various values of pH are given in Table IV. The results are averages of at least duplicate determinations. It is seen that pH 0·3–0·4 is favourable for separating the 4-oxidation states from the remaining oxidation states by the extraction procedure.

Table III.—Per cent extraction of U^{IV} and U^{VI} by 0·4*M* TTA *vs.* acetate concentrations at pH 4·2

Ammonium acetate, *M*	U^{IV}	U^{VI}
0·55	96·5	96·4
2·20	95·6	35·9
4·40	97·3	22·5
8·80	96·8	9·7
11·00	97·8	4·4

In the case of uranium^{IV}, repeated separations performed 2 hr apart on different aliquots showed increasing activity in the raffinate from the extraction and in the supernatant solution from the precipitation. Because this indicates gradual atmospheric oxidation of uranium^{IV}, the earliest recorded results have been taken as the most indicative of uranium^{IV} behaviour.

At pH 4·2 plutonium^{III}, plutonium^{IV}, uranium^{IV} and neptunium^{IV} are extracted.

Table IV.—Per cent extraction of uranium, neptunium and plutonium oxidation states by 0·4*M* TTA from distilled water and sea water at various values of pH

State	pH	Distilled water	Sea water
U^{IV}	0·3	93·3	94·3
	1·5	97·5	98·4
	4·3*	98·8	98·7
U^{VI}	0·4	3·4	1·7
	4·3*	4·4	3·6
Np^{IV}	−0·3	87·7	80·1
	0·3	98·7	98·8
	4·3*	100·0	92·0
Np^{VI}	0·3	0·1	0·1
	4·1	0·2	5·0
Pu^{III}	0·0	3·5	1·2
	0·3	4·6	2·8
	1·1	10·5	7·5
	2·0	—	79·4
	4·3*	99·0	100·0
Pu^{IV}	0·3	95·1	96·5
	4·2*	98·2	99·5
Pu^{VI}	0·0	0·1	5·2
	0·3	0·5	9·2
	4·2*	2·9	3·5

* Ammonium acetate is $>10M$.

The per cent of each oxidation state carried by lanthanum fluoride precipitation in the presence and absence of uranyl ion holdback or hydrochloric acid is given in Table V.

TABLE V.—PER CENT CARRYING OF URANIUM, NEPTUNIUM AND PLUTONIUM OXIDATION STATES ON LANTHANUM FLUORIDE FROM DISTILLED WATER AND SEA WATER UNDER VARIOUS CONDITIONS

State	Distilled water			
	Without UO_2^{2+} carrier		With UO_2^{2+} carrier	
	No HCl	1 ml of HCl	No HCl	1 ml of HCl
U^{IV}	—	—	97·3	98·2
U^{VI}	—	20·0	—	3·8
Np^{IV}	95·9	96·2	96·2	97·4
Np^{VI}	18·2	13·4	4·6	3·8
Pu^{III}	94·5	93·5	94·4	95·6
Pu^{IV}	—	—	—	99·0
Pu^{VI}	18·0	10·2	3·0	3·8
	Sea water			
U^{IV}	—	91·5	98·9	96·9
U^{VI}	40·1	3·4	34·6	2·6
Np^{IV}	94·6	97·6	96·2	99·1
Np^{VI}	39·7	1·6	27·9	1·3
Pu^{III}	96·4	97·8	97·4	97·5
Pu^{IV}	99·0	—	99·0	98·0
Pu^{VI}	14·0	3·6	12·5	5·0

Here again, the uranium results, as well as those for neptunium and plutonium, are averages of at least duplicate determinations. No design experiments were run to determine the optimum amounts of uranium and lanthanum carriers. It was noted, however, that less than 2·5 mg of lanthanum carrier was insufficient to carry all of the uranium^{IV}. With the exception that hydrofluoric acid was the last reagent added, no preferred order of reagent addition was noted. Without uranyl ion holdback carrier, as is seen in Table V, uranium^{VI} tends to coprecipitate with lanthanum fluoride from distilled water. The best results were achieved using both 2 mg of uranyl ion and 1 ml of hydrochloric acid.

The results for neptunium and plutonium in Table IV are in general agreement with those of Lai, *et al.*[12] which are presented in Table VI.

We did not obtain any results for neptunium^{V} in distilled water or sea water. Because little difference in the behaviour of the other actinide oxidation states between distilled water, salt water and sea water has been noted, and because the +5-state should be least affected by complex ion formation, the results with sodium chloride solutions have been taken as being applicable to the other two media.

It is seen from Tables IV and V that near-optimum conditions for neptunium oxidation state separation correspond closely to those used for uranium, namely, a pH of 0·4 for extraction and the use of uranyl ion holdback carrier and hydrochloric acid for precipitation. In the case of uranium, either the extraction at low pH or the precipitation method could be used to distinguish between uranium^{IV} and uranium^{VI}.

TABLE VI.—PER CENT EXTRACTION AND CARRYING OF NEPTUNIUM AND PLUTONIUM OXIDATION STATES FROM SODIUM CHLORIDE SOLUTION

State	TTA Extraction, pH 0·4	TTA Extraction, pH 4·2	LaF_3 precipitation, 2 mg of UO_2^{2+}
Np^{IV}	—	97–100	96
Np^{V}	—	0–5	95–100
Np^{VI}	—	2[b]	2
Pu^{III}	4	98–100	96
Pu^{IV}	97–100	97–100	96
Pu^{V}[b]	not extracted	not extracted	carried
Pu^{VI}	4	5–12[a]	4

[a] See section on Results.

[b] Predicted behaviour.

Lai prepared neptunium^{V} by fusing the tracer in sodium chloride for 1 hr at 850°–875°, cooling and dissolving the residue in dilute hydrochloric acid.

In the case of neptunium, because of the additional oxidation state, both methods must be used. The results are then interpreted as

$$\begin{aligned}
\mathrm{Np(TTA)} &= \mathrm{Np^{IV}}\\
\mathrm{Np(Raf.)} &= \mathrm{Np^{V}} + \mathrm{Np^{VI}}\\
\mathrm{Np(LaF_3)} &= \mathrm{Np^{IV}} + \mathrm{Np^{V}}\\
\mathrm{Np(Sup.)} &= \mathrm{Np^{VI}}\\
\mathrm{Np(Total)} &= \mathrm{Np^{IV}} + \mathrm{Np^{V}} + \mathrm{Np^{VI}}
\end{aligned}$$

where, for simplicity, separations are written as being quantitative. This overdetermined system of five equations in three unknowns can then be solved by the method reported by Wilson[13] in order to obtain the most consistent distribution.

It is seen that near optimum conditions for extracting plutonium^{IV} or holding plutonium^{VI} in solution during lanthanum fluoride precipitation correspond closely to those found for uranium. In the case of plutonium, because of its additional oxidation state, two extractions and a lanthanum fluoride precipitation must be carried out. The first extraction is done from pH 0·4 solution. The aqueous phase may then be adjusted to 4·2.

The behaviour of plutonium^{VI} towards extraction did not agree with that expected from the results of Heisig and Hicks[14] because of the acetate concentration. It appears that the plutonium^{VI} is complexed during the extraction.

As in the case of neptunium, the lanthanum fluoride precipitation should then be carried out on a separate aliquot. The results are then interpreted as

$$\begin{aligned}
\mathrm{Pu(TTA,\ pH\ 0{\cdot}4)} &= \mathrm{Pu^{IV}}\\
\mathrm{Pu(TTA,\ pH\ 4{\cdot}2)} &= \mathrm{Pu^{III}}\\
\mathrm{Pu(Raf.,\ pH\ 4{\cdot}2)} &= \mathrm{Pu^{V}} + \mathrm{Pu^{VI}}\\
\mathrm{Pu(LaF_3)} &= \mathrm{Pu^{III}} + \mathrm{Pu^{IV}} + \mathrm{Pu^{V}}\\
\mathrm{Pu(Sup.)} &= \mathrm{Pu^{VI}}\\
\mathrm{Pu(Total)} &= \mathrm{Pu^{III}} + \mathrm{Pu^{IV}} + \mathrm{Pu^{V}} + \mathrm{Pu^{VI}}.
\end{aligned}$$

Here again, separations have been written as being quantitative, and again, the unknowns are overdetermined.

DISCUSSION

Ideally, in order to demonstrate that two oxidation states of the same tracer element can be separated from each other by a given procedure, is should be shown that:

(1) tracer solutions have been prepared for each state, and that in each solution the given state is quantitatively maintained;

(2) the states are not altered by the separation process, and the results of the separation process are not affected by the substances introduced with the tracer (*e.g.*, oxidising or reducing agents);

(3) the separation is quantitative.

In practice, the second requirement may be modified with regard to oxidation state perturbation. Provided that sequential separation procedures are not utilised, it is only necessary that the final states be separable, and that the separated quantities correspond to the original distribution. For example, consider the LaF_3 method in separating the two oxidation states neptunium^{IV} and neptunium^{VI}. The neptunium^{VI} remains in the supernate and the neptunium^{IV} is coprecipitated. Now, if the procedure changes the oxidation state of neptunium^{IV} to neptunium^{V}, and neptunium^{V} coprecipitates when present, no error is incurred by overlooking the change, provided the supernate is not subjected to any further separations. The investigator must consider each case on individual merit and decide whether likely redox effects are or are not going to lead to bias in his results.

The above ideal has been approached in varying degrees by the methods described. What has been achieved is a self-consistent interpretation of a series of preparation and separation procedures, which is also consistent with published procedures for, and properties of, the various oxidation states, the procedures being "nearly quantitative." This interpretation is summarised in Table VII.

TABLE VII.—SUMMARY OF OXIDATION STATE BEHAVIOUR OF URANIUM, NEPTUNIUM AND PLUTONIUM AT TRACER CONCENTRATIONS

Precipitation by LaF_3		Extraction by TTA	
		pH 0·4	pH 4·3
M^{3+}	Carried	Not extracted	Extracted
M^{4+}	Carried	Extracted	Extracted
MO_2^+	Carried	Not extracted	Not extracted
MO_2^{2+}	Not carried	Not extracted	Extracted, unless complexed

Without further information, it is uncertain whether lack of quantitativeness in the separations results from the behaviour of the oxidation state, the presence of small fractions of other oxidation states in the stock solutions, or partial changes of oxidation state by the procedure. In some instances, this could be determined by re-extraction or reprecipitation. If the same distribution ratio were obtained for successive performances of the same separation, it could then be argued that the species was originally present in pure form. The use of inert carriers in the extraction procedures might serve to sharpen separations and should also be tried.

In practice[15] for a solution containing all three elements, the following separation scheme is adhered to. First a 25-ml portion of the solution is made 0·5M with respect to hydrochloric acid and the uranium^{IV}, neptunium^{IV} and plutonium^{IV} are extracted with an equal volume of $0{\cdot}4M$ 2-thenoyltrifluoracetone for 10–15 min. The pH of the raffinate is then raised to 4·3 with $11M$ ammonium acetate, and plutonium^{III} is extracted with a second portion of 2-thenoyltrifluoracetone. The lanthanum fluoride carrying step is then performed on a separate 25-ml portion of the solution being analysed. In rapid succession, 2 mg of natural uranium holdback carrier, 2·5 mg of lanthanum carrier, 1 ml of hydrochloric acid and 1 ml of hydrofluoric acid are added. Uranium^{VI}, neptunium^{VI} and plutonium^{VI} remain in the supernatant solution. Radiochemical analysis of each fraction is then carried out using Wish's method.[10] The results may then be interpreted using the equations described above, or more general equations may be used to incorporate the distribution ratios present.

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Zusammenfassung—Der vorliegende Bericht beschreibt die Entwicklung, Erprobung und Anwendung chemischer Methoden zur Ermittelung der Verteilung von Uran, Neptunium und Plutonium in ihren verschiedenen Wertigkeitsstufen in wässrigem Medium und bei Anwesenheit in Tracermengen. Die erzielten Trennungen sind in der Grössenordnung von 95%. Die mitgeteilten Daten zeigen die perzentuelle Extraktion der drei Metalle in ihren verschiedenen Oxydationsstufen durch 0,4 m 2 Thenoyltrifluoroazeton bei verschiedenen pH-Werten. Radiochemische Analyse wurde auf die Bestimmungen in den Fraktionen angewandt.

Résumé—Ce rapport décrit le développement, l'essai et l'application d'un procèdé chimique pour déterminer les répartitions des différents degrès d'oxydation de l'uranium, du neptunium et du plutonium dans divers milieux aqueux à l'état de traces. Les séparations effectuées donnent une pureté de l'ordre de 95%. Les résultats indiquent le pourcentage d'extraction par la 2 thénoyltrifluoracétone 0,4 M des degrès d'oxydation de l'uranium, du neptunium et du plutonium à différentes valeurs de pH et le pourcentage donné par le fluorure de lanthane à partir de l'eau distillée et de l'eau de mer dans diverses conditions. L'analyse radiochimique des parties fractionnées peut alors être utilisée pour déterminer les séparations demandées des degrès d'oxydation.

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SOME OBSERVATIONS ON THE ZERO-CURRENT BEHAVIOUR OF ANTIMONY INDICATOR ELECTRODES

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Summary—Methods are described for the preparation and handling of antimony electrodes of precise area and good reproducibility, and for the determination of potential-pH and potential-log P_{O_2} relationships under controlled conditions. Conditions affecting the response characteristics are defined and critically examined: they include the purity of the antimony, the history of the electrode, the temperature, agitation, poising, ionic strength and composition of the solution, the working pH range, the condition of the electrode surface and the oxygen content of the solution. The marked influence of the presence of buffering materials, of the condition of the electrode surface and of the oxygen content of the solution are emphasised. Phosphates cause changes of the electrode surface. The current situation is reviewed in the context of the present work, and electrode mechanisms are discussed.

During the course of fundamental investigations of the differential electrolytic potentiometry of acid-base reactions[1] and of the polarisation of antimony electrodes,[2] the necessity arose for a close enquiry into the zero-current behaviour of antimony electrodes.[3] Despite the general superiority of the glass electrode, antimony, the best of the metal-metal oxide electrodes, has advantages of cheapness, simplicity, robustness, ease of fabrication, cleaning and activation, comparative insensitivity to poisoning, low impedance, a reasonable exchange current and fast response speed, and claims continuing interest in many situations, such as in non-aqueous titrimetry,[4] and in polarisation methods.[1] The literature, however, contains much confusion and contradiction, and not until comparatively recently has this been recognised[5,6] as probably arising from a lack of standardisation of conditions of preparation, handling and use of the electrodes, in turn the result of a lack of appreciation of influential factors. This derogates much of the virtue of earlier work on the subject. The present investigation was undertaken in the hope of resolving some of the points of contention, and it has been thought worth offering a summary of the current situation. To avoid repetition, the present work is intermingled as comment with the review.

EXPERIMENTAL

Preparation of electrodes

Spectrographically pure antimony (Johnson Matthey Ltd.) is melted in a quartz crucible in air. A short length (the bottom) of Pyrex tubing of appropriate diameter sealed to a 5-inch length (the top)

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of 10-11-mm tubing is clamped vertically with the lower end just above the molten antimony. The tube is preheated by flaming and lowered to dip into the molten antimony, and the liquid metal is drawn into the tube to about 1 cm above the seal by suction applied from a rubber bulb attached to the top. A tight metal-glass junction results on cooling, and electrical contact is effected by pouring molten solder into the upper tube and sealing into this a length of tinned copper wire. The connecting lead is fixed at the top with wax, and a fresh surface of antimony is exposed at the bottom by cutting off a slice of the assembly at 90° to the tube axis with a diamond wheel. A plane surface of area equal to the internal cross-section of the tube is obtained. Many sets of electrodes were made of areas ranging from 0·126 cm^2 to 0·00102 cm^2, mean diameters being determined by a vernier microscope. Matched pairs of micro electrodes are made by drawing out a thick-walled capillary, cutting in the middle and sucking antimony into the two sections. Larger, cylindrical electrodes are made by cutting back the glass sheath to expose a rod of metal.

Electrodes are usable immediately after sawing, or may be aged (oxidised) by storage in water. No pre-treatment other than wiping with tissue before use has been found necessary—a process now meeting with general acceptance.[7] Electrodes are never allowed to dry out.

Reagents

Water, of chloride, nitrogen and silica content less than $10^{-11}M$, prepared in a quartz still,[8] is boiled out in borosilicate glass, handled under nitrogen in polythene, and protected from carbon dioxide as previously described.[1] This water, never stored for more than 36 hr, is used throughout the experimental work and for the preparation of all solutions.

Carbon dioxide-free perchloric acid solutions are prepared as required by dilution of standardised $0{\cdot}1M$ solutions prepared from the 72% AnalaR acid.

Barium hydroxide solutions are prepared as before.[1]

The background electrolytes, usually potassium chloride, occasionally sodium sulphate, of AnalaR grade, are selected for neutral reaction. Buffer and other materials are of AnalaR grade. Calibrated glassware is used throughout.

Procedure

(*a*) *Potential-pH measurements:* A 400-ml beaker is charged with 200 ml of water and 0·5 g of potassium chloride ($\equiv 0{\cdot}03M$) and fitted with a cover carrying a mounted set of three (or more) antimony electrodes, a calibrated E.I.L. GHS23 lithium-barium glass electrode, the salt bridge, terminated with a low leakage rate ceramic plug, a high-capacity saturated calomel cell of area 30 cm^2, a burette and a gas inlet which so dips into the solution that gas bubbles do not break on the electrode surfaces. Coating the beaker with hard paraffin wax to obviate attack of the glass and dissolution of alkali was found to make no difference to the results. The solution is magnetically stirred just at cavitation speed with a PTFE-coated paddle of a length just less than the diameter of the beaker. The potentials of the electrodes with respect to the reference electrode are read on an E.I.L. model 23A pH meter, from which a Cambridge DE 2-sec recorder is driven. By means of helipots, the recorder scale can be expanded and backed off to provide more sensitive discrimination and to observe potential drift. Scale expansion to incipient noise level can also be used to overcome recorder dead space in establishing the attainment of equilibrium and in examining low drift rates. Electrode circuits are selected by a Doran high impedance switching unit. An interval of at least 30 min is allowed for potential equilibration at each pH value, and the pH is changed by addition of increments of $0{\cdot}001M$ perchloric acid or $0{\cdot}0005M$ barium hydroxide from the burette. More concentrated solutions are used outside the pH range 4–10. Supplementary results are provided from numerous perchloric acid—barium hydroxide titrations.[1] A vigorous stream through the solution of the appropriate gas at constant pressure is maintained throughout.

(*b*) *Variation of partial pressure of oxygen:* As in (*a*), with the addition that pure oxygen and "oxygen-free" (white spot) nitrogen are passed through separate banks of calibrated rotameters of sizes such that a nominal variation from 0·1% to 100% of oxygen in the gas stream bubbling through the solution can be effected. The gas flow from the cylinder reducing valves is further regulated by calibrated needle valves. The attainment of potential equilibrium is observed on the recorder trace, and a series of measurements is started with the lowest required oxygen partial pressure because equilibration is much more rapid in the direction of increasing oxygen concentration.

Each series of experiments was replicated many times, both with the same and with fresh electrodes and/or solutions, and each run was carried out with at least three electrodes. Replicability is discussed below. Sets of results are illustrated graphically in Figs. 1 and 2. The laboratory was thermostatted at 20°. The pH values indicated by the glass electrode agreed with those calculated from solution composition.

REVIEW, RESULTS AND DISCUSSION

Factors recognised[9] as affecting the performance of antimony electrodes in aqueous media are:

(*a*) the purity of the antimony and the history of the electrode;
(*b*) temperature and agitation of the solution;
(*c*) the poising, ionic strength and composition of the solution;
(*d*) the working pH range;
and (*e*) the oxygen content of the solution or partial pressure of oxygen in the atmosphere in contact with the solution.

It is therefore necessary to describe meticulously the preparation, handling and conditions of use of the electrodes if the results are to be of significance and their validity is to be appraised. The factors will be discussed as grouped above.

Potential-governing equilibria of metal–metal oxide electrodes

Imprimis, as a metal–metal oxide electrode, it is tacitly assumed that the following equilibria are applicable:

$$Sb_2O_3 + 3H_2O \rightleftharpoons 2Sb(OH)_3 \qquad (1)$$

$$Sb(OH)_3 \rightleftharpoons Sb^{3+} + 3OH^- \qquad (2)$$

whence the solubility product $S_{Sb_2O_3}$ is

$$S_{Sb_2O_3} = [Sb^{3+}][OH^-]^3 = [Sb^{3+}]\frac{K_w{}^3}{[H^+]^3} \qquad (3)$$

and that the electrode responds to antimony^{III} ions by the Nernst relationship

$$E = E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e [Sb^{3+}] \qquad (4)$$

From (3) and (4)

$$E = E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e S_{Sb_2O_3}\frac{[H^+]^3}{K_w{}^3} \qquad (5)$$

$$= E_{0_{Sb/Sb^{3+}}} + \frac{RT}{3F}\log_e \frac{S_{Sb_2O_3}}{K_w{}^3} + \frac{RT}{3F}\log_e [H^+]^3 \qquad (6)$$

The first two terms on the right hand side of (6) are assumed to be constant, and may be combined as the single term E_0', so that

$$E = E_0' + \frac{RT}{F}\log_e [H^+] = E_0' - \frac{2{\cdot}303RT}{F}\,\text{pH} \qquad (7)$$

DISCUSSION

Equilibria (1) and (2) can be strongly challenged. The hydration process is undoubtedly complex, and strongly dependent on conditions; it may be represented by

$$aSb_2O_3 + (3a - 2b)H_2O \rightleftharpoons 2Sb_aO_b(OH)_{(3a-2b)} \qquad (8)$$

and it is unlikely that Sb^{3+} ions will be formed, of a concentration adequate to control electrode potentials, the over-all ionisation being either

$$Sb_aO_b(OH)_{(3a-2b)} \rightleftharpoons Sb_aO_b{}^{(3a-2b)+} + (3a - 2b)OH^- \qquad (9)$$

or

$$Sb_aO_b(OH)_{(3a-2b)} \rightleftharpoons Sb_aO_{(3a-2b)}{}^{(3a-2b)-} + (3a - 2b)H^+ \qquad (10)$$

with an isoelectric region of overlap of the two modes of ionisation, which are themselves complex equilibria. This does not affect the pH dependence, because the relevant term in either case resolves to

$$\frac{RT}{(3a - 2b)F} \log_e [\mathrm{H}^+]^{(3a-2b)} = \frac{RT}{F} \log_e [\mathrm{H}^+] \tag{11}$$

but the constancy of the term E_0' is no longer assured, and the second term in (6) may well vary with conditions. This possibility has not received sufficient attention in the past, but suspicion has recently been turned upon the constancy of normal electrode potentials.[7]

(*a*) *Purity and history of the electrode*

After early confusion, Perley's careful work established the detrimental effects of traces of copper, which are now confirmed; but otherwise antimony is comparatively insensitive to impurity,[6] notably to arsenic and sulphur.[10] Many methods of preparation have been examined.[6,11] Electrodeposition gives variable quality[6] because of deficiency of oxygen in the metal lattice, inclusion of electrolyte (*cf.* "explosive" antimony[12]) and variable surface activity. Casting in air is found to give the most satisfactory electrodes. Compression of mixtures of powdered metal and oxide[11] has been advocated for ensuring uniform distribution of oxide.

Pretreatment to secure a clean reproducible surface by electrolysis,[13] chemical activation,[13] abrasion[14] and scraping[15] has been advocated; simple wiping with tissue has been found perfectly satisfactory. Electrodes after drying out, or prolonged storage in aerated water, behave erratically when returned to use because of too thick an oxide film on the surface. Activity is quickly restored by the differentiating current in DEP,[1] so that cathodic polarisation at $\sim 10\ \mu\text{A cm}^{-2}$ is effective; but normal practice is to saw a thin slice off the end of the electrode to expose a fresh surface. The electrode is then used immediately, or after ageing for 24–48 hr in aerated water. Electrodes are not exposed to solutions outside the pH range 2–10, otherwise marked hysteresis occurs. Electrodes prepared and handled as described show good reproducibility (± 5 mv). No specific area effects[16] have been observed.

(*b*) *Temperature and agitation of the solution*

The scant work on temperature effects[17] indicates far from theoretical behaviour at temperatures above 30°, and no consistent theory has been advanced to account for the deviations. The present work has been confined to a temperature of 20°, but polarisation measurements up to 50° have been analysed.[2a]

Stirring affects the electrode potentials.[9,14,18] The effect has been reviewed,[6] and Gatty and Spooner have plausibly applied the local action theory of corrosion.[9] The electrode surface consists of anodic (bare metal) and cathodic (oxide layer) sites, and the advent of dissolved oxygen increases the proportion of cathodic sites, causing a positive potential drift. Stirring either increases the rate of diffusion of oxygen to the bare metal, to increase the proportion of cathodic sites causing a positive deviation, or enhances anodic dissolution to expose more bare metal, causing a negative drift; both effects have been observed under appropriate conditions.[9] The versatility of the theory makes it difficult to prove or disprove the interpretation of a given observation.

(*c*) *Poising, ionic strength and composition of the solution*

Poising: Perley[14] alone appears to have observed that the potential at a fixed pH differs in the presence or absence of buffering substances. That good linear plots of near theoretical slope result from calibration of the electrode in a series of buffer solutions is no guarantee that the behaviour will be similar in unpoised solutions, or in solutions of low buffer concentration or low ionic strength. For example, at pH 7 and 20° in a pure oxygen atmosphere, the antimony electrode potential with respect to the SCE was -320 mv in unpoised solution. Addition of ammonium acetate (pH 6·98) lowered the potential to -356 mv. In ordinary nitrogen ($\sim$1 % oxygen) these potentials became -405 ± 5 and -411 ± 2 mv, respectively. Change of atmosphere may cause a change in electrode reaction,[9,20] or removal of oxygen overvoltage;[20] but the negative shift on addition of buffer is unlikely to be caused by reduction of the solubility of oxygen on the addition of electrolyte[6] because the high supporting electrolyte concentration ensures that the ionic strength is hardly altered. The concentration of ammonium acetate is not critical; variation from 0·005*M* to 0·03*M* made no significant difference to the potentials.

Ionic strength: Effects claimed to result from changes in ionic strength[14,21,22] can more probably be ascribed to adventitious addition of impurities with the electrolytes, to change in hydrogen ion activity, or to change in oxygen solubility,[6] or, at low ionic strengths, to activation overpotential.

Composition of solution: Oxidising, reducing or complexing (particularly oxygen-ligand) substances will naturally affect the potential of the antimony electrode by upsetting the equilibria on which it depends. For example, buffers containing tartrate or citrate must be avoided.[23] Silver[24] and copper ions, and, presumably, other metal ions, such as mercury, displaceable by antimony, produce abnormal potentials. The effect of phosphate ion is discussed below.

(*d*) *Working pH range. Potential-pH relationships and* E_0' *values*

Linearity, slope and range of response: The reasonably linear pH response has repeatedly been affirmed, but it is generally recognised that the useful range is limited to pH 1–12, and that excursions to these limits give rise to hysteresis, so that the electrode functions best in the range pH 3 to 10. Most results refer to calibration in aerated buffer solutions. Perley, however, has shown[14] that different slopes for the emf-pH plot result, depending on whether the solution pH is greater or less than 8: a break occurs in the region around neutrality. Others have noted this phenomenon.[15] The emf-pH plots of Fig. 1 show that for unbuffered, oxygenated solutions, the antimony electrode yields a line of slope 58 mv/pH unit over the range pH 3–6 in agreement with Perley's results; but the plot becomes non-linear at higher pH values,[25] and shows a flat portion over the range pH 6·5–7·5, somewhat resembling that observed by Kolthoff and Hartong.[15] Under ordinary ($\sim$1 % of oxygen) nitrogen, the slope in the region pH 8–11 is 52 mv/pH unit, again in agreement with Perley's results. The effect of oxygen is greatest in unpoised neutral or weakly alkaline media, and addition of buffer causes an immediate negative shift of potential towards the value in nitrogen. The change in slope could well indicate a change in active ion from hydrogen to hydroxyl, *i.e.*, a change in electrode order, as happens with silver-halide systems,[16] or of electrode reaction [*cf.* refs. (9) and (10)].

Formal potential, E_0': Assuming that equation (7) is valid, extrapolation of the emf-pH plot should give values for E_0', but in practice the extrapolation extends over 2–8 orders of concentration, casting doubt on its reliability. Moreover, slopes vary between 50 and 60 mv/pH unit; potentials at a given pH value may vary by 100 mv according to the conditions of measurement; and temperature coefficients are uncertain. The diversity of reported E_0' values[6] is not surprising, and any attempt to draw conclusions from such evaluations must be approached with caution. Pourbaix *et al.*[26] give the theoretical value of E_0' on the hydrogen scale as 0·167 v: most quoted values are about 0·1 v higher.[6] Values from Fig. 1 are 0·274 v in a pure oxygen atmosphere, and 0·245 v in ordinary nitrogen. Mehta and Jatkar,[27] surveying a large number of reported values, discern a tendency towards the formation of two distinct groups, one around 0·275 v, the other around 0·25 v. It is tempting to ascribe the higher value to determinations in aerated or oxygenated solutions, and the lower to de-aerated solutions; but the correlation is vitiated by certain exceptions and by lack of definition of experimental conditions.

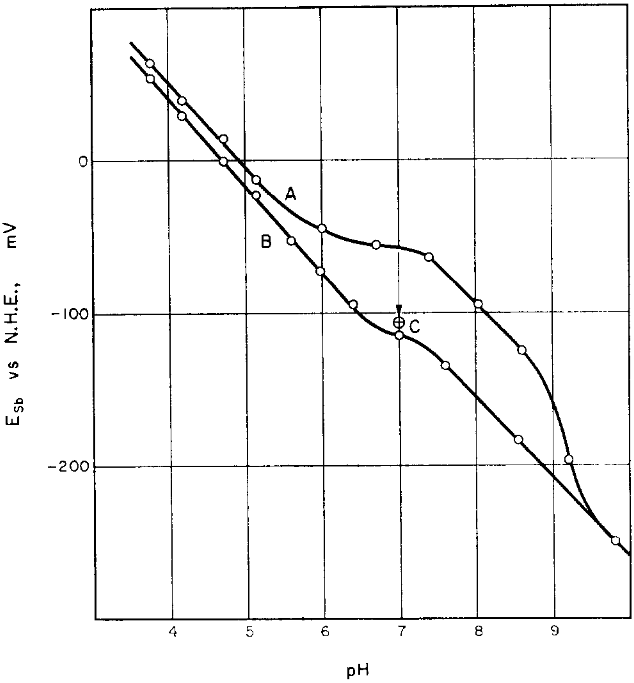

FIG. 1.—Emf—pH relationships of antimony electrodes.
Curve A: In an atmosphere of pure oxygen. Point C illustrates the effect of the addition of a buffering material to the solution.
Curve B: In an atmosphere of nitrogen containing a trace (about 1 %) of oxygen. Potentials have been converted to the hydrogen scale using the value 0·245 v for the SCE.

Under customary conditions, the electrode does not accord with the simple concept (7), but does approach theoretical behaviour under strictly anaerobic conditions[17,28] for which E_0' values of 0·16 v have been reported, and deoxygenation shifts the potentials towards the theoretical values. The electrode reaction must therefore be complex rather than simple, *e.g.*, (8), and may be a mixed process. For instance,

$$2Sb + 3H_2O \rightleftharpoons Sb_2O_3 + 6H^+ + 6\varepsilon \tag{12}$$

gives a potential linearly dependent on pH, and an E_0' value of 0·16 v, while

$$O_2 + 4H^+ + 4\varepsilon \rightleftharpoons 2H_2O \tag{13}$$

gives the same pH dependence and an E_0 value of 1·23 v, but the potential is also dependent on log P_{O_2}. At a constant partial pressure of oxygen, the electrode should show a linear pH response, with an E_0 between 0·16 and 1·23 v, depending on the partial pressure of oxygen and the state of the electrode surface. Several theories attempt a more detailed mechanistic explanation,[9,20] probably the most successful being the local action theory of corrosion; but none has yet been completely vindicated. Clearly, however, the buffering and oxygen content of the solution are intimately involved in the response of the electrode, and the E_0' value is a function of conditions of use.

(*e*) *Oxygen response of antimony electrodes*

Most reports refer to aerated solutions, one or two to pure oxygen or pure nitrogen atmospheres. Tourky and Moussa[20] examined the response in carefully de-aerated solutions of electrodes prepared in an atmosphere of hydrogen, and found a step-like emf-pH plot with alternating high and low slopes showing five breaks which they attempted to interpret in terms of neutralisation of hydroxyl and hydrogen groupings on antimony oxide. No investigation of the effect of variation of oxygen content appears to have been reported other than those of Holmqvist[29] and of Kauko and Knappsberg.[13] From equation (13) the plot of emf against $\log_{10} P_{O_2}$ at constant pH should have a slope of $2{\cdot}3\ RT/4F$, which Kauko and Knappsberg claim for polished antimony electrodes at pH 5·9, 7 and 9 in phosphate and borate buffers over the partial pressure range of 3–100% of oxygen. Holmqvist found an S-shaped plot with the potential of the antimony electrode changing rapidly at about 10% of oxygen and reaching constancy at high and low levels.

Results

Effect of buffers: The present work was done at pH 7 in 0·03*M* potassium chloride, with or without the addition of ammonium acetate or a phosphate buffer, and subjected to manyfold replication. Typical results are shown in Fig. 2 and support Holmqvist. Notable is the effect of buffers in shifting the potentials to more negative values and in diminishing the potential swing for a given change in oxygen pressure. The concentration of buffering substance in the solution is not critical, provided that it exceeds a minimum value of about 0·005*M*: determinations have been made in concentrations up to 0·3*M* without revealing any concentration-dependent effect. The reproducibility of the slopes is not good, but the slope $\partial E/\partial \log_{10} P_{O_2}$ in buffered solutions tends to be less than in unpoised solution. Freshly cut electrodes give lower slopes and more negative potentials than oxidized electrodes.

Equilibration time: Kauko and Knappsberg attribute Holmqvist's results to failure to attain equilibrium; and certainly equilibration is sluggish, especially at oxygen partial pressures below 10%. Accordingly, two oxygen levels falling on the straight portion between 0·5% and 10% oxygen of the emf–$\log_{10} P_{O_2}$ plot were selected, and the potential at each pressure was recorded for 6 hr repeatedly. After the initial rapid drift for 10 min, and a slow drift for a further 20 min, the potentials varied by no more than 0·25 mv. The slopes calculated from these measurements in ammonium acetate, assuming linearity of the plot, were 30 mv for freshly sawn electrodes and 57 mv for oxidised electrodes, each of these being means of three separate determinations showing a maximum scatter of 3 mv.

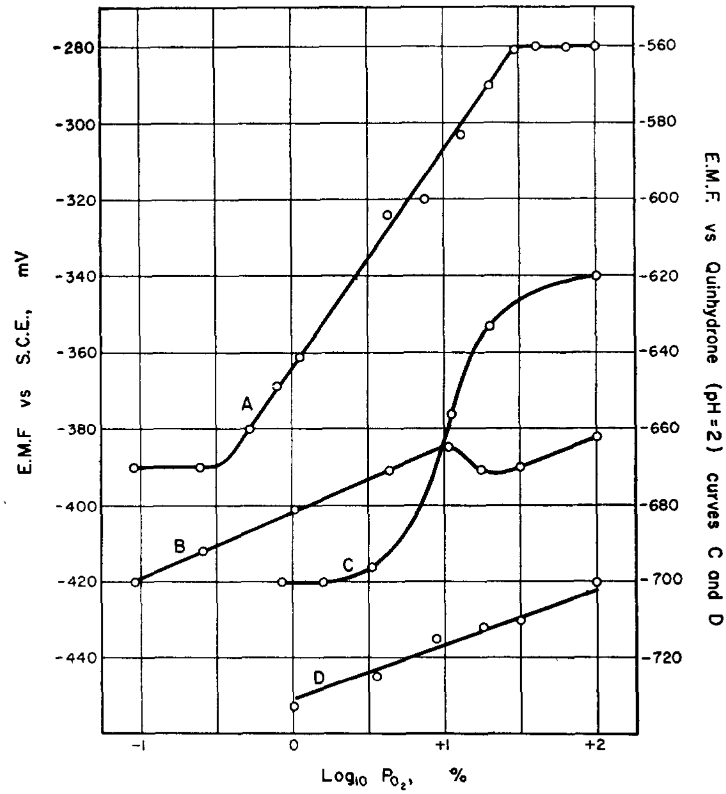

FIG. 2.—Variation of partial pressure of oxygen at pH 7.
Curve A: Unpoised solution, 0·03*M* KCl.
Curve B: Phosphate buffer.
Curve C: From Holmqvist's data.
Curve D: From Kauko and Knappsberg's data.

Discussion

The approach to constant potential at low oxygen levels can be explained by postulating either that this represents the residual partial pressure of oxygen in "white spot" nitrogen, probably about 0·1%; or that this level represents the "failure point" of the electrode response,[16,30] *i.e.*, the concentration below which no further change in potential occurs with change in concentration of the reactive species. Constancy of potential at high oxygen levels is not so easily explained. Possibly in this region the antimony surface is fully populated with oxygen doublets, so that further increase in oxygen partial pressure does not change the potential,[31] a view in accord with the postulate of Tourky *et al.*[17,20] that antimony electrode behaviour is governed by a layer of chemisorbed oxygen on the metal surface.

The disaccord of Kauko and Knappsberg's results may be resolved on the basis of the presence of phosphate in their solutions. Electrode surfaces, even if initially dull and thickly coated with oxide, become bright and shiny after immersion in solutions containing phosphate ion. Phosphate ion evidently reacts with antimony oxide species, probably to form a phosphate antimonate-III ion, though no report of such a reaction has been traced in the literature. The measurements in phosphate media provide emf–$\log_{10}P_{O_2}$ slopes closest to the theoretical value claimed by Kauko and Knappsberg, and indicate participation of the bare metal surface in reaction (13).

The slopes of the emf–$\log_{10}P_{O_2}$ plots vary from 20 to 60 mv depending on whether electrodes are fresh or aged, and whether or not buffering substances or phosphate ion are present, forcing the conclusion that the precise involvement of oxygen in the electrode reaction is condition-dependent. Processes involving one, two or four [reaction (13)] electrons per oxygen molecule can be written:

$$2H^+ + 2Sb + 2O_2 + 2\varepsilon \rightleftharpoons Sb_2O_3 + H_2O \tag{14}$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,\mathrm{pH}}} = \frac{2{\cdot}3RT}{F};$$

$$6H^+ + 2Sb + 3O_2 + 6\varepsilon \rightleftharpoons Sb_2O_3 + 3H_2O \tag{15}$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,\mathrm{pH}}} = \frac{2{\cdot}3RT}{2F};$$

but reactions involving three electrons are less plausibly formulated:

$$18H^+ + 2Sb + 6O_2 + 18\varepsilon \rightleftharpoons Sb_2O_3 + 9H_2O$$

with a slope of

$$\frac{\partial E}{\partial(\log_{10}P_{O_2})_{T,\mathrm{pH}}} = \frac{2{\cdot}3RT}{3F}.$$

Values of the oxygen response slopes can be accounted for on a basis of such a reaction series, one or other reaction preponderating as conditions change.

CONCLUSIONS

When used merely as an indicator electrode for locating titrimetric end-points, the antimony electrode performs satisfactorily, provided that it is not exposed to solutions outside the pH range 2–10, or solutions containing ligands that will combine with, or metal ions displaceable by, antimony; but reproducible results will be accessible only if all conditions are rigorously standardised.

The formal potential E_0', and electrode slope, are dependent on the oxygen content of the solution, the presence or absence of buffering material and the condition of the electrode surface. The oxygen response also depends on the same factors, and is markedly affected by the presence of phosphate. For the determination of pH, the response is so much dependent on conditions that the electrodes should be calibrated and used under as nearly identical conditions as possible.

The method of preparation and handling which has been described gives electrodes of excellent reproducibility independent of electrode area; but the simple mechanism of metal-metal oxide electrodes is inadequate to describe their behaviour. It seems likely that equilibrium (12) combined with (13), (14) and (15), in the presence of oxygen, is responsible for the mixed behaviour of antimony electrodes, but the marked influence of buffering materials is difficult to explain.

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Zusammenfassung—Herstellung und Handhabung von gut reproduzierbaren Antimonelektroden genau definierter Fläche und Bestimmung der Potential-p_H-und Potential-log p_{O_2}-Beziehungen unter definierten Bedingungen werden beschrieben. Die das Ansprechen beeinflussenden Parameter werden definiert und kritisch untersucht: Reinheit, Vorgeschichte der Elektrode, Temperatur, Rührung, Ionenstärke und Zusammensetzung der Lösung, p_H, Oberflächenzustand der Elektrode und Sauerstoffgehalt der Lösung. Nachdruck wird gelegt auf den starken Einfluß von Puffern, des Oberflächenzustandes der Elektrode und des Sauerstoffgehalts der Lösung. Phosphate verändern die Oberfläche der Elektrode. Eine Ubersicht über das Verhalten bei Stromfluß wird gegeben und Elektrodenmechanismen diskutiert.

Résumé—On décrit des méthodes de préparation et de manipulation des électrodes d'antimoine, de surface précise et de bonne reproductibilité, et des méthodes de mesures potentiométriques du pH et des relations potentiel-log P_{O_2} dans des conditions controles. Les facteurs susceptibles d'affecter les caractéristiques de la réponse ont été définis et étudiés: ils comprennent la pureté de l'antimoine, les antécédents de l'électrode, la température, l'agitation, l'équilibration, la force ionique et la composition de la solution, le domaine de pH utilisé, les conditions de surface de l'électrode et la teneur en oxygéne de la solution. L'influence déterminante qu'ont les facteurs suivants: présence de tampons, conditions de surface de l'électrode et teneur en oxygéne de la solution, a été mise en lumiére. Les phosphates perturbent la surface de l'électrode. Les théories actuelles et le mécanisme des électrodes sont résumés dans le contexte de cet article.

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THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF EUROPIUM^{III} OXALATE AND SOME EUROPIUM^{II} SALTS*

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Summary—The differential thermal analysis curves of $Eu_2(C_2O_4)_3$, EuC_2O_4 and $EuCO_3$ exhibit prominent exothermic peaks in the region of 420° because of the oxidation of europium^{II} to europium^{III}. The first step in the decomposition of $Eu_2(C_2O_4)_3$, after completion of dehydration, is $Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$. The reasons for some conflicting differential thermal analysis curves of the rare earth oxalates obtained by various authors are explained. The europium^{II} oxalate, $EuC_2O_4 \cdot 1.7H_2O$, is prepared.

INTRODUCTION

THE oxalates of the rare earths are of special importance for the separation and quantitative analysis of this group of elements. There is also a wide interest in other aspects of the rare earth oxalates, as evidenced by the numerous investigations on their thermal behaviour published during the last decade. Mostly thermogravimetric (TG)[1] and differential thermal analytical (DTA)[2] methods have been employed, but the thermal curves obtained were complicated and their interpretation was often dubious.

In a series of studies carried out in this laboratory[3] the mechanism and stepwise decomposition of many of the rare earth oxalates has been elucidated by analysing the solid residues and the gaseous products formed in vacuum or in various atmospheres.[4] It was found that $Eu_2(C_2O_4)_3$[4] and $Yb_2(C_2O_4)_3$[4] were internally reduced to the bivalent cation in the first step of their decomposition, at about 300° and 340°, respectively. In the presence of oxygen the cations were soon re-oxidised to the tervalent state. In vacuum or in an inert atmosphere, bivalent carbonates (or oxycarbonates) were found to be stable well above 400°. In the light of these results a re-examination of the TG and DTA curves of $Eu_2(C_2O_4)_3$ was thought to be desirable. A few bivalent europium salts, such as EuC_2O_4, $EuCO_3$ and $EuSO_4$, were also prepared and their thermal curves were compared to that of the tervalent europium salts. Disregarding minor fluctuations, the recorded thermal curves were found to be consistent with the previously proposed mechanisms of decomposition.

EXPERIMENTAL

Reagents

Eu_2O_3 (Lindsay, code 1013, 99·9% purity) served as the starting material for all of the preparations examined in this work.

$Eu_2Ox_3 \cdot 5.8H_2O$ (or 10 H_2O): Prepared in the usual manner by precipitation with oxalic acid from a nitric acid solution[4] and kept in an evacuated desiccator over phosphorus pentoxide.

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* This paper contains part of the Ph.D. thesis submitted to the Senate of the Hebrew University by E. L.

$EuSO_4$ and $EuCO_3$: Prepared as described by Cooly and Yost;[5] the solution from the Jones' reductor was allowed to pass directly into a 4*M* sulphuric acid solution and the precipitated $EuSO_4$ was filtered, washed and dried.

A batch of $EuSO_4$ was further digested in a 10% sodium hydroxide plus sodium carbonate mixture to yield the greenish-yellow $EuCO_3$, which, after drying, was found by analysis to conform to the formula $EuCO_3 \cdot 0.21H_2O$. The infrared absorption spectrum of this preparation, by the potassium bromide disc method, is shown in Fig. 1.

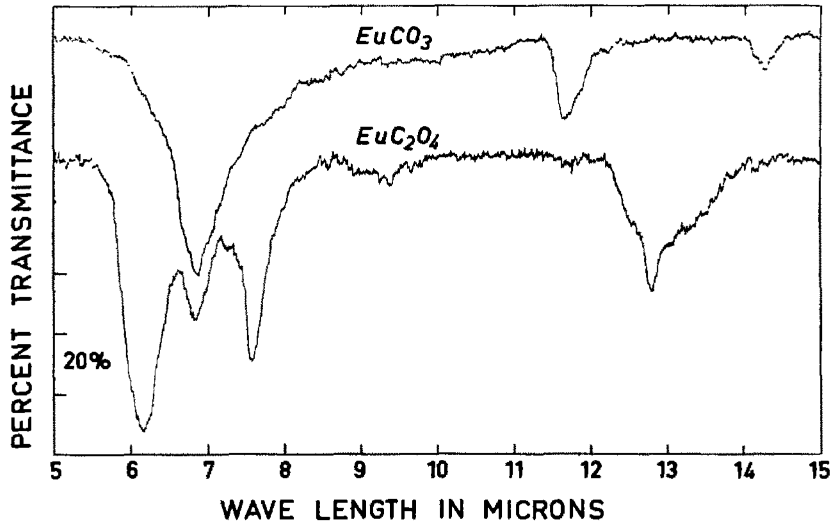

Fig. 1.—Infrared spectra of EuC_2O_4 and $EuCO_3$ showing absorption bands characteristic for the anions.

EuC_2O_4: Its preparation has not yet been described in the literature. Various procedures were investigated. On either adding the reduced solution from the Jones' reductor to a saturated solution of oxalic acid (previously boiled to expel oxygen) or dissolving $EuCO_3$ in 1*M* hydrochloric acid and adding the oxalic acid to this solution, a beige coloured precipitate was obtained. An elementary analysis* of the last preparation gave:

	Found	Theoretical		
		EuC_2O_4	$EuC_2O_4 \cdot 0 \cdot 5H_2C_2O_4$	$Eu_2(C_2O_4)_3$
C, %	13·08	10·0	12·64	12·68
H, %	0·18	0·0	0·315	0·00

and its composition is evidently undefined.

Pouring a saturated oxalic acid solution onto the solid $EuCO_3$ proved more successful. Evolution of carbon dioxide, but no dissolution of the solid (which turned from yellow to a rusty red) was observed. At this stage two volumes of distilled ethyl alcohol were added, and the red crystals were filtered and dried at 90°. If no alcohol is added, the red crystals change slowly to the beige modification, but no similar change occurs when the dry material is contacted with water. The elementary analysis of the red preparation gave 8·86% of carbon and 1·28% of hydrogen. Assuming that all hydrogen is from absorbed water or from water of crystallisation, the formula for the preparation should be $EuC_2O_4 \cdot 1 \cdot 72H_2O$, in excellent agreement with the 8·86% of carbon found. This formula was

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* For which we are grateful to Mrs. M. Goldstein of the Organic Chemistry Department of the Hebrew University.

further confirmed by igniting a weighed portion of the preparation in air at 1000°:

	H, %	C, %	Wt. loss at 1000°, %
Theoretical for			
$EuC_2O_4 \cdot 1{\cdot}7H_2O$	(1·28)	8·86	35·0 (Eu_2O_3)
Found	1·28	8·86	34·5

The infrared absorption spectrum of this preparation, obtained by the potassium bromide disc method, is shown in Fig. 1.

$Eu_2(SO_4)_3 \cdot nH_2O$: Crystallised from a sulphuric acid solution of Eu_2O_3 by evaporation. It was collected on a fritted glass crucible and washed with a small amount of water and dry acetone. This product was not analysed, and it is therefore possible only to estimate its water content or surplus sulphuric acid, from the thermogravimetric curve.

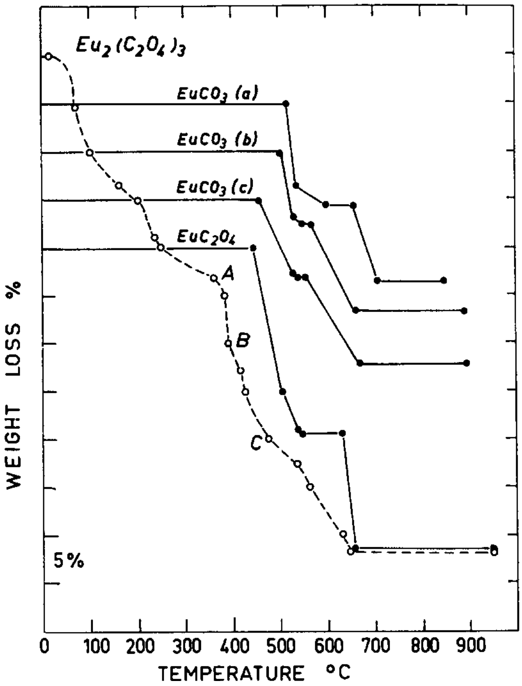

FIG. 2.—Thermogravimetric curves of $Eu_2(C_2O_4)_3 \cdot 10H_2O$, $EuC_2O_4 \cdot 1{\cdot}7H_2O$, two samples of $EuCO_3$ (a and b), and $EuCO_3$ mixed with alumina (c).

Apparatus

For the thermogravimetric measurements a Stanton decimilligram model thermobalance was used. The heating rate was maintained at 6°/min and the furnace temperature control is generally correct within ±2°. Samples weighing 100 mg each were taken for all of the experiments, so that weight losses can be directly read on the recorded thermograms in percentages.

For the DTA measurements a Gallenkamp tube furnace, provided with a ceramic heating block and ceramic twin crucibles, was employed. One of the crucibles contained the sample, mostly weighing 500 mg, mixed with an equal weight of α-alumina (previously ignited at 1000°), and the other crucible 1 g of the pure inert reference material. The rate of heating was maintained at 10°/min. Temperatures were measured with chromel-alumel thermocouples. The temperature of the alumina was taken as reference and recorded on a Kent multilec instrument, whilst the temperature difference between the two crucibles was recorded on a Kent microvolt instrument.

RESULTS

Fig. 2 shows the percentage weight loss (TG curves) obtained on heating $Eu_2(C_2O_4)_3$, EuC_2O_4 and $EuCO_3$ and Figs. 3, 4 and 5 the thermal spectra (DTA curves) of the same materials.

Europium^{III} *oxalate.* There are no distinct plateaux on the thermogram of the tervalent hydrated oxalate (Fig. 2), but one may attribute definite compositions to the decomposing sample at most points of inflection. Thus the percentage loss at *A* (350°) corresponds to the anhydrous salt $Eu(C_2O_4)_3$, the decomposition of which has been retarded by the presence of the last traces of water. The steep slope to *B* (390°) corresponds approximately to the formation of EuC_2O_4, although a partial re-oxidation of the europium by air may have taken place. Re-oxidation and decomposition of the oxalate to carbonate is completed at *C* (475°), where the weight loss indicates the composition: $(EuCO_3)_2O$. The decomposition to the sesquioxide is completed at about 650°.

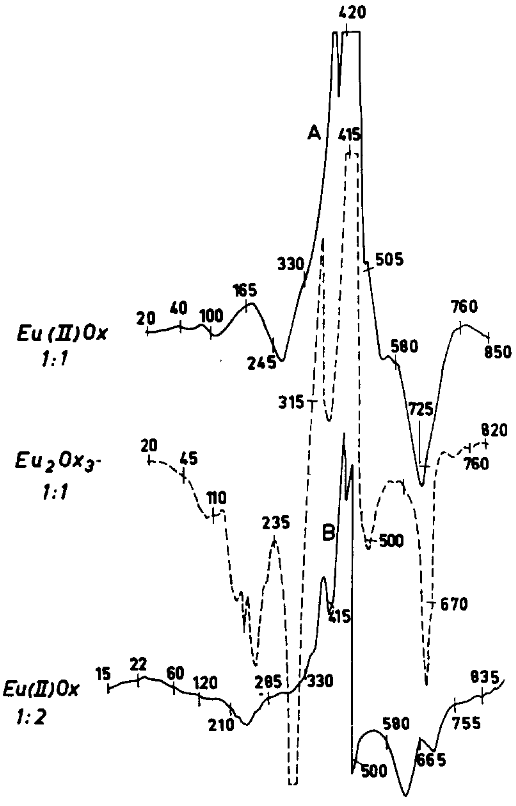

FIG. 3.—DTA curves of $Eu_2(C_2O_4)_3{\cdot}5{\cdot}8H_2O$ and $EuC_2O_4{\cdot}1{\cdot}7H_2O$. Weight ratio of oxalate to alumina for curve B was 1 : 2. Numbers on curves indicate temperatures (°C).

The most prominent feature of the DTA curves in Figs. 3 and 4 (inclusive of the $EuCO_3$ curves) is a broad and high exothermic peak at 410°–420°. For the sake of comparison, the thermal spectrum of $La_2(C_2O_4)_3{\cdot}10H_2O$ is also shown in Fig. 5, with

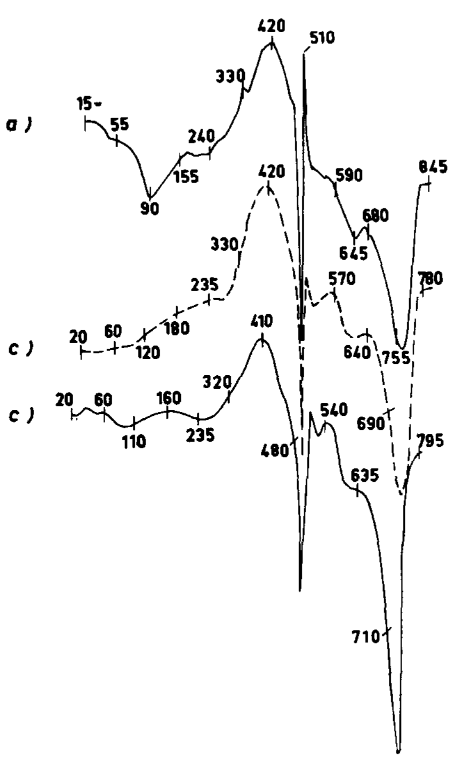

FIG. 4.—DTA curves of $EuCO_3 \cdot 0{\cdot}2H_2O$ (a), and $EuCO_3 \cdot 0{\cdot}04H_2O$ (c).

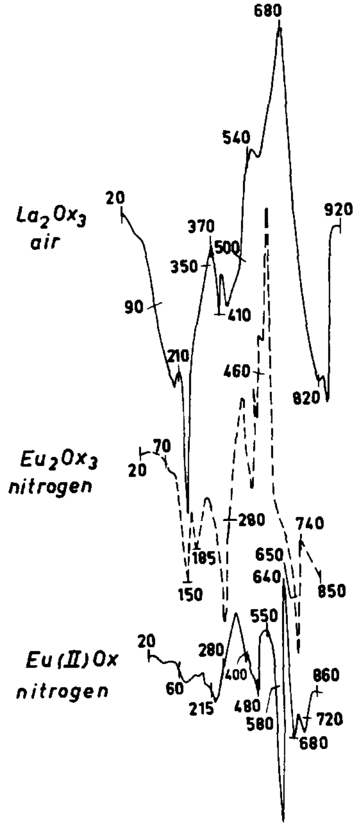

FIG. 5.—DTA curves of $La_2(C_2O_4)_3 \cdot 10H_2O$ in air, and of europium^{II} and europium^{III} oxalates in an atmosphere of nitrogen.

endothermic reactions in this range of temperatures and a prominent exothermic peak at 680°, in good agreement with the measurements of Wendlandt *et al.*[2] Hence the exothermic peaks at 420°, common to the bivalent and tervalent europium salts, are most probably from the air-oxidation of the europium, and imply a previous reduction of the tervalent europium according to the equation

$$Eu_2(C_2O_4)_3 \rightarrow 2\,EuC_2O_4 + 2\,CO_2 \tag{1}$$

This reduction took place at a lower temperature, as indicated by the endothermic peak at ~300°.

The complete interpretation of the DTA curve of $Eu_2(C_2O_4)_3 \cdot 5{\cdot}8\ H_2O$ is therefore as follows. The endothermic peaks below 235° are from partial dehydration. The peak at about 300° is a combined effect of the final dehydration and decomposition (reduction) according to equation (1). The latter endothermic peak terminates in a narrow pointed exothermic peak because of some re-oxidation of the europium, and is soon followed by the main exothermic peak at 415° (the pointed head of this peak came beyond the limits of the paper), which hides most of the endothermic effect from the conversion of the oxalate to a carbonate

$$2EuC_2O_4 + 0{\cdot}5O_2 \rightarrow (EuCO_3)_2O + 2CO \tag{2}$$

Reaction (2) terminates in a small endothermic peak at 490° in good agreement with the point *C* on the TG curve. The last endothermic peak at about 660° also corresponds to the formation of the oxide Eu_2O_3 indicated by the TG measurement. Some of the more prominent thermal data obtained from the TG and DTA curves are recorded in Table I for the sake of ease of comparison. The heading of each column shows the composition of the residue formed at the temperature indicated.

TABLE I.—TEMPERATURES OF FORMATION

Sample	System	$Eu_2(C_2O_4)_3$	EuC_2O_4	$Eu(CO_3)_2O$	$(EuO)_2CO_3$	Eu_2O_3
$Eu_2(C_2O_4)_3{\cdot}10H_2O$	TG	350°	390°	475°	—	650°
$Eu_2(C_2O_4)_3{\cdot}5{\cdot}8H_2O$	DTA	~250°	300°	490°	—	660°
$EuC_2O_4{\cdot}1{\cdot}7H_2O$	TG	—	450°	550°	—	660°
	DTA	—	270°	545°	—	700°
$EuCO_3{\cdot}0{\cdot}21H_2O$	TG	—	—	—	>540°	>665°
	DTA	—	—	—	500°	750°
	Vacuum[a]	—	—	—	400°	620°

[a] After heating at constant temperature for 24 hr.

Europium^{II} *oxalate.* The similarity between the DTA curves of the two europium oxalates (Fig. 3) above 310° is most striking, precluding any doubts with respect to the assumed reduction of $Eu_2(C_2O_4)_3$ to EuC_2O_4 [reaction (1)] at a temperature below 310°. The endothermic peak on the EuC_2O_4 curve at ~270° is from dehydration ($1{\cdot}7$ MH_2O per formula weight), but we have no explanation for the small exothermic peak at ~180°.

Fig. 3, curve *B*, shows another DTA run with EuC_2O_4 and α-alumina mixed in the weight ratio of 1:2. As expected, the thermal effects are less pronounced, but better resolved in this case; three exothermic peaks are followed by three endothermic peaks, all at temperatures corresponding to those which may also be observed on curve *A* with the 1:1 mixture.

Two more DTA curves, one of EuC_2O_4 and one of $Eu_2(C_2O_4)_3$, obtained on passing a current of nitrogen through the cylinder which contained the double crucible, are shown in Fig. 5. The exothermic peaks were not eliminated in these experiments, but they were shifted to considerably higher temperatures. In other aspects the two thermal spectra are similar to the two corresponding curves obtained in air (Fig. 3). Hence it may be inferred that under conditions of limited access of oxygen, the exothermic oxidation of europium^{II} to europium^{III} is completed at 560° and at 640°, when the initial salts were $Eu_2(C_2O_4)_3{\cdot}5{\cdot}8H_2O$ and $EuC_2O_4{\cdot}1{\cdot}7H_2O$, respectively.

On the thermogram of EuC_2O_4 (Fig. 2), no change of weight corresponding to the DTA peaks up to 420° was observed. (Apparently the alumina admixed with the sample in the DTA experiments assists dehydration and consequently promotes the whole sequence of the decomposition reactions.) Decomposition starts at 450°, with a steep loss of weight ($19{\cdot}5$%). The plateau between 550° and 630° indicates the stability of the intermediate oxycarbonate $(EuCO_3)_2O$, which again decomposes in one step to the oxide Eu_2O_3. The agreement between the latter half of the TG and the DTA curves is good.

Europium^{II} *carbonate.* Three thermograms of the decomposition of $EuCO_3$ are shown (Fig. 2): (a) the analysed sample which contained $0{\cdot}21$ M H_2O per formula weight, (b) another preparation which contained only about $0{\cdot}04$ M H_2O, and (c) a sample of the latter preparation admixed with an equal weight of alumina, as in the DTA experiments. In all three cases decomposition occurred in two steps, as shown in detail in Table II.

TABLE II.—COMPILED DATA OF TG RUNS ON $EuCO_3$

	Temp. range of 1st step, °C	Wt. loss for $(EuO)_2CO_3$, %		Temp. range of 2nd step, °C	Wt. loss for Eu_2O_3, %	
		Calc.	Found		Calc.	Found
a	520–605	8·3	10·5	665–715	18·5	18·4
b	505–550	6·9	7·5	570–665	17·1	16·6
c	455–540	6·9	8·0	555–675	17·1	17·0

The final weight loss indicates in all three runs the formation of Eu_2O_3 at about 700°. On the other hand, the loss at the intermediate stage is always larger than that calculated for $(EuO)_2CO_3$. This difference suggests that the bivalent europium has been only partially oxidised to the tervalent state (complete oxidation gives a *gain* in weight of 3·7%).

It is of interest to note the lowering of the temperature of the initial decomposition in sample *b*, containing less water, and again in run *c*, where the admixed alumina assists dehydration.

On the DTA curve (Fig. 4) of sample *a* one can actually observe the endothermic dehydration peak at 95°, which is absent on the two parallel runs of sample *c*. The parallel runs exemplify the excellent reproducibility of these analyses. The prominent exothermic peaks at 410°–420°, which testify to the oxidation of the europium, occur at the very same temperature as those on the DTA curves of the oxalates. The absence of parallel changes of weight on the TG curve (Fig. 2, curve *a*) are understandable if it is assumed that alumina assists dehydration and that the dehydrated carbonate is more prone to oxidation. (In the thermogravimetric runs there may also be a partial cancellation of the loss of weight from dehydration and the weight gained by oxidation).

A pointed narrow endothermic peak at 500° shows evidence of another reaction, namely the decomposition to the oxycarbonate, proceeding simultaneously with the oxidation of the europium. The oxidation reaction is indeed completed only at 510°, as indicated by a second pointed exothermic peak. The final decomposition to the oxide was shifted to higher temperatures (750°) in the DTA experiments as compared with the TG experiments (see Table I).

It should be emphasised that on heating $EuCO_3$ at temperatures above 400°, the evolving carbon dioxide may oxidise the europium to the tervalent state, even in the absence of air. This is illustrated in Table III, which shows the composition of

TABLE III.—COMPOSITION OF GASES EVOLVED FROM $EuCO_3$ ON HEATING

Temp., °C	Wt. of sample, *mg*	Expected total pressure, μ	Partial pressures			
			μ (CO_2)	μ (CO)	CO_2, %	CO, %
400	3·47	62·8	15	12	23·9	19·1
620	5·33	96·5	54	41	55·9	42·5
1000	7·48	135·4	62	62	45·8	45·8

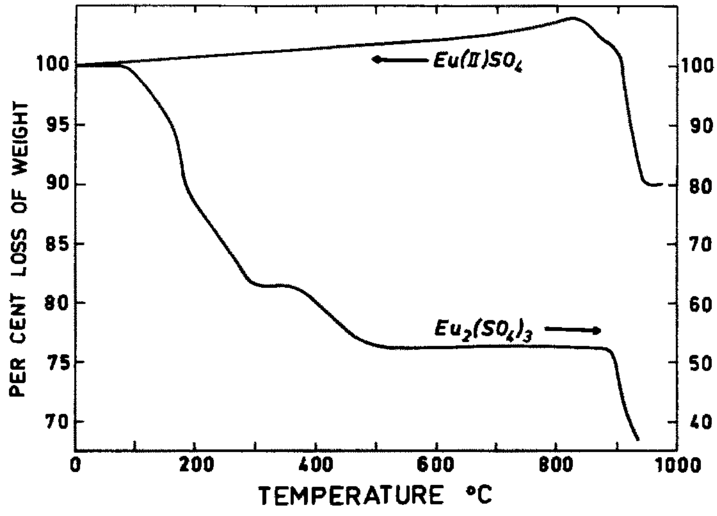

FIG. 6.—Thermogravimetric curves of europium^{II} and europium^{III} sulphates. Arrows indicate ordinate scale to be used.

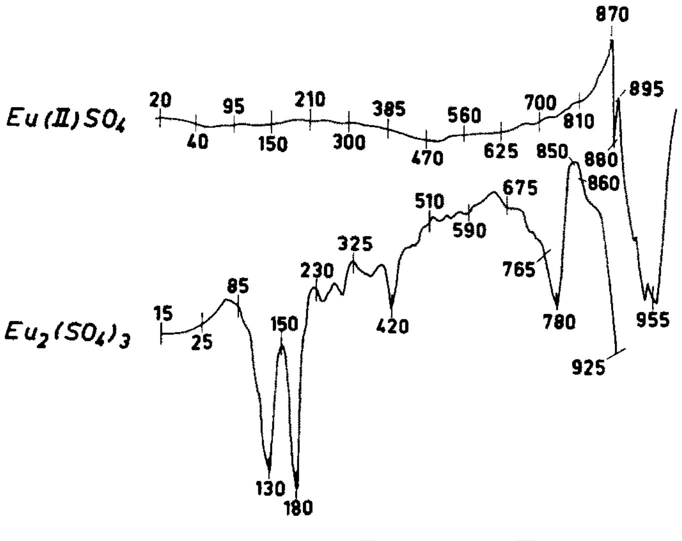

FIG. 7.—DTA curves of europium^{II} and europium^{III} sulphates.

the gases accumulated in the vacuum apparatus after heating for 24 hr at the indicated temperatures.

At 400° the residue approximates to the composition of the oxycarbonate $(EuO)_2CO_3$, while at 620° the decarbonisation is complete, but the oxidation of the europium seems to be 100% only at higher temperatures.

The TG and DTA curves of the europium sulphates are shown in Figs. 6 and 7. On the thermogravimetric curve of $EuSO_4$ the oxidation of the europium is indicated by a slow continuous increase in weight up to 830°. At this point decomposition of $(EuSO_4)_2O$ sets in, proceeding at an increased rate from 910° upwards, to form the oxysulphate $(EuO)_2SO_4$ at 950°. The oxidation peak at 870° and the endothermic peaks at 940°–960° on the DTA curve are in good agreement with this interpretation.

The thermal decomposition of $Eu_2(SO_4)_3$, among other rare earth sulphates, has been recently studied by Nathans and Wendlandt.[6] The starting points for the decomposition of the anhydrous salt indicated by our curves are: 880° (870°, TG) and 855° (810°, DTA) (the results of Nathans and Wendlandt are given in the brackets).

The dehydration of our hydrated sample proceeded in three steps, indicated by three endothermic peaks at 130°, 180° and 420°, and by the corresponding changes in the slope of the weight-loss curve.

An additional endothermic peak at 780° is inexplicable, considering the level plateau between 500° and 880° on the TG curve.

There is an intermediate plateau on the TG curve, between 300° and 360° at about 37% weight loss, which suggests the intermediate composition $Eu_2(SO_4)_3{\cdot}H_2SO_4{\cdot}H_2O$ and the formula $Eu_2(SO_4)_3{\cdot}H_2SO_4{\cdot}24H_2O$ for the initial sample.

DISCUSSION

The DTA curves of Wendlandt *et al.* for the rare earth oxalates[2] show, as a rule, endothermic peaks in the temperature range 350°–600°, with the exception of $Eu_2(C_2O_4)_3$ which exhibits a prominent exothermic peak at 390°. In contrast, Blum and Maguire[7] obtained with the oxalates of yttrium, lanthanum, neodymium, samarium and gadolinium a series of exothermic peaks in the same range of temperatures, and stated that "the curves could be re-run with extremely good reproducibility".

Claudel, in a thesis[8] on the thermal decomposition of thorium oxalate, investigated the occasional appearance of an exothermic peak in the region of 400°, observed by Padmanabhan *et al.*,[9] but absent on the curve of Wendlandt *et al.* Claudel attributes the exothermic reaction to the air oxidation of carbon monoxide evolving from the decomposing oxalate (catalysed by thorium dioxide). He demonstrates that the oxidation is promoted by a metallic container and the use of alumina (absorbed oxygen) as the inert diluent, while in an atmosphere of nitrogen only an endothermic peak was obtained under any condition. Hence, it seems plausible that Blum and Maguire's experiments were carried out under exceptionally good oxidising conditions.

A comparison of the $La_2(C_2O_4)_3$ curves shows that our experimental conditions were very much the same as those of Wendlandt *et al.*, the exothermic peak from the oxidation of carbon monoxide or deposited carbon, appearing at 680° (Fig. 5). The same curve is reproduced on flushing the apparatus with nitrogen, and it is supposed that the oxygen adsorbed on the alumina serves as oxidant in this case.

It is interesting to note that, particularly in the case of $La_2(C_2O_4)_3$, there is no exothermic, but a broad shallow endothermic peak in the region of 700° on Blum and Maguire's DTA curve. Evidently, all carbon monoxide and carbon has been burned away below 600°.

Attribution of the prominent exothermic peaks at 420° on the thermograms of the salts of europium to the oxidation of europium^{II} to europium^{III} is, therefore, the only straightforward conclusion to the above considerations. In the case of $Eu_2(C_2O_4)_3$, reaction (1) obviously precedes all other reactions in the consecutive steps of decomposition,[4] and hence the great similarity between the thermograms of the europium^{II} and europium^{III} oxalates above 400°.

By flushing the DTA chamber with nitrogen, the oxidation of europium^{II} to europium^{III} could not be prevented, but it proceeded at a slower rate and was shifted to higher temperatures. The probable source of oxygen in this case was the gas adsorbed by the bulky alumina powder, yet the infiltration of some air with the stream of nitrogen cannot be excluded. The oxidation of europium^{II} in $EuSO_4$ is rather slow, and the exothermic peak on the DTA curve appears only at 870°. On the TG curve, on the other hand, the continuous gain in weight is clearly discernable. Hence, the proneness of the europium^{II} salts to oxidation appears to be in the following increasing order: $EuSO_4 < EuC_2O_4 < EuCO_3 < EuO$.

In conclusion, it should be remarked that DTA curves may supply useful information only in conjunction with data from other methods of investigation. Unexpected complications that might arise are well exemplified in the case of the oxalates. In a well aerated apparatus the evolving carbon monoxide may be oxidised at a comparatively low temperature ($\sim$400°),[4] but the sample will overheat only if the oxidation takes place in the bulk of the material. With a limited supply of oxygen disproportionation occurs and the exothermic peak is shifted to a temperature above 600°, when the deposited carbon burns away. The exothermic peak from the oxidation of europium^{II}, on the other hand, is not subject to such irregularities.

Zusammenfassung—Die DTA-Kurven von $Eu_2(C_2O_4)_3$, EuC_2O_4 und $EuCO_3$ zeigen um 420° deutliche exotherme maxima, die auf Oxydation von Europium^{II} zu Europium^{III} beruhen. Die erste Stufe der Zersetzung von $Eu_2(C_2O_4)_3$ nach beendeter Entwässerung wird durch die Gleichung $Eu_2(C_2O_4)_3 \rightarrow 2EuC_2O_4 + 2CO_2$ beschrieben. Gründe für nicht übereinstimmende DTA-Kurven der Oxalate seltener Erden von verschiedenen Autoren werden angegeben. Ein Europium^{II}-oxalat mit $1 \cdot 7H_2O$ wurde dargestellt.

Résumé—Les courbes DTA des systèmes $[Eu^{(III)}]_2Ox_3$, $[Eu^{(II)}]Ox$ et $[Eu^{(II)}]CO_3$ présentent des pics exathermiques importants dans la région des 420°C, dûs à l'oxydation de l'ion europeux en ion europique. La première étape de la décomposition de Eu_2Ox_3 après deshydration complète est donnée par l'équation

$$Eu_2Ox_3 \rightarrow 2EuOx + 2CO_2.$$

Les raisons de discordance de quelques courbes DTA d'oxalates de terres rares obtenues par différents auteurs sont éclaircies. Le préparation d'un oxalate, $[Eu^{(II)}]Ox \,.\, 1 \cdot 7H_2O$ est décrivé.

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AN INVESTIGATION OF 2-AMINO-4-CHLOROBENZENETHIOL HYDROCHLORIDE AS A SPECTROPHOTOMETRIC REAGENT FOR THE DETERMINATION OF MOLYBDENUM

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Summary—2-Amino-4-chlorobenzenethiol hydrochloride forms a green precipitate with molybdenum^{VI} at pH 2. The precipitate can be extracted into chloroform and has an absorbance maximum at 720 mμ. The sensitivity of the reaction is 0·0054 μg of molybdenum per cm^2 for log $I_0/I = 0{\cdot}001$. Development of the spectrophotometric method for the determination of molybdenum included a study of the effect of pH, reagent concentration, rate of complex formation and extraction, temperature and conformity to Beer's law. The method has been applied to the determination of molybdenum in steel and cast iron.

A SYSTEMATIC qualitative investigation of the reactivity of a number of aromatic mercapto compounds with 78 inorganic ions was undertaken utilising the spot-test procedure of Yoe.[1] It was found that 2-amino-4-chlorobenzenethiol hydrochloride reacts with molybdate ions in aqueous solution over a wide range of pH to form an insoluble green complex. The precipitate can be extracted into chloroform and other non-polar and polar solvents. The variables governing formation and extraction of the complex have been studied, and a method for the spectrophotometric determination of traces of molybdenum has been developed and applied to the analysis of steel and cast iron.

PRELIMINARY QUALITATIVE STUDIES

2-Amino-4-chlorobenzenethiol hydrochloride hydrolyses in water to the free base, which is insoluble in water. The hydrochloride is quite soluble in ethanol, however, and a 1% solution in 95% ethanol was used to investigate the reactivity of the compound with metal ions.

The reagent forms colours or precipitates with a number of metal ions. Between pH 2 and 10 it forms precipitates with molybdenum (green), palladium (orange), bismuth (orange), lead (yellow), nickel (pale green), cobalt (brown), copper (pale green), tungsten (white), cadmium (white) and zinc (white). The reagent also precipitates slowly when the alcoholic solution is added to the aqueous metal ion solution. No reaction was observed between molybdenum and the reagent between pH 1 and 4 in the presence of a large amount (greater than 1000-fold excess over the molybdenum present) of EDTA, citrate, tartrate, oxalate and fluoride, although the presence of excess potassium cyanide did not affect the reaction.

The molybdenum complex can be extracted into chloroform, carbon tetrachloride, benzene, isoamyl alcohol, isopropyl ether and petroleum ether between pH 1 and 4. When freshly precipitated from aqueous solution it can also be dissolved by the addition of ethanol, methanol, acetone, isopropyl alcohol, pyridine, dioxan or dimethylformamide. The solvents used to dissolve the precipitate all produce a clear solution whose green colour fades rapidly. Of the solvents used to extract the complex, only chloroform, carbon tetrachloride and benzene produce a green organic phase whose colour is sufficiently stable for spectrophotometric measurement. Under standardised conditions for the colour formation and extraction, the absorbance spectra of the complex dissolved in these three non-polar solvents are virtually identical with respect to both the wavelength and intensity of the absorption maximum. Chloroform was chosen as the extractant, because it was preferred to use a solvent of density greater than water. The free reagent also extracts into chloroform and produces an organic phase which is yellow in colour. The intensity of the yellow colour is dependent upon the extraction pH.

The palladium and bismuth complexes of the reagent can also be extracted into chloroform, but the precipitates formed with the other metal ions mentioned previously are either insoluble in chloroform or only slightly soluble and produce a colourless organic phase.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman Spectrophotometers, Models DU and DK-2, with matched 1-cm Corex cells.

pH meter: Beckman Model G, with general-purpose glass electrode.

Reagents

2-Amino-4-chlorobenzenethiol hydrochloride: Obtained from Eastman Kodak (No. 3279) in the form of pale yellow crystals. It is only slightly soluble in water, and was used as a 4% solution in 95% ethanol. The pale yellow solution becomes deep yellow over a period of several days and appears to undergo slow decomposition. The reagent solution was therefore prepared fresh every 2 days.

Standard molybdenum solution: 1·840 g of dry ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, ('Baker Analyzed' A.C.S.) was dissolved in distilled water and diluted to 1 litre. The solution was standardised by precipiting the molybdenum with α-benzoinoxime, igniting the precipitate and weighing as the oxide.[8] The 1000 ppm of molybdenum^{VI} standard stock solution was diluted as required.

Buffer solutions: Clark and Lubs buffers were used throughout.

Na_2H_2EDTA (*disodium salt of ethylenediaminetetra-acetic acid*): 3% aqueous solution.

Solutions of diverse ions: Reagent-grade salts were used to prepare solutions of various ions. The solutions were made to contain 1 g of the ion per litre of solution.

All other reagents were analytical reagent grade.

Preparation of calibration curves

(*a*) *Pure solution:* Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of standard molybdenum solution (10 μg of Mo per ml) to 50-ml separating funnels. Add 3 ml of pH 2·2 buffer solution and dilute each solution to 10 ml with distilled water. Add 0·25 ml of 4% 2-amino-4-chlorobenzenethiol hydrochloride reagent solution, mix, and allow to stand for 15 min. Add 10·0 ml of chloroform and shake vigorously for 1 min. When the phases have separated, measure the absorbances at 720 mμ using a chloroform blank.

(*b*) *Steel analysis:* Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5·0 ml of the standard molybdenum solution (10 μg of molybdenum per ml) to 50-ml separating funnels. Add to each funnel a volume of ferric chloride solution (10 mg/ml) which contains approximately the equivalent amount of iron to that present in the steel or cast iron sample. Add just sufficient 3% Na_2H_2EDTA solution to complex the ferric iron added, and add 5 ml of pH 2·4 buffer. Dilute each solution to the same volume with distilled water. Add 0·25 ml of 4% 2-amino-4-chlorobenzenethiol hydrochloride solution, mix, and allow to stand for 15 min. Add 10·0 ml of chloroform and shake vigorously for 1 min. Measure the absorbances of the chloroform phases at 720 mμ against a reagent blank.

Preparation of samples for analysis

Dissolve the sample (0·2–0·5 g) in a mixture of 10 ml of hydrochloric acid and 3 ml of nitric acid. Evaporate the solution to small volume, dilute with 10 ml of water and boil. Dilute the solution to 40–50 ml with distilled water, adjust the pH of the solution to 1·5–2·0 with dilute aqueous ammonia solution, transfer the solution to a 100-ml volumetric flask, and dilute to volume. Take a 1-ml aliquot of the solution for analysis, and, assuming the sample to contain 100% ferric iron, add the required volume of 3% Na_2H_2EDTA solution (0·45–1·2 ml) to complex the iron present. After the addition of the buffer and reagent, determine the molybdenum content as described for calibration curve (*b*).

The conditions, the volume of the solution, pH and time of shaking, *etc.*, should be carefully controlled in order to obtain good reproducibility.

DETERMINATION OF OPTIMUM CONDITIONS

Spectral characteristics

The absorbance spectra for 2-amino-4-chlorobenzenethiol and its molybdenum complex in chloroform are shown in Fig. 1. The molybdenum complex has a well-defined absorption maximum at 720 mμ. The reagent exhibits no absorbance at 720 mμ, and only begins to absorb appreciably at wavelengths less than 450 mμ. The 720 mμ absorbance maximum is suitable for spectrophotometric absorbance measurements and no reagent blank is required.

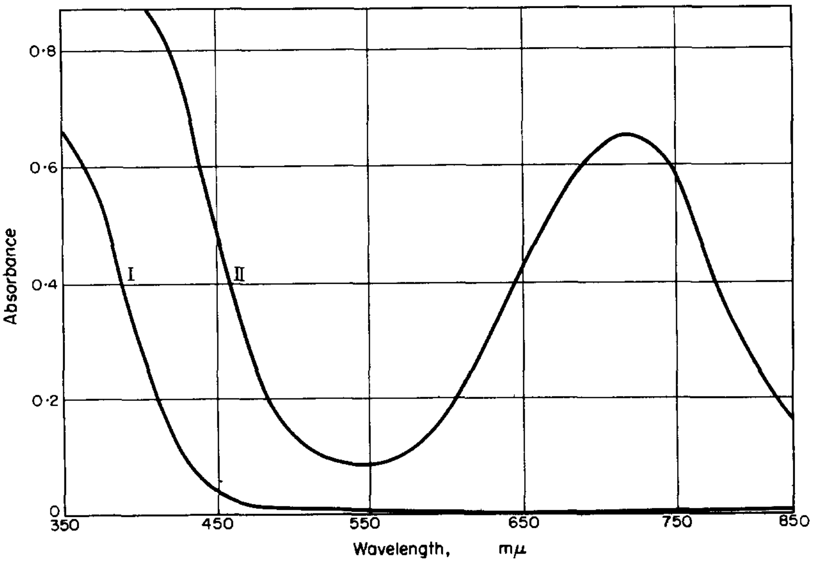

FIG. 1.—Absorbance spectra for (I) reagent and (II) molybdenum complex against chloroform at pH 2 (20 μg of Mo).

Effect of pH

(*a*) *Complex formation.* Curve (I) in Fig. 2 shows the effect of pH on the formation of the molybdenum complex in aqueous solution. A constant large excess of reagent solution was added to buffered solutions containing 20 μg of molybdenum^{VI}, and the mixture was allowed to stand for 15 min. The solutions were then brought to pH 1 by the dropwise addition of dilute hydrochloric acid, and extracted with 10 ml of chloroform for 1 min. The absorbances of the chloroform extracts were measured at 720 mμ using a chloroform blank. The optimum pH for complex formation is at 1·9–3·3.

(*b*) *Solvent extraction.* Curve II in Fig. 2 shows the effect of pH on the extraction of the molybdenum complex into chloroform. The precipitate of the complex was formed at pH 2·8 and allowed to stand for 15 min. The pH of the solutions was adjusted to between 1 and 5 by the addition of a large excess of the required buffer, and the solutions were shaken immediately with 10 ml of chloroform for 1 min. The absorbance of the chloroform extracts was measured at 720 mμ against a chloroform blank. For solvent extraction the pH of the solution should be adjusted to between 1 and 2·3. The complex can also be extracted at pH < 1, in dilute hydrochloric acid medium, and there is no significant variation in the absorbance with acid concentration when the medium is 0·1–0·3M with respect to hydrochloric acid. All pH values are uncorrected for ionic concentration.

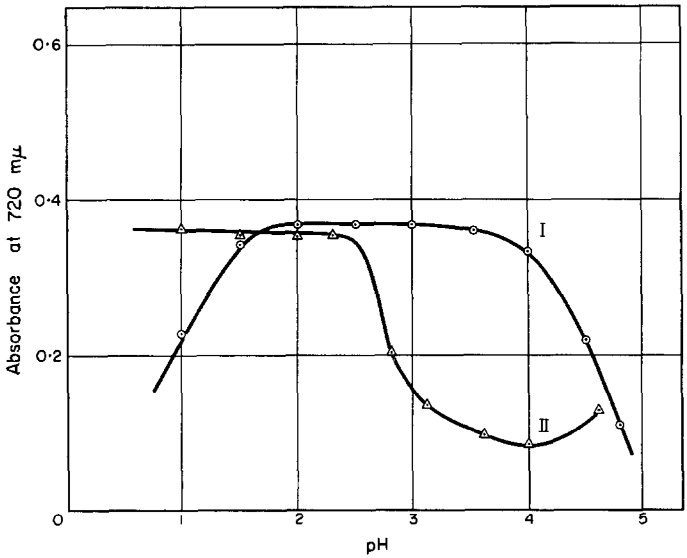

FIG. 2.—Effect of pH on absorbance at 720 mμ: (I) complex formation and (II) solvent extraction.

Order of addition of reactants

The ethanolic solution of 2-amino-4-chlorobenzenethiol must be added to the buffered molybdenum^{VI} solution. Because of the precipitation of the reagent in aqueous solution, sufficient excess of reagent does not remain in solution to give a rapid quantitative reaction if the molybdenum solution is added to the buffered reagent solution.

Effect of reagent concentration and time of shaking

It was found satisfactory to use 1 ml of a 1% reagent solution in ethanol. When the effect of the time of shaking on the absorbance at 720 mμ was studied using this reagent concentration, however, it was found that the absorbance decreased considerably when the shaking time was extended above 1 min. Further investigation revealed that the decrease was related to the volume of ethanol present, and that the rate of decrease was considerably less when a smaller volume of a more concentrated reagent solution was used. As shown in Fig. 3, when 0·25 ml of a 4% reagent solution in ethanol was used no change in absorbance was produced when the mixture was extracted between 30 and 60 sec.

Time required for complex formation

At least 5 min are required for the formation of the extractable molybdenum complex in order to obtain constant absorbance after extraction. The mixture may be allowed to stand for as long as 1 hr before extraction without change in the absorbance of the chloroform extract at 720 mμ. A 15-min standing time was adopted for convenience.

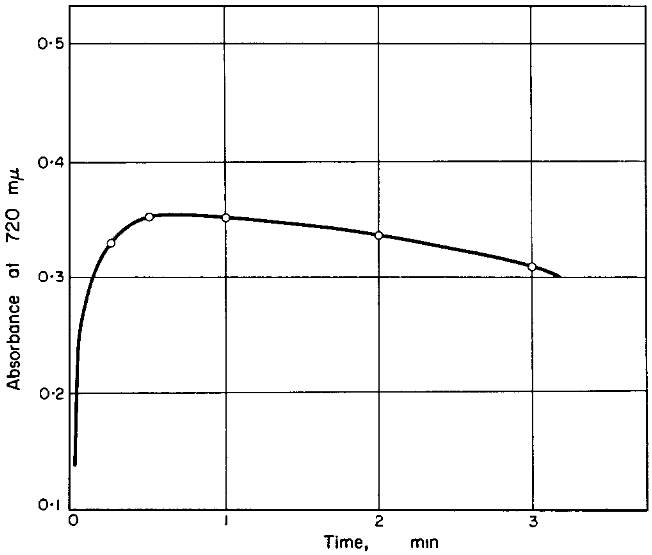

FIG. 3.—Effect of extraction time on absorbance.

Effect of temperature

The complex formation was conducted at temperatures between 10° and 40° in a water bath. No significant variation in the absorbance of the chloroform extract was observed.

Beer's law and sensitivity

The calibration curve follows Beer's law in the range 5–45 μg of molybdenum in 10 ml of chloroform. The optimum range for absorbance measurements on the spectrophotometer is 0·2–0·7 unit. With the recommended procedure these values correspond to 10–35 μg of molybdenum in 10 ml of chloroform.

According to Sandell's expression of sensitivity,[3] *i.e.*, μg of Mo per cm^2 for log $I_0/I = 0{\cdot}001$, the sensitivity was found to be 0·0054 μg of Mo per cm^2. A more practical sensitivity, however, based on an absorbance reading of 0·005 unit, is 0·027 μg of Mo per cm^2.

Stability

The absorbance of the chloroform solution of the molybdenum complex was found to decrease by 6% after standing for 4 hr and 9% after 6 hr. The absorbance should be measured at 720 mμ within 30 min after the extraction.

Precision

To obtain the precision of the method in pure molybdenum solutions, the same amount of molybdenum was determined 12 times. The average absorbance was 0·351 and the standard deviation 0·004 or 1·1%. This precision, however, is not obtained when complex mixtures are analysed. The values for the precision of three such analyses are given in Table I.

TABLE I.—ANALYSIS OF NBS SAMPLES

NBS Sample	Mo, %		Difference, %
	NBS	Found[a]	
72a chromium-molybdenum steel	0·202	0·199	
		0·201	
		0·197	
		0·203	
	Av.	0·200	−1·0%
Standard deviation = 0·0026 or 1·3%			
36 chromium-molybdenum steel	1·01	1·02	
		1·01	
		1·00	
		1·04	
	Av.	1·02	+1·0%
Standard deviation = 0·017 or 1·7%.			
107 nickel-chromium-molybdenum cast iron	0·687	0·678	
		0·675	
		0·670	
		0·690	
	Av.	0·678	−1·31%
Standard deviation = 0·0085 or 1·24%.			

[a] Each value represents the average of three aliquots in good agreement.

Interference studies

The preliminary qualitative investigation revealed that the most serious interfering ions in the determination of molybdenum were the transition metal ions. These ions consume the reagent and form non-extractable precipitates. Other interferences result from metal ions which are precipitated as their hydrated oxides at the recommended pH, and from certain complexing anions which interfere with the formation of the molybdenum complex.

Solutions were prepared containing 20 μg of molybdenum and varying concentrations of each ion to be tested. The molybdenum was then determined by the recommended procedure. The limiting value of the concentration of foreign ion was taken as that which caused an error of 3% in the absorbance. This corresponds to an error of 0·01 absorbance unit.

The presence of a 100-fold excess (2 mg) of the following ions caused no interference: Al^{3+}, Ba^{2+}, Ca^{2+}, Cr^{3+}, Fe^{2+}, K^+, Mg^{2+}, Mn^{2+}, NH_4^+, Na^+, Sr^{2+}, VO_2^{2+}, VO_3^-, Br^-, I^-, SO_4^{2+}, HSO_3^- and $B_4O_7^{2-}$. A 100-fold excess of the following caused the negative error given in parentheses: F^- (31%), CO_3^{2-} (12·5%), CNS^- (6·5%), acetate (7·5%), citrate (15%), oxalate (22%), phosphate (7%), silicate (15%), tartrate (13%), ascorbic acid (7%). A 100-fold excess of EDTA produced less than 3% error in the absorbance.

The following ions caused not greater than 3% error in the absorbance produced by 20 μg of molybdenum when present in the number of fold excess given in parentheses: Au^{3+} (5), As^{3+}(50), Bi^{3+} (20), Ce^{4+} (40), Co^{2+} (0·5), Cr^{6+} (2), Cu^{2+} (1), Fe^{3+} (50), Ga^{3+} (20), Ge^{2+} (35), Hg^{2+} (4), Ni^{2+} (3), Pb^{2+} (25), Pd^{2+} (2), Pt^{2+} (25), Th^{4+} (50), W^{6+} (0·5), Zn^{2+} (10).

Ag^+ is precipitated as its chloride. Se^{4+} and Te^{4+} give a yellow precipitate with the reagent which is extracted into chloroform. Ti^{4+} and Zr^{4+} are precipitated and cause negative errors.

Nature of complex

The complex was isolated as a green precipitate by the addition of a slight excess of the reagent solution to 100 ml of $10^{-2}M$ molybdate solution at pH 2. The precipitate was filtered off, washed with a mixture of 2 volumes of ethanol and 1 volume of water, and dried to constant weight at 50°. The molybdenum content was then determined by igniting a weighed portion to molybdenum trioxide at 500°. The results of the duplicate analyses were 15·9% and 16·0% of Mo. A 3:1 complex of reagent to molybdenum requires 15·8% Mo, *e.g.*, $MoO(OH).[C_6H_5NSCl]_3$.

A study was made to determine the empirical formula of the molybdenum complex in solution. The mole ratio method of Yoe and Jones[4] gave indication of a 3:1 complex of reagent to molydbenum, and the subsequent formation of a higher complex. The complex appears to be appreciably dissociated, because no sharp breaks were observed. The continuous variations method of Job,[5] as modified by Vosburgh and Cooper,[6] gave results in agreement with those obtained from the mole ratios studies and the determination of the molybdenum content of the solid complex. It seems that a 3:1 complex of reagent to molybdenum is formed and there is some indication of the existence of a higher complex.

ANALYSIS OF COMPLEX MIXTURES

The principal interferences, from a practical viewpoint, are iron^{III}, copper, cobalt, nickel and tungsten. The permissible concentrations of these ions, with the exception of iron^{III}, are high enough to allow the determination of molybdenum in a range of steel and cast iron samples. Although an appreciable excess (1 mg) of iron^{III} can be tolerated, this value is too low to permit the analysis of these samples without masking or prior separation of the iron.

An attempt was made to separate the iron by precipitation as ferric hydroxide. Coprecipitation errors, even after repeated precipitation by the method recommended by Lundell and Hoffman,[7] prevented complete recovery of the molybdate. The interference from iron^{III} was successfully overcome by the addition of EDTA to the sample solution. An appreciable excess of EDTA (2 mg) can be tolerated, but it was preferred to add only the required amount, calculated assuming the steel and cast iron samples contained 100% of iron. Under these conditions, high results were obtained when the sample absorbance is compared with a calibration curve obtained using pure molybdenum solutions. A calibration curve was produced from standard molybdenum solutions containing a large excess of iron^{III} and the equivalent amount of Na_2H_2 EDTA. Comparison of absorbance values against this calibration curve gave better accuracy, although slightly lower precision, than when the calibration curve obtained from pure solution was used.

To test the efficiency of the method, three National Bureau of Standards samples were analysed for molybdenum. The results are shown in Table I.

Acknowledgements—We are indebted to the Pratt Trace Analysis Laboratory for the grant of a Fellowship to one of us (G. F. K.), and wish to thank Ann Kirkbright for her assistance with this work.

Zusammenfassung—2-Amino-4-chlorthiophenolhydrochlorid bildet bei pH 2 mit Molybdän(VI)-Ionen einen grünen Niederschlag. Dieser kann mit Chloroform extrahiert werden und hat ein Absorptionsmaximum bei 720 mμ. Die Empfindlichkeit der Reaktion beträgt 0,0054 μg Mo pro cm^2 für log $I_0/I = 0,001$. Die Entwicklung der spektralphotometrischen Mo-Bestimmung schloß eine Untersuchung über p_H-Einflüß, Konzentration des Reagenses, Komplexbildungs- und Extraktionsgrads, Temperaturabhängigkeit und Gültigkeit des Beerschen Gesetzes ein. Die Methode wurde auf die Molybdänbestimmung in Stahl und Gußeisen angewandt.

Résumé—Le chlorhydrate de l'amino-2-chloro-4-benzènethiol fournit un précipité vert avec les ions molybdène(VI) à pH 2. Le précipité peut être extrait au chloroforme et présente une absorption maximum à 720 mμ. La sensibilité de la réaction est de 0,0054 μg de molybdène par cm^2 pour log $I_0/I = 0,001$. Le développement de la méthode spectrophotométrique de dosage du molybdène comprend une étude sur l'influence du pH, la concentration des réactifs, le taux de formation du complexe et de son extraction, la température et la conformité à la loi de Beer. Cette méthode a été appliquée au dosage du molybdéne dans l'acier et la fonte.

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PHOTOMETRIC TITRATIONS—VII*

THE CONSECUTIVE TITRATION OF CADMIUM AND ZINC

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Summary—Zinc and cadmium can be determined in one solution in the following manner. The sample is adjusted to pH 10 with an ammonia-ammonium chloride buffer so that the total ammonia concentration is 0·02–0·03*M*. Murexide is added so that its amount is in at least 5-fold excess over the amount of zinc present. The titration is performed photometrically at about 450 mμ with ethyleneglycol bis(β-amino-ethylether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid (EGTA) as the titrant. The titration curve obtained shows two breaks which are related to the consecutive titration of cadmium and zinc. The influence of calcium impurities in the reagents used has been studied and a method of pretitration is proposed. For this purpose a small amount of zinc is pretitrated and then the sample solution is added. Thus the calcium blank is established for each titration.

In a previous paper of this series,[1] it was shown that calcium and magnesium can both be determined from a single photometric titration curve. This is achieved by the addition of Calmagite[2] in an amount greater than equivalent to the sum of the two metals, or at least to the magnesium. In that titration, Calmagite does not function in the usual manner as a "step indicator" but, in combination with the magnesium, gives a self-indicating system. Because calcium forms a stronger complex with the titrant (EDTA) than does magnesium, the self-indicating Mg-Calmagite system serves as a "slope indicator" for calcium. Thus a titration curve with two breaks is obtained, the first and second slope changes marking the end-points for calcium and magnesium, respectively.

In the EDTA titration of zinc in ammoniacal solution with Erio T as indicator, the amount of pH 10 buffer added has little influence on the colour change at the end-point. With cadmium, however, increasing amounts of buffer pH 10 cause a decrease in the sharpness of the end-point. Experiments have shown that the addition of large amounts of ammonia pH 10 buffer to a solution containing cadmium and Erio T progressively diminishes the red colour of the cadmium-indicator complex until the pure blue of the free indicator is essentially restored. Under the same conditions, the red colour of the Zn-Erio-T complex is little affected. As expected, Calmagite behaves in exactly the same manner as Erio T but is preferable because it is stable in solution.

From these considerations, it would seem that a Cd-Zn determination analogous to that used for Ca-Mg is feasible. EDTA, however, is not the appropriate titrant in this case because the stabilities of its zinc and cadmium complexes are almost identical. Ethyleneglycol bis(β-amino-ethylether)-*N*,*N*,*N'*,*N'*-tetra-acetic acid (EGTA) is a more favourable titrant because its cadmium complex is stronger than its zinc

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* Part VI—see ref. 1.

complex, the constants being log $K_{Cd} = 16{\cdot}7$ and log $K_{Zn} = 14{\cdot}5$.[3] Of course, the apparent stability constants must be compared, and these are obtained from a knowledge of the stability constants of the metal-ammonia and metal-dye complexes. At the high ammonia concentrations necessary to decompose the Cd-Calmagite complex, the value of the β_{NH_3}-factor (pH = 10) for zinc is close to 100 times that for cadmium. Because the Zn-Calmagite complex is not decomposed, the Zn-Calmagite β-factor is significant, and thus the logs of the β-factors for cadmium and zinc will differ by more than two units. This indicates that the apparent stabilities of the Cd-EGTA and Zn-EGTA differ by a factor somewhat greater than 10^4, so that a selective titration should be possible. Unfortunately, however, the Zn-EGTA complex is not sufficiently more stable than the Zn-Calmagite complex, so that even a photometric end-point is unsatisfactory. Moreover, galvanometer drift after titrant addition indicated that the reaction ZnY + CdI → ZnI + CdY is quite slow. Changing the titration conditions did not improve the situation, so it was necessary to find a more suitable dye.

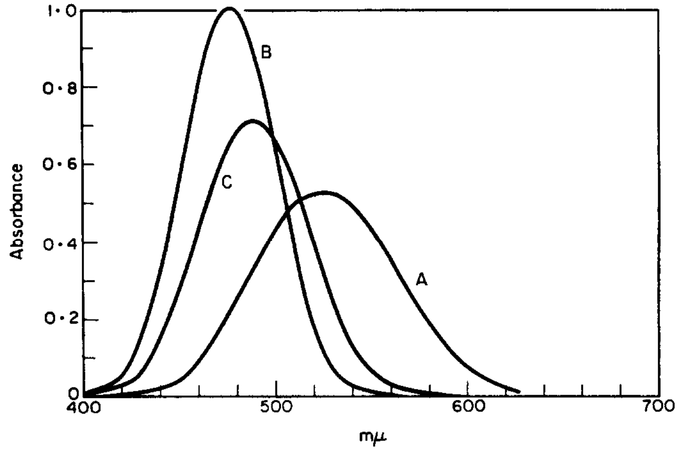

FIG. 1.—Absorbance curves for free Murexide (A), Zn-Murexide (B) and Cd-Murexide (C) at pH 10 (ammonia-ammonium chloride buffer).

Many common metallochromic indicators were investigated and eventually Murexide was found to meet the necessary requirements. Murexide has already been used as indicator in the titration of zinc at pH 8–8·5 in ammonia-free solutions.[4] It was found that the yellow Zn-Murexide complex also persists in solutions buffered to pH 10 with ammonia provided that the ammonia concentration does not exceed certain limits. Also, at some ammonia concentrations where the Zn-Murexide complex is still formed to a considerable degree, the Cd-Murexide complex is largely decomposed. These qualitative findings were substantiated by later quantitative investigations. The spectral curves of free Murexide (A), its zinc (B) and its cadmium (C) complexes at pH 10 are represented in Fig. 1. These curves were obtained with the same total concentration of Murexide and with excess metal ions present to assure complete complex formation. Fig. 2 shows a plot of the difference curve, Zn-Murexide minus Murexide (B-A from Fig. 1), to aid in the selection of an appropriate wavelength. The maximum difference is at 470 mμ and for highest sensitivity this wavelength should be chosen. In practice, however, a somewhat shorter wavelength is more convenient for two reasons. Under the conditions of the titration an excess of Murexide is required, which would provide a considerable background absorbance at 470 mμ. In itself, this is no detriment, although instrument settings are simplified when it is avoided. A second more serious consideration is the instability of the free Murexide in solution. Thus, when considerable amounts of free Murexide are present, and no measures are taken to inhibit its decomposition, a drift of the galvanometer occurs. The decomposition is partly caused by oxidation of the dye, because it is inhibited by deaeration of the solution with nitrogen or by the addition of ascorbic acid. Part of the decomposition is caused by hydrolysis of the dye. At a wavelength of about 450 mμ, the difference is still sufficiently high but the absorptivity of free Murexide is so low that the influence of the decomposition of free Murexide on the optical behaviour of the system is negligible. It may be mentioned in this connection that, as is the case for many other unstable complexing agents, complexed Murexide is stabilised against decomposition. The yellow colour of a solution of Zn-Murexide persists long after the red-violet colour of a solution containing an equal amount of Murexide alone has disappeared.

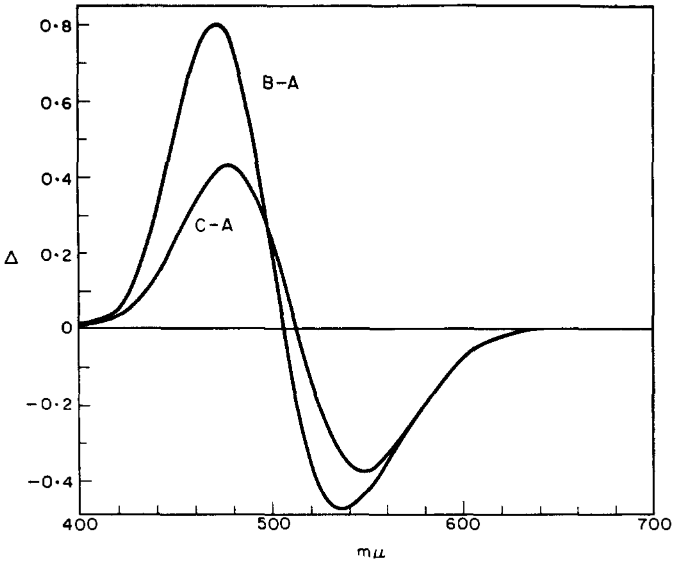

FIG. 2.—Difference curves obtained from Fig. 1.

The difference curve, Cd-Murexide minus Murexide (C-A from Fig. 1), is also shown in Fig. 2. Unless cadmium can be masked completely against the reaction with Murexide, the absorbance of the Cd-Murexide complex must also be considered. (See later.)

The conditions for a working, self-indicating system, zinc-Murexide-EGTA at pH 10, were established as follows. Titrations were performed using $10^{-5}M$ zinc and $10^{-2}M$ EGTA solutions in a 1-cm cell with a 456-mμ interference filter. At first the amount of pH 10 buffer was held constant, and the amount of Murexide was varied. In order to obtain a straight titration curve before the equivalence point, at least a 5-fold Murexide excess over the zinc was necessary; larger excesses did no harm. Next the Murexide concentration was held constant at a sufficient excess and the buffer concentration was varied. Up to approximately 0·01M in total ammonia ($[NH_3] + [NH_4^+]$), identical titration curves were obtained. Upon addition of more buffer, the slopes of the titration curves decreased, as was to be expected. A buffer concentration of 0·01M is not always sufficient to prevent the precipitation of zinc hydroxide; however, the excess Murexide keeps the metal in solution. This fact makes it necessary to add the Murexide to the titration solution before the sample, when the buffer concentration is low.

Titrations of solutions containing both cadmium and zinc were attempted next.

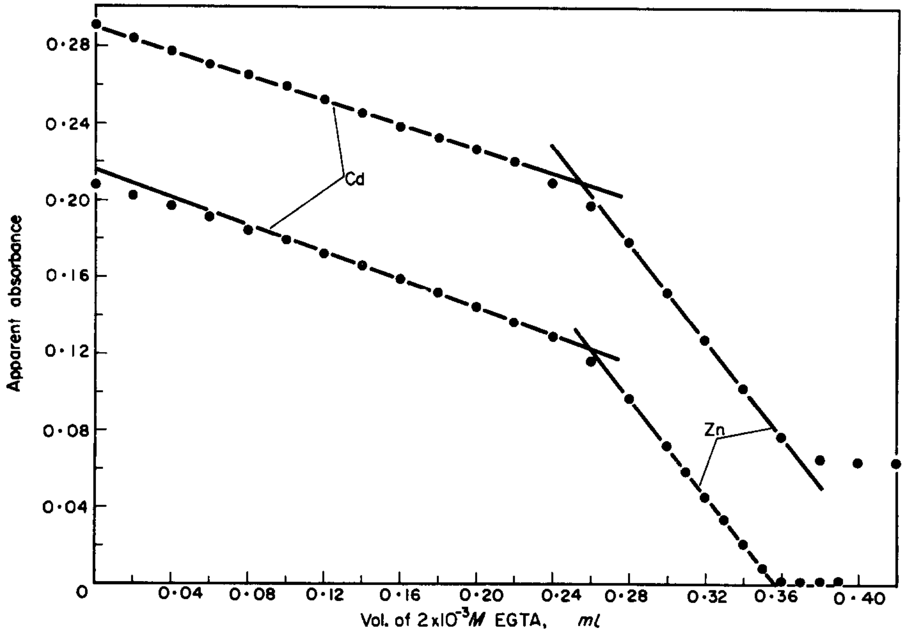

FIG. 3.—Typical curves obtained by titration of a sample containing cadmium and zinc with EGTA.

As expected, cadmium reacts with the titrant before zinc. At low ammonia concentrations (0·01M and below), the cadmium segment of the titration curve shows an appreciable slope. With increasing buffer concentration, however, the cadmium segment approaches the horizontal as predicted. The effect of buffer concentration on the zinc segment is less pronounced. Thus a concentration of 0·02–0·03M in total ammonia gives the best possible angle at the cadmium end-point without seriously affecting the zinc segment of the curve. The cadmium segment, of course, becomes steeper when the concentration of Murexide is increased. The amount of Murexide necessary is governed only by the amount of zinc present. When the excess of Murexide is not sufficient to complex all the cadmium, the titration curve is nearly horizontal at the beginning and then bends down to the usual cadmium slope. This, however, does not affect the determination because, for the location of the cadmium end-point, only the straight line portion immediately before the abrupt slope change is necessary for the extrapolation.

Typical titration curves with sufficient excess of Murexide showing all three straight portions in nearly perfect fashion are presented in Fig. 3.

It is generally expected that with a very weak complex a curvature should be produced in a titration curve. Thus it is rather unexpected that, with the deliberately weakened Cd-Murexide complex, such a perfect straight line is obtained. Similar reasoning holds as for the analogous conditions of the calcium segment of the Ca-Mg-titration described in a previous paper of this series.[1] The full mathematical treatment of this situation is reserved for another publication, and here only a simplified derivation will be given.

Consider a metal ion, M, reacting with a dye, I, according to

$$\mathrm{M} + \mathrm{I} \rightleftarrows \mathrm{MI}.$$

(Charges are omitted because they are irrelevant to the point in question.) Only MI is assumed to absorb at the wavelength selected. Hence

$$A = \varepsilon b \times [\mathrm{MI}].$$

The stability constant of the complex MI is given by

$$K = \frac{[\mathrm{MI}]}{[\mathrm{M}] . [\mathrm{I}]} \tag{1}$$

The following two equations must hold:

$$C_{\mathrm{M}} = [\mathrm{MI}] + [\mathrm{M}] \tag{2}$$

$$C_{\mathrm{I}} = [\mathrm{MI}] + [\mathrm{I}] \tag{3}$$

When the dye is in considerable excess the condition $C_{\mathrm{I}} \gg C_{\mathrm{M}}$ is given and consequently also

$$C_{\mathrm{I}} \gg [\mathrm{MI}].$$

Using this and substituting (2) and (3) in the expression for the equilibrium constant (1), one obtains

$$K = \frac{[\mathrm{MI}]}{(C_{\mathrm{M}} - [\mathrm{MI}])C_{\mathrm{I}}} \tag{4}$$

Solving for [MI] results in

$$[\mathrm{MI}] = \frac{KC_{\mathrm{I}}}{KC_{\mathrm{I}} + 1} . C_{\mathrm{M}} = \text{const.} \times C_{\mathrm{M}} \tag{5}$$

and finally,

$$A = \varepsilon b. \text{ const.} \times C_{\mathrm{M}} = \text{const.}' \times C_{\mathrm{M}} \tag{6}$$

Thus the absorbance is directly proportional to the total metal ion concentration regardless of how weak the complex may be. If these findings are applied to a titration the following reasoning holds: assume that the metal is titrated with a complexing agent, Y, and that the titration complex, MY, is of so high a stability that its dissociation can be neglected to a first approximation. Then C_{M} in equation (6) is the concentration of metal ion not complexed by the titrant, and consequently a straight-line titration curve is obtained even with a very weak metal-dye complex.

It is of interest to speculate in this connection as follows. Many photometric determinations (not titrations!) employ rather weak complexes and the procedure requires "addition of a considerable excess of chromogenic agent in order to shift the equilibrium to virtual completion, so that a straight calibration curve is obtained". It is entirely possible that there is no shift to completion at all, but rather that the straight calibration curve is a consequence of the situation discussed above.

Because many other metal ions (of notable interest are lead, copper, nickel and cobalt) also give yellow Murexide complexes, the selectivity of the proposed titration is not expected to be high. Selective masking and demasking may improve the situation but no investigations in this direction were undertaken. Separation of Cd + Zn is possible by several methods (ion exchange, paper chromatography, solvent extraction) so that the method described may be applied after such a separation is effected. Only the influences of magnesium and calcium were investigated, because these two metals, present as impurities in the reagents used, or introduced by dust, may affect the results seriously, especially when small amounts of zinc and cadmium are to be determined.

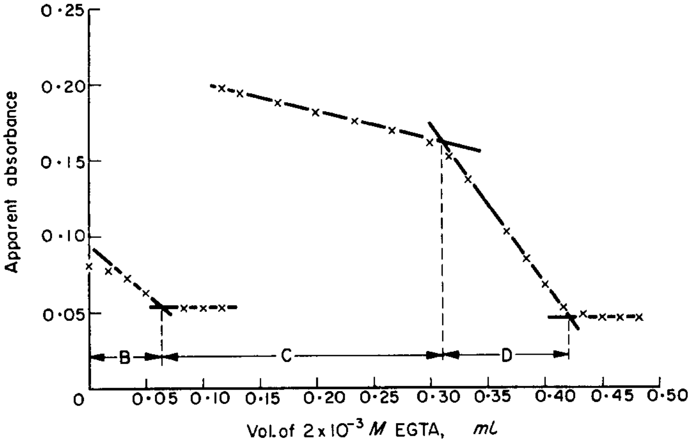

FIG. 4.—Calculation of an analysis of a Cd-Zn mixture using the pretitration method. Let A stand for the EGTA (ml) equivalent to the known amount, P, of zinc added for the pretitration.

Then: pretitrated impurity of Ca $\hat{=}$ B − A ml
Cd $\hat{=}$ C + A ml
Zn $\hat{=}$ D − A ml.

Magnesium was found not to interfere at all, as was to be expected from the low stability constant of its EGTA complex (log K = 5·4) and the fact that it shows only very little tendency to complex with Murexide. Calcium is titrated after cadmium and before zinc. The slope of the calcium segment is virtually identical to that of the cadmium segment so that the sum Cd + Ca is obtained at the "cadmium end-point". Thus cadmium may be corrected for any calcium blank established. Unfortunately the calcium blank is not constant over a long period of time. Water and reagent solutions prepared in the way described in the experimental part are at the beginning virtually free from calcium. But on the repeated opening of the plastic bottles dust enters the solution and the blank becomes noticeable and increases with time. It is, therefore, most convenient to establish the blank for each titration *via* a pretitration. For this purpose the buffer solution containing the Murexide is placed in the titration cell and diluted to the desired volume. Then a small, accurately known amount of zinc is introduced and titrated. After this pretitration the sample solution is introduced and the titration is performed as usual. The amounts of titrant required for the cadmium and zinc in the sample are obtained from the titration curve as shown in Fig. 4. This method, of course, corrects for only those impurities (calcium or any other metals with similar interference mechanisms) present in the reagents, but any calcium in the sample solution is still cotitrated with the cadmium.

Zinc or cadmium alone may also be titrated using the pretitration technique and in this case the amount of zinc added initially need not be accurately known. The amount of metal present in the sample is obtained simply from the difference of two zinc end-points.

The accuracy and precision of the method are satisfactory. Table I shows a selection of results for titrating zinc alone and cadmium alone, as well as zinc and cadmium together, using the pretitration technique.

EXPERIMENTAL

Apparatus

The phototitrator described in Part II of this series was used.[5] An improvement was found to be necessary. At the wavelength selected, strong deviations from Beer's law were observed initially. These were eventually traced to insufficient monochromacy. The filter used not only passed light of the nominal wavelength but showed also a transmittance peak in the near infrared. Hence a heat ray absorbing filter was permanently positioned in the light beam behind the interference filter. Some titrations were initially performed in the micro cell assembly described in Part VI of this series.[1] It was then possible to titrate as little as a few μg of cadmium and zinc. In this case a Beckman Spinco ultra-microburette was employed. Again, however, serious dust problems were encountered under the prevailing conditions. Therefore a macro cell of 35-ml capacity and a light path of 2 cm were used, and the titrant was delivered from a 1-ml micro burette. An interference filter of 456 mμ and in some cases of 444 mμ nominal wavelength has employed.

Reagents

All reagents were of highest purity. The water used was deionised water, redistilled using a condenser tube of polyethylene. All solutions were stored in polyethylene bottles. The buffer solution was prepared by mixing ammonia and hydrochloric acid solutions which had been purified by isothermal distillation. The distillations were accomplished by placing a beaker containing the concentrated commercial reagent along with a polyethylene beaker containing redistilled water in a desiccator (without desiccant) for a day or two. The total concentration of ammonia in the buffer was $2M$.

Stock solutions of zinc and cadmium (about $0{\cdot}1M$) were prepared by dissolving appropriate amounts of highest purity metal in HNO_3 followed by dilution with redistilled water.

Stock solutions of chelons (of about $0{\cdot}1M$) were prepared by dissolution of the reagent in redistilled water (a few pellets of NaOH were added, if necessary, to effect solution).

The stock solutions were standardised by well established complexometric methods.

More dilute solutions were prepared by quantitative dilution of these stock solutions.

Procedure

Place about 25 ml of water in the absorption cell. Add 0·2 ml of buffer and about 0·5–1 mg of Murexide.* Adjust the light to give a galvanometer reading of about 90 S.D. (or 180 S.D. with zero suppressed to −100). Add 0·2–0·5 ml (exactly measured) of a $5 \times 10^{-4}M$ zinc solution and titrate with $2 \times 10^{-3}M$ EGTA until the curve shows 2–3 points of the horizontal after the zinc end-point (see Fig. 4). Add the unknown sample and titrate again.† Plot the results and evaluate the curve as shown in Fig. 4.

* It is not necessary to weigh the Murexide accurately. One may dilute Murexide by grinding it with sodium chloride and add a certain amount with a spoon of appropriate size. However, it is much simpler to add Murexide (diluted or undiluted) to the solution containing buffer until a predetermined galvonometer reading is obtained. The amount of Murexide is not at all critical as long as there is a sufficient excess over the zinc.

† For samples with very high metal contents it may be necessary to operate with a "sectioned titration curve". See Part VI in this series for details.[1]

TABLE I.—TITRATION OF ZINC AND CADMIUM WITH EGTA

Zinc						Cadmium					
$4{\cdot}71 \times 10^{-4}M$, *ml*			$10^{-7}g$			$5{\cdot}06 \times 10^{-4}M$, *ml*			$10^{-7}g$		
Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.	Taken	Found	Diff.
0·474	0·477	+0·003	146	147	+1						
0·480	0·484	+0·004	148	149	+1						
0·514	0·511	−0·003	158	157	−1						
0·578	0·576	−0·002	178	177	−1						
0·627	0·620	−0·007	193	191	−2						
0·742	0·756	+0·014	228	233	+5						
0·881	0·871	−0·010	271	268	−3						
0·910	0·910	±0·000	280	280	±0						
1·121	1·100	−0·021	345	339	−6						
						0·916	0·914	−0·002	521	520	−1
						1·063	1·068	+0·005	605	607	+2
						1·313	1·306	−0·007	747	743	−4
0·353	0·340	−0·013	109	105	−4	0·521	0·530	+0·009	296	301	+5
0·429	0·427	−0·002	132	131	−1	1·526	1·530	+0·004	868	870	+2
0·500	0·492	−0·008	154	151	−3	1·000	0·997	−0·003	569	567	−2
0·500	0·495	−0·005	154	152	−2	1·000	0·983	−0·017	569	559	−10
0·529	0·552	+0·023	163	170	+7	5·005	5·000	−0·005	2846	2844	−2
0·555	0·564	+0·009	171	174	+3	1·036	1·038	+0·002	589	590	+1
0·735	0·716	−0·019	226	220	−6	1·637	1·621	−0·016	931	922	−9
1·915	1·910	−0·005	590	588	−2	0·577	0·569	−0·008	328	324	−4

Acknowledgment—Part of this work was performed under a grant of the National Science Foundation. This aid is gratefully appreciated.

Zusammenfassung—Zink und Cadmium können in einer Lösung wie folgt bestimmt werden. Die Probe wird mit Ammoniak-Ammoniumchlorid-Puffer auf pH 10 gebracht, sodass die totale Ammoniak-Konzentration 0.02–0.03 m beträgt. Sodann wird Murexid in mindestens fünffachem molaren Überschuss (auf Zink bezogen) eingetragen. Es wird photometrisch bei 450 mμ titriert. Die erhaltene Titrationskurve zeigt zwei Knicke, deren erster dem Cadmium- und deren zweiter dem Zink-Endpunkt entspricht. Der Einfluss von Calciumverunreinigungen in den Reagenzien wurde studiert und eine Vortitration wird vorgeschlagen. Hierbei wird erst eine kleine, genau bekannte Menge an Zink vortitriert und dann die Probe zugesetzt. So lässt sich der Cacliunblindwert der Reagenzlösung für jede Titration in Rechnung stellen.

Résumé—Le zinc et le cadmium peuvent être dosés dans une solution unique de la manière suivante. L'échantillon est amené à pH 10 par addition d'une solution tamponnée ammoniaque-chlorure d'ammonium et composée de telle sorte que la concentration totale en ammoniaque soit de 0,02–0,03 M. On ajoute du murexide en quantité telle su'elle représente un excès d'au moins cinq fois sur la quantité de zinc présente. Ce dosage est effectué par photométrie à environ 450 mμ et en présence d'EDTA comme agent titrant. La courbe de dosage obtenue montre deux cassures correspondant aux neutralisations successives du cadmium et du zinc. L'influence des impuretés calciques dans les réactifs utilisés a été étudiée et une méthode de prédosage proposée. Dans ce but, une petite quantité connue de zinc est prédosée et l'on ajoute la solution à analyser. Ainsi le taux de calcium dans l'essai témoin est établi pour chaque dosage.

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SELECTIVE DETERMINATION OF TRACE AMOUNTS OF COBALT USING THE SORPTION OF $Co(Phen)_3^{2+}$ ON SILICA

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Summary—Sorption of $Co(Phen)_3^{2+}$ on silica is not affected by EDTA or citric acid in appropriate conditions of acidity. This fact has been used for the selective determination of microgram amounts of cobalt. Desorption of $Co(Phen)_3^{2+}$ is carried out from an alkaline aqueous-methanolic solution of ammonium formate, and cobalt is determined indirectly, colorimetrically, *via* ferroïn. Special attention has been paid to the determination of trace amounts of cobalt in the presence of iron.

As previously mentioned,[1] the complex of Co^{II} with 1,10-phenanthroline (Phen), $[Co(Phen)_3^{2+}$ (pK = 20·1)], can be sorbed on silica quantitatively over a large pH range even in the presence of EDTA and citric acid. Anionic complexes of metals with EDTA and citric acid are not sorbed on silica, and therefore it is possible to use these reagents to increase the selectivity of the sorption of $Co(Phen)_3^{2+}$, and thus also to permit the determination of cobalt. The formation of ion association complexes $[Co(Phen)_3^{2+}, 2X^-]$ which increases at high concentrations of X^- has been similarly used for the desorption of $Co(Phen)_3^{2+}$, sorbed on silica, as well as for the desorption of ferroïn.[2,3] Complexes of this type, where X^- indicates anions of some monobasic acids, *e.g.*, formic, acetic, trichloro- and monochloroacetic, are, to a certain degree soluble in water, and are very soluble in a mixture of methanol and water.

After elution of the $Co(Phen)_3^{2+}$, cobalt is determined in the solution colorimetrically;[4] the cobalt bound in the phenanthroline complex is oxidised with $iron^{III}$, and the concentration of the resulting ferroïn is determined colorimetrically.

This paper describes a number of influences on the sorption of $Co(Phen)_3^{2+}$ on silica, and on its use for the selective determination of trace amounts of cobalt. Special attention has been paid to the determination of cobalt in the presence of $iron^{III}$ which results in the oxidation of $cobalt^{II}$ to $cobalt^{III}$ with an excess of Phen, and the formation of an equivalent amount of ferroïn.

EXPERIMENTAL

Reagents

Silica: Silica of pore size 85 Å and particle size 0·15–0·20 mm, activated at 120° was used (if not stated otherwise) for the sorption, which was carried out on a column of 16 mm internal diameter and 50 mm in height. The "silica pH" was adjusted to the required value by washing with a suitable buffer solution.

1,10-Phenanthroline solution: 0·1*M*: Prepared by dissolving 18 g of reagent-grade 1,10-phenanthroline in hot water, acidifying with 5 drops of acetic acid and diluting to 1 litre.

Cobalt chloride solution: $10^{-4}M$: Prepared by dissolving $CoCO_3$ (Kahlbaum, Ni-free) in a minimum amount of HCl and diluting it with water.

Salt solutions: 1*M* solutions of ammonium formate, acetate, tri- and monochloroacetate were prepared by the solution of the appropriate salts or acids in redistilled water, and adjusting the pH to 9·5 with aqueous ammonia.

EDTA solution: 1M: Prepared by dissolving 372 g of reagent-grade EDTA in warm water, making alkaline with aqueous ammonia (1 : 1) and diluting to 1 litre. The pH of the resulting solution should be 8.

Buffer solutions: Prepared by potentiometric neutralisation of suitable acids (trichloro-, monochloroacetic, acetic or boric acid (with aqueous ammonia) to give a final concentration of *ca.* 1*M*.

Other solutions prepared from reagent-grade chemicals, and standardised by recommended procedures.

Apparatus

Optical densities were measured with a Pulfrich photometer (Zeiss, Jena, East Germany) equipped with an arrangement for objective measuring—Elpho II. pH values were measured with a glass electrode and pH meter Multoscop V (Labor. potřeby, Prague, Czechoslovakia).

Sorption of $Co(Phen)_3^{2+}$ *on silica*

In most cases the influence of factors on the sorption of $Co(Phen)_3^{2+}$ on silica was followed by a kinetic method, which was also used for analytical purposes. As already mentioned, the changes in the concentration of the Co^{II} complex with phenanthroline were followed by indirect colorimetric measurements, *via* ferroïn. The reaction used occurs quantitatively even in an aqueous-methanolic medium, under identical conditions. The procedure, except in cases mentioned explicitly, was as follows.

Procedure: To a measured amount of 10^{-4} or $10^{-3}M$ $CoCl_2$ was added a known amount of 1*M* EDTA solution or 1*M* citric acid; alternatively the pH was adjusted by addition of 5 ml of 1*M* buffer solution. To this solution, 1 ml of 0·1*M* phenanthroline was added, and after a further adjustment of the pH, the volume of the solution was adjusted to ~25 ml. The sorption on the silica column was carried out, after adjusting the pH of the silica, at a flow rate of about 2 ml/min. The washing of the column after the sorption was carried out with 25 ml of a 0·1*M* buffer solution with a pH of the same value as during the sorption, and, finally, with 10 ml of water. The desorption of the sorbed $Co(Phen)_3^{2+}$ was carried out with 15 ml of *ca.* 1*M* solution of ammonium formate of pH 9·5, containing, in every 100 ml, 1 ml of 0·1*M* phenanthroline* and 15 ml of methanol. The desorption can be carried out reliably at the same rate as the sorption. The washing of the column was carried out with 10 ml of water. The pH of the solution, containing $Co(Phen)_3^{2+}$, was adjusted with HCl (1 : 1) to ~3. One ml of 0·1*M* phenanthroline was added, and 2 ml of *ca.* $10^{-3}M$ $FeCl_3$ (containing no Fe^{II}). The volume was adjusted to 50 ml, and the extinction of the ferroïn was measured after 15 min, in 2-cm cells at 510 mμ, against a blank at pH 3, containing, in the same volume, the same amount as the sample of $FeCl_3$ and Phen. The evaluation was read from a calibration curve, obtained by adding to 2–15 ml of $10^{-4}M$ $CoCl_2$, 1 ml of 0·1*M* Phen, 1 ml of $10^{-3}M$ $FeCl_3$ and 5 ml of buffer solution of pH *ca.* 3, and diluting to 50 ml as in the case of the sample solution.

RESULTS AND DISCUSSION

Influence of pH, EDTA and citric acid

The influence of pH, EDTA and citric acid was studied on the sorption of 29·5 μg of cobalt. The curves in Fig. 1 show that the sorption of cobalt is complete in the pH range 2–7·5 (curve 1), even in the presence of citric acid (curve 2). In the solution of 0·1*M* EDTA the sorption of $Co(Phen)_3^{2+}$ is not influenced in the pH range 6·5–8·5. At lower pH values, however, EDTA interferes by forming chelates. At higher pH values, the presence of EDTA reduces the hydrolysis of Co^{II} (curve 3). These examples show the dependence of the apparent stability constants of $Co(Phen)_3^{2+}$ and of the Co–EDTA complex on pH.

Influence of rate of sorption, dilution and ionic strength

Under given conditions, the sorption of 29·5 μg of cobalt in 25 ml of solution is quantitative, even at a flow rate of 6 ml/min, which was, in our case, the maximum possible rate.

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* Phenanthroline must be present in the solution, otherwise there will be a partial hydrolysis of $Co(Phen)_3^{2+}$, and its desorption is then not quantitative.

The influence of the ionic strength was tested by sorption of $Co(Phen)_3^{2+}$ from saturated solutions of some salts of alkali metals (*e.g.*, 29·5 μg of Co were sorbed with an error of −4·2% from a saturated solution of NaCl.

Capacity of silica

It was found by using a kinetic method that a silica column (50 mm high and 16 mm in diameter) at pH 3·5 and a flow rate of 2 ml/min sorbs quantitatively as much as 1·16 mg of Co as $Co(Phen)_3^{2+}$.

Using a static method the capacity of the silica was determined in the following way: 1 g of silica was shaken intensively for 5 hr on a shaking machine with a solution of 5 ml of 5×10^{-2} *M* $CoCl_2$, 5 ml of 1*M* buffer solution of pH 3·5, 10 ml of 10^{-1} *M* Phen, the volume being adjusted to 25 ml. The change of the concentration of Co $(Phen)_3^{2+}$ was determined colorimetrically by measuring the intensity of the yellow coloration of the complex at 410 mμ (pH *ca.* 3.)[5] It was found that at pH *ca.* 3·5 6·35 mg of cobalt is sorbed on 1 g of silica. During the study of the mechanism of the sorption,[6] it was found that the capacity of silica for $Co(Phen)_3^{2+}$ is effectively unaltered in the pH range 1·5–9·5.

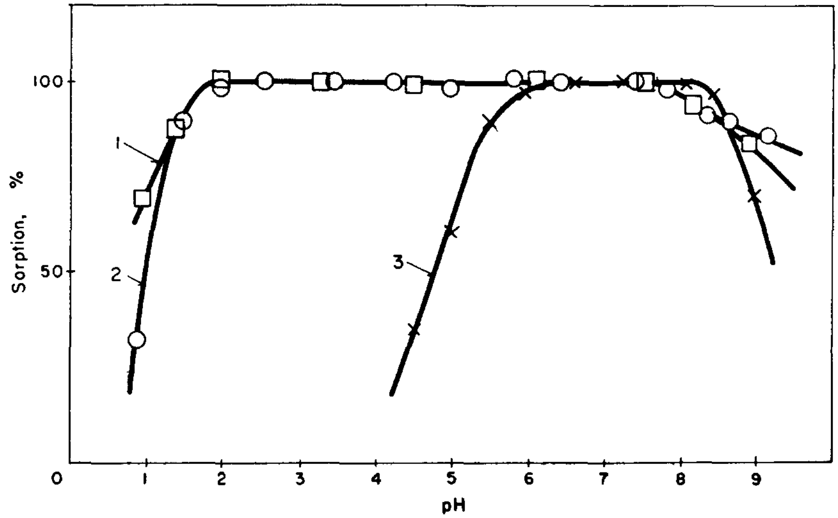

FIG. 1.—Influence of pH on sorption of $Co(Phen)_3^{2+}$ on silica

1—in 0·1*M* buffer solutions.
2—in 0·1*M* citric acid.
3—in 0·1*M* EDTA.

The capacity of silica is influenced by the size of grain and of pores in the same way as in the sorption of ferroïn.[2] These results apply to the commonly used silica (pore size 85 Å, grain size 0·15–0·20 mm). With decreasing grain size of silica the capacity rises abruptly. Because of the resistance of a column of finer silica, the application to sorption under kinetic conditions is rather problematical. For the determination of trace amounts of Co— which is the aim of the work described in this paper—silica with a higher capacity is not necessary. The pore size in a given range does not influence appreciably the sorption of $Co(Phen)_3^{2+}$(32·65 and 85 Å); larger pore silica (150 Å), however, has a very small capacity.

Reagents for desorption

Alkaline solutions (pH 9·5–10) of ammonium salts of some acids may be used in the same way as for the desorption of ferroïn sorbed on silica. Instead of the more usual ammonium formate, it is possible to use, under the same conditions, ammonium salts of trichloroacetic, monochloroacetic and acetic acids. To prevent the hydrolysis of $Co(Phen)_3{}^{2+}$, the presence of phenanthroline is necessary just as when formic acid is used. The minimum volume necessary for the desorption under the same conditions was obtained when ammonium formate and trichloroacetate were used. Methanol lowers still further the volume of the minimum amount of elution mixture.

Analytical application

It is advantageous for the analytical application that the sorption of $Co(Phen)_3{}^{2+}$ on silica is quantitative, even from solutions of high ionic strength. Very dilute solutions can be concentrated by sorption from a large volume and desorption by a minimum volume. It is possible to use the masking properties of EDTA and citric acid to increase the selectivity of the determination of cobalt. For a rapid determination of cobalt it is important that the sorption of $Co(Phen)_3{}^{2+}$ on silica can be carried out reliably at a comparatively high flow rate and that the final colorimetric determination does not need a special treatment of the solution of $Co(Phen)_3{}^{2+}$, and is rapid.

Also, the fact that the sorption is carried out on an inexpensive type of silica, needing no special treatment, is an advantage in the analytical application. The procedure for the analytical utilisation of the sorption of $Co(Phen)_3{}^{2+}$ on silica is practically identical with the procedure for the sorption. In the sequel, only results will be given, and any digressions from the given working procedure.

Reliability of determination

With the above procedure, at pH 7, a number of determinations of 29·5 μg–1·16 mg of cobalt were carried out, taking care to maintain the excess of phenanthroline during the sorption at least to ten-fold (molar). In the case of larger concentrations of cobalt, the solution containing $Co(Phen)_3{}^{2+}$ was adjusted to a volume suitable for a sensitive determination of cobalt *via* ferroïn. The results obtained show that, in the given concentration range, cobalt is determined with an average relative error of $\pm 3·7\%$.

Selectivity of determination

The influence of interfering ions on the formation and sorption of $Co(Phen)_3{}^{2+}$ (pK = 20·1) on silica is identical to that in the case of $Fe(Phen)_3{}^{2+}$ (pK = 21). The formation of complexes of cobalt^{II} is affected especially by those ions which also form with Phen stable soluble complexes or less soluble ion associates (*e.g.*, Ni, Cu, Zn, Cd, Hg, Ag, W, Mo). The course of the sorption on silica is also affected by other metal ions which hydrolyse at optimal conditions, forming hydroxo complexes (which are also sorbed on silica), giving in water partly soluble hydroxides which inhibit the smooth course of the reaction (*e.g.*, Bi, Ti, Cr, Al, Sn, Sb, *etc.*)

To avoid the separation of cobalt from these interfering ions, their influence can be prevented, in most cases, by utilising the complex-forming properties of EDTA and citric acid, complexes of these reagents not being sorbed on silica, because of their anionic character.

Masking with EDTA

In the pH range 6·5–8·5 it is possible, with EDTA, to mask those metals which, under given conditions with this reagent, form complexes which are stable enough to prevent a reaction with phenanthroline or a hydrolysis.

Working procedure: To a solution of 29·5 μg Co and of the interfering metal, an amount of 1*M* solution of EDTA is added, sufficient to bind the metal quantitatively. The pH of the solution is adjusted to *ca.* 7, the volume to *ca.* 25 ml, and 1 ml of 0·1*M* Phen is added. The sorption of $Co(Phen)_3^{2+}$ and its determination is carried out according to the procedure used during the sorption. Metals which hydrolyse easily and do not form very stable complexes with Phen can be masked with EDTA to allow the determination of trace amounts of cobalt in their presence.

In this way 29·5 μg of cobalt were determined in the presence of *ca.* 100 mg of Pb, Mn, Be, Zr, Sc, In, La, Al, Cr or Bi with an error not exceeding ±4% rel. It is probable that the determination of cobalt is possible in the presence of an even larger excess of these metals. In the case of Al and Cr it is necessary to boil the solution after adding EDTA—both ions react slowly with EDTA at normal temperature. During the sorption of $Co(Phen)_3^{2+}$ in the presence of higher concentrations of Cr bound with EDTA, a sorption of hydroxo complexes of chromium occurs (a violet layer on the column); these are not desorbed in alkaline medium by formate, and do not influence the determination. The elution can be carried out with dilute acid.

Only limited concentrations of metals which form stable complexes with Phen and which have stability constants nearly equal to, or higher than, the complexes of EDTA (Cu, Ni, Cd, Zn, Fe) can be screened. In this way 29·5 μg of Co were determined with an error not exceeding ±5% rel., in the presence of 23·6 mg of Ni, 15·5 mg of Cu, 225 mg of Cd and 130 mg of Zn. In the case of Cd and Zn it is necessary to boil and cool the solution after adjustment of pH and addition of Phen, otherwise the Co^{II} complex forms, and the results are low.

Masking with citric acid

Citric acid does not affect the sorption of $Co(Phen)_3^{2+}$ on silica, even at high concentrations. For a number of metals, pH 3·5–4 is optimal, as in the masking of metals which affect the formation and sorption of ferroïn. Most multivalent metals, *e.g.*, Sn, Sb, Bi, Tl and Zr, can be screened by citric acid when hydrolysis is to be prevented; the same applies to metals which form with Phen practically insoluble associates (W, Mo). An excess of sodium citrate must be used in most cases to prevent hydrolysis, and therefore the formation of complexes with Phen.

Procedure: For example for the determination of 29·5 μg of cobalt in the presence of 47 mg of Mo (as molybdate). About 10 ml of 1*M* sodium citrate are added to the solution, the pH is adjusted to 3·5–4, and 1 ml of 0·1*M* Phen is added. The sorption, desorption and determination of cobalt *via* ferroïn is carried out in the same way as before.

With the method described, the same amount of cobalt was determined even in the presence of 75 mg of W and 82 mg of Bi. The relative error of the determination did not exceed ±3·5%.

Determination of cobalt in the presence of iron

Special attention was paid to this case because Fe^{III} and Fe^{II} form with Phen very stable complexes, and because of the redox reaction[8] which occurs over a large pH range in the presence of cobalt, bound as $Co(Phen)_3^{2+}$:

$$Fe_2(OH)_2(Phen)_4^{4+} + 2Co(Phen)_3^{2+} + 2HPhen^+ \leftrightharpoons 2\,Fe(Phen)_3^{2+} + 2Co(Phen)_3^{3+} + 2H_2O \quad (2)$$

which is the reaction used for the final indirect colorimetric determination of cobalt.

For the determination with milligram amounts of Fe^{III}, the amount of ferroïn formed corresponds to the concentration of cobalt, which permits the determination of this metal[4]. Reaction (2) can be applied even for the concentration or separation of ferroïn from a mixture.

With a molar ratio Fe:Phen = 1:1, reaction (2) proceeds quantitatively, but all the excess of Fe^{III} bound as $Fe_2(OH)_2(Phen)_4^{4+}$ (which is of cationic nature) is sorbed along with ferroïn, and is desorbed by ammonium formate. This phenomenon causes a positive error in the determination, because the yellow-orange coloration of the $Fe_2(OH)_2(Phen)_4^{4+}$ complex is measured together with the coloration of ferroïn. The formation of $Fe_2(OH)_2(Phen)_4^{4+}$ can be considerably reduced by the presence of EDTA, according to the following equation:

$$Fe_2(OH)_2(Phen)_4^{4+} + 2H_2Y^- + 2H^+ \rightleftarrows 2FeY^- + 2H_2O + 2OH^- + 4HPhen^+, \quad (3)$$

which is strongly influenced by the pH. At higher pH values weaker complexes of Fe^{III}-EDTA than FeY^- can be formed (*e.g.*, $FeOHY^{2-}$), shifting the equilibrium to the left and raising the concentration of the hydro complex Fe^{III}-Phen in equivalent conditions.

When the absolute concentration of Fe^{III} is small, and the excess of EDTA is large, the formation and sorption of $Co(Phen)_3^{2+}$ occurs in the solution at pH 6·5–8·5 in the presence of Phen, and the course of the determination of cobalt does not differ from that already described. At concentrations higher than a few mg of Fe^{III}, the redox reaction (2) occurs even in the presence of EDTA, because the absolute equilibrium concentration of the complex $Fe_2(OH)_2(Phen)_4^{4+}$ is sufficient. It is, however, necessary to carry out the sorption at pH 4–5, and at higher concentrations of iron a blank sorption experiment must be made.

Working procedure: (*a*) To a solution containing 5–100 μg of cobalt and a maximum of 25 mg of Fe sufficient EDTA is added to complex all iron, and then 50% excess. The pH of the solution is adjusted to 4·5, and 1 ml of 0·1*M* Phen is added. After 15 min, the sorption of ferroïn, after the oxidation of cobalt, is carried out, and the ferroïn is desorbed in the same way as described for the sorption of $Co(Phen)_3^{2+}$. The extinction of the ferroïn is measured against water, and the result is evaluated against a calibration curve in the same way as described above. The error in the determination of 29·5 μg of Co in the presence of 25 mg of Fe^{II} does not exceed ±5% rel.

(*b*) In the presence of more than 26 mg of iron a blank has to be carried out with a solution of the same concentration as the sample, in order to eliminate the influence of the coloration of $Fe_2(OH)_2(Phen)_4^{4+}$ which is sorbed and desorbed as ferroïn. The procedure is analogous to that with the sample. After elution the pH is adjusted to the same value, and the resulting solution serves as a comparison in the colorimetry of ferroïn. It is also possible to measure the absorption (at 510 mμ) against water, and subtract the resulting value from the value of the extinction of the sample at the same wavelength. This procedure is suitable for routine determinations of cobalt with similar amounts of Fe (one blank is sufficient). It may be presumed that the above principle and procedure can be used for the determination of small amounts of cobalt in special steels.

Zusammenfassung—Es wurde die Sorption von $Co(phen)_3^{2+}$ an Silicagel studiert, welche bei geeigneten Aciditätsbedingungen weder durch EDTA noch durch Zitronensäure gestört wird, was zur selektiven Bestimmung von μg-Mengen Co ausgenützt wurde. Die Desorption des $Co(phen)_3^{2+}$ wurde mit einer alkalischen, wässrig-methanolischen Ammoniumformiatlösung durchgeführt. Die eigentliche Kobaltbestimmung erfolgte kolorimetrisch auf indirektem Wege über Ferroin. Besondere Aufmerksamkeit wurde der Bestimmung von Spuren Co neben Fe gewidmet.

Résumé—La sorption de $Co(Phen)_3^{2+}$ sur silice n'est pas perturbée par l'addition d'EDTA ou d'acide citrique dans des conditions d'acidité convenables. Ce fait a été utilisé pour le dosage sélectif de quantités de cobalt de l'ordre du μg. La désorption de $Co(Phen)_3^{2+}$ s'effectue au moyen d'une solution alcaline composée de formiate d'ammonum en solution dans le méthanol aqueux, et le cobalt dosé indirectement, par colorimétrie, par l'intermédiaire de la ferroïne. Considérations spéciales sur le dosage des traces de Co en présence de Fe.

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ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—I

SELEKTIVE SORPTION DES FLIESSMITTELS AUF CELLULOSE UND ENTSTEHUNG DER 2. FRONT IN DER PAPIERCHROMATOGRAPHIE

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Zusammenfassung—Es wird der Verlauf der Entmischung der Lösungsmittel als Wirkung des Trägers (Cellulose, Silicagel) untersucht. Durch Studium der Verhältnisse bei Gemischen von Alkohol, Wasser und Säure konnte bewiesen werden, daß es bei der Verteilungschromatographie zur Entmischung des Fließmittels kommt und daß der Verlauf dieser Entmischung von der Konzentration der Komponenten im ursprünglichen Gemisch abhängt. Es wird die Hypothese ausgesprochen, daß sich an der Grenze zwischen Träger und Lösungsmittelsystem eine Zwischenschicht bildet, an deren Aufbau alle Komponenten des Lösungsmittelsystems beteiligt sind.

NACH der heute allgemein anerkannten Hypothese von Hanes und Isherwood[1] beruht der Trennvorgang bei der Papierchromatographie in erster Linie auf der Einstellung eines Verteilungsgleichgewichts zwischen einem Cellulose-Wasser-Komplex als stationäre Phase und dem Fließmittel als mobile Phase. Dabei ist allerdings zu berücksichtigen, daß die Zusammensetzung des Lösungsmittelgemischs während des Trennvorganges nicht konstant bleibt.

Horner, Emrich und Kirschner[2] verfolgten die Veränderung der Fließmittelzusammensetzung durch das Papier auf die Weise, daß sie in einem geschlossenen Raum ein Lösungsmittelgemisch über das Papier laufen liessen und die abtropfende Flüssigkeit dann refraktometrisch untersuchten. Sie bewiesen dabei, daß beim Durchfluß eine Entmischung des Lösungsmittelsystems eintritt, welche durch die Bindung von Wasser an die Cellulose hervorgerufen wird. Andererseits fanden sie aber bei Gemischen von Phenol mit Wasser eine bevorzugte Sorption der organischen Komponente durch die Cellulose. Sie schlossen daraus, daß die Verhältnisse beim Aufbau der stationären Phase nicht so einfach sind und sprachen die Vermutung aus, daß ein ternärer Komplex aus Cellulose, Wasser und organischem Lösungsmittel entsteht.

Martin[3] benutzte in seiner Arbeit die von Krulla[4] vorgeschlagene Methode und kam damit zum Schluß, daß das Papier Wasser aus dem Lösungsmittelgemisch bis zur Bildung eines bestimmten Gleichgewichtes adsorbiert und daß dabei die Cellulosefasern stark aufquellen.

Da einerseits die bisher erschienenen Arbeiten der einzelnen Autoren recht wenig sichere Ergebnisse enthalten, andererseits aber die Ursache für die Veränderung der Zusammensetzung des Fließmittels für den Trennvorgang und seine theoretische Behandlung von großer Bedeutung ist, erschien uns eine weitere Bearbeitung dieses

Fragenkomplexes wünschenswert. Dabei war zu erwarten, daß mit Hilfe der erhaltenen Ergebnisse auch gleichzeitig die Entstehung der 2. Front bei der papierchromatographischen Trennung aufgeklärt werden kann.

WAHL DER UNTERSUCHUNGSMETHODE

Für die Versuche benutzten wir zunächst die von Martin[3] beschriebene Methode. Sie besteht darin, daß das Fließmittel an einem bei 110°C getrockneten Papierstreifen im geschlossenen, lösungsmitteldampf-gesättigten Raum in üblicher Weise aufsteigt. Nachdem die Flüssigkeitsfront eine bestimmte Höhe erreicht hat, wird der Versuch abgebrochen und das Chromatogramm schnell in vorher markierte Streifen von 2 × 5 cm zerschnitten. Diese werden sofort in getrocknete, austarierte Wägegläser gegeben und gewogen. Durch Subtraktion der Masse des bei 110°C getrockneten Papierstreifens bestimmt man die Flüssigkeitsmenge auf dem Papier in den einzelnen Chromatogrammteilen. Durch Auswaschen mit Wasser und Titration mit 0,05 N Natriumhydroxidlösung beim Studium des Gemisches Alkohol-Wasser-Säure und durch Extraktion mit Alkohol und anschließende Titration mit Karl-Fischer-Reagens beim Studium des Gemisches Alkohol-Wasser wurden die Konzentrationsänderungen im Verhältnis zur Menge des Gemisches in den einzelnen Streifen untersucht.

Abb. 1 zeigt typische Kurven, welche wir dadurch erhielten, daß wir die Masse des Fließmittels (Äthanol 3M an Salzsäure) und die Konzentration der Säure im Verhältnis zu den Rf-Werten des Lösungsmittels verfolgten.

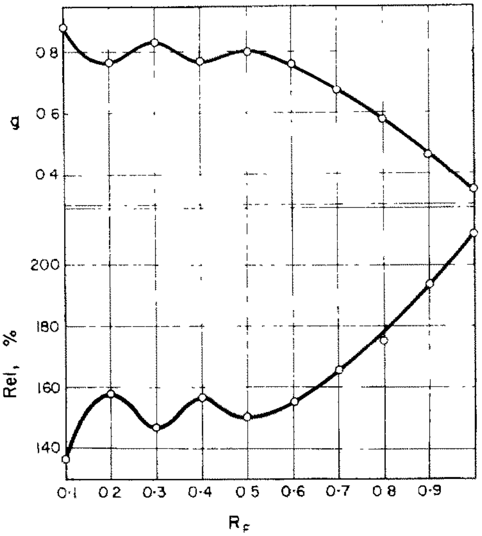


ABB. 1.—Masseänderung des Lösungsmittels (in g) und Änderung der Chlorwasserstoffsäurekonzentration (bezogen auf den Säuregehalt der Ausgangslösung)

Aus den Kurven geht hervor, daß mit der absoluten Masse-Abnahme des Lösungsmittels auf dem Papier der Gehalt an Salzsäure zunimmt. Da sich jedoch diese Abhängigkeit nicht nur im Gesamtbild der Kurve zeigt, sondern auch an den Stellen, an denen es bei der Durchführung der Versuche zu Unregelmäßigkeiten gekommen war, entstand der Verdacht, daß während der Bearbeitung der einzelnen Chromatogrammteile eine selektive Verdampfung auftritt. Es liegt nahe, daß dieser Effekt dann die Form der Kurven maßgeblich bestimmt. Das bedeutet aber, daß das Studium der Entmischung der Fließmittel mit Hilfe des gewählten Untersuchungsverfahrens zu fehlerhaften Ergebnissen führen muß.

Um diese Vermutung zu stützen, haben wir das angewandte Arbeitsverfahren noch etwas näher überprüft.

Für die folgenden Versuche benutzten wir als Fließmittel Methanol, Äthanol, Isopropanol und Butanol mit einem Wassergehalt von 5 Mol/l bei einem Chlorwasserstoff-Gehalt von 3 Mol/l.

Papierstreifen (Whatman Nr. 1, 2 × 7 cm), auf welchen mit Bleistift bei 1 und 6 cm Marken angebracht waren, tauchten wir mit dem unteren Ende in das zu untersuchende Fließmittel und ließen die Front genau bis zur oberen Marke aufsteigen. Danach haben wir die Papierstreifen aus dem Entwicklungsgefäß genommen, den Teil zwischen 1 und 6 cm schnell abgeschnitten und in ein vorher tariertes Wägeglas gebracht, gewogen und anschließend den Gehalt an Wasser bzw. Säure durch Titration bestimmt.

Diesen Vorgang wiederholten wir mit dem Unterschied, daß wir nach Entnahme des Papiers aus der Entwicklungskammer die Streifen 1, 2, 3, 4 und 5 min an der Luft hängen ließen und sie erst dann wie beschrieben behandelten.

Als Beispiel für weitere völlig gleichartig ausgefallene Versuche zeigt Abb. 2 das Verhalten des Gemisches Butanol-Wasser.

Aus Abb. 2a erkennt man, daß erwartungsgemäß mit steigender Lagerzeit an der Luft eine beträchtliche Gewichtsabnahme festgestellt werden kann. Bezieht man, wie Abb. 2b zeigt, die bei der Titration gefundene Wassermenge auf die nach Abb. 2a vorhandene Gesamtflüssigkeit, so ist gegenüber der Ausgangslösung eine erhebliche Zunahme des Wassergehaltes festzustellen, d. h. aber, daß aus dem Fließmittel während der Verarbeitung selektiv der Alkohol verdampft.

Aus diesen Versuchen geht eindeutig hervor, daß mit Hilfe der von Martin[3] beschriebenen Methode keine exakten Aussagen über die Veränderung der Fließmittelzusammensetzung auf dem Papier gemacht werden können.

Wir haben uns deshalb für die Methode der Säulen-Chromatographie entschieden, in welcher wir das zu untersuchende Flüssigkeitssystem über eine Säule aus Cellulosepulver fließen ließen. Es mußte zuvor noch geklärt werden, ob die Verhältnisse auf der Säule mit denen auf dem Papierblatt verglichen werden können.

Zu diesem Zweck untersuchten wir die Trennung von Nickel, Kobalt und Kupfer mit einem Gemisch Aceton-Wasser-Salzäure (8,7 + 0,5 + 0,8) sowohl auf Whatman-Papier wie auch auf der Cellulosesäule. In beiden Fällen arbeiteten wir nach der aufsteigenden Methode. Das Austauscherrohr wurde dazu der Länge nach in 2 Teile zerschnitten und mittels Klebestreifen zusammengehalten.[5] Nach Beendigung der Entwicklung und Öffnen der Säule wurden beide Chromatogramme mit 5%iger Natriumsulfidlösung behandelt. Wie Abb. 3 zeigt, wirken tatsächlich beide Verfahren ähnlich, so daß wir für die weiteren Versuche ohne Bedenken zur Prüfung der Entmischung von Fließmittelsystemen Cellulosesäulen verwenden konnten.

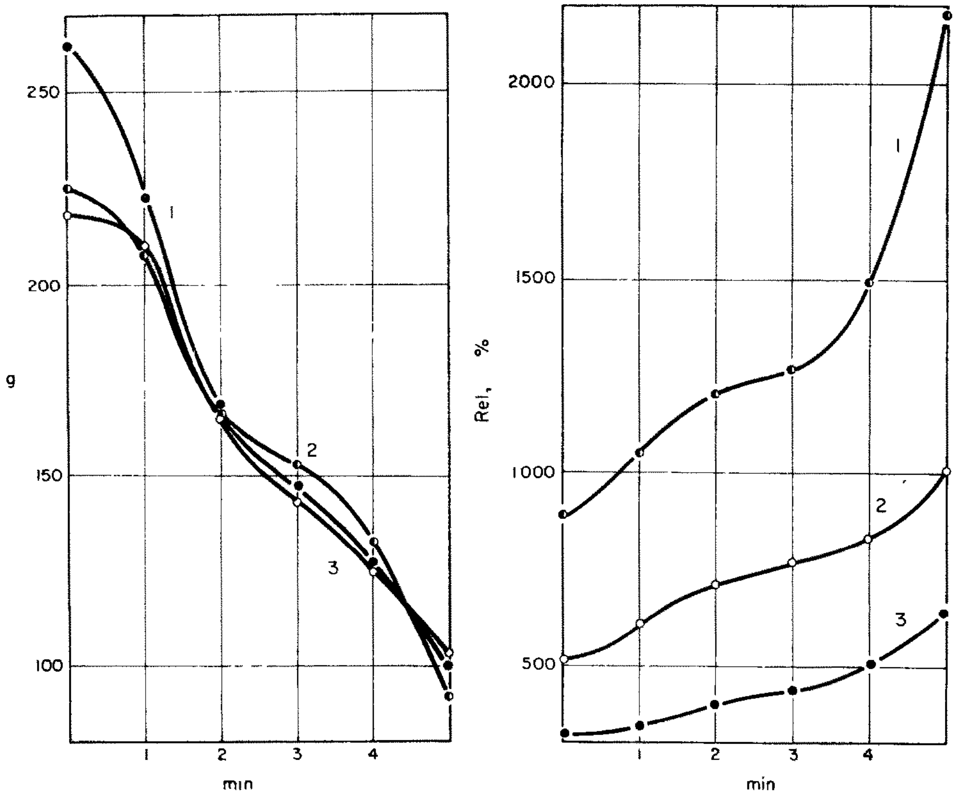
ENTMISCHUNG DER FLIESSMITTEL AN DER CELLULOSESÄULE

Zum Studium des Entmischungsvorganges verwendeten wir Gemische aus Alkohol, Wasser und Chlorwasserstoffsäure. An Alkoholen setzten wir Methanol, Äthanol, n-Propanol, n-Butanol und Benzylalkohol ein.

Durchführung

Über eine an der Luft getrocknete Cellulosesäule (Durchmesser 2,5 cm, Höhe 40 cm, 35 g Cellulosepulver Whatman Standard Grade) floß die zu untersuchende Mischung mit einer Geschwindigkeit von 2 ml pro Minute. Das Eluat wurde in Meßzylindern aufgefangen, aus welchen wir Portionen von 2 ml entnahmen und nach Verdünnung mit dest. Wasser mit 0,05 N Natronlauge gegen Methylrot titrierten.

Alle Alkohol-Säure-Gemische stellten wir so her, daß, 2 ml konz. Salzsäure in einem 100 ml Meßkolben mit reinem, mehrfach destilliertem Alkohol bis zur Marke aufgefüllt wurden.



(a) (b)

ABB. 2.—Veränderung der Zusammensetzung des Fließmittels durch Verdampfen der Alkoholkomponente.

(1) Butanol mit 8% Wasser
(2) Butanol mit 4% Wasser
(3) Butanol mit 2% Wasser

(a): Abnahme der absoluten Lösungsmittelmasse (g Wasser/Mol Cellulose) mit der Zeit
(b): Zunahme des Wassergehaltes mit der Zeit

Abb. 4 zeigt die bei der Untersuchung verschiedener Alkohol-Säure-Gemische erhaltenen Meßergebnisse.

Aus dem Diagramm geht hervor, daß in allen Fällen das Filtrat zu Anfang des Versuches einen wesentlich geringeren Säuregehalt aufweist als die Ausgangslösung. Außerdem kann man erkennen, daß die Menge der von der Säule zurückgehaltenen Salzsäure von der Art des Alkohols bestimmt wird und mit dessen Molekulargewicht wächst. Die Veränderung in der Zusammensetzung des Fließmittels wird

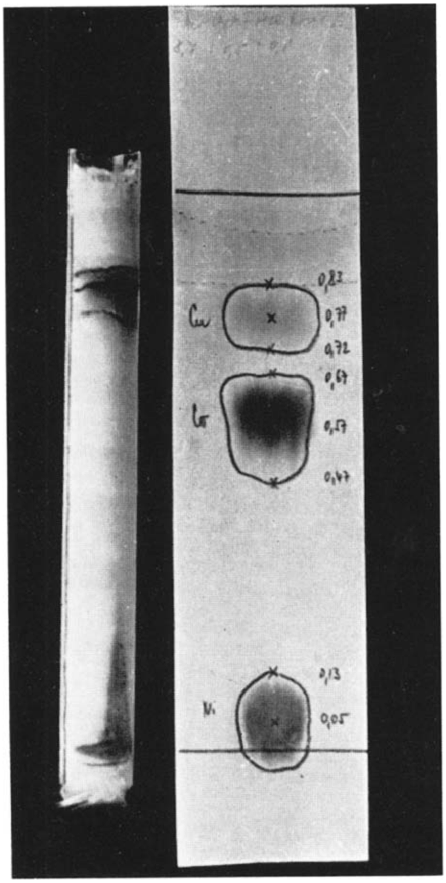


Abb. 3.—Trennung von Nickel, Kobalt und Kupfer mit Aceton-Wasser-Salzsäure. Säulenchromatogramm und Papierchromatogramm

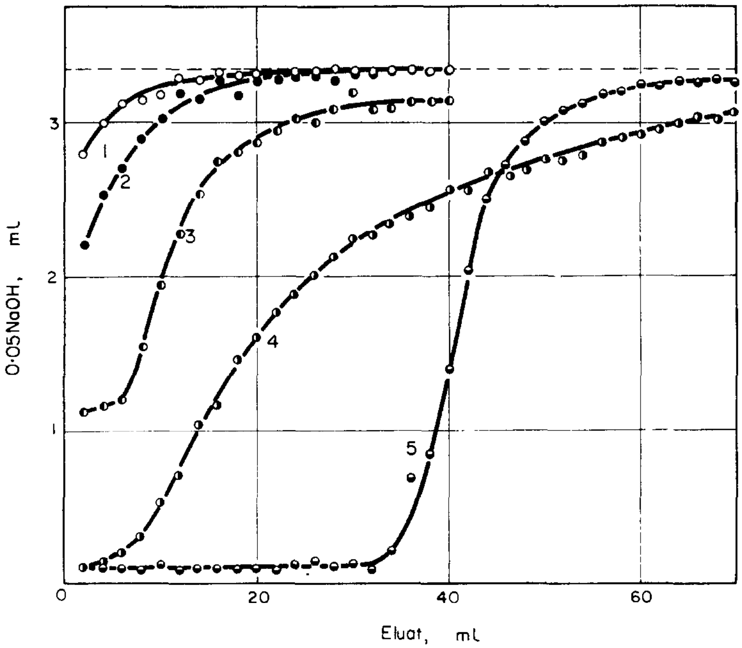


Abb. 4.—Konzentrationsänderung der Chlorwasserstoffsäure im Filtrat. Cellulosesäule, lufttrocken

(1) Methanol-Salzsäure
(2) Äthanol-Salzsäure
(3) n-Propanol-Salzsäure
(4) n-Butanol-Salzsäure
(5) Benzylalkohol-Salzsäure

augenscheinlich dadurch hervorgerufen, daß die Cellulose selektiv Komponenten des Gemisches bindet und erst nach Sättigung das Lösungsmittel die Säule in seiner ursprünglichen Zusammensetzung durchläuft.

Um zu prüfen, ob die beobachteten Effekte auf den unterschiedlichen Wassergehalt der verwendeten Alkohole zurückzuführen sind, bestimmten wir diesen.

Durchführung

3 ml des verwendeten Alkohols werden mit Karl-Fischer-Lösung nach der Dead-stop-Methode titriert. Das Reagens bereiteten wir auf folgendem Wege. 252 g sublimiertes Jod werden in 400 ml reinem Pyridin gelöst und so lange Schwefeldioxid eingeleitet, bis die Gewichtszunahme 131 g beträgt. Nach Abkühlung wird mit reinstem Methanol auf 2000 ml aufgefüllt. Man läßt 24 Stunden stehen und bestimmt dann den Wirkungswert der Lösung durch Titration einer bekannten Wassermenge. Die Bestimmung erfolgte unter Luftabachluß.

Bei den benutzten Alkoholen fanden wir die folgenden Wassergehalte:

Methanol	4,80%
Äthanol	8,02%
n-Propanol	8,64%
n-Butanol	4,20%
Benzylalkohol	4,03%

Wie man erkennt, ist der Wassergehalt der Alkohole etwas unterschiedlich. Aus dem Vergleich des Verhaltens von Methanol, n-Butanol und Benzylalkohol, die annähernd den gleichen Prozentsatz Wasser enthalten, muß man schließen, daß die

Form der Kurven in Abb. 4 in erster Linie durch die Art des Alkohols bestimmt wird. Äthanol und n-Propanol lassen sich zwanglos in das Bild einorden, obwohl sie etwas mehr Wasser enthalten.*

Unter ähnlichen Bedingungen untersuchten wir auch die Mischung von Aceton bzw. Methyläthylketon mit Salzsäure (2 ml konz. Salzäure mit Keton auf 100 ml aufgefüllt).

Abb. 5 zeigt, daß es auch bei diesen Systemen zu einer Entmischung kommt und daß der Effekt sogar noch deutlicher als bei den Alkoholen auftritt.

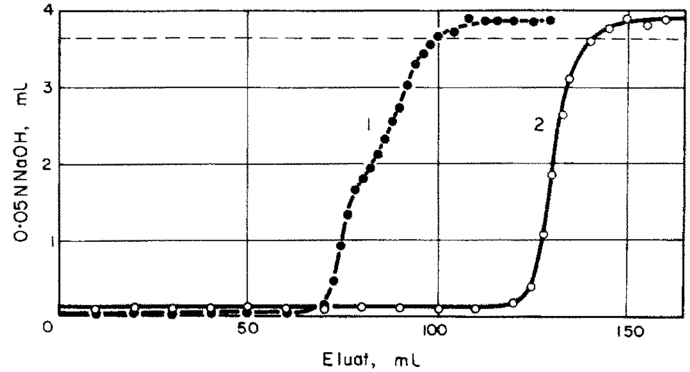


ABB. 5.—Konzentrationsänderung der Chlorwasserstoffsäure im Filtrat. Cellulosesäule, lufttrocken
(1) Aceton-Salzsäure (2) Methyläthylketon-Salzsäure

Um zu klären, ob die Entmischung der Lösungsmittel nur durch Cellulose hervorgerufen wird, prüften wir Gemische von Benzylalkohol mit Chlorwasserstoffsäure und Aceton mit Chlorwasserstoffsäure auch auf einer Silicagelsäule.

Durchführung

Über eine Säule (Durchmesser 2,5 cm, Höhe 40 cm) mit 55 g getrocknetem Silicagel (Korngröße 0,3 bis 0,6 mm) floß die zu untersuchende Mischung mit einer Geschwindigkeit von 2 ml/min. Das Filtrat wurde in gleicher Weise wie bei den vorangegangenen Versuchen geprüft.

Die Kurven der Abb. 6 zeigen, daß die Entmischung des Fließmittels an der Silicagelsäule mit dem Verhalten an Cellulose vergleichbar ist.

Die Befunde beweisen, daß in der Verteilungschromatographie die Entmischung des Lösungsmittels durch den Träger hervorgerufen wird. Die bei den Alkoholen und Ketonen festgestellte Abhängigkeit deutet darauf hin, daß der Zustand an der Grenze zwischen fester und flüssiger Phase nicht so einfach ist wie es im allgemeinen bisher angenommen wurde. Besser charakterisiert werden die Verhältnisse wahrscheinlich durch die Vermutung welche von Horner und Mitarbeitern[2] ausgesprochen worden ist, daß sich nämlich an der Cellulose ein ternärer Komplex Cellulose-Wasser-organisches Lösungsmittel ausbildet.

Die angeführten Versuchsergebnisse sprechen für diese Erklärung, wenn sie auch diese Hypothese noch nicht exakt beweisen. Nehmen wir die Bindung aller Komponenten des Lösungsmittelsystems an der Oberfläche der festen Phase an, so können wir die Verschiebung der Konzentrationskurven bei einer Reihe von Alkoholen und

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* Über die genauerer Wirkung des Wassergehaltes bei den einzelnen Alkoholen wird später berichtet.

Ketonen durch Änderung des Mengenverhältnisses der Komponenten an der festen Phase erklären.

Über weitere Untersuchungen zu diesem Fragenkomplex soll später berichtet werden.

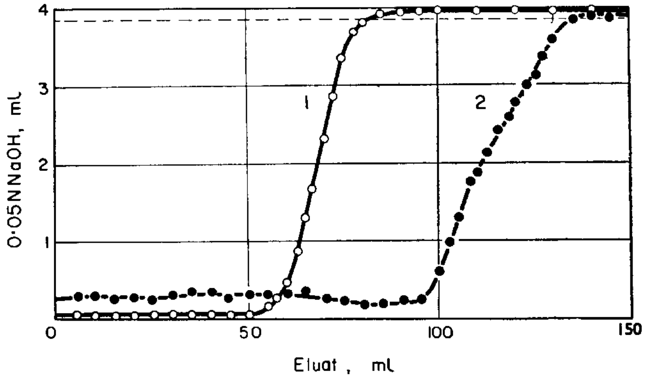

Abb. 6.—Konzentrationsänderung der Salzsäure im Filtrat. Silicagelsäule, getrocknet
(1) Benzylalkohol-Salzsäure (2) Acteon-Salzsäure

ENTSTEHUNG DER ZWEITEN FRONT BEI DER PAPIERCHROMATOGRAPHISCHEN TRENNUNG

Bei den Gemischen von Benzylalkohol mit Chlorwasserstoffsäure und noch deutlicher bei Methyläthylketon-Chlorwasserstoffsäure ist die Abnahme der Säurekonzentration in den ersten Teilen des Filtrates so bedeutend, daß dieser Teil praktisch säurefrei ist. Erst in einiger Entfernung nach dieser praktisch neutral reagierenden Front folgt dann die Säurefront.

Die Bildung zweier Fronten in der Papierchromatographie wird häufig beobachtet. Da sie mit der Entmischung des Fließmittels in unmittelbarer Beziehung stehen muß, widmeten wir auch dieser Erscheinung unsere Aufmerksamkeit. Weil eine selektive Verdampfung des Lösungsmittels hier keine wesentliche Rolle spielen kann, haben wir uns entschlossen, zum Studium der zweiten Front wieder die Methode der Papierchromatographie zu benutzen.

Durchführung

Chromatographiert wurde nach der aufsteigenden Methode auf Streifen von Whatman Papier Nr. 1 (2 × 30 cm). Die Chromatogramme besprühten wir sofort nach Entnahme aus der Entwicklungskammer mit einer 0,05% igen Thymolblaulösung. Der saure Teil des Chromatogramms bis zur zweiten Front erschien dabei rot gefärbt, die Zone darüber gelb.

Um zu zeigen, daß der Einfluß der selektiven Verdampfung bei diesen Versuchen tatsächlich vernachlässigt werden kann, haben wir die Lage der zweiten Front auf der Cellulosesäule (Abb. 4, Kurve 5) mit der auf dem Papier beim Gemisch Benzylalkohol-Chlorwasserstoffsäure verglichen. Für die Säule konnte ein formaler Rf-Wert von 0,81 errechnet werden. Auf dem Papier erhielten wir Rf-Werte von 0,76, 0,78 und 0,76.

Wenn auch die Eigenschaften des Trägers maßgebend für den Verlauf der Entmischung sind und die große Ähnlichkeit der Meßwerte zufällig sein kann, so beweist sie dennoch die Möglichkeit des Einsatzes der Papierchromatographie bei der Untersuchung des gegebenen Problems.

Nach der o. a. Methode prüften wir systematisch Gemische aus Aceton, Wasser und Salzsäure. Um gleichzeitig den Einfluß der Papierqualität mit zu erfassen, führten wir die Versuche parallel auf Whatman Papier Nr. 1 und Nr. 3 MM durch.

Wie Abb. 7 zeigt, verschiebt sich die 2. Front in Richtung höherer Rf-Werte, wenn man bei konstanter Salzsäurekonzentration den Wassergehalt auf Kosten des Acetons erhöht.

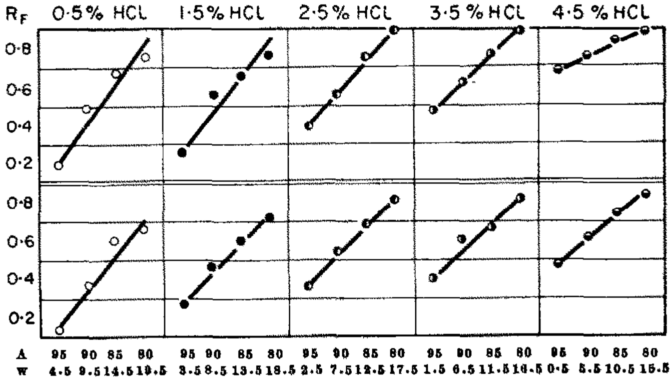

ABB. 7.—Abhängigkeit der Rf-Werte der 2. Front vom Verhältnis Wasser:Aceton bei konstantem Salzsäuregehalt

Hält man den Acetongehalt konstant, dann verschiebt sich die 2. Front zu höheren Rf-Werten mit steigendem Säuregehalt. Die Ergebnisse dieser Versuche sind in Abb. 8 dargestellt.

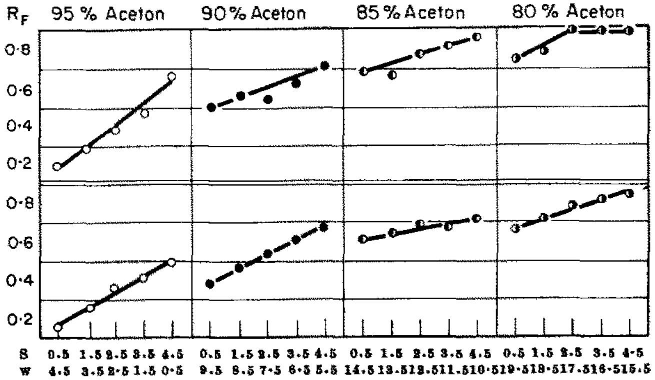

ABB. 8.—Abhängigkeit der Rf-Werte der 2. Front vom Verhältnis Wasser:Salzsäure bei konstantem Acetongehalt.

Aus den Abb. 7 und 8 geht hervor, daß sich die Verhältnisse prinzipiell bei beiden Papiersorten gleichen, daß aber auf der Sorte 3 MM (untere Reihe) die Rf-Werte der 2. Front niedriger liegen.

Diese Versuchsreihe beweist ebenfalls, daß das Fließmittel bei der papierchromatographischen Trennung entmischt wird. Aus den gefundenen Abhängigkeiten geht weiter hervor, daß, wie bei der Säule, die Verhältnisse an der Grenze zwischen mobiler und stationärer Phase nicht durch Bildung einfacher Wasser-Cellulose-Komplexe erklärt werden können. Auch bei der Trennung auf dem Papierbogen nehmen sicher alle Komponenten des Fließmittels am Aufbau der stationären Phase teil.

Es wird Gegenstand weiterer Untersuchungen sein diese Hypothese zu beweisen und die dabei entstehenden Gleichgewichte an der Grenzfläche zwischen Träger und Lösungsmittel zu untersuchen.

Summary—The course of separation of the components of a solvent mixture by the carrier (cellulose or silica gel) has been investigated. By a study of alcohol-water-acid mixtures it has been shown that in partition chromatography the components of the eluting solvent are partially separated, and that the course of the separation depends on the composition of the original solvent mixture. The hypothesis is proposed that at the boundary between the carrier and the solvent system an intermediate layer forms, in which all the compounds of the solvent are present.

Résumé—On a examiné la marche de la séparation des constituants du solvant par le support (cellulose ou gel de silice). Par l'étude de mélanges alcool-eau-acide, on a montré qu'en chromatographie de partage les constituants du solvant d'élution sont partiellement séparés, et que la marche de cette séparation dépend de la composition du mélange solvant initial. On propose l'hypothèse selon laquelle, à la séparation entre le support et le système solvant, il se forme une couche intermédiaire, dans laquelle sont présents tous les constituants du solvant.

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ZUR ENTMISCHUNG DER LÖSUNGSMITTEL BEI DER CHROMATOGRAPHISCHEN TRENNUNG—II*

SELEKTIVE SORPTION DER MISCHUNGEN ALKOHOL–WASSER UND ALKOHOL–WASSER–SÄURE AN DER CELLULOSESÄULE

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Zusammenfassung—Bei der Untersuchung von Gemischen aus Alkohol und Wasser bzw. Alkohol, Wasser und Säure wird festgestellt, daß der Charakter der selektiven Sorption sich in der Reihe der Alkohole und mit steigendem Wassergehalt ändert. Bei Gemischen mit sehr geringem Wasseranteil kommt es in einigen Fällen zu bevorzugter Sorption des Alkohols. Mit steigendem Wassergehalt ändert sich der Charakter der Entmischung und es kann bevorzugte Wasseraufnahme festgestellt werden. Bei den Mischungen Alkohol–Wasser–Säure wurde bewiesen, daß an der Bildung der Zwischenschicht auf der Cellulose auch die Säure beteiligt sein muß. Im Falle des Verhaltens der Mischungen auf lufttrockener Cellulose konnte ein weiteres Argument dafür erhalten werden, daß sich offenbar am Aufbau der Grenzschicht zwischen fester und flüssiger Phase alle Komponenten des Lösungsmittelsystems beteiligen.

IN der 1. Mitteilung[1] haben wir gezeigt, daß aus einem Lösungsmittelgemisch einzelne Komponenten an der Cellulosesäule selektiv festgehalten werden. Auf Grund unserer Meßergebnisse gelangten wir zur Ansicht, daß sich am Aufbau der Grenzschicht zwischen Träger und Fließmittelsystem wahrscheinlich alle Komponenten des Lösungsmittels beteiligen. Es muß vermutet werden, daß dabei Gleichgewichtssysteme entstehen, deren Zusammensetzung von Art und Mischungsverhältnis des Fließmittels bestimmt wird.

Im folgenden soll dieser Entmischungsvorgang an Gemischen aus Alkohol–Wasser bzw. Alkohol–Wasser–Salzsäure näher betrachtet werden. Aus experimentellen Gründen wird dabei zunächst die Aufnahme von Wasser und von Säure in die stationäre Phase untersucht werden.

VERSUCHSANORDNUNG

Es wurden wieder Säulen mit einem Durchmesser von 2,5 cm und einer Höhe von 40 cm verwendet, die stets 35 g Cellulose enthielten. Das Cellulosepulver (Whatman Standard Grade) wurde in der unten beschriebenen Weise vorbehandelt, wobei wir auf genaue Einhaltung der Versuchsbedingungen besonderen Wert legten.

Die benutzten Alkohole reinigten wir durch mehrfache Destillation und bewahrten sie in Flaschen mit Schliffstopfen auf. Den Wassergehalt der Alkohole bestimmten wir wieder durch Titration mit Karl-Fischer-Lösung. Die vorbehandelte Cellulose füllten wir in die Säule bis zur Marke, welche einer Cellulosemenge von 35 g entsprach, ein. Das zu untersuchende Gemisch lief dann wieder mit einer Geschwindigkeit von 1–2 ml/min über die Säule. Das Eluat wurde in Meßzylindern aufgefangen aus denen wir jeweils 2 ml Lösung für die Wasserbestimmung entnahmen.

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* I. Mitteilung: Literatur Punkt 1.

SYSTEM ALKOHOL–WASSER

Die einfachsten Systeme, welche zum Studium des Entmischungsvorganges der Fließmittel in der chromatographischen Analyse benutzt werden können, sind Gemische der niederen Alkohole mit Wasser. Diese Alkohole sind infolge ihrer Affinität zur Cellulose und der Größe ihrer Dielektrizitätskonstanten aus der großen Reihe der organischen Lösungsmittel, die man in der Verteilungschromatographie benutzt, dem Wasser am nächsten. Sie geben uns durch ihre unbegrenzte Mischbarkeit mit Wasser die Möglichkeit Änderungen an der Grenze zwischen fester und flüssiger Phase unter verschiedenen Bedingungen zu verfolgen.

Das verwendete Cellulosepulver wurde wie folgt vorbehandelt:

(1) 12 Std. bei 110°C im Trockenschrank getrocknet
(2) 12 Std. bei 110°C im Trockenschrank getrocknet und anschließend 12 Std. in wasserdampfgesättigter Atmosphäre aufbewahrt.
(3) 12 Std. bei 110°C im Trockenschrank getrocknet und anschließend 12 Std. dem Dampf des verwendeten Alkohols ausgesetzt.

Methanol-Wasser

Die Mischung wurde mit mehrmals destilliertem reinem Methanol hergestellt. Der Wassergehalt betrug 4,5 mg/ml Methanol.

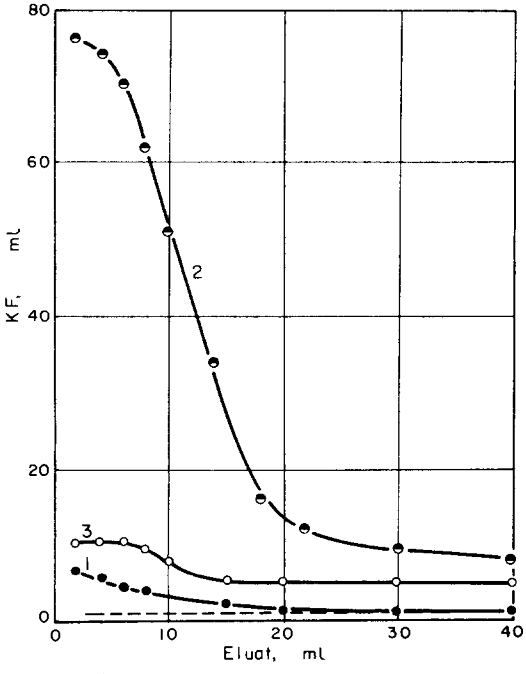

ABB. 1.—Änderung der Wasserkonzentration im Filtrat. Methanol–Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.
(3) Cellulose bei 110°C getrocknet und mit Methanoldampf gesättigt.

In Abb. 1 ist die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

Aus der Figur muß man die erstaunliche Tatsache ableiten, daß es bei allen 3 Versuchsreihen zu einer bevorzugten Alkoholaufnahme aus dem Gemisch Methanol-Wasser kommt. Nach dem Durchfluß durch die mit getrockneter Cellulose gefüllte Säule sind die ersten Fraktionen des Eluats reicher an Wasser als die ursprüngliche Mischung. Eine ähnliche Erscheinung war auch an der mit Alkoholdämpfen gesättigten Säule zu beobachten. Der gleiche Effekt trat bei der mit Wasserdampf gesättigten Säule auf, wobei hier der Wassergehalt des Eluats besonders hoch lag. Auf Grund dieser Versuchsreihe ist es allerdings noch nicht möglich zu erklären, ob bei diesen Versuchen das an die Cellulose gebundene oder nur das "freie" Wasser an das Filtrat abgegeben wird.

Äthanol-Wasser

Die Mischung wurde mit mehrmals destilliertem reinem Äthanol hergestellt. Der Wassergehalt betrug 40,2 mg/ml Äthanol.

In Abb. 2 ist wieder die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

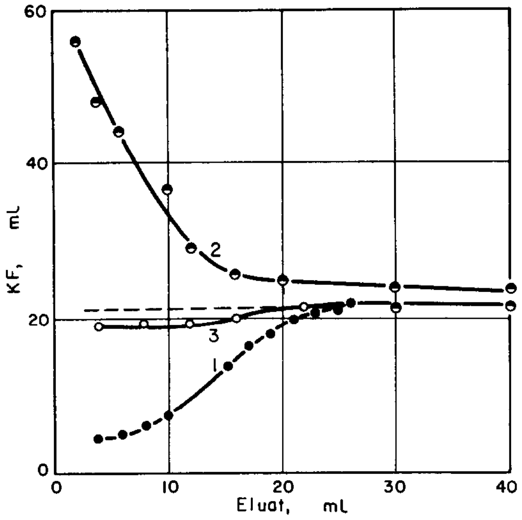

Abb. 2.—Änderung der Wasserkonzentration im Filtrat.
Äthanol-Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.
(3) Cellulose bei 110°C getrocknet und mit Äthanoldampf gesättigt.

Die an der trockenen und mit Alkoholdampf gesättigten Säule erhaltenen Meßwerte sprechen für die bisher gültigen Vorstellungen vom Aufbau eines Cellulose-Wasser-Komplexes, denn die ersten Anteile des Eluats sind wasserärmer als die Ausgangslösung. Bei der mit Wasserdampf gesättigten Säule ist allerdings das Filtrat wie beim Methanol zu Anfang wasserreicher als die Ausgangslösung.

n-Propanol-Wasser

Die Mischung wurde mit reinem mehrfach destilliertem n-Propanol hergestellt. Der Wassergehalt betrug 3,8 mg/ml n-Propanol.

In Abb. 3 ist wieder die Änderung des Wassergehaltes im Eluat in Abhängigkeit von dessen Gesamtvolumen dargestellt.

Der Charakter des Entmischungsvorganges entspricht merkwürdigerweise sowohl auf der trockenen wie auf der mit Wasserdampf gesättigten Säule wieder dem Befund beim Gemisch Methanol–Wasser.

Da diese Unregelmäßigkeit in der Reihe der Alkohole auffallend war, schenkten wir den Bedingungen, unter welchen diese Resultate erhalten worden waren besondere Aufmerksamkeit. Es ist auffallend, daß Methanol und n-Propanol bedeutend wasserärmer sind als das verwendete Äthanol. Es mußte daher kontrolliert werden, ob die Wassermenge in der Ausgangslösung auf den Charakter der bevorzugten Sorption Einfluß hat.

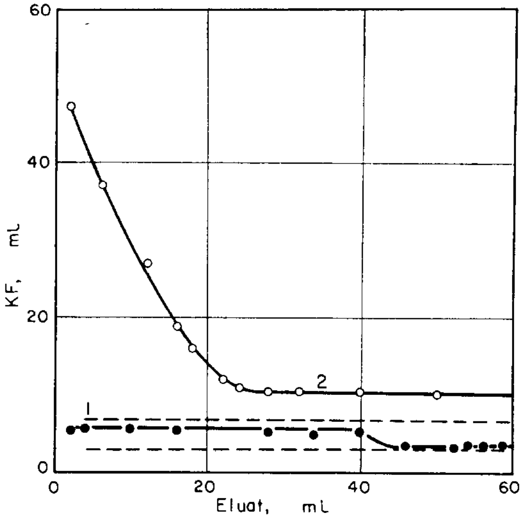

ABB. 3.—Änderung der Wasserkonzentration in Filtrat. n-Propanol–Wasser
(1) Cellulose bei 110°C getrocknet.
(2) Cellulose bei 110°C getrocknet und mit Wasserdampf gesättigt.

Wir wiederholten deshalb zunächst diese Versuche an der getrockneten Cellulosesäule mit n-Propanol–Wasser–Mischungen, die 3,8 mg bzw. 11,5 mg bzw. 26,5 mg Wasser/ml n-Propanol enthielten. Die Resultate dieser Versuchsreihe sind in Abb. 4 wiedergegeben.

Es muß angenommen werden, daß sich die für das Propanol gefundenen Verhältnisse im Prinzip auch auf die anderen Alkohole übertragen lassen. Weitere Versuche, über die später noch berichtet wird, bestätigen diese Vermutung.

Man kann also feststellen, daß die Zusammensetzung des Fließmittels von bestimmenden Einfluß auf den Charakter der selektiven Sorption der Lösungsmittel für die Cellulose ist. Während es bei Gemischen mit geringem Gehalt an Wasser zur bevorzugten Aufnahme des Alkohols kommt, ändert sich mit steigendem Wasseranteil der Charakter der Kurven und es kommt zur bevorzugten Sorption des Wassers.

SYSTEM ALKOHOL–WASSER–SÄURE

Um die Verhältnisse auch bei komplizierteren Mischungen zu klären, haben wir die ternären Systeme Alkohol–Wasser–Säure studiert. Wir wählten wieder Methanol, Äthanol, Isopropanol (und Benzylalkohol) und—in allen Fällen—Chlorwasserstoffsäure. Die Mischungen waren etwa 0,05 M an Salzsäure und enthielten 50–100 mg Wasser/ml Lösung.

Das verwendete Cellulosepulver wurde wie folgt vorbehandelt:

(1) 12 Std. bei 110°C im Trockenschrank getrocknet

(2) An der Luft bei Zimmertemperatur getrocknet

(3) Lufttrockenes Pulver 12 Std. dem Dampf des verwendeten Alkohols ausgesetzt

(4) Lufttrockenes Pulver 12 Std. dem Dampf des verwendeten Fließmittels ausgesetzt

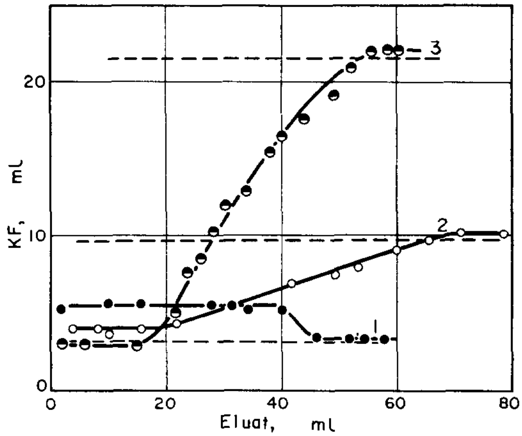

Abb. 4.—Änderung der Wasserkonzentration im Filtrat. n-Propanol–Wasser

(1) Wassergehalt 3,8 mg/ml.

(2) Wassergehalt 11,5 mg/ml.

(3) Wassergehalt 26,5 mg/ml.

In allen Fällen sind wir prinzipiell so vorgegangen, wie wir es beim Studium der Mischungen Alkohol–Wasser beschrieben haben. Das Eluat verwendeten wir abwechselnd einmal zur Wasserbestimmung mit Karl-Fischer-Reagens und zum anderen zur Bestimmung des Säuregehaltes durch Titration mit 0,05 N Natronlauge.

Methanol–Wasser–Chlorwasserstoffsäure

Die Abb. 5 und 6 zeigen die Abhängigkeit des Wasser- bzw. des Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

Äthanol–Wasser–Chlorwasserstoffsäure

Die Abb. 7 und 8 zeigen die Abhängigkeit des Wasser- bzw. Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

Isopropanol–Wasser–Chlorwasserstoffsäure

Die Abb. 9 und 10 zeigen die Abhängigkeit des Wasser- bzw. Säuregehaltes vom Gesamtvolumen des Eluats. Die Diagramme enthalten auch gleichzeitig als gestrichelte Linie Angaben über den Wasser- bzw. Säuregehalt der Ausgangslösung.

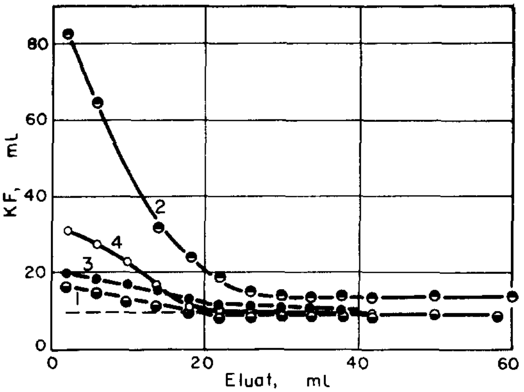

ABB. 5.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge. Methanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet. (3) Cellulose, lufttrocken, mit Methanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

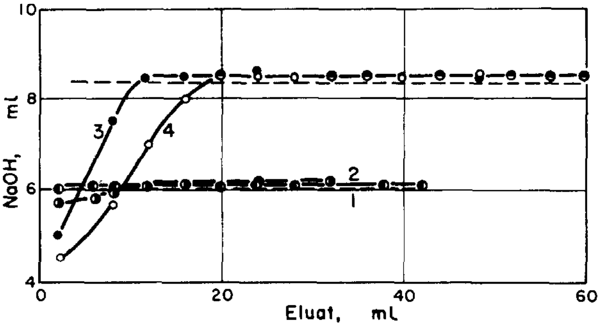

ABB. 6.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge. Methanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet. (3) Cellulose lufttrocken, mit Methanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

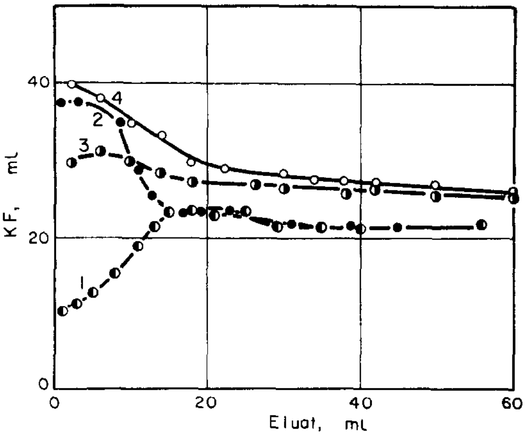

ABB. 7.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge. Äthanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet. (3) Cellulose, lufttrocken, mit Äthanoldampf gesättigt.
(2) Cellulose, lufttrocken. (4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

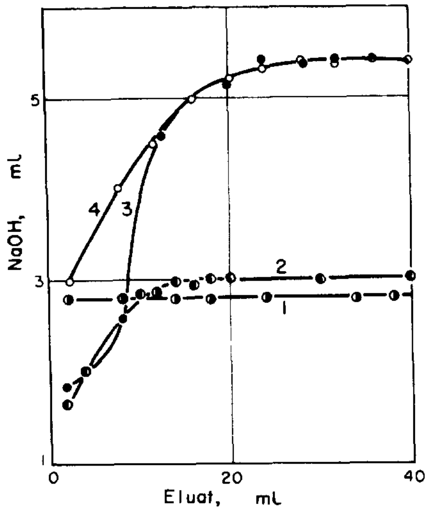

ABB. 8.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge.
Äthanol–Wasser–Salzsäure
(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit Äthanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

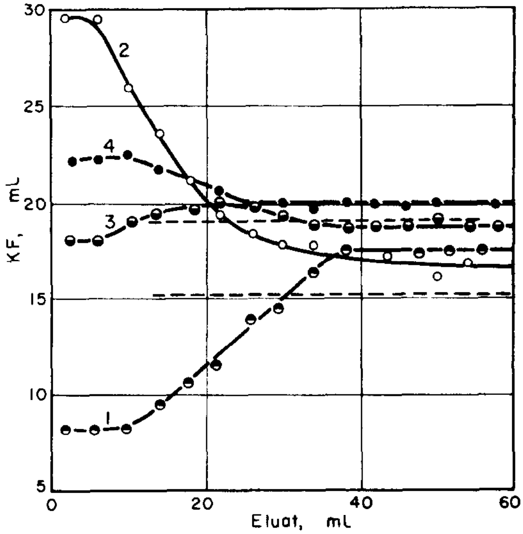

ABB. 9.—Abhängigkeit des Wassergehaltes im Filtrat von dessen Gesamtmenge.
i-Propanol–Wasser–Salzsäure
(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit i-Propanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

Auch bei den untersuchten 3-Komponenten-Systemen können wir beobachten, daß es beim Durchlauf der Lösungsmittelgemische durch die Cellulosesäulen zu einer Veränderung in deren Zusammensetzung kommt. Mit wechselndem Alkohol ändert sich der Charakter der Kurven nicht prinzipiell. Allerdings sind bei den einzelnen Versuchen in den ersten Teilen des Eluats recht unterschiedliche Mengen an Wasser und an Chlorwasserstoffsäure enthalten. Vergleicht man die beiden Serien von Meßreihen miteinander, so kann man erkennen, daß die Veränderung der Salzsäure- und der Wasserkonzentration im Eluat im entgegengesetzten Sinn verlaufen. Eine Ausnahme bildet die bei 110°C getrocknete Cellulose, wo die Salzsäurekonzentration im Eluat konstant bleibt und praktisch der Säurekonzentration in der ursprünglichen Mischung gleicht. In allen anderen Fällen wird Säure von der Säule aufgenommen.

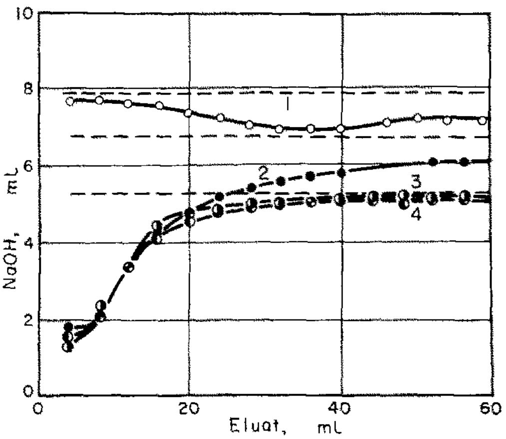

ABB. 10.—Abhängigkeit der Salzsäurekonzentration im Filtrat von dessen Gesamtmenge.

i-Propanol–Wasser–Salzsäure

(1) Cellulose, bei 110°C getrocknet.
(2) Cellulose, lufttrocken.
(3) Cellulose, lufttrocken, mit i-Propanoldampf gesättigt.
(4) Cellulose, lufttrocken, mit Fließmitteldampf gesättigt.

Zu einem interessanten Ergebnis kommen wir noch, wenn wir uns den Wassergehalt der Eluate bei den verschiedenen Alkoholen [Abb. 5, 7 und 9, Kurve (2)] in den Lösungen ansehen, die die bei 110°C getrockneten Säulen passiert haben. Die entsprechenden Kurven sind nochmals in Abb. 11 zusammengefaßt.

Obwohl der Wassergehalt in den untersuchten Gemischen nicht exakt gleich ist, geht aus dem Bild hervor, daß die verschiedenen Alkohole aus der Celluslose unterschiedliche Wassermengen verdrängen. Methanol steht wieder an der Spitze, während aus Benzylalkohol im Gegenteil von der Säule noch Wasser aufgenommen wird.

Da bei allen Versuchen die Cellulose in gleicher Weise präpariert und aufbewahrt wurde, können wir aus den erhaltenen Elutionskurven wieder den Schluß ziehen, daß offensichtlich alle Komponenten des Lösungsmittelsystems an der Oberfläche der Cellulose gebunden werden. Das Verhältnis ist aber nicht nur durch die Konzentrationsverhältnisse der Komponenten in der Ausgangsmischung, sondern auch durch die Eigenschaften der organischen Lösungsmittel bedingt. Bei diesen Versuchen wird das Methanol am stärksten gebunden. Mit ansteigenden Gliedern aus der Reihe der Alkohole fällt dann der Gehalt des an der Oberfläche der Cellulose gebundenen Alkohols.

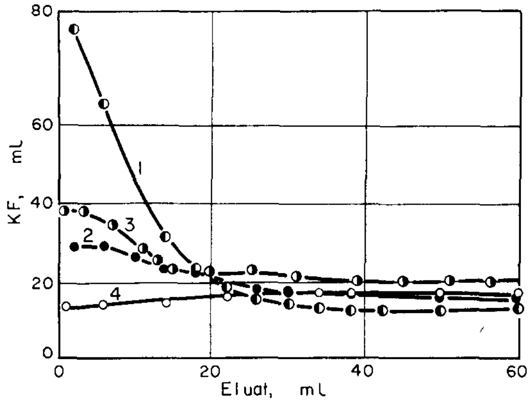

Abb. 11.—Abhängigkeit der Wasserkonzentration im Filtrat bei verschiedenen Alkoholen. Cellulose lufttrocken

(1) Methanol–Wasser–Salzsäure.
(2) Äthanol–Wasser–Salzsäure.
(3) i-Propanol–Wasser–Salzsäure.
(4) Benzylalkohol–Wasser–Salzsäure.

Es muß Gegenstand weiterer Untersuchungen sein diese Abhängigkeit quantitativ zu erfassen und die exakten Verhältnisse an der Grenze zwischen Träger und Lösungsmittel zu untersuchen.

Summary—The character of the selective sorption of alcohol–water and alcohol–water–acid mixtures has been shown to alter on ascending the alcohol series, and with increasing water content. From some mixtures with very low content the alcohol is preferentially sorbed. As the concentration of water increases preferential sorption of water can be shown to occur. For alcohol–water–acid mixtures the acid also participates in the formation of the boundary layer on the cellulose. In the case of air-dried cellulose, it further appears that all the components of the solvent system participate in the formation of the boundary layer between the solid and liquid phases.

Résumé—On a montré que le caractère de sorption sélective de mélanges alcool-eau et alcool-eau-acide est modifié lorsqu'on s'élève dans la série des alcools, et lorsque croît la teneur en eau. A partir de quelques mélanges à très faible teneur en eau, l'alcool est sorbé préférentiellement. Lorsque croît la concentration en eau, on peut montrer qu'il apparaît une sorption préférentielle de l'eau. Pour des mélanges alcool-eau-acide, on a établi que l'acide doit aussi participer à la formation de la couche de jonction sur la cellulose. Dans le cas de la cellulose séchée à l'air, on a acquis un argument supplémentaire quant au fait que tous les constituants du système solvant participent à la formation de la couche de jonction entre les phases solide et liquide.

LITERATUR

[1] J. Michal u. G. Ackermann, *Talanta*, 1964, **11**, 441.

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CYANOMETRIC TITRATIONS IN NON-AQUEOUS SOLUTIONS*

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Summary—Elemental sulphur can be titrated directly in a benzene-acetone medium with potassium cyanide dissolved in isopropyl alcohol. A potentiometric or visual indicator (bromothymol blue) end-point can be used. Elemental selenium can be determined by dissolving it in an excess of a standard solution of potassium cyanide in isopropyl alcohol and back-titrating the excess with a standard solution of sulphur in benzene-acetone. Selenium and sulphur can also be determined simultaneously. With these titrants, salts of quaternary ammonium bases, dissolved in a mixture of isopropyl alcohol and acetone, can be titrated.

OUR cyanometric titrations in a non-aqueous medium may be divided into three groups: the determination of elemental sulphur, the determination of elemental selenium and the determination of heterocyclic quaternary ammonium salts.

For the determination of elemental sulphur many methods are known. Most methods suggest a preliminary dissolution in acetone or some other solvent for the purpose of separation or enrichment. For the determination of the sulphur content of this extract, gravimetric as well as titrimetric methods are known. A direct titrimetric method in non-aqueous solution has been reported by Skoog and Bartlett.[1] They used acetone as solvent and were able to prepare a $0{\cdot}01F$ solution of sulphur. The titration was carried out with a standard solution of potassium cyanide in isopropyl alcohol. For the determination of substances of higher elemental sulphur content this method could only be used with satisfactory accuracy if a solvent could be found in which sulphur is more soluble than in acetone. For that special purpose we wanted to improve this method and to extend its field of application.

We found that by using benzene and acetone mixed in a ratio of 4 to 1, sulphur solutions may be prepared of $0{\cdot}1F$ concentration. Experience has shown that the sulphur content of sulphur solutions prepared in benzene-acetone mixtures is stable. Consequently, such solutions may be used as standard solutions for the titration of cyanide and indirectly for the determination of elemental selenium.

The titration is based on the fact that cyanide ion, which is a strong Lewis base, is converted to the less basic thiocyanate or selenocyanide ion in the presence of sulphur or selenium; when an excess of cyanide is added there is a sudden increase in the basicity of the solution. On the other hand, when titrating cyanide with standard sulphur solution, the basicity of the solution suddenly decreases at the equivalence point.

In accordance with Skoog and Bartlett,[1] we confirm that bromothymol blue indicates precisely the equivalence point. In order to follow the reaction occurring

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during the titration, we first carried out potentiometric titrations. A 0·1*F* stock solution of sulphur in benzene-acetone, prepared from sulphur recrystallised several times from carbon disulphide and dried at 60°, was titrated with a 0·1*F* standard solution of potassium cyanide in isopropyl alcohol.

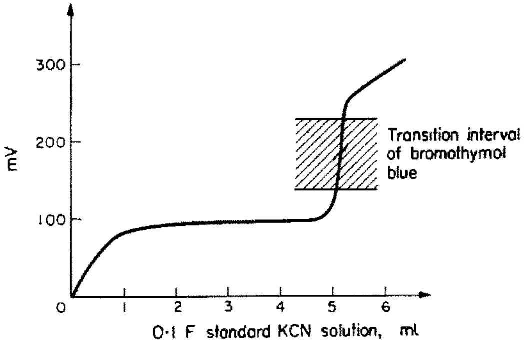


Fig. 1.—Potentiometric titration of a benzene-acetone solution of sulphur with a standard solution of potassium cyanide in isopropyl alcohol.

For the potentiometric titrations a glass indicator electrode and a calomel reference electrode were used, without a salt bridge. This was possible because the small water content of the isopropyl alcohol solution is sufficient for dissolution of the potassium cyanide and at the same time it does not decompose the benzene-containing solution. Twenty-five ml of the sulphur stock solution were titrated with potassium cyanide at 50–60° with magnetic stirring and nitrogen bubbling through the solution. A Metrohm potentiometer was used as the measuring instrument.

Table I.—Titration of a solution of sulphur in benzene-acetone with a standard solution of potassium cyanide in isopropyl alcohol using bromothymol blue as indicator.

KCN consumed, *ml*		Sulphur found, *mg*	Sulphur taken, *mg*	Deviation, %
4·99	0·1*F*	16·00	16·03	−0·18
5·00		16·03	16·03	−0·00
9·92		31·80	32·06	−0·81
9·97		31·99	32·06	−0·22
19·87		63·74	64·13	−0·60
19·95		63·99	64·13	−0·22
9·90	0·01*F*	3·171	3·206	−1·03
9·86		3·161	3·206	−1·40

In order to ascertain the transition interval of bromothymol blue the potentiometric titrations were also carried out in the presence of this indicator. Fig. 1 shows the titration curve thus obtained. Bromothymol blue is seen to change colour at the potential change which corresponds with the equivalence point. Consequently, the titration can also be carried out with visual end-point indication. The results of some titrations with the visual indicator, performed in the same way as the potentiometric titration, are shown in Table I. The deviation from the true value is seen to vary between 0·0 and −0·8% with 0·1*F* potassium cyanide solution, and between −1 and −1·4% with a 0·01*F* solution.

The method was next applied to various technical materials. Thus, to determine the elemental sulphur content of sulphur recovered from gases, after appropriate pretreatment of a weighed sample it was washed with benzene into a volumetric flask. The flask was shaken until dissolution of the sulphur, then diluted to the mark with acetone. Two–three drops of a 0·1% isopropyl alcohol solution of bromothymol blue indicator were added to an aliquot of this stock solution. After warming to 50–60°, it was titrated with potassium cyanide standard solution until the appearance of a blue coloration. In the neighbourhood of the end-point it is advisable to titrate slowly, because the reaction becomes slow and part of the sulphur may remain untitrated. Some results are summarised in Table II.

TABLE II.—DETERMINATION OF THE ELEMENTAL SULPHUR CONTENT OF SULPHURS RECOVERED FROM GASES

0·1*F* KCN consumed, *ml*	Sulphur found, *mg*	Substance taken, *mg*	Sulphur content of substance, %
I (purified sample)			
10·34	33·15	33·17	99·9
11·97	38·38	38·30	100·2
9·25	29·68	29·71	99·9
II (impure sample)			
8·71	27·93	30·25	92·4
9·55	30·63	33·21	92·2
10·49	33·65	36·23	92·8

TABLE III.—DETERMINATION OF THE ELEMENTAL SULPHUR CONTENT OF PLANT PROTECTIVES

Substance	0·05*F* KCN consumed /10 ml, *ml*	Substance taken, *mg*	Sulphur found, *mg*	Sulphur found, %	Sulphur present, %
"Sulfex"	3·62	178·6	58·03	32·49	30–33
	5·55	269·7	88·98	32·99	
	7·71	385·8	123·61	32·04	
"Sulfarol"	2·29	55·6	41·61	74·98	74–75
	14·00	301·2	224·78	74·53	
	16·24	350·0	260·40	74·40	
"Netzschwefel-Pahlberg"	8·21	217·8	131·74	60·49	60–63
	3·94	103·1	63·30	61·40	
	7·91	206·2	126·91	61·55	

We have also determined the elemental sulphur content of various plant protectives, as did Bartlett and Skoog.[1] The sulphur content of the sample may be extracted either by shaking the test sample with benzene in a volumetric flask or by means of an extractor. The latter procedure must be used if a volume correction should be applied because of a large amount of accompanying material. Aliquots of the resulting stock solution were titrated both potentiometrically and with visual end-point indication (bromothymol blue), the results of these titrations being given in Table III.

The data of this table prove that the method is well suited to the determination of the elemental sulphur content of sulphur-containing plant protectives. The method is rapid and the difference between parallel titrations does not exceed ±1 %.

TABLE IV.—DETERMINATION OF ELEMENTAL SULPHUR IN SULPHUR-CONTAINING MEDICINAL CARBON (NEOCARBOLAX)

Elemental sulphur present, *mg/pill*	Sulphur found, *mg*	
	Visual end-point	Potentiometric indication
50	50·10	50·11
50	49·75	49·94
50	49·95	49·99
50	50·02	49·98
50	49·98	50·09

The titration with potassium cyanide was also applied to the determination of the elemental sulphur content of sulphur-containing medicinal carbon (Neocarbolax). Because of the high carbon content the titration must be carried out potentiometrically. Visual end-point indication can only be used after filtration. Table IV shows the results of some titrations. The determination is of sufficient accuracy, the greatest observable error being about ±0·2 %.

An attempt was made to apply the sulphur titration to the determination of cyanide. A 0·1*F* isopropyl alcohol solution of cyanide was titrated with a 0·1*F* standard sulphur solution in acetone-benzene using both potentiometric and visual end-point indication. The curve of our potentiometric titration carried out by using a glass and a saturated calomel electrode in the presence of bromothymol blue or titan yellow can be seen in Fig. 2 and the results of the titrations carried out in the presence of titan yellow are to be seen in Table V. The standard deviation calculated on the basis of 20 parallel titrations, in which 65 mg of potassium cyanide were taken as test, was ±0·014 ml of 0·1*F* sulphur solution.

TABLE V.—TITRATION OF A 0·1*F* SOLUTION OF POTASSIUM CYANIDE IN ISOPROPYL ALCOHOL WITH A 0·1*F* STANDARD BENZENE-ACETONE SOLUTION OF SULPHUR IN THE PRESENCE OF TITAN YELLOW

0·1*F* Sulphur solution consumed, *ml*	KCN found, *mg*	KCN taken, *mg*	Deviation, %
4·98	32·42	32·56	−0·42
4·96	32·29	32·56	−0·82
4·97	32·36	32·56	−0·61
9·97	64·92	65·12	−0·30
9·95	64·79	65·12	−0·50
9·94	64·72	65·12	−0·61
9·98	64·98	65·12	−0·21
9·95	64·79	65·12	−0·50
Deviation from true value			−0·49

The possibility of titrating potassium cyanide in a non-aqueous solution with a standard solution of elemental sulphur led us to try and extend the method to the determination of selenium. Elemental selenium was found to dissolve easily in an excess of an isopropyl alcohol solution of potassium cyanide to form selenocyanide. The excess cyanide can be titrated with a 0·1*F* standard solution of elemental sulphur to titan yellow or potentiometrically. Some results of the determination of purified selenium are shown in Table VI.

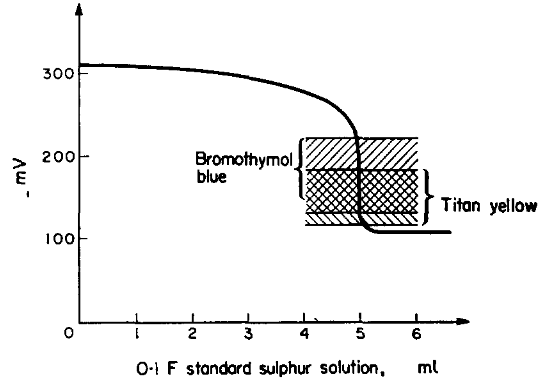


FIG. 2.—Potentiometric titration of a solution of potassium cyanide in isopropyl alcohol with a standard solution of sulphur in benzene-acetone.

TABLE VI.—INDIRECT TITRATION OF PURIFIED SELENIUM WITH A STANDARD SOLUTION OF SULPHUR IN BENZENE-ACETONE

0·1*F* KCN soln. used, *ml*	0·1*F* Sulphur soln. consumed, *ml*	Selenium found, *mg*	Selenium taken, *mg*	Deviation, %
10·00	5·47	35·82	35·60	+0·62
10·00	5·79	33·24	33·10	+0·45
10·00	6·39	28·58	28·39	+0·99
10·00	6·16	30·34	30·65	+1·01
10·00	6·13	30·60	30·45	+0·59

Elemental sulphur and selenium can be determined in the presence of each other, because elemental sulphur dissolves in benzene whereas selenium does not. The dissolved sulphur can be titrated directly with a standard solution of potassium cyanide in isopropyl alcohol. After the whole of the sulphur has been converted to thiocyanate, which may be indicated either visually or potentiometrically, the solid selenium is dissolved in an excess of standard potassium cyanide solution. The excess cyanide solution is then back-titrated with a standard solution of sulphur in benzene-acetone. Fig. 3 shows a potentiometric titration curve obtained with glass and saturated calomel electrodes in the presence of tital yellow. One can observe definite potential changes at the end-point of both reactions. Table VII shows some results of the titration carried out in the presence of titan yellow as indicator. The greatest deviation from the theoretical value is 1·3% for sulphur and +1·0% for selenium.

In a previous method[2] elementary sulphur or selenium was determined by treatment with an excess of potassium cyanide solution, the excess of which was determined by adding excess nickel solution and titrating the uncomplexed nickel with EDTA. It was not possible to determine sulphur and selenium in admixture as in the present method. Furthermore, the present method enables sulphur to be extracted from a sample containing ions which would interfere in a complexometric titration.

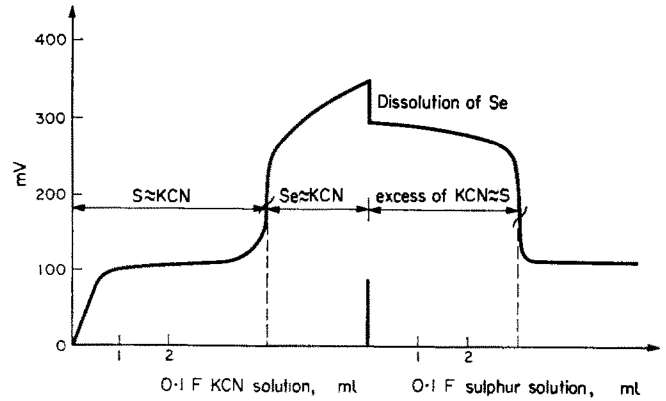
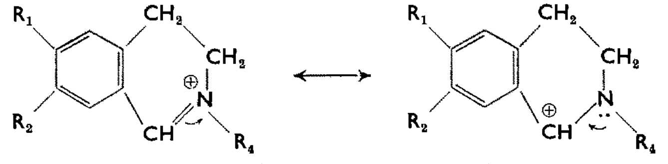


FIG. 3.—Potentiometric titration of elemental sulphur and selenium in the presence of each other.

TABLE VII.—TITRATION OF SULPHUR AND SELENIUM IN THE PRESENCE OF EACH OTHER

Sulphur found, *mg*	Sulphur taken, *mg*	Selenium found, *mg*	Selenium taken, *mg*	Deviation from true value	
				Sulphur, %	Selenium, %
17·86	17·98	28·40	28·34	−0·66	+0·21
17·90	17·98	25·28	25·20	−0·44	+0·35
17·74	17·98	30·30	30·20	−1·33	+0·33
17·85	17·98	29·30	29·00	−0·72	+1·02

It has also been found possible to titrate the salts of heterocyclic quaternary ammonium bases with a standard solution of potassium cyanide in isopropyl alcohol. These salts react quite easily with cyanide ion, the carbon atom next to the quaternary nitrogen atom binding it with a covalent bond. The stability of the resulting cyanide compound depends upon the polarity of the solvent. Heterocyclic quaternary ammonium salts have two mesomeric forms:



quaternary ammonium ion carbonium ion

In polar solvents the quaternary ammonium is the stable form, whereas the non-polar solvents favour the formation of the carbonium ion. The strongly nucleophilic cyanide ion attacks the carbonium ion with the formation of a covalent bond. Because the reaction takes place rapidly and quantitatively, it is well suited for quantitative determinations.

After the heterocyclic quaternary ammonium salt is consumed, the cyanide ion will be in excess and behave in a non-aqueous medium as a strong base. Consequently, the end-point of the titration can be indicated either with acid-base indicators or potentiometrically.

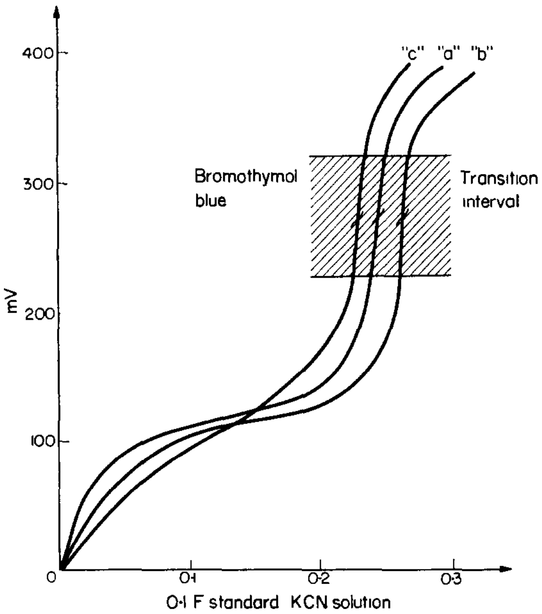
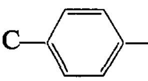


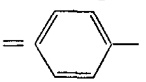
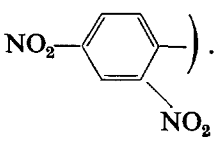
FIG. 4.—Potentiometric titration of heterocyclic quaternary ammonium salts with a standard solution of potassium cyanide in isopropyl alcohol:
(a) cotarnine chloride,
(b) *p*-chlorophenylnorcotarninium chloride,
(c) 2,4-dinitrophenyl-6,7-dimethoxyisoquinolinium chloride.

The method was tested by using the following three heterocyclic quaternary ammonium salts:

(a) cotarnine chloride ($R_1 + R_2 = CH_2O_2$, $R_3 = CH_3O$—, $R_4 = CH_3$-),
(b) *p*-chlorophenylnorcotarninium chloride

($R_1 + R_2 = CH_2O_2$, $R_3 = CH_3O$—, $R_4 =$ C— ),

(c) 2,4-dinitrophenyl-6,7-dimethoxyisoquinolinium chloride

($R_1 = R_2 = CH_3O$—, $R_3 =$  , $R_4 =$ ).

The substance to be analysed or an aliquot of a previously prepared stock solution was transferred to a titration vessel and the volume adjusted to about 20 ml with a mixture of acetone and isopropyl alcohol (1 : 1). Potentiometric titrations were carried out with a glass and saturated calomel electrode using a 0·1*F* standard solution of potassium cyanide in isopropyl alcohol. Fig. 4 shows the titration curves obtained.

The potentiometric titrations were repeated in the presence of bromothymol blue as indicator. As can be seen, the titration can be carried out with visual end-point indication, because the inflection point of the potentiometric curve coincides with the colour transition of bromothymol blue.

TABLE VIII.—TITRATION OF HETEROCYCLIC QUATERNARY AMMONIUM SALTS WITH A STANDARD SOLUTION OF POTASSIUM CYANIDE IN ISOPROPYL ALCOHOL

Substance	Concentration of standard soln., *F*	Standard soln. consumed, *ml*	Substance found, *mg*	Substance taken, *mg*	Deviation, %
Cotarnine chloride	0·05	0·58	7·4	7·5	−1·3
		0·57	7·3	7·5	−2·6
		1·19	15·2	15·4	−1·3
	0·01	3·13	80·0	80·2	−0·3
p-Chlorophenyl-norcotarninium chloride	0·01	0·95	3·05	3·12	−2·2
		1·91	6·14	6·24	−1·6
	0·05	0·85	15·44	15·60	−1·0
2,4-dinitrophenyl-6,7-dimethoxy-isoquinolinium chloride	0·01	0·78	3·07	3·16	−2·8
		5·41	21·2	21·0	+0·9
	0·01	3·19	62·6	63·0	−0·6
		4·20	82·3	82·4	−0·1

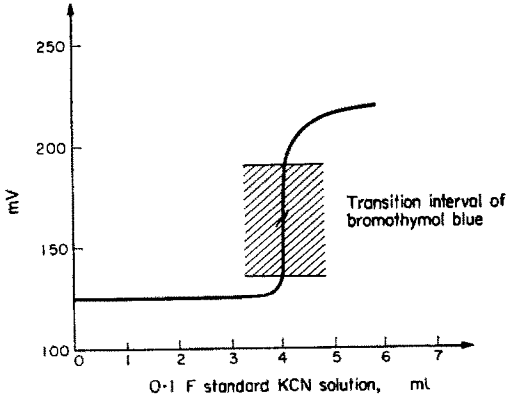


FIG. 5.—Potentiometric titration of cotarnine chloride in the presence of free cotarnine base.

The results of some titrations carried out in the presence of bromothymol blue are summarised in Table VIII. The data show that for titrations performed on the micro scale (10 mg of substance taken and 0·01*F* standard solution used), the error was about 0–3 %, whereas by taking greater amounts of sample, the deviation is only 0·1 %. The standard deviation of the method using 30 mg of substance is ±0·05 ml of 0·05*F* potassium cyanide solution.

It was later found that heterocyclic quaternary ammonium bases in non-aqueous solution do not react with an isopropyl alcohol solution of potassium cyanide. This made it possible to determine quaternary ammonium salts in the presence of their free bases. Fig. 5 shows the curve of the potentiometric titration of cotarnine chloride in the presence of free cotarnine. It is seen from the curve that the medium has a buffer effect and the potential changes only just before the equivalence point giving a definite and well perceptible jump.

In conclusion, a standard solution of potassium cyanide in isopropyl alcohol is seen to be well suited to the titration of many substances. We have succeeded in extending the field of its application for the titration of elemental sulphur. Furthermore, new methods have been developed for the determination of elemental selenium and heterocyclic quaternary ammonium salts. By the last method it is also possible to follow the formation of quaternary salts from the corresponding free bases.

Zusammenfassung—Elementarer Schwefel kann in einer Benzol-Aceton-Lösung mit in Isopropanol gelöstem Kaliumcyanid direkt titriert werden. Es kann potentiometrische oder visuelle (Bromthymolblau) Endpunktsanzeige verwendet werden. Elementares Selen kann bestimmt werden durch Lösen in einem Überschuß eingestellter Kaliumcyanidlösung in Isopropanol und Rücktitration mit einer eingestellten Schwefellösung in Benzol-Aceton. Selen und Schwefel können auch nebeneinander bestimmt werden. Mit diesen Titranten können auch Salze heterocyclischer quartärer Ammoniumbasen, gelöst in Isopropanol-Acton, titriert werden.

Résumé—On peut doser directement le soufre élémentaire en milieu benzène-acétone au moyen de cyanure de potassium en solution dans l'isopropanol. Le point final peut être déterminé potentiométriquement ou au moyen d'un indicateur visuel (bleu de bromothymol). Le sélénium élémentaire peut être dosé par dissolution dans un excès d'une solution titrée de cyanure de potassium en isopropanol, et dosage en retour de l'excès par une solution titrée de soufre dans un mélange acétone-benzène. On peut aussi doser simultanément le sélénium et le soufre. Au moyen de ces solutions titrées, on peut doser des sels de bases hétérocycliques à fonction ammonium quaternaire, dissous dans un mélange isopropanol-acétone.

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INVESTIGATION OF REAGENTS FOR THE COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF CYANIDE—I

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Summary—The König synthesis of pyridine dyestuffs by reaction of cyanogen bromide and suitable aromatic amines with pyridine, used as the basis of standard British and American colorimetric methods for the determination of small amounts of cyanide, is reinvestigated. After consideration of the carcinogenic properties of amines capable of being used in a method for cyanide, *p*-phenylenediamine is selected for further examination.

A REVIEW[1] of methods available for the determination of small amounts of cyanide indicates that the colorimetric determination is far superior to others, including titrimetric, polarographic and chromatographic methods. The standard methods for trade wastes and effluents[2,3,4,5] and for waters[4,6] are based either on the colorimetric procedure developed by Aldridge[7,8] or on that of Epstein,[9] which themselves are based on the König reaction[10,11] for the synthesis of pyridine dyestuffs. The latter are formed by reaction of cyanogen bromide or chloride with pyridine and an aromatic amine. Aldridge's method utilises a pyridine/benzidine mixture reacting with cyanogen bromide; Epstein uses cyanogen chloride reacting with pyridine/1-phenyl-3-methyl-5-pyrazolone and a small amount of bis-(1-phenyl-3-methyl-5-pyrazolone). Other workers[12] have used a variation of the Aldridge procedure employing barbituric acid in place of benzidine.

The pyridine/pyrazolone colour development requires the preparation of a relatively unstable reagent, whilst the benzidine method has the distinct disadvantage that the aromatic amine is a well known active carcinogen and the developed colour only obeys Beer's law up to concentrations of the order of 1–2 μg/ml so that it cannot be used for effluents containing more than 2 ppm of cyanide in the measured sample. The barbituric acid method requires a relatively large sample (25 ml) and a relatively long period of heat treatment (40 min at 40°); furthermore, the reagent becomes discoloured on standing for short periods of time.

In view of these criticisms it was decided to reinvestigate the König synthesis as the basis of a method for the determination of cyanide, examining aromatic amines in addition to those considered by König for colour production, and heterocyclic amines other than pyridine as the parent reagent for dyestuff formation.

Examination of heterocyclic amines other then pyridine in the König synthesis

Replacement of pyridine by other heterocyclic amines and their reaction with benzidine and cyanogen bromide (produced from 1 μg of cyanide) produced the results shown in Table 1.

TABLE I

Amine	Colour obtained
Pyridine	Red
Piperidine	None
Morpholine	None
Piperazine	None
Quinoline	None
Isoquinoline	None
2,6-Lutidine	None
α-Picoline	Golden yellow

Apart from pyridine, only α-picoline produced a colour and in this case a much lower maximum absorbance was obtained. Pyridine is, therefore, the best common heterocyclic amine to use.

Examination of aromatic amines other than benzidine in the König synthesis

König synthesised dyes from a number of aromatic amines using pyridine and relatively large quantities of cyanogen bromide. Goris and Larsonneau[13] utilised this reaction for the characterisation of small amounts of pyridine, using aniline as the aromatic amine. One drop of pyridine, 1 drop of aniline and 50–100 mg of cyanogen bromide in 1–20 ml of water, when mixed, yield an intense red colour and a crystalline precipitate; but with traces of pyridine a yellow colour is first produced, which changes after 30–40 min to an orange colour. Přibyl[14] used benzidine instead of aniline for the determination of small amounts of pyridine in aromatic hydrocarbons, measuring the extinction of the solutions at 518 mμ. With only traces of cyanogen bromide, some amines produce different colours from those of the dyes originally synthesised by König. Accordingly, a number of amines were substituted for benzidine in the Aldridge procedure, and the colours produced by reaction with 1 μg of cyanide (as cyanogen bromide) were compared to the corresponding colours of the dyes reported by König (see Table II).

TABLE II

a. *Benzene derivatives*

Number	Amine	Colour of dye	
		As reported by König	Aldridge procedure
1	Aniline	Orange	Yellow, changing to orange (20 to 30 min)
2	*p*-Toluidine	Orange	Yellow, changing to orange (20 to 30 min)
3	*p*-Chloraniline	Orange	Yellow changing to orange (20 to 30 min)
4	*p*-Nitro-aniline	Orange	None detected

TABLE II (*continued*)

b. *Naphthalene derivatives*

Number	Amine	Colour of dye	
		As reported by König	Aldridge procedure
5	*o*-Anisidine	Salmon-pink, with yellowish-red fluorescence	Orange
6	*p*-Phenetidine	Rose-red	Orange, changing to pink
7	*o*-Aminophenol	Rose-red	None detected
8	*p*-Aminophenol	Rose-red	Yellow, changing to orange (20 to 30 min)
9	Anthranilic acid	Bright red, with yellowish-red fluorescence	Yellow, changing to pink (20 to 30 min); fading always occurs
10	Sulphanilic acid	Orange, with greenish fluorescence	Yellow
11	*p*-Aminobenzoic acid	Red	Yellow
12	*o*-Phenylenediamine	Red	Orange (detectable only by spectrophotometer)
13	*m*-Phenylenediamine	Red	None detected (reagent too strongly coloured; evidence of reaction when diluted 125 times)
14	*p*-Phenylenediamine	Red	Cherry-red
15	*p*-Bromo-aniline	—	Yellow
16	α-Naphthylamine	Rose-red	Yellow
17	β-Naphthylamine	Rose-red	Yellow, changing to orange

c. *Amino-azo-compounds*

18	Amino-azobenzene	Heliotrope	None detected

d. *Benzidine derivatives*

19	Benzidine	Lilac	Red
20	*o*-Dianisidine	Blue-violet	Red

TABLE II (*continued*)

e. *Miscellaneous amines not used by König*

Number	Amine	Aldridge procedure colour
21	*p*-Aminodiphenylamine	Cherry-red
22	*p*-Amino-*N*,*N*-dimethylaniline	Red
23	*p*-Acetamido-aniline	Yellow (fades during 10 to 20 min)
24	*p*-Amino-acetophenone	Yellow (fades during 20 to 20 min)
25	4,4'-Diaminodiphenylene oxide	Yellow (fades)
26	*N*-Benzyl-*p*-phenylenediamine	Yellow (fades)
27	*N*-(4-Aminophenyl)piperidine	Yellow[a]
28	*N*-(2-Aminophenyl)piperidine	Yellow[a]
29	*N*-(4-Aminophenyl)pyrrolidine	None detected (red solutions)
30	*N*-(2-Aminophenyl)pyrrolidine	Yellow[a]
31	*N*-(4-Aminophenyl)morpholine	Red
32	*N*-(2-Aminophenyl)morpholine	Yellow (fades rapidly)[a]
33	*N*-(4-Aminophenyl)piperazine	Orange
34	*N*-(2-Aminophenyl)piperazine	None detected (green solutions)
35	Diphenylamine	None detected
36	*p*-Cyclohexylaniline	Yellow, changing to pink (fades)
37	3-Amino-4-cyclohexylaniline	Yellow, changing to orange (fades)
38	4-Aminophenazone	Yellow (fades)
39	Rosaniline	Impossible to detect[b]
40	*N*-(1-Naphthyl)ethylenediamine	None detected
41	Benzylamine	None detected
42	2-Piperidino-3-aminopyridine	None detected
43	2-Pyrrolidino-3-aminopyridine	None detected
44	2-Morpholino-3-aminopyridine	None detected
45	3-Amino-4-morpholinopyridine	None detected
46	2-Aminopyridine	None detected

[a] Certain amines (Nos. 27, 28, 30, 32) only show evidence of reaction with 50 and 100 μg of cyanide (as cyanogen bromide).

[b] With a strongly coloured amine (No. 39), the initial solution is intensely coloured and reaction with 100 μg of cyanide is impossible to detect even at great dilution of the amine solution.

In every case where a yellow colour is produced initially, fading always occurs. Where an orange or red colour is obtained, fading is not so apparent. Therefore, from the amines investigated only *o*-anisidine, *p*-phenetidine, *p*-phenylenediamine, benzidine, *o*-dianisidine, *p*-aminodiphenylamine, *p*-amino-*N*,*N'*-dimethylaniline, *N*-(4-aminophenyl)morpholine and *N*-(4-aminophenyl) piperazine are worth further consideration. For comparison purposes 3-amino-4-cyclohexylaniline was also examined.

By dilution with cyanide-free water of a suitable stock solution, previously standardised with silver nitrate by potentiometric titration and by titration using *p*-dimethylaminobenzylidenerhodanine as indicator, the following 6 cyanide solutions were prepared for each of the 10 amines: (i) 0·0 μg, (ii) 0·1 μg, (iii) 0·2 μg, (iv) 0·5 μg, (v) 1·0 μg, and (vi) 2·0 μg of CN^-. These were examined using a method similar to the Aldridge procedure, the alkaline solutions of cyanide being acidified with 0·6 ml of glacial acetic acid, treated with 0·2 ml of saturated bromine water, mixed thoroughly, excess bromine in the solution removed with 0·2 ml of arsenious acid (2% w/v in water, refluxed until solution is complete) and bromine vapour in the tube removed by air. Before addition of mixed amine/pyridine reagent, the volume of solution was adjusted to 50·0 ml and a 5·0 ml-aliquot taken for the rest of the procedure.

Cyanide solution (v) was examined first in every case. A freshly prepared mixture of 3·0 ml of pyridine reagent (1 litre of 60% w/w aqueous pyridine plus 100 ml of concentrated hydrochloric acid) and 1·0 ml of amine reagent (0·1 g of amine dissolved in 50 ml of 0·5*M* hydrochloric acid; where difficulty was experienced in effecting solution, the mixture was heated to boiling point, cooled and filtered) was added and the absorbance of the solution measured between 450 and 550 mμ at different time intervals using a recording spectrophotometer to ascertain a suitable wavelength to use for each amine reagent. The other test solutions were then treated with the relevant mixed pyridine/amine solutions and the absorbances measured at the appropriate wavelength for each amine reagent, after 20 and 30 min, using a manual spectrophotometer. In most cases the wavelength chosen was that wavelength at which the spectral curve after 30 min crossed the spectral curve after 20 min (isosbestic point). The relatively low concentration of the amine reagent (0.2%) was chosen to enable some amines which were themselves highly coloured in more concentrated solution, to be included in any comparison tests. The same concentration was also used for the benzidine reagent.

Further tests were made altering the conditions simultaneously as follows:

1. The concentration of the amine reagent was increased to 1·0% for amines Nos. 1, 5, 6, 7 and 10.
2. The solutions containing cyanide were arranged so that a volume of 1·0 ml contained the cyanogen bromide before addition of mixed pyridine/amine reagent.

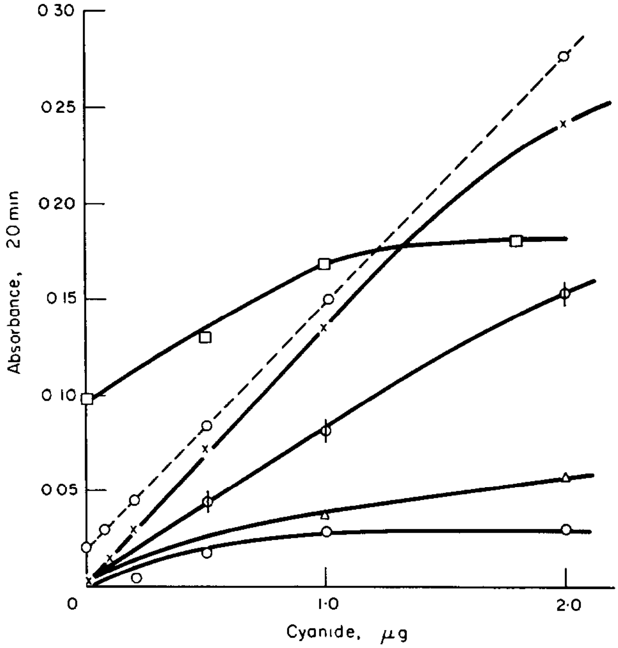

Fig. 1—Calibration curves using 0·2% amine reagents:

——×—— benzidine,
——○—— *o*-anisidine,
——△—— *o*-dianisidine,
——□—— *p*-amino-*N*,*N*-dimethylaniline,
——⏀—— *p*-phenetidine,
- - -○- - - *p*-phenylenediamine.

The results obtained with the 0·2 and 1·0% amine reagents are given in Tables III and IV, respectively, and the corresponding calibration curves in Figs. 1–3.

It appears that a number of amines would be satisfactory for the determination of concentrations of cyanide between 0·1 and 1·0 μg. For more concentrated cyanide solutions, however, the number of amines is restricted. The best amines are benzidine, *p*-phenylenediamine and *p*-aminodiphenylamine. Using the stated conditions and a concentration of 0·2% amine in 0·5*M* hydrochloric acid, *p*-phenylenediamine is the best of the three. At a higher amine concentration (1·0%), benzidine produces the most intense colour and has an absolute absorbance of 0·636 (2·0 μg of cyanide/1·0 ml test solution), whereas *p*-phenylenediamine has an absolute absorbance of only 0·540 but gives a better calibration curve than does benzidine (see Fig. 3). It was necessary at this junction to consider the carcinogenic properties of the amines.

Carcinogenic hazards of aromatic amines

The carcinogenic properties of benzidine are well known. Related compounds, such as 3,3′-dihydroxybenzidine, tetramethylbenzidine and dichlorobenzidine, and other binuclear compounds like 4-aminodiphenyl, 2,3-dimethyl-4-aminodiphenyl and

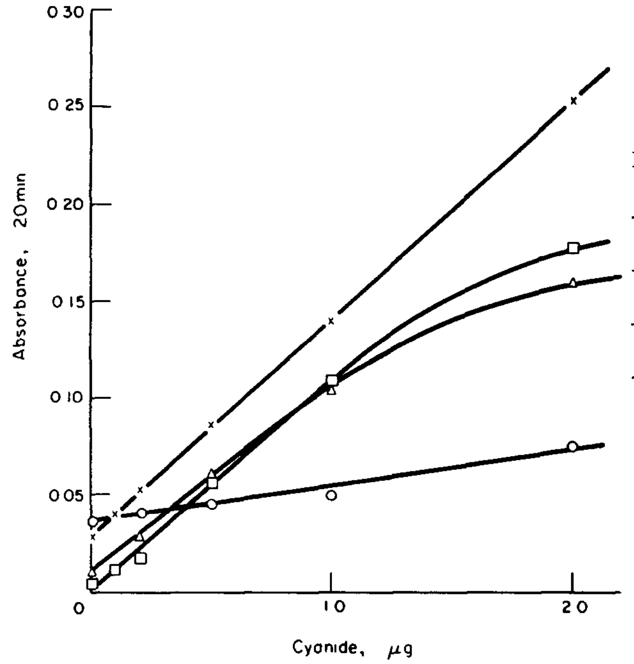

Fig. 2.—Calibration curves for 0·2% amine reagents:

——×—— *p*-amino-diphenylamine,
——○—— *N*-(4-aminophenyl) piperazine,
——□—— 3-amino-4-cyclohexyl-aniline,
——△—— *N*-(4-aminophenyl) morpholine.

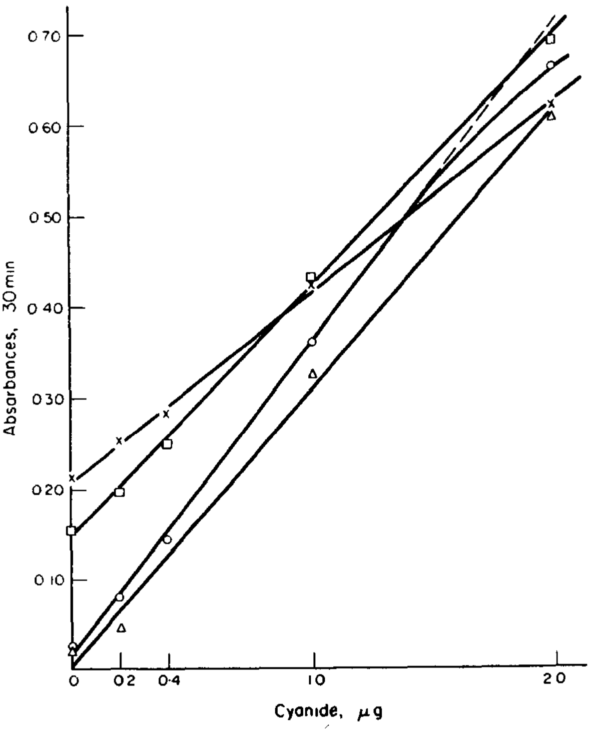

Fig. 3—Calibration curves for 1·0% amine reagents:

——○—— benzidine,
——□—— *p*-phenylenediamine,
——△—— *p*-phenetidine,
——×—— *p*-aminodiphenyl-amine.

TABLE III—0.2% amine reagent

No.	Amine	Wavelength, *mμ*	Time after mixing, *min*	Absorbance referred to water						Observations
				Cyanide[a], μg						
				0·0	0·1	0·2	0·5	1·0	2·0	
1	Benzidine	522 (isosbestic)	20 30	0·004 0·003	0·015 0·017	0·031 0·034	0·071 0·076	0·135 0·140	0·241 0·251	Good calibration curve (Fig. 1)
2	*o*-Anisidine	508 (isosbestic point)	20 30	0·000 0·000	0·001 0·000	0·005 0·004	0·018 0·016	0·029 0·025	0·031 0·024	Yellow colour fades badly (Fig. 1)
3	*o*-Dianisidine	548	20 30	0·000 0·000	0·006 0·008	0·010 0·010	0·023 0·023	0·039 0·039	0·056 0·051	Similar to *o*-anisidine (Fig. 1)
4	*p*-Amino-*N*,*N*-dimethylaniline	528	30	0·099			0·136	0·169	0·180	Reagent blank highly coloured (Fig. 1)
5	*p*-Phenetidine	510 (peak maximum)	20 30	0·000 0·000	0·005 0·005	0·015 0·015	0·046 0·051	0·089 0·086	0·151 0·159	Yellow colour turns to pink tint and change increases with time (Fig. 1)
6	*p*-Phenylenediamine	508 (isosbestic point)	20 30	0·021 0·026	0·029 0·033	0·044 0·047	0·084 0·089	0·150 0·154	0·273 0·277	Better calibration curve than benzidine (obeys Beer's law better; Fig. 1)
7	*p*-Amino-diphenylamine	541 (isosbestic point)	20 30	0·029 0·032	0·041 0·043	0·052 0·058	0·087 0·093	0·140 0·147	0·252 0·264	Good calibration curve (Fig. 2)
8	*N*-(4-Aminophenyl)-morpholine	517	20 30	0·011 0·015	0·021 0·025	0·029 0·032	0·061 0·064	0·107 0·110	0·159 0·154	Fading at 2.0 μg of cyanide (Fig. 2)
9	N-(4-Aminophenyl)-piperazine	500	20	0·035	0·038	0·042	0·044	0·049	0·073	Poor sensitivity (Fig. 2)
10	3-Amino-4-cyclohexylaniline	504 (isosbestic point)	20 30	0·005 0·006	0·011 0·013	0·021 0·023	0·046 0·057	0·109 0·108	0·176 0·169	Fading at 2.0 μg of cyanide (Fig. 2)

[a] Volume of final mixture of reagents: 9·0 ml.

TABLE IV—1·0% amine reagent[a]

No.	Amine	Wavelength, $m\mu$	Time after mixing, *min*	Absorbance referred to water				
				Cyanide[b], μg				
				0·0	0·20	0·40	1·0	2·0
1	Benzidine	510 (isobestic point)	20	0·027	0·080	0·139	0·359	0·663
			30	0·026	0·080	0·139	0·359	0·662
			40	0·029	0·080	0·139	0·358	0·665
5	*p*-Phenetidine	510 (peak maximum)	20	0·018	0·040	—	0·321	0·600
			30	0·021	0·041	—	0·323	0·611
			40	0·021	0·043	—	0·322	0·611
6	*p*-Phenylene-diamine	515 (peak maximum)	20	0·114	0·163	0·255	0·408	0·673
			30	0·152	0·197	0·250	0·432	0·692
			40	0·189	0·231	0·383	0·463	0·718
7	*p*-Amino-diphenylamine	509 (isobestic point)	20	0·186	0·230	0·262	0·413	0·599
			30	0·212	0·248	0·248	0·423	0·618
10	3-Amino-4-cyclohexylaniline	515	30	0·072	0·120	—	0·381	—
10	3% Amine solution	515 (peak maximum)	20	0·222	—	0·335	0·490	0·818
			30	0·238	—	0·352	0·505	0·839
			40	0·247		0·362	0·509	0·853

[a] Absorbances after 30 min are recorded in Fig. 3 for amines 1, 5, 6 and 7.
[b] Volume of final mixture of reagents: 5·0 ml.

naphthalene derivatives, such as 1-amino-2-naphthol, 2-amino-1-naphthol, α-naphylamine and β-naphthylamine, have been reported as being highly active.[15] Dianisidine and the tolidines are suspected of being carcinogenic.

Because there is no published evidence that amines with only a single ring are active, it was decided to confine further investigations to *p*-phenylenediamine.

Zusammenfassung—Die Farbstoffsynthese nach König, die Reaktion von Bromcyan nit geeigneten Aminen, die britischen und US-Standardmethoden zugrundeliegt, wird an 46 Aminen unter geeigneten Bedingungen nachgeprüft. Nach Erörterung der carcinogenen Eigenschaften von Aminen, die zur analytischen Bestimmung kleiner Cyanidmengen geeignet sind, wurde *p*-Phenylendiamin zur weiteren Untersuchung gewählt.

Résumé—Les auteurs ont repris l'étude de la synthèse de König des colorants dérivés de la pyridine, par action du bromure de cyanogène et d'amines aromatiques appropriées sur la pyridine, sur laquelle sont fondées les méthodes colorimétriques étalons britannique et américaine de détermination de petites quantités de cyanure. Tenant compte des propriétés cancérigènes des amines susceptibles d'être utilisées dans une telle méthode, ils ont choisi a p-phenylènediamine pour une étude plus poussée.

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CHELATING RADIOMETRIC TITRATIONS BY ION EXCHANGE FOR DETERMINATION OF TRACES OF METALS

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Summary—A new type of radiometric titration has been developed. Using EDTA solutions, the negatively charged or neutral metal chelates are formed, and these can easily be separated from the excess of unreacted metal ions using a cation exchanger. Titration curves are constructed from the activities of the eluates. The method has been used for the determination of microgram amounts of indium using ^{114m}In as an isotopic tracer, and for the determination of submicrogram traces of cobalt using the same indicator as a non-isotopic tracer.

IN radiometric titrations the radiotracer is involved in the chemical reaction which is the basis of the determination. The compound formed during the titration must be easily separated from the excess of the unreacted ions and the end-point is determined from the change in the activity of the residual solution or of the other phase. Two types of radiometric titration have previously been described. In precipitation titrations the second phase is a precipitate, and the end-point can be determined by the appearance of the activity in the aqueous phase, or by its disappearance from the aqueous phase, according to circumstances.[1] Precipitation titrations are difficult to apply, because of the necessity for handling precipitates, to less than milligram amounts and impossible at the submicrogram level.

Extractive titrations[2,3] are based on the formation of metal chelates which can be separated from the unreacted metal ions by solvent extraction. The end-point is determined similarly from the change in activity either of the aqueous phase or of the organic phase. This type of titration is far more sensitive, but has been applied only to a limited number of determinations.

In the present paper a new type of radiometric titration using EDTA is proposed and its utility is verified.

RADIOMETRIC TITRATIONS USING EDTA

EDTA titrations are widely used for determination of many metals, but their sensitivity is limited by the sensitivity of the determination of the end-point. However, using radiometric indication the determination of submicrogram amounts of metals can be carried out without difficulty.

Radiometric titrations using EDTA are based on the formation of negatively charged or neutral chelates which can easily be separated from the excess of the unreacted metal ions on a cation exchanger. The end-point is determined from the activities of the eluates obtained. As in other radiometric titrations, isotopic or non-isotopic tracers can be used. In the first case the radioactive indicator is a radioisotope of the element being determined. In the second case the titration of the element to be assayed is followed by means of an element which is chelated after all the metal being determined is bonded in the EDTA complex (*i.e.* the stability constant of the complex of the radioactive tracer with EDTA is much lower than that of the metal to be determined).

The optimum pH for the titration can be calculated from the basic theory given in our paper on isotope dilution by ion exchange.[4] From this theory it follows that the determination of metals forming very stable chelates (*e.g.*, Co^{III}, Zr^{IV}, Fe^{III}, In^{III}, Th^{IV}, *etc.*[5]) can be carried out at pH 2–3 using 10^{-6}–10^{-7} M EDTA solutions. The pH for the determination of metals having lower stability constants must, however, be much higher.

This method has been applied to the determination of microgram amounts of indium by means of an isotopic tracer, and to the determination of traces of cobalt using a non-isotopic tracer.

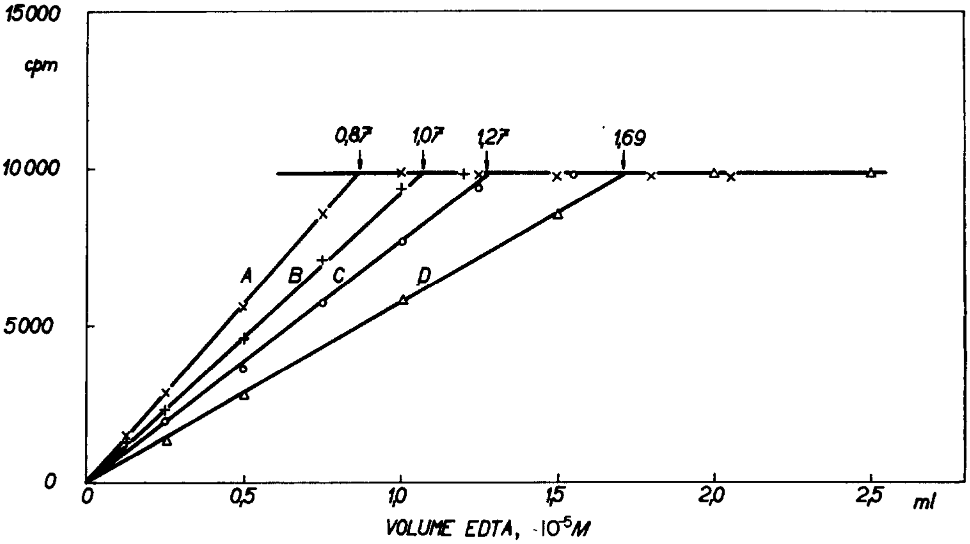

FIG. 1.—Radiometric titration of indium using ^{114}In tracer with $10^{-5}M$ EDTA solution: A—1·00 ml of radio-indium standard solution; B, C, D—1·00, 2·00, 4·00 ml of inactive indium solution mixed with 1·00 ml of radio-indium standard solution.

DETERMINATION OF TRACES OF INDIUM USING ISOTOPIC TRACER

Procedure

The pH of a series of equal, known volumes of analysed solution of indium (2·0 ml containing about 1 μg/ml), labelled with a known amount of radio-indium (^{114m}In, $t_{\frac{1}{2}} = 50$ days), is adjusted approximately to a value of 2–3. Any $iron^{III}$ present, which can interfere, is reduced to $iron^{II}$ by adding 2 drops of 10% ascorbic acid. The solutions thus prepared are carefully mixed with known, increasing amounts of titrating solution ($10^{-5}M$ EDTA) and are simultaneously passed through a series of cation-exchanger columns. The eluate from each column is made up to 10 ml and the activity of 4-ml aliquots are measured by a well-type scintillation counter. Each value of activity measured represents a point on the titration curve (Fig. 1).

The results obtained are also summarised in Table I. The amount of the indium in the non-active sample being analysed can be determined from the difference between the end-point of the standard curve, A (solution containing only standard labelled indium), and the end-points of the corresponding curves, B, C, D (solutions prepared by mixing the standard labelled samples with the sample to be analysed).

TABLE I.—DETERMINATION OF INDIUM

Curve	Indium added, μg	Radio-indium added, μg	Total indium present, μg	Total indium found, μg
A	0·00	1·02	1·02	1·00
B	0·22	1·02	1·24	1·23
C	0·44	1·02	1·46	1·46
D	0·88	1·02	1·90	1·94

DETERMINATION OF TRACES OF COBALT USING NON-ISOTOPIC TRACER

Because of much higher stability with EDTA of the cobalt^{III} complex than of the indium complex it is possible to use radio-indium as non-isotopic tracer for the determination of traces of cobalt.

Procedure

To the series of solutions containing equal, known volumes of the analysed solution (slightly acid), known, increasing amounts of EDTA ($10^{-5}M$) are added. Each of these solutions is carefully mixed in a polyethylene flask with 0·5 ml of 0·01M aqueous ammonia containing 1·5% hydrogen peroxide. The pH of the solutions thus prepared should be 6–8. The solutions are heated on a boiling water bath for 5 min (formation of Co^{III}-EDTA complex). After cooling to room temperature the pH of all the solutions is readjusted to approximately 2–3, and the radio-indium tracer is added. The remainder of the procedure is carried out as before.

The results obtained are given in Fig. 2 and Table II.

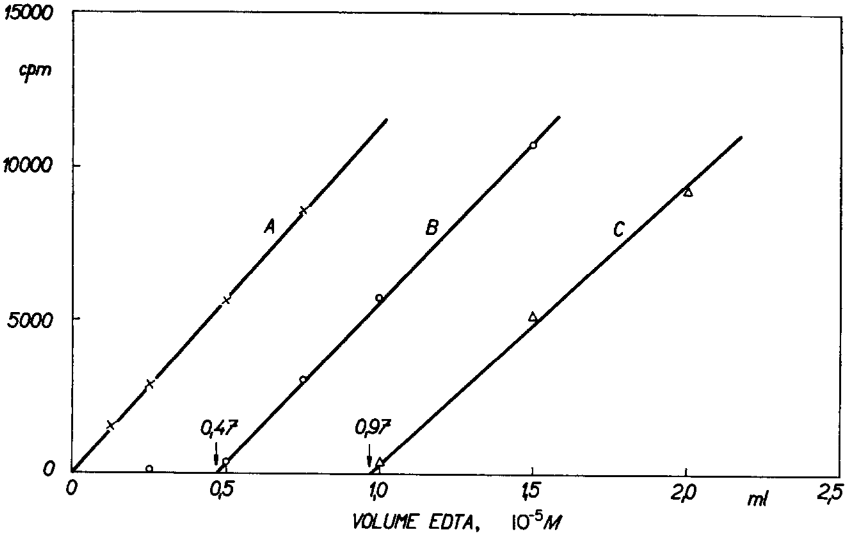

FIG. 2.—Radiometric titration of cobalt using ^{114}In tracer with $10^{-5}M$ EDTA solution: A—1·00 ml of radio-indium standard solution; B, C—1·00, 2·00 ml of inactive cobalt solution.

TABLE II.—DETERMINATION OF COBALT

Curve	Cobalt added, μg	Cobalt found, μg
A	0·00	0·00
B	0·29	0·27
C	0·58	0·56

DISCUSSION

Radiometric titrations such as those described above can in general be used for the same determinations as common complexometric titrations, but their sensitivity is much higher. They have the advantage that the selectivity can be easily predicted from the stability data of EDTA-complexes, which are well known. Thus, for example, in the determination of traces of indium uni- and bivalent metal cations will not interfere, because of their lower stability constants. This has been verified in the present work. However, titrations using isotopic tracers are limited to instances where suitable radioisotopes are available. This restriction does not hold for determinations using non-isotopic tracers. The non-isotopic tracer most suitable for achieving the highest selectivity can also be chosen using the stability constants of the EDTA complexes. The stability constant of the EDTA complex of the tracer must be lower than that of the metal to be determined, but higher than the stability constants of interfering metals which might be present.

Compared with extractive titrations, radiometric titrations using EDTA have the advantage of high stability of the titrant even in very dilute solutions.

Acknowledgement—The authors thank Professor V. Majer, D. Sc. for his interest in this work and to Professor C. L. Wilson for his critical discussion.

Zusammenfassung—Eine neue Art radiometrischer Titration wurde entwickelt. Mit EDTA-Lösungen werden negative oder neutrale Metallchelate gebildet, die leicht mittels Kationenaustauscher von den nicht gebundenen Metallionen abgetrennt werden können. Die Titrationskurven werden aus der Aktivität der Eluate konstruiert. Die Methode wurde an der Bestimmung von Mikrogramm-Mengen Indium mit ^{114m}In als isotopem Tracer und an der Bestimmung von Submikrogramm-Mengen Kobalt mit ^{114m}In als nichtisotopem Tracer verifiziert.

Résumé—On a mis au point un nouveau type de titrage radiométrique. Par l'emploi de solutions d'EDTA, on forme les chélates du métal chargé négativement ou du métal neutre, et ceux-ci peuvent être. aisément séparés des ions en excès qui n'ont pas réagi au moyen d'un échangeur cationique. On trace des courbes de titrage à partir des activités des éluats. On a utilisé la méthode pour doser des quantités d'indium de l'ordre du microgramme par l'emploi de ^{114m}In comme traceur isotopique, ainsi que pour doser des traces de cobalt en quantités inférieures au microgramme au moyen du même indicateur, utilisé comme traceur non isotopique.

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SOME SULPHUR-CONTAINING ORGANIC COMPOUNDS AS REAGENTS FOR THE PHOTOMETRIC DETERMINATION OF SELENIUM

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Summary—The reactions of diethylphosphorodithioate, 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine with selenous acid have been studied. Diethylphosphorodithioate and 2-mercaptobenzimidazole react with selenous acid in a 4:1 molar ratio, and with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacelyl-*p*-toluidine in a 2:1 ratio. New extraction-photometric methods for the determination of small amounts of selenium in various materials not containing tellurium, have been developed, using 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine as reagents.

THE photometric determination of selenium is carried out mainly in the form of a colloidal solution of elementary selenium or in the form of the piazselenol formed by the reaction of selenous acid with 3,3′-diaminobenzidine.[1,2] No other reagents have found practical application.[3]

Of sulphur-containing reagents it has been reported that selenous acid can react with diethyl phosphorodithioate[4] and with 2-thiopyrogallol,[5] giving yellow compounds which can be extracted with organic solvents. More recent experiments have shown[6,7,8] that many reagents containing sulphydryl groups react with selenous acid, forming yellow compounds which possess sufficient stability to be used for the determination of small amounts of selenium. Some of these reagents possess high sensitivity and selectivity.

In the present work the results are given of a study of the reaction of selenous acid with diethyl phosphorodithioate, 2-mercaptobenzimidazole, and some products of the condensation of thioglycollic acid with primary aromatic amines, together with the photometric methods developed for determining small amounts of selenium in various materials.

Diethyl phosphorodithioate, $(C_2H_5O)_2PSSH$

When an aqueous solution of nickel or potassium diethyl phosphorodithioate, $[(C_2H_5O)_2PSS]_2Ni$ or $(C_2H_5O)_2PSSK$, is added to an aqueous solution of selenous acid at an acidity of between about pH 3 and not greater than 2*M* in hydrochloric acid, a yellowish precipitate is formed. Under these conditions, selenium is quantitatively precipitated by an excess of the reagent. The compound formed consists of needle-shaped, bright yellow crystals with a melting point of 81–82°.[6] Chemical analysis (Se: 17·4%; P:13·6%; S:30·9%) shows that the compound corresponds to the formula $[(C_2H_5O)_2PSS]_2Se$. Therefore selenous acid appears to react with nickel diethyl phosphorodithioate according to the equation:

$$2[(C_2H_5O)_2PSS]_2Ni + H_2SeO_3 + 4HCl \rightarrow [(C_2H_5O)_2PSS]_2Se + [(C_2H_5O)_2PSS]_2 + 2NiCl_2 + 3H_2O.$$

The diethyl phosphorodithioate salt of bivalent selenium is completely stable. In the dry state it can be kept in diffuse daylight for not less than 4 months without visible changes. Its solutions in chloroform have been kept without change for 1 year. Unfortunately, nickel diethyl phosphorodithioate cannot be used to determine selenium either by the gravimetric method (the precipitation takes place slowly) or by the photometric method {the disulphide $[(C_2H_5O)_2PSS]_2$ formed strongly interferes with the photometric determination of the selenium (Fig. 1)}, although the reagent is quite sensitive: the molar absorption coefficient of extracts of the diethyl phosphorodithioate salt of bivalent selenium is 1900.

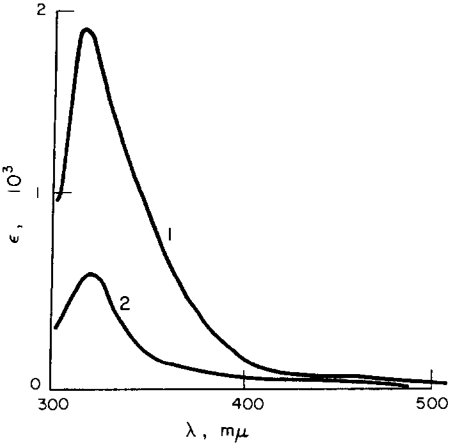
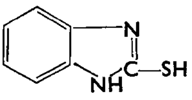


FIG. 1—Absorption curves of the diethyl phosphorodithioate salt of bivalent selenium (1) and the disulphide $[(C_2H_5O)_2PSS]_2$ (2).

2-Mercaptobenzimidazole,



2-Mercaptobenzimidazole has been used for the gravimetric determination of bismuth, copper, cadmium, lead, mercury and gold.[9] Experiments have now shown that 2-mercaptobenzimidazole permits the photometric determination of small amounts of selenium. When a 1 % ethanolic solution of 2-mercaptobenzimidazole is added to an acid solution [the optimum optical density is found at an acidity of from 1 to 3*M* hydrochloric acid (Fig. 2)] of selenous acid, it gives a yellow coloration or a bright yellow crystalline precipitate, depending on its concentration. The compound formed is not extracted by benzene, toluene or ether, is poorly extracted by isoamyl and isobutyl alcohols, is somewhat better extracted by dichloroethane and chloroform, and is well extracted by a 1:5 mixture of butyl alcohol and chloroform, the coloration being very stable. It does not change during several months. The extraction takes place practically completely in a single treatment.

It has not been possible to isolate in the pure state and analyse the compound formed by the reaction of selenous acid with 2-mercaptobenzimidazole, because when it is filtered on paper it decomposes after some minutes with the liberation of red elementary selenium.

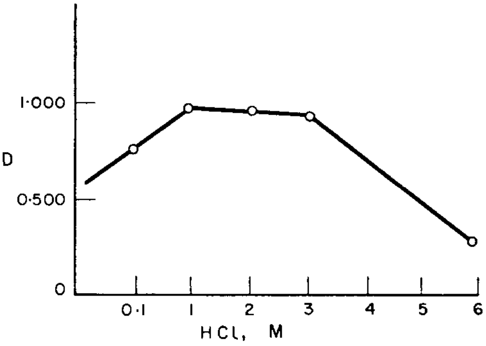


FIG. 2.—Absorption at 335 mμ of the compound of selenium with 2-mercaptobenzimidazole as a function of the acidity of the solution.

The extracts of the compound of 2-mercaptobenzimidazole with selenous acid in a 1:5 mixture of butyl alcohol and chloroform have a maximum light absorption at 330 mμ. The optical density was measured relative to the pure extractant (Fig. 3). If the optical density is measured relative to an extract of the reagent with a mixture of butyl alcohol and chloroform, the maximum light absorption is found at 335 mμ.

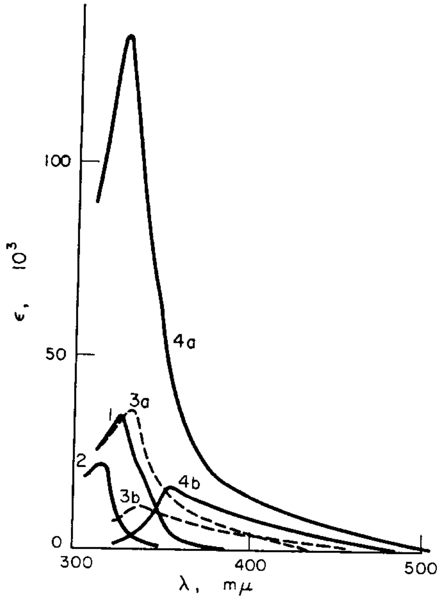


FIG. 3.—Absorption curves of 2-mercaptobenzimidazole (1), $(C_7H_5N_2S)_2$ (2), and the compounds of 2-mercaptobenzimidazole with selenium (3a, 3b) and with tellurium (4a, 4b) relative to the pure extractant (3a, 4a) and relative to an extract of the reagent (3b, 4b).

Under the experimental conditions, the reagent is itself extracted to a large extent and it absorbs light intensely; its maximum absorption is at 325 mμ (Fig. 3). The molar absorption coefficient of extracts of the compound of selenium with 2-mercaptobenzimidazole was found to be 10,500.

The method of isomolar series has shown that selenous acid reacts with 2- mercaptobenzimidazole in a molar ratio of 1:4. This suggests that the reaction between selenous acid and 2-mercaptobenzimidazole takes place according to the equation:

$$4C_7H_6N_2S + H_2SeO_3 \rightarrow (C_7H_5N_2S)_2Se + (C_7H_5N_2S)_2 + 3H_2O.$$

Extracts of the compound of selenium with 2-mercaptobenzimidazole obey Beer's law within the range of concentrations from 1 to 10 μg/ml at 360–380 mμ and 1–40 μg/ml at 420 mμ (Fig. 4). Satisfactory results for the determination of selenium are obtained by measuring the optical density of extracts of its compound with 2-mercaptobenzimidazole in the region of wavelengths greater than 360 mμ or, best, at 420 mμ. At wavelengths less than 360 mμ, the reagent itself absorbs light and thereby prevents satisfactory results being obtained.

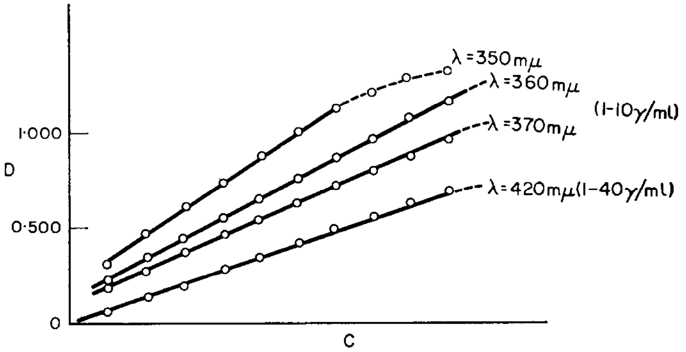
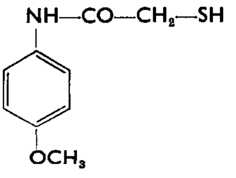


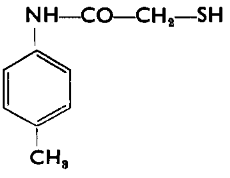
Fig. 4.—Obedience to Beer's law of the compound of selenium with 2-mercaptobenzimidazole at various wavelengths.

Derivatives of thioglycollic acid

A series of derivatives of thioglycollic acid, RNH-CO-CH_2-SH, (where R is -$C_6H_4OCH_3$-*p*, -$C_6H_4CH_3$-*p*, -C_6H_4Cl-*m*, -$C_6H_4NO_2$-*m*, *etc.*) has been used for the detection and gravimetric and photometric determination of silver, lead, mercury^{I}, mercury^{II}, copper, cadmium, bismuth, tin, zinc, cobalt, nickel and molybdenum.[10,11] Experiments have now shown that some of these derivatives can be used for the photometric determination of small amounts of selenium. As examples, the results are given of a study of two derivatives of thioglycollic acid obtained by the condensation of the latter with *p*-anisidine and *p*-toluidine, respectively:



N-mercaptoacetyl-*p*-anisidine



N-mercaptoacetyl-*p*-toluidine

When a solution of selenous acid is added to an acid solution of either of these reagents [the optimum optical density is found at an acidity of 0·05–1M hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-anisidine and 0·05–0·5M hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-toluidine (Fig. 5)], a yellow coloration or pale yellow turbidity or precipitate is immediately formed which can be extracted with many organic solvents: benzene, chloroform, *etc.* The extracts are yellow and are very stable. The extraction of selenium in the form of the coloured compounds takes place practically completely in a single extraction with a 1:5 mixture of butyl alcohol and chloroform.

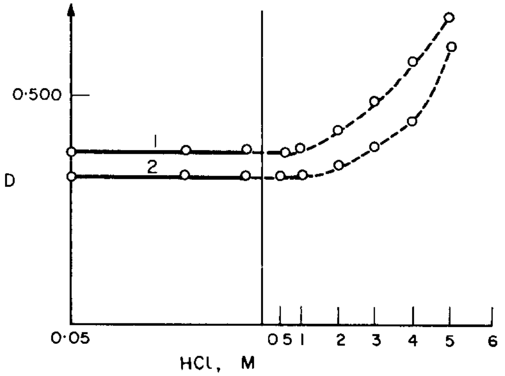


Fig. 5.—Absorption of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine (1) and *N*-mercaptoacetyl-*p*-toluidine (2) as a function of the acidity of the solution.

The absorption curves of the extracts of the compound of selenium with *N*-mercaptoacetyl-*p*-anisidine have a maximum at 310 mμ relative to the pure extractant and at 315 mμ relative to an extract of the reagent (Fig. 6). The extract of the reagent itself under the experimental conditions also absorbs light intensely; its absorption curve has a maximum at 306 mμ (Fig. 6).

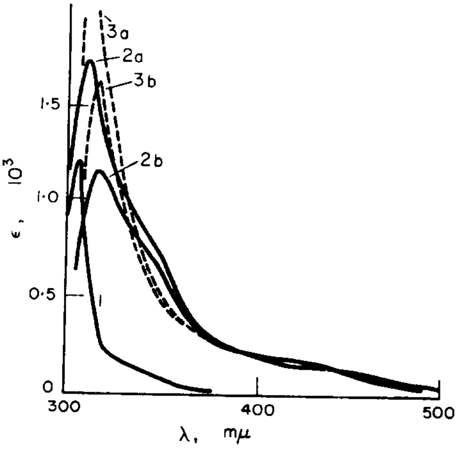


Fig. 6.—Absorption curves of *N*-mercaptoacetyl-*p*-anisidine (1) and its compounds with selenium (2a, 2b) and with tellurium (3a, 3b) relative to the pure extractant (2a, 3a) and to an extract of the reagent (2b, 3b).

N-Mercaptoacetyl-*p*-toluidine is also extracted well under the experimental conditions, but its extract absorbs light very feebly and therefore all the absorption curves of extracts of the compound of selenium with *N*-mercaptoacetyl-*p*-toluidine relative to the pure extractant and relative to an extract of the reagent have maxima in the same position at 318 mμ (Fig. 7). The molar absorption coefficients of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine are similar at 1200.

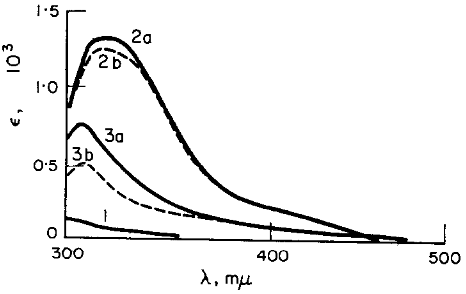


FIG. 7.—Absorption curves of *N*-mercaptoacetyl-*p*-toluidine (1) and its compounds with selenium (2a, 2b) and with tellurium (3a, 3b) relative to the pure extractant (2a, 3a) and to an extractant of the reagent (2b, 3b,).

The molar ratio in which selenous acid reacts with these reagents was found to be 1:2 (Fig. 8). Thus selenous acid probably reacts according to the following equations:

$$2C_9H_{11}O_2NS + H_2SeO_3 \rightarrow (C_9H_{10}O_2NS)_2SeO + 2H_2O$$

$$2C_9H_{11}ONS + H_2SeO_3 \rightarrow (C_9H_{10}ONS)_2SeO + 2H_2O.$$

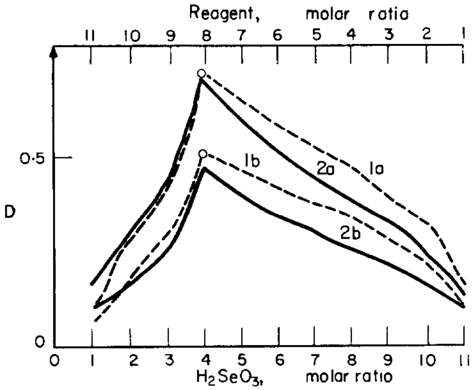


FIG. 8.—Determination of the molar ratios in the reaction of selenous acid with *N*-mercaptoacetyl-*p*-anisidine (1a, 1b) and *N*-mercaptoacetyl-*p*-toluidine (2a, 2b) at 340 mμ (1a, 2a) and 360 mμ (1b, 2b).

It has not been possible to isolate in the pure state and analyse the selenium compounds formed because they are unstable. After they have been filtered, red selenium appears on the filter after a few minutes.

Extracts of the compounds of selenium with *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine obey Beer's law within the range of concentrations from 8 to 70 μg/ml at wavelengths from 340 mμ to 380 mμ. At wavelengths greater than

380 mμ, the extracts still follow Beer's law, but the sensitivity is considerably less. At wavelengths less than 340 mμ, *N*-mercaptoacetyl-*p*-anisidine itself absorbs light and thereby prevents satisfactory results being obtained. In the case of *N*-mercaptoacetyl-*p*-toluidine, the lower limit of obedience of the extracts to Beer's law can be reduced to concentrations below 7 μg/ml, but it is then necessary to work with a hydrogen lamp.

It must be mentioned that 2-mercaptobenzimidazole, *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine permit the determination of selenium only in the absence of tellurium. Tellurous acid, as can be seen from Figs. 3, 6 and 7, behaves completely analogously to selenous acid under the experimental conditions. It reacts with the reagents mentioned, likewise forming either a yellow coloration or a precipitate. The tellurium compounds formed are also extracted by organic solvents. The light-absorption maxima of the extracts of the tellurium compounds and the corresponding selenium compounds are very close to one another (Table I). Consequently, in order to determine selenium in materials containing tellurium, the latter must previously be removed.

TABLE I.—ABSORPTION MAXIMA OF COMPOUNDS OF SELENIUM AND TELLURIUM WITH VARIOUS REAGENTS

Reagent	λ_m(Se)	λ_m(Te)
2-Mercaptobenzimidazole	335	350
N-Mercaptoacetyl-*p*-anisidine	315	325
N-Mercaptoacetyl-*p*-toluidine	318	308

Bismuth and copper interfere with the determination of selenium by the proposed reagents, with which they form either greyish-yellow or pale yellow precipitates which are partially extractable with organic solvents, giving yellow extracts. Moderate amounts of mercury, silver, gold, cadmium and lead cause practically no interference. Bromate and iodate interfere with the determination of selenium with 2-mercaptobenzimidazole, and molybdate interferes with its determination by means of *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine.

Determination of selenium in various materials not containing tellurium

A 0·1 to 0·5-g sample of the material to be analysed is dissolved by means of a mixture of nitric, hydrochloric and sulphuric acids.[12] Any excess of nitrous acid is removed by the addition of urea.[13] The resulting solution is diluted with twice its volume of distilled water and any insoluble residue is filtered off through a loose filter. The filtrate is diluted in volumetric flasks with appropriate volumes of water to give concentrations of selenium in the resulting solution within the range 50 to 200 μg/ml.

One-five ml of the solution to be analysed is added by means of a pipette to an acid solution of the reagents namely 3 ml 1% ethanolic solution of 2-mercaptobenzimidazole, or 3 ml 0·2% ethanolic solution of *N*-mercaptoacetyl-*p*-anisidide or *N*-mercaptoacetyl-*p*-toluidine (final concentration 2*M* hydrochloric acid in the case of 2-mercaptobenzimidazole and 0·5*M* hydrochloric acid in the case of *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine) in a separating funnel and the mixture is well shaken, then extracted with 5 ml of a 1:5 mixture of butyl alcohol and chloroform. It is left to stand for 1 hr for complete separation of the aqueous and organic phases. The extracts are filtered through a dry filter paper into 10·00-mm cells and the optical density measured on a spectrophotometer Beckman DU at the appropriate wavelength (420 mμ for 2-mercaptobenzimidazole and 360 mμ for *N*-mercaptoacetyl-*p*-anisidine and *N*-mercaptoacetyl-*p*-toluidine). The selenium content is found from a calibration curve.

Calibration curves are obtained as above, using different amounts of a standardised solution of selenous acid. The completion of a single selenium determination requires 4 hr.

Some results for the determination of selenium are given in Tables II, III and IV.

TABLE II.—DETERMINATION OF SELENIUM IN A PURE COMPOUND BY MEANS OF 2-MERCAPTOBENZIMIDAZOLE

SeO_2 taken, *mg*	Se found, *mg*	Error, %
100·0	72·0	+1·5
50·0	36·3	+2·6
10·0	7·3	+2·6
2·0	1·5	+5·4

TABLE III.—DETERMINATION OF SELENIUM IN MATERIALS NOT CONTAINING TELLURIUM BY MEANS OF 2-MERCAPTOBENZIMIDAZOLE

Material to be analysed	Weight of sample, *g*	Composition, %	Se found, %	Absolute error, %
Dust from a sintering plant	0·500	Se 0·51; Tl 0·11; Ge 0·0011; In 0·0009;	0·54	+0·03
Sinter	0·100	4·42; remainder unknown	4·57	+0·15
Se-Hg sludge	0·100	Se 14·6; Hg 9·5; remainder $PbSO_4$	14·2	−0·4
Sublimate from Se-As filter-cake	0·100	Se 30·0; As about 20; Pb present	31·25	+1·25

TABLE IV.—DETERMINATION OF SELENIUM IN MATERIALS NOT CONTAINING TELLURIUM BY MEANS OF *N*-MERCAPTOACETYL-*p*-ANISIDINE AND *N*-MERCAPTOACETYL-*p*-TOLUIDINE

		Se found, %			
Material to be analysed	Composition, %	With *N*-mercapto acetyl-*p*-anisidine	Absolute error, %	With *N*-mercapto acetyl-*p*-toluidine	Absolute error, %
Dust from a sintering plant	Se 0·51; Tl 0·11; Ge 0·0011; In 0·0009	0·49	−0·02	0·46	−0·05
Sinter	Se 4·42; remainder unknown	4·60	+0·18	4·11	−0·31
Se-Hg sludge	Se 14·6; Hg 9·5; remainder $PbSO_4$	14·85	+0·25	14·37	−0·23
Sinter	Se 0·03; remainder unknown	0·028	−0·002	0·026	−0·004

Acknowledgement—Hoang Minn-Chau took part in the experimental work.

Zusammenfassung—Die Reaktion von Diäthylphosphorodithioat, 2-Mercaptobenzimidazol, N-Mercaptoacetyl-*p*-anisidin und N-Mercaptoacetyl-p-toluidin mit seleniger Säure wurden untersucht. Die ersten zwei Verbindungen reagieren mit seleniger Säure im Verhältnis 4:1, die andern beiden im Verhältnis 2:1. Neue extraktionsphotometrische Methoden zur Bestimmung kleiner Selenmengen in verschiedenen nicht tellurhaltigen Materialien wurden entwickelt mit 2-Mercaptobenzimidazol, N-Mercaptoacetyl-p-anisidin und N-Mercaptoacetyl-p-toluidin als Reagentien.

Résumé—On a étudié des réactions du diéthylphosphorodithioate, de la mercapt-2-benzimidazole, de la N-mercaptoacétyl-p-anisidine et de la N-mercaptoacétyl-p-toluidine, avec l'acide sélénieux. Le diéthylphosphorodithioate et la mercapto-2-benzimodazole réagissent avec l'acide sélénieux dans le rapport moléculaire de 4/1. La N-mercaptoacétyl-p-anisidine et la N-mercapto-p-toluidine réagissent dans le rapport 2/1. Etude de nouvelles méthodes photométriques d'extraction pour le dosage de petites quantités de sélénium dans des produits variés et ne contenant pas de tellure; on utilise la mercapto-2-benzimidazole, la N-mercaptoacétyl-p-anisidine et la N-mercaptoacétyl-p-toluidine comme réactifs.

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ANION-EXCHANGE BEHAVIOUR OF SCANDIUM IN CHLORIDE-THIOCYANATE MEDIA

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Summary—A method is described for the separation of scandium from rare earths and thorium by anion exchange. The method utilises the adsorption of a negatively-charged thiocyanato complex of scandium on the strongly-basic anion exchanger Dowex 1-X8 from a $2M$ solution of ammonium thiocyanate in $0{\cdot}5M$ hydrochloric acid. Rare earth elements are not retained on the column, while scandium and thorium show moderate adsorptions and can be separated chromatographically by elution with $3M$ hydrochloric acid. The distribution coefficient data for elements in this medium suggest many possible analytical separations of scandium.

MOST ion-exchange separations of scandium have been based on the use of cation exchangers with eluents containing an organic complexing agent. Thus, elution with citric acid,[1] nitrilotriacetic acid,[2] ethylenediaminetetra-acetic acid,[2] hydrazine diacetic acid[3] and ammonium acetate-ammonium oxalate solution[4] seem to provide an excellent cation-exchange separation of scandium from rare earth elements. There has been little published information about the effective anion-exchange separation of scandium from rare earths and thorium. Vickery[5] has demonstrated that scandium in citrate or oxalate solution is adsorbed on an anion-exchange resin. Scandium is also weakly adsorbed from $13{\cdot}3M$ hydrochloric acid, which affords the basis of a simple separation from rare earths,[6] but thorium also behaves like scandium. Walter[7] has effected the separation of scandium, titanium and vanadium by anion exchange from oxalic-hydrochloric acid mixtures and Schindewolf and Irvine[8] worked out the separation of traces of scandium from the same elements by anion exchange from 0·5 to $15M$ hydrofluoric acid solution. The adsorption of several metals, including scandium, on Dowex-1 from potassium thiocyanate solution has been reported by Turner, Philp and Day,[9] the separation of scandium and chromium having been accomplished. In a recently published study Fritz and Pietrzyk[10] have reported distribution coefficients for dysprosium, lanthanum and scandium in mixtures of hydrochloric acid and several alcohols. Yttrium and scandium were separated from lanthanum in hydrochloric acid-ethanol mixtures by Wilkins and Smith,[11] while Faris and Warton[12] worked out an extensive spectrographic determination of distribution coefficients for scandium, yttrium and rare earths in nitric acid-methanol mixtures, giving a promising separation factor for scandium from rare earths.

A study of the anion-exchange behaviour of scandium in an ammonium thiocyanate-hydrochloric acid system was, therefore, undertaken to provide information which would give a method for the sharp separation of scandium from the whole of the lanthanide elements and thorium as well as from several common metals.

EXPERIMENTAL

Ion-exchange resin

Dowex 1-X8, 100–200 mesh, was used in the thiocyanate form. Before use the resin was placed in a large column and back-washed with distilled water to remove fine particles. It was then washed with 3*M* hydrochloric acid, followed by a sufficient amount of 3*M* ammonium thiocyanate solution to convert it to the thiocyanate form. After washing with distilled water the resin was dried at 50° for 1 hr, then placed in a large desiccator containing saturated potassium bromide solution.

Resin column

Ten g of dried resin were slurried with distilled water and poured into a conventional ion-exchange column, 1·1 cm in diameter, packed at the bottom with glass wool. The column bed usually had a height of approximately 18 cm. Eluent was added dropwise from a conventional separatory funnel attached to the top of the column through a rubber stopper.

Reagents and tracer

Scandium^{III} solution (0·600 mg of scandium/ml) was made by dissolving *ca.* 100 mg of 99·9% purity Sc_2O_3 in 3*M* hydrochloric acid, evaporating to dryness and diluting to 100 ml with 0·5*M* hydrochloric acid. Lanthanum and lutetium chloride solutions (2·85 mg of lanthanum/ml; 1.83 mg of lutetium/ml) were prepared by dissolving the appropriate amount of the respective oxide (99·9% purity) in 3*M* hydrochloric acid, evaporating to dryness and diluting to a definite volume with 0·5*M* hydrochloric acid. Thorium chloride solution (4·85 mg of thorium/ml) was made by simply dissolving *ca.* 820 mg of thorium chloride in 100 ml of 0·5*M* hydrochloric acid.

The strengths of the above solutions were determined by titration with 0·001*M* EDTA solution previously standardised against primary-standard zinc metal. All other reagents used were of analytical-reagent quality.

^{46}Sc (half-life 85 day) and ^{160}Tb (73 day) tracers were produced by irradiating 40 mg of the appropriate oxide in the Japan Research Reactor JRR-1 for 15 hr at a power level of 50 kW and a neutron flux of 3×10^{11} neutron.cm^{-2}.sec^{-1}. After cooling for a sufficient period of time each oxide was dissolved in hydrochloric acid, evaporated to dryness and the residue taken up in 0·5*M* hydrochloric acid to give a final volume of 100 ml. An aliquot, usually 0·5 ml for scandium and 1 ml for terbium, was used for elution work. A 0·5*M* hydrochloric acid solution of carrier-free ^{152}Eu (13 year) was obtained commercially. An aliquot was taken, evaporated and diluted to 100 ml of 0·5*M* hydrochloric acid, to give a suitable level of activity. Each tracer was carefully checked for radiochemical purity before use by gamma spectrometry.

Column separation of scandium

A sample solution containing scandium and rare earth or thorium is evaporated and taken up in a minimum amount of 2*M* ammonium thiocyanate in 0·5*M* hydrochloric acid. The resin bed should be previously equilibrated with the same solution. Load the sample solution onto the top of the column. When the liquid level in the column has almost reached the top of the resin bed, elution is started with 3*M* hydrochloric acid at room temperature. The rate of flow of eluent through the column is adjusted to be approximately 0·17 ml/min and the effluent is collected in 5- or 10-ml fractions. These fractions are transferred to a beaker, diluted with water and titrated with 0·001*M* EDTA using Xylenol Orange as indicator. In the cases of separation of europium or terbium from scandium a quantitative measure of their concentration in the effluent fractions is obtained by counting the respective total gamma activity using a standard well-type scintillation counter.

RESULTS AND DISCUSSION

Like hydrochloric acid, thiocyanic acid (a pseudohalogenic acid), forms stable thiocyanato complexes with a number of metals and it has been put to analytical use in connection with solvent extraction using diethyl ether. Some attention[9,13,14,15,16] has been paid to the use of thiocyanate with or without hydrochloric acid in ion-exchange separations. Korkisch and Hecht[16] devised a separation of gallium, iron and aluminium, by the use of a thiocyanate elution system. In a weakly acid solution gallium and iron form negatively-charged thiocyanato complexes which are adsorbed on an anion-exchange column, while aluminium passes through the column with no sign of adsorption. Gallium and iron are then chromatographically desorbed by elution with hydrochloric acid which decreases the stability of the respective thiocyanato complexes.

It is of interest to note here that the elution system enhances the tendency of scandium and thorium to behave as anionic species; from a hydrochloric acid medium both elements do not show any marked adsorption on an anion-exchange resin.

Fig. 1 illustrates the quantitative elution profile curves when scandium and rare

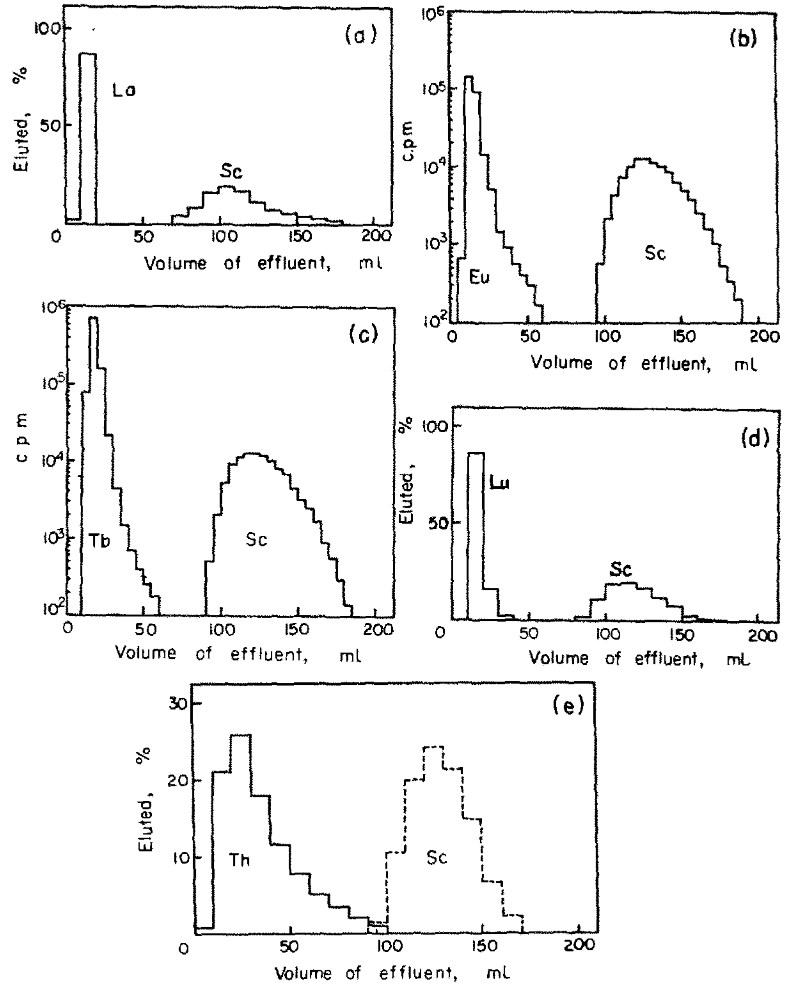

FIG. 1.—Elution profile curves

(*a*) The elution with 3*M* HCl of La and Sc from an 18 × 1·1 cm column of Dowex 1 X8, 100–200 mesh, previously treated with 2*M* NH_4SCN in 0·5*M* HCl. La 2·9 mg, Sc 0·6 mg present with recovery of 98% for La and 99% for Sc.

(*b*) The elution with 3*M* HCl of ^{152}Eu and ^{46}Sc from the same column as in (*a*). Eu carrier-free, Sc 130 μg present with recovery of 87% for Eu and 98% for Sc.

(*c*) The elution with 3*M* HCl of ^{160}Tb and ^{46}Sc from the same column as in (*a*). Tb 350 μg, Sc 130 μg present with recovery of 99% for Tb and 99% for Sc.

(*d*) The elution with 3*M* HCl of Lu and Sc from the same column as in (*a*). Lu 1·8 mg, Sc 0·6 mg present with recovery of 100% for Lu and 98% for Sc.

(*e*) The elution with 3*M* HCl of Th and Sc from the same column as in (*a*). Th 4·9 mg, Sc 0·6 mg present.

TABLE I.—DISTRIBUTION COEFFICIENT OF SOME ELEMENTS IN NH_4SCN-HCl MEDIUM ON DOWEX 1-X8

Element	Concentration of NH_4SCN in 0·5*M* HCl, *M*				
	0·2	0·4	0·6	0·8	1·0
Sc	56	250	905	5040	2818
La	<1	<1	<1	<1	<1
Sm	<1	<1	<1	<1	<1
Lu	<1	<1	<1	<1	<1
Th	3·3	19	43	74	106
Ca	0·0	0·0	0·0	0·0	0·0
Al	0·0	0·0	0·7	0·7	0·9
Cu	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Zn	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Cd	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
In	579	646	734	580	706
Hg	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$

Kd value of Sc in 2*M* NH_4SCN—0·5*M* HCl is $>10^4$.

TABLE II.—SEPARATION OF SCANDIUM FROM OTHER ELEMENTS IN NH_4SCN-HCl MEDIUM

Scandium µg		Foreign ions used, *mg*		Foreign ions		Remark
Taken	Found			Break-through	Elution complete	
600	598	Al	3·4	0	60	Al eluted first, then Sc with 3*M* HCl.
600	599	Ca	2·0	0	60	Ca eluted first, then Sc with 3*M* HCl.
600	601	Fe	1·0	—	—	Sc eluted first with 3*M* HCl; Fe strongly adsorbed on resin.
600	592	Zn	1·3	210	300	Sc eluted first with 3*M* HCl, then Zn with H_2O.
600	588	Cd	1·1	210	300	Sc eluted first with 3*M* HCl, then Cd with H_2O.
600	594	In	1·8	210	270	Sc eluted first with 3*M* HCl, then In with 0·005*M* HCl.
600	592	La	2·9	0	20	La eluted first, then Sc with 3*M* HCl.
600	588	Lu	1·8	10	40	Lu eluted first, then Sc with 3*M* HCl.

earth or thorium are eluted by 3*M* hydrochloric acid. It can be seen that scandium can be separated successfully from lanthanum, europium, terbium and lutetium. Scandium tends to give slightly asymmetrically-shaped elution bands. This would result either from rather slow approach to exchange equilibrium or from non-linearity of the adsorption isotherm. According to an equilibrium study by a batch method it takes more than 20 hr for scandium to attain exchange equilibrium in the anion exchanger-thiocyanic acid system at room temperature.

In cation-exchange chromatography with elution by hydrochloric acid-ammonium thiocyanate, heavy rare earth elements ranging from europium to lutetium can be separated from scandium with difficulty.[14] Extreme difficulty has been encountered in separating scandium from heavier rare earths, even in lactate, citrate and EDTA eluent systems coupled with a cation exchanger. Scandium is eluted between thulium and erbium in close proximity to thulium in the form of a complex with EDTA by anion-exchange chromatography.[17] The anion-exchange separation of scandium presented here is likely to offer a simple, rapid and convenient way to separate scandium successfully with a rather shorter column.

The separation of thorium is not very satisfactory, but it may be achieved by the use of a slightly longer column or, more effectively, by the proper choice of eluent system, say 0·2*M* ammonium thiocyanate in 0·5*M* hydrochloric acid. In this case it is preferable to desorb scandium with hydrochloric acid after elution of the thorium fraction in order to minimise the tailing of scandium elution.

In Table I the weight distribution coefficient values, Kd, are given for several elements.

Increasing the concentration of thiocyanate resulted in an increased adsorption of scandium and thorium. The adsorption of scandium was found to be almost independent of the concentration of hydrochloric acid over the range 0·25*M* to 2·0*M*. The feasibility of the separation of scandium from common metal ions was investigated briefly. In Table II several of the results obtained are recorded. Scandium is completely eluted by a 130 ml-fraction of 3*M* hydrochloric acid, while the breakthrough of aluminium and calcium occurred in the effluent from the sample solution. Because iron, copper, indium and mercury are not desorbed with 3*M* hydrochloric acid, the separation of scandium from most metal ions which form strong thiocyanato complexes should be feasible.

Zusammenfassung—Eine Methode zur Trennung von Scandium von seltenen Erden und Thorium durch Anionenaustausch wird beschrieben. Dabei wird der negativ geladene Rhodanokomplex von Scandium am stark basischen Anionenaustauscher Dowex 1-X8 aus einer Lösung mit 2m NH_4SCN und 0,5m HCl adsorbiert. Seltene Erden werden auf der Säule nicht zurückgehalten, Scandium und Thorium werden mäßig stark adsorbiert und können chromatographisch durch Elution mit 3m HCl getrennt werden. Die Verteilungskoeffizienten für verschiedene Elemente in diesem Medium weisen auf viele mögliche analytische Abtrennungsverfahren für Scandium hin.

Résumé—On décrit une méthode de séparation du scandium des terres rares et du thorium par échange d'anions. La méthode utilise l'adsorption, sur l'échangeur anionique fortement basique Dowex 1-X8, d'un complexe sulfocyané du scandium chargé négativement, à partir d'une solution 2*M* de sulfocyanure d'ammonium en acide chlorhydrique 0,5*M*. Les éléments des terres rares ne sont pas retenus sur la colonne, cependant que le scandium et le thorium sont moyennement adsorbés et peuvent être séparés chromatographiquement par élution à l'acide chlorhydrique 3M. Les données sur les coefficients de distribution des éléments dans ce milieu suggèrent de nombreuses séparations analytiques possibles du scandium.

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EINE PHOTOMETRISCHE METHODE ZUR BESTIMMUNG GERINGER MENGEN VON GOLD MIT *N,N'*-TETRAMETHYL-*o*-TOLYDIN (TETRON)

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Zusammenfassung—Anhand einer Möglichkeit, die vorher grundsätzlich aufgeklärt war, wurde eine photometrische Methode zur Bestimmung geringer Goldmengen mit *N,N'*-Tetramethyl-*o*-tolydin (Tetron) entwickelt. Das Gold wurde von den Begleitelementen zunächst durch Mitfällung mit Tellur, ferner durch Extraktion mit Äther aus Bromwasserstoffsäurem Medium getrennt und schliesslich mit Tetronlösung behandelt. Es entstand eine orangegelbe Färbung, die in etwa 4 Minuten zur vollen Intensität gelangte. Man verdünnte und photometrierte bei Blaulichtfilter. Die Färbung blieb 20 bis 25 Minuten bestehen, verblasste dann allmählich. Das Verfahren wurde zur Bestimmung von Gold in Kupfer-, Blei- und gemischten Konzentraten sowie im Anodenkupfer verwendet. Die Aussagen wurden statistisch ausgewertet.

BEKANNT sind zahlreiche Farbreaktionen für Gold(III)-ionen mit verschiedenen organischen Reagentien.[2–18] Den meisten von ihnen liegen photometrische Methoden zur Bestimmung geringer Goldmengen zugrunde. Eine kritische Bewertung derselben ergibt,[19] dass am empfindlichsten diejenige ist, bei der das o-Tolydin als Reagens verwendet wird.

Unsere Untersuchungen zeigten,[1] dass *N,N'*-Tetramethyl-o-tolydin (Tetron) etwa zweimal so empfindliche Reaktionen bewirkt als das o-Tolydin; auch ist hierbei die Färbung seiner Oxydationsform tiefer und nachhaltiger. Der Extinktionskoeffizient der unter der Einwirkung von Gold(III)-ionen entstandenen Oxydationsform des Tetrons beträgt 50,000 bei Blaulichtfilter des ФЭК–М. Die Geschwindigkeit des Redoxprozesses hängt von der Acidität des Mediums ab. In schwefelsaurem Medium (1 :20) kommt die Färbung zur vollen Entwicklung in 3 bis 4 Min., bleibt 20 bis 25 Min. unverändert und verblasst dann allmählich. Direktes Sonnenlicht beschleunigt die Entfärbung, daher sind die Lösungen davor zu schützen.

Dass hierbei Fe(III), Cu, Mn(II), Pb, As, Sb, Sn, Ni, Co, Zn, Ag, Hg, Se, Te und Tl nicht störend wirken, wohl aber Ce(IV), Mn(IV), Ir(IV), Chromat- und Nitritionen, ergibt sich eindeutig aus dem Vergleich des Redoxpotentials des Tetrons mit dem zahlreicher anderer Stoffe, die das Gold in Gesteinen, Konzentraten oder Halbprodukten begleiten können.

Wir nahmen uns vor, dieses Verhalten des Tetrons zu verwerten, um eine empfindlichere, selektivere und zugleich weniger anspruchsvolle Methode zur Bestimmung von geringen Goldmengen zu schaffen.

EXPERIMENTELLER TEIL

Reagentien

Goldstandartlösung: 0,0250 g Gold wird in etlichen ml Königswasser aufgelöst, mittels IR-Glühlampe zur Trockne eingedampft, der Rückstand mit 1 ml Konz. Salzsäure versetzt, wieder zur Trockne eingedampft und in einem Messkolben auf 250 ml mit 1M Salzsäure verdünnt. Dieser Lösung, die 100 μg Au(III)/ml enthält, entnimmt man 10 ml, verdünnt sie mit frisch destilliertem Wasser auf 100 ml und erhält eine Lösung von 10 μg Au(III)/ml.

0,1 %*ige Tetronlösung:* 0,1 g Tetron, aufgelöst in 100 ml verd. Schwefelsäure (1:20).

0,1 %*ige Lösung von Kaliumtellurit:* 0,1 g K_2TeO_3 werden in etlichen ml 2,5M Salzsäure aufgelöst und mit Wasser auf 100 ml verdünnt.

10%*ige Zinn*(II)*-chloridlösung:* Frisch bereitete Auflösung von 10 g $SnCl_2$ in 2,5M Salzsäure unter Erhitzen.

3M Bromwasserstoffsäure

Äthyläther: p.a.

2,5M Salzäure

konz. Salzsäure; konz. Salpetersäure.

ERGEBNISSE

Eine der wesentlichsten Schwierigkeiten, auf die man bei der Bestimmung geringer Mengen von Gold stösst, ist seine Trennung. Dazu benutzt man: die Mitfällung des Goldes durch ein geeignetes Fällungsmittel (Tellur,[14] Bleisulfid,[21,22] ein Gemisch von Quecksilber-(II)-chlorid und Magnesium[20] u.a.); ferner die Extraktion des Goldes mit Äthyläther,[23,24] Isopropyläther[25] oder Äthylacetat[23] aus Chlor- bzw. Bromwasserstoff-säurem Medium und schliesslich Ionenaustausch[26] oder Adsorption über Kohle, Zellulose u.a.

Unsere Versuche zeigten, dass es bei der Aufarbeitung zusammengesetzter Proben wie Gesteine, Erze und Konzentrate am zweckmässigsten ist, das Gold zunächst durch Mitfällung mit Tellur von den Begleitelementen abzutrennen und anschliessend die Gold(III)-ionen mit Äther aus einem Medium von 3M Bromwasserstoffsäure zu extrahieren.

Bestimmung des Goldes in Kupfer-Eisen- und gemischeten Konzentraten

Analysegang: 0,5 bis 2,0 g der fein verriebenen Probe werden im Gemisch von Lunge aufgelöst. Man dampft die Lösung auf Sandbad zur Trockne ein. Einwirkenlassen von 3 bis 4 ml konz. Salzsäure auf den Rückstand mit nochmaligem Eindampfen zur Trockne. Nach Zugabe von 60 bis 70 ml der 2,5M Salzsäure und 2 ml Kaliumtelluritlösung erwärmt man fast bis zum Sieden und reduziert mit 15–20 ml Zinn(II)-chloridlösung.* Es entsteht eine dunkelbraune kolloidale Lösung von Elementartellur, die beim Liegenlassen flockig wird wobei sich das Tellur auf den Boden setzt. Der Niederschlag wird nach einer Stunde abfiltriert (Weissbandfilter) und mit 0,2M Salzsäure ausgewaschen. Das Filter wird samt Niederschlag im Porzellantiegel bei 800–900° verbrannt und geglüht. Unter diesen Bedingungen entweicht das Tellur als Oxyd, und im Tiegel verbleibt das Gold, gelegentlich mit einigen Platinmetallen, geringen Mengen von Siliciumsäure, Kupfer, Blei und Eisen vermischt. In das Becherglas, in dem die Mitfällung erfolgt war, bringt man 2 bis 3 ml Königswasser, deckt mit dem Uhrglas zu und erhitzt auf dem Sandband 15–20 Min. lang. Das Säurengemisch wird in den Tiegel eingegossen, mit Uhrglas bedeckt und 15–20 Min. erwärmt. Nach Abnahme des Uhrglases dampft man die Lösung mittels IR-Glühlampe zur Trockne ein.† Dem Trockenrückstand werden 10 ml 3M Bromwasserstoffsäure zugesetzt; nach heftigem Umrühren mit Glasstab wird die Lösung samt dem Niederschlag der Siliciumsäure in den Scheidetrichter gebracht und darin 3 Min. lang mit 10 ml Äthyläther extrahiert. Praktisch geht das Gold schon bei der ersten Extraktion in die organische Phase über. Um grössere Gewissheit zu erlangen führt man am besten eine zweite Extraktion durch.‡ Die vereinten ätherische Auszüge werden in einem 25 ml-Becherglas mit Hilfe der IR-Glühlampe langsam zur Trockne eingedampft. Auf den Rückstand lässt man 10–15 Tropfen Königswasser einwirken, dann erhitzt man 15 Min. mit aufgesetztem Uhrglas und dampft vorsichtig zur Trockne ein. Nach Versetzen mit 1 ml 0,1 % iger Tetronlösung entsteht orangegelbe Färbung, die allmählich

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* Die Menge an Zinn(II)-chlorid muss dazu ausreichen, nicht nur das Tellur, sondern auch die vorhandenen Eisen(III)- und Kupfer(II)-ionen reduzieren zu können.

† Die Temperatur darf 70–80° nicht übersteigen, sonst könnte sich das Gold(III)-chlorid zersetzen. Die Luft darf nicht verstaubt noch verqualmt sein (kein Tabakrauch!), da Reduktion des Gold(III)-chlorids zu Elementargold eintreten könnte.

‡ Geringe Mengen an Siliciumsäure bleiben dispergiert in der Wasserphase zurück und halten an den Trichterwänden. Damit sie nicht vom Äther mitgerissen werden, giesst man diesen durch die obere Öffnung des Scheidetrichters ab.

intensiver wird. Nach 3 bis 4 Min. verdünnt man mit frisch destilliertem Wasser* auf ein angemessenes Volumen (10-, 20- oder 50 ml) und photometriert bei Blaulichtfilter.

Goldbestimmung in Bleikonzentraten

Analysengang: 0,5 bis 2,0 g der Probe werden mit 10 bis 15 ml konz. Salzsäure übergossen und bis zum Aufhören der Entwicklung von Schwefelwasserstoff erhitzt. Dann gibt man 5 bis 10 ml konz. Salpetersäure hinzu und lässt die Lösung auf dem Sandbad zur Trockne verdunsten. Der weitere Gang der Analyse ist derselbe wie bei der Analyse von Kupferkonzentraten.

Bleibt bei der Verdünnung, die der Mitfällung des Goldes mit Tellur vorausgeht, noch ungelöstes Bleichlorid zurück, so wird es nach Abfiltrierung dadurch entfernt, dass man den gesamten Niederschlag mit 15–20 ml heissem Wasser auswäscht.

Goldbestimmung im Anodenkupfer

Bei der Aufarbeitung von Proben mit einfacher Zusammensetzung, z.B. von Anodenkupfer, kann die Abrennung des Goldes mit Hilfe eines Ionenaustauschers vorgenommen werden.

Bekanntlich haftet $[AuCl_4]^-$-an-Anionit in einem ziemlich weiten pH-Intervall: von 0,1 bis 12 n HCl.[27] Auf dieser Eigenschaft beruht das von S. Hirano, A. Mizuike und Y. Yida[26] angewandte Verfahren zur Bestimmung geringer Goldmengen im Kupfer.

Bei unseren Versuchen bedienten wir uns des Ionenaustauschers Dowex II 310 mesh in Cl^--Form. Die Säule stellte ein mit Hülse versehenes Filtrierröhrchen dar,[28] das bis zur Höhe von 10 mm mit dem Ionenaustauscher gefüllt war. Durch Aufsaugen mittels Wasserstrahlpumpe wird die Ausströmungsgeschwindigkeit auf etwa 1 ml/min eingestellt.

Analysengang: 0,1 bis 0,5 g Anodenkupfer werden in 6 ml salpetersäure (1:1) aufgelöst; der Lösung setzt man 2 ml konz. Salzsäure hinzu und verdünnt mit Wasser auf etwa 20 ml. Man lässt die Lösung durch die Säule fliessen. Diese wäscht man dann mit etwa 10 ml Salzsäure (1:10) durch. Die Filtrierpapierhülse wird mit dem Glasstab aus der Säule in einen Porzellantiegel geschoben, verbrannt und auf 800° geglüht. Den kaum merklichen Rückstand versetzt man mit ein paar Tropfen Königswasser, dampft mit Salzsäure ein, setzt 1 ml Tetronlösung hinzu, verdünnt und photometriert.

Aufnahme der Standardgeraden

Die Goldkonzentration in der zu untersuchenden Probe kann nach einer vorher aufgenommenen Standardgeraden ermittelt werden. Zur Vermeidung gelegentlicher methodischer Fehler müssen die Punkte, mit deren Hilfe die Gerade aufgenommen werden soll, das Resultat der Goldbestimmung in Lösungen sein, die bestimmte Goldkonzentration aufweisen und an denen der entsprechende Analysengang angewendet worden ist.

Da Zufallsfehler während der Bestimmung unterlaufen können, wird man die wahrscheinlichste Gerade nur erhalten, wenn jeder Punkt das arithmetische Mittel aus mehreren Berechnungsaussagen ist.

In den Konzentraten schwankt der Goldgehalt meist zwischen 0,5 und 50 g/t. Aus diesem Grunde ist es zweckmässig, zwei Standdardgeraden aufzunehmen: eine für Konzentrationen von 1 bis 7 g/t und die andere für solche von 5 bis 30 g/t. Bei der ersten werden die zu photometrierenden Lösungen auf 10 ml verdünnt, bei der zweiten auf 25 ml. Benutzt wird eine Küvette von 2 cm-Stärke des absorbierenden Mediums.

BEURTEILUNG DER ERGEBNISSE

Bewertung der Genauigkeit der Methode

Im Laufe der Analyse kommen methodische Fehler vor, deren Betrag von dem gewählten analytischen Arbeitsgang abhängig ist. Das Vorliegen solcher Fehler stellten wir bei der Aufnahme der Standardgeraden unter verschiedenen Bedingungen fest: eine bei der direkten Bestimmung von Gold(III)-chlorid mit Tetron (s. Abb. 1, Gerade I), die zweite nach vorausgegangenem Haftenbleiben des Goldes am Anionit (Gerade II) und die dritte nach der Mitfällung des Goldes mit Tellur und anschliessender Extraktion des komplex an Goldbromids mit Äther (Gerade III). Der Betrag jedes den Goldmengen 2, 4, 6, 8 μg entsprechenden Punktes stellt das arithmetische

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* Ist das Wasser nicht frisch destilliert, enthält es Mikro-organismen, durch deren reduzierende Wirkung die Entfärbung der Lösung beschleunigt wird.

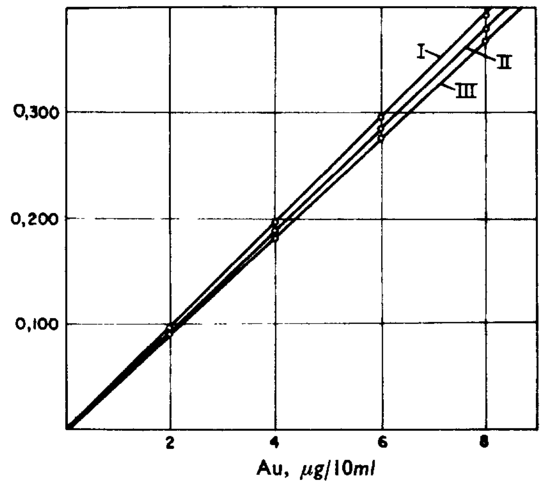

ABB. 1

Mittel aus zehn Bestimmungen dar. Die Abweichung der Geraden II and III von der Geraden I um entsprechend 2,5 oder 5,6% besagt, dass im Gange der Analyse infolge der Unvollständigkeit der Mitfällung, der Extraktion oder des Ionenaustausches Gold teilweise verloren geht. Es leuchtet daher ein, dass es zweckmässig ist, die Aufnahme der Standardgeraden auf den jeweiligen Analysengang abzustimmen, um methodische Fehler dieser Art zu vermeiden. Ist diese Anforderung erfüllt, dann wird die Reproduzierbarkeit bzw. Genauigkeit der Methode von den unbestimmten Fehlern abhängig sein. Da diese meist aus Variationen der bestimmten Fehler herrühren, müssen sie selbst variabel sein, wie dies aus Tab. I hervorgeht.

TABELLE I

	I			II			• III		
Au in 10 ml, µg	Direkte Bestimmung			Nach vorheriger Trennung von Au mit Anionit			Nach vorheriger Mitfällung von Au mit Te		
	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$	$\bar{E}$	ς	$\frac{\varsigma}{\bar{E}} \cdot 100$
2	0,098	0,0018	1,8	0,095	0,0019	2,0	0,093	0,0031	3,3
4	0,195	0,0031	1,6	0,190	0,0037	1,9	0,184	0,0056	3,0
6	0,294	0,0040	1,4	0,287	0,0050	1,7	0,275	0,0068	2,5
8	0,397	0,0056	1,4	0,383	0,0060	1,6	0,372	0,0075	2,0

$\bar{E}$—arithmetischer Mittelwert der Extinktion bei N = 10

ς—Standardabweichung

$\frac{\varsigma}{\bar{E}} \cdot 100$—Prozentfehler

Demnach liegt der Relativfehler innerhalb der Grenzen ±7,5 bis ±4,5%, wenn Gold einmalig in Kupfer-, Blei- oder gemischten Konzentraten mit Goldgehalt 2 bis 8 g/t bei 95% statistischer Sicherheit bestimmt wird. Handelt es sich um Bestimmung des Goldes im Anodenkupfer, so wird sich der Relativefehler unter denselben Bedingungen auf ±3,6 bis ±4,5% belaufen.

TABELLE II

No.	Probe	Au g/t nach photometrischer Methode	Au g/t Mittelwert	Au g/t nach der Kupellationsmeth.
1	Goldkonzentrat	60,0; 59,5; 60,0; 58,5	59,8	60,0
2	Komplexes Konzentrat	56,6; 56,6; 55,7	56,3	57,4
3	Blei/Kupfer-Konzentrat	22,0; 22,0; 23,0	22,3	23,0
4	Kupferkonzentrat No 1	8,9; 9,1	9,0	8,8
5	Kupferkonzentrat No 2	2,8	2,8	2,5
6	Bleikonzentrat	0,9; 0,8; 1,0	0,9	1,0

Anwendungsgebeit der Methode

Das Verfahren wurde bei industriellen Objekten angewendet: Gold-, Kupfer-, Blei- und gemischten Konzentraten.

Tabelle II veranschaulicht die gute Reproduzierbarkeit der Ergebnisse, die mit denen der Kupelationsmethode in Einklang stehen.

Bestimmt wurde auch der Goldgehalt im Anodenkupfer. Zur Trennung des Goldes wurden die beiden Varianten eingesetzt: einmal durch Ionenaustauscher und zum andern durch Mitfällung mit Tellur und anschliessende Extraktion.

Die erste Variation ergab bei $N = 10$; $\bar{C} = 59{,}3$ g/t; $\varsigma = 0{,}89$; $\frac{\varsigma}{\bar{C}} \cdot 100 = 1{,}5\%$.

Nach der zweiten Variante bei $N = 10$; $\bar{C} = 58{,}5$ g/t; $\frac{\varsigma}{\phi} = 1{,}25$; $\frac{\varsigma}{\bar{C}} \cdot 100 = 2{,}1\%$.

Summary—A photometric method can be used for the determination of small amounts of gold with *N,N'*-tetramethyl-*o*-tolidine (Tetron). The gold is separated by precipitation with tellurium and extraction by ether from an HBr medium, and is then treated with Tetron solution. An orange-yellow colour develops and reaches its full intensity in about 4 min. The solution is diluted, and the colour is measured using a blue filter. The colour is stable for 20–25 min, and then fades gradually. The procedure may be applied to the determination of gold in copper-, lead- and mixed-concentrates or in anode-copper. The results have been evaluated statistically.

Résumé—En vertu d'une possibilité préalablement éclaircise est proposée une méthode de determination de petites quantités d'or a l'aide de la *N,N'*-tetramethyl-*o*-tolydine (tètrone). L'or est coprécipite avec le tellure, puis extrait par l'ether en milicu bromhydrique et á la fin traité par une solution de la *N,N*-tetramethyl-*o*-tolydine. On obtient une coloration jaune orangée, qui se develloppe 4 minutes. On amene a un volume convenable et effectue la photometue en utilisant un filtre bleu, la coloration est stable 20–25 minutes, après quoi elle commence a s'affaiblir. La méthode est appliquèe a l'analyse de l'or dans des concentrés différens et dans le cuivre anodique. Les résultats sont interprétés par le calcul statistique.

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PHASE TITRATIONS—III*

NEW APPLICATIONS AND THE PHASE TITRATION OF BINARY SOLUTIONS OF CHEMICALLY SIMILAR COMPONENTS

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Summary—Results are given for the phase titration of 27 new binary solutions of the water-immiscible components dichloromethane, cyclohexane, allyl bromide, benzene, toluene and xylene in combination with the water-miscible components methanol, ethanol, isopropanol, dioxan, acetone and acetic acid. A new method for the phase titration of binary solutions of liquids which are chemically similar is described. Results are given for the phase titration of binary solutions of the chemically similar liquids methyl aniline–aniline, nitrobenzene–aniline, carbon tetrachloride–chloroform, n-butyl bromide–n-butyl acetate and cyclohexane–benzene. Sampling procedures and sources of error are discussed.

MOST of the titrations of binary solutions reported in this series depend on great differences in solubility of the components. For example, solutions of carbon tetrachloride, which is completely immiscible with water, and methanol, which is completely miscible, can be analysed using water as a titrant. Part of this work has been devoted to extending the original technique to 27 new systems of this kind.

Bogin[1] showed that it is possible to take advantage of differences in solubility even when the components of a binary solution are chemically similar. Thus he was able to titrate solutions of butanol in propanol because of the partial immiscibility of butanol with water.

We will describe a method for the analysis, by phase titration, of binary solutions made up of components which are not only chemically similar but also have almost identical solubilities in water. The method is so sensitive to slight differences in solubility characteristics that it is possible to analyse solutions of chloroform in carbon tetrachloride and solutions of cyclohexane in benzene.

The new technique, like the old one, is capable of extremely wide application.

THEORY

Consider, as an illustrative binary solution, carbon tetrachloride and chloroform (solubilities: 0·077 and 0·822 g/100 ml of water respectively[2]). The phase titration of each in combination with water-miscible organic liquids has been reported.[3,4] Although they are both regarded as being completely immiscible with water, the solubility curve of the carbon tetrachloride-ethanol-water phase diagram is slightly higher than the solubility curve of the chloroform-ethanol-water phase diagram[5] as shown in Fig. 1.†

It has been shown[3] that a higher solubility curve gives a lower phase-titration calibration curve and *vice versa*. This is shown in Fig. 2. In the discussion that

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* Part II, *Talanta*, 1963, **10**, 633.

† In the actual experiment described, acetic acid was used instead of ethanol but the principle is the same. Ethanol is referred to in this discussion because the phase diagrams are readily available.

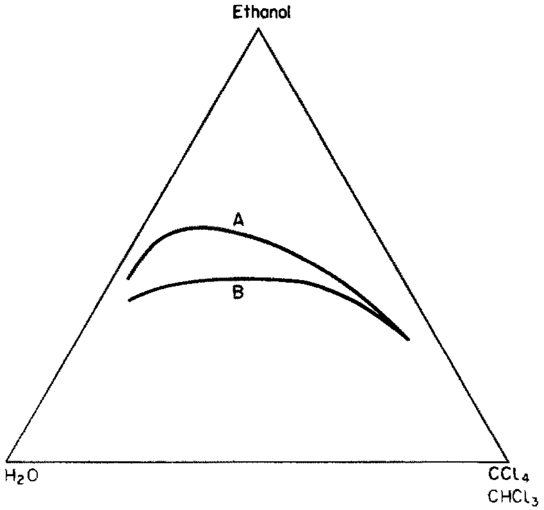

FIG. 1.—Ternary phase diagrams at 0°
A: carbon tetrachloride–ethanol–water:
B: chloroform–ethanol–water.
Taken from the International Critical Tables.[5]

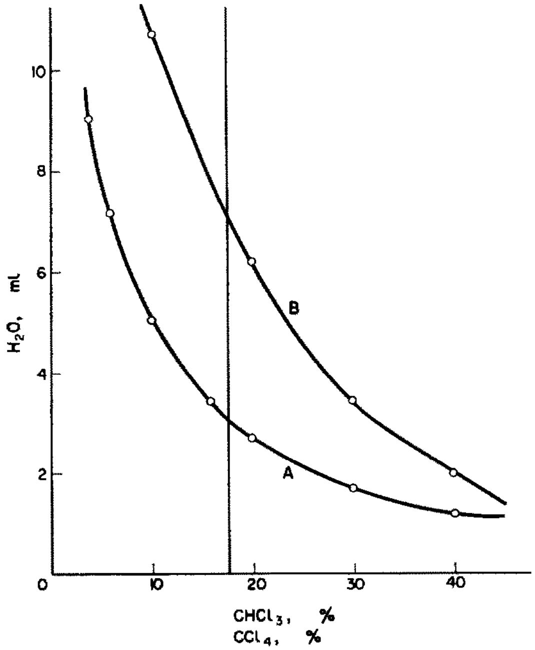

FIG. 2.—Type A solubility curves
A: carbon tetrachloride–ethanol,
B: chloroform–ethanol,
titrated with water.
The vertical line segment represents a constant composition with respect to ethanol.

follows, phase-titration calibration curves of the kind shown in Fig. 2 will be referred to as Type A solubility curves.

If, instead of titrating binary solutions of ethanol and immiscible component with water, one titrates ternary solutions of carbon tetrachloride, chloroform and ethanol with water, the titres will fall in the area between the Type A solubility curves shown in Fig. 2. The locus of the number of ml of water necessary to cause turbidity, as a function of the composition of the three component system titrated, is the three-dimensional surface shown in Fig. 3. The Type A solubility curves are the XZ plane and the outer edge of the solubility surface which is parallel to it. Notice that the concentration of water necessary to cause turbidity as a function of three other composition variables is not a surface in four dimensions because, of the four composition variables, only three are independent.

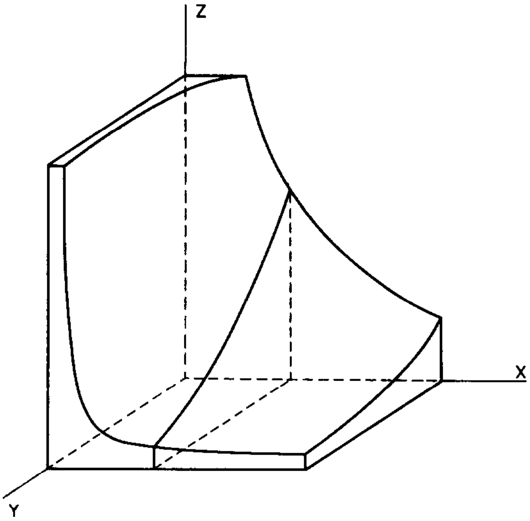

Fig. 3.—The solubility surface for the ternary system carbon tetrachloride–chloroform–ethanol titrated with water.

The axes are: X, 100 − % ethanol; Y (ml of carbon tetrachloride/ml of carbon tetrachloride + ml of chloroform), 100, *i.e.*, % carbon tetrachloride before the addition of any ethanol or water; and Z, ml of water necessary to cause turbidity.

The vertical plane parallel to the YZ plane shown in the diagram indicates constant ethanol composition.

Now simplify the problem by holding the amount of ethanol constant and allowing variation in the ratio of carbon tetrachloride to chloroform. Let the constant composition of ethanol be represented by the vertical line in Fig. 2. This line and an intersecting line perpendicular to the plane of the page define a plane. The plane so defined intersects the solubility surface as shown in Fig. 3. Its projection on the YZ plane is Fig. 4, the number of ml of water necessary to cause turbidity as a function of carbon tetrachloride percentage at constant amount of ethanol. Fig. 4 will be referred to as a Type B solubility curve. Its use as a calibration curve for the phase titration of binary solutions of carbon tetrachloride and chloroform is described in detail in the Experimental section.

The projection of the Type B solubility curve on its vertical axis gives the vertical line segment between the two Type A solubility curves in Fig. 2. The intersection of

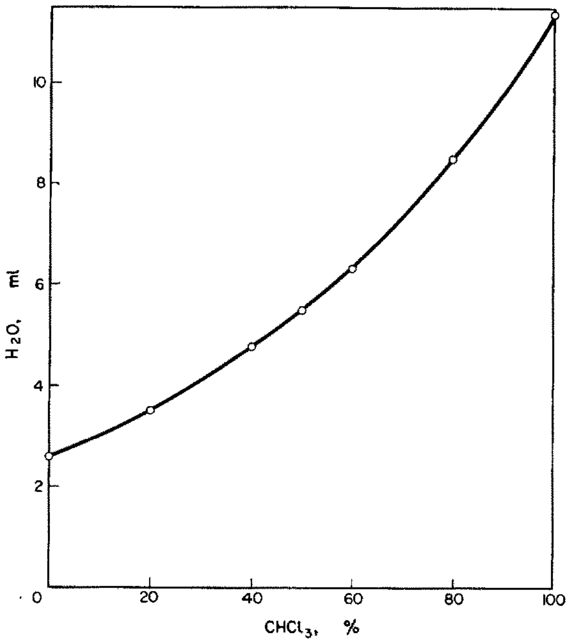

FIG. 4.—Type B solubility curve for the system carbon tetrachloride–chloroform. The horizontal axis represents the % chloroform before addition of ethanol.

the vertical line segment with the Type A solubility curves gives the upper and lower limits of the Type B solubility curve, *i.e.*, 0% and 100%. The greater the separation of the Type A solubility curves, the greater will be the slope of the Type B solubility curve and the greater will be the accuracy of any determination which depends on it.

The separation of the Type A solubility curves depends on the following factors:

The nature of the immiscible component is of prime importance.

The amount of miscible component added determines the position of the vertical line in Fig. 2. Sometimes advantage can be taken of flat portions and bulges in the Type A solubility curves to achieve a wider separation. Generally, the Type A solubility curves converge as they approach the horizontal axis, so that a wider separation is achieved at higher proportions of the miscible component. On the other hand, the end-point is usually sharper at lower proportions of the miscible component. There is an optimum proportion of miscible component which best satisfies both of these conditions.

Shifting the position of the vertical line in Fig. 2 also determines the size of the titre. It is generally best placed so that the limits of the Type B solubility curve are about 1 and 12 ml.

Doubling the sample size doubles each titre and doubles the separation of the Type A curves. Thus, advantage can be taken, by appropriate increase in the sample size, of subtle differences in the solubility characteristics of the substances titrated.

There are exceptions to this rule, but inspection of over one hundred Type A solubility curves showed that the miscible component has little effect on the separation of the curves. Factors of availability and price were most important in determining the choice of the miscible component, and we expect that a change in the miscible component in the systems reported in Table II would have little effect on the results.

Bogin[1] has suggested, but not carried out, the application of this principle to analogous systems in which the ratio of two completely water-miscible components can be determined by phase titration with water in the presence of a constant amount of a water-immiscible or slightly water-miscible component. He suggests that ethanol–propanol mixtures can be titrated with water in the presence of a constant amount of butanol. Bogin has also devised a method for the titration of chemically similar components using as the titrant, not water, but binary and even ternary solutions in which one of the components is water. Such a method involves titration surfaces like the one shown in Fig. 3, but is less easily visualised because the addition of titrant causes a variation in two or even three of the composition variables. The selection of the composition of the mixed solvent titrant was empirical. The disadvantages involved in the use of a mixed-solvent titrant, which must be exactly the same in composition from one titration to the next, as contrasted to water, which never need be standardised, are discussed by Bogin.

EXPERIMENTAL

Reagents

Reagent-grade carbon tetrachloride and benzene were obtained from E. Merck A. G., Darmstadt. Reagent-grade aniline and xylene were obtained from Mallinckrodt Chemical Works, New York and reagent-grade nitrobenzene from Fischer Scientific Co., Fair Lawn, N.J. Technical methyl aniline was obtained from Amend Drug and Chemical Co., New York, and practical-grade cyclohexane from Eastman Organic Chemicals, Rochester, N.Y.

TABLE I.—RESULTS FOR THE TITRATION OF 27 HOMOGENEOUS BINARY SYSTEMS WITH WATER,
The end-point was indicated by the appearance of a distinct permanent turbidity.

Sample	Optimum range, %	Number of titrations	Average error, *absolute* %
Dichloromethane-methanol	13–50	9	0·21
Dichloromethane-ethanol	15–50	12	0·19
Dichloromethane-isopropanol	17–38	6	0·23
Dichloromethane-dioxan	7–22	12	0·19
Dichloromethane-acetone	6–20	10	0·22
Dichloromethane-acetic acid	15–50	14	0·23
Cyclohexane-methanol	1–10	12	0·10
Cyclohexane-ethanol	1–20	12	0·06
Cyclohexane-isopropanol	5–45	12	0·04
Cyclohexane-dioxan	1–15	12	0·13
Cyclohexane–acetone	1–25	12	0·03
Cyclohexane–acetic acid	1–7	12	0·05
Allyl bromide-methanol	4–35	12	0·01
Allyl bromide-ethanol	5–40	15	0·05
Allyl bromide-isopropanol	10–45	12	0·08
Allyl bromide-dioxan	4–25	12	0·07
Allyl bromide-acetone	3–20	12	0·09
Allyl bromide-acetic acid	5–30	12	0·22
Benzene-dioxan	3–20	12	0·05
Benzene-acetone	4–25	12	0·05
Benzene-acetic acid	5–30	12	0·06
Toluene-dioxan	2–20	12	0·04
Toluene-acetone	3–23	12	0·16
Toluene-acetic acid	2–25	12	0·06
Xylene-dioxan	1–20	6	0·09
Xylene-acetone	2–25	12	0·04
Xylene-acetic acid	2–20	12	0·11

Chemicals of unspecified grade were toluene and dichloromethane (density 1·322–1·324) from E. Merck; and allyl bromide (3-bromopropene, b.p. 70–71°, lot no. 370220) from Matheson Coleman and Bell, New Jersey. All other reagents have been described elsewhere, and their sources given.[6]

Sampling procedure

Aliquot portion method: An appropriate volume of the water-insoluble or least water-soluble component was pipetted into a 50-ml volumetric flask and diluted to the mark with the water-soluble or most water-soluble component. For example, in Table I, cyclohexane was diluted to the mark with methanol; and in Table II carbon tetrachloride was diluted to the mark with chloroform. Aliquot portions (10 ml unless otherwise noted) were withdrawn for titration with water. The first was arbitrarily taken as a point on the calibration curve and the remaining three were taken as synthetic unknowns.

TABLE II.—RESULTS FOR THE TITRATION OF 5 HOMOGENEOUS BINARY SYSTEMS WITH WATER
A soluble component was added to each before titration

Sample	Soluble component added	Sample taken, *ml*	Soluble component added, *ml*	No. of titrations	Average error, *absolute* %
Methylaniline–aniline	Ethanol	10	10	12	0·16
Carbon tetrachloride–chloroform	Acetic acid	10	25	10	0·65
n-Butyl bromide–n-butyl acetate	Ethanol	10	15	10	1·0
n-Butyl bromide–n-butyl acetate	Ethanol	10	15	9	0·32
Nitrobenzene-aniline	Ethanol	10	10	12	0·43
Cyclohexane-benzene	90% ethanol 10% water	3	25	15	1·1
Cyclohexane-benzene	Ethanol	5	25	15	0·59

Individual portion method: An appropriate volume of each component was measured into a titration vessel. The volume percentage of the least soluble component was calculated, disregarding volume changes caused by mixing. Alternatively, weight percentages could have been used. After constructing the calibration curve, synthetic unknowns were prepared by the same method and determined by comparison. Compositions of the synthetic unknowns were, in most cases, different from the solutions used to construct the calibration curve.

Titration procedure

The results in Table I were obtained as described in the first paper of this series.[3]

The data in Table II were obtained by placing 3–10 ml of the unknown binary solution in a beaker and diluting with 10–25 ml of a liquid miscible with water and both components of the solution to be analysed. The amount of each liquid used, and the miscible component chosen are given in Table II. The criteria for the choice of the miscible component are maximum separation of the Type A solubility curves and a sharp end-point. The criteria for choosing the amount of miscible component are similar: maximum separation of the solubility curves consistent with a good end-point and a convenient titre. The criteria for good end-points have been discussed elsewhere.[4]

The ternary solution so obtained is then titrated with water. The behaviour of the solution during titration and the end-point is in all respects similar to the phase titration of binary solutions with water. A Type B solubility curve is constructed from known samples, and synthetic unknowns are determined by comparison.

Calculations

The calculations are straightforward, except that in the single sample method, if the final volume of all the samples is not the same, they must be normalised to one another. Thus, if one sample is made up by adding 2 ml of one component to 10 ml of the other, and if the second sample is made up by adding 3 ml to 10 ml. the titres could be normalised by multiplying the second by 12/13.

RESULTS AND DISCUSSION

Table I shows the results of the titration of 27 binary systems containing one water-miscible component. All end-points are fair to good except cyclohexane-acetic acid and allyl bromide-acetone. Even those titrations with fair or poor end-points gave small errors because the calibration curves are steep in the optimum titration range.

Table II shows the results for 5 binary systems both components of which are insoluble in water. The maximum titre was 10–15 ml, and the separation of the 0% and 100% titres was about 10 ml. The two series of determinations on the system n-butyl bromide–n-butyl acetate only differed in that the first was by the single sample method and the second by the aliquot portion method. A mixed solvent was added to the first of the cyclohexane-benzene systems to bring the titre into a more convenient range. All end-points were good to excellent with the exception of the first cyclohexane-benzene system, which was fair to poor. All systems in Table II showed a gradual opalescence followed by a sharp turbidity. This effect has been discussed before[6] but was much more noticeable in the systems given in Table II than in any other systems we have studied. The end-point is similar to, but not identical with, the end-point of a 100% sample of the less soluble of the two components. All calibration curves increased in slope with increasing titre, as shown in Fig. 3.

Errors

Of the systems given in Table I, those in which dichloromethane is one of the components were done by the single sample method, and the others were done by the aliquot portion method. The error reported for the latter may be called titration error, and largely results from uncertainty in the end-point. The error reported for the dichloromethane systems is the sum of the titration error, the errors arising from sample mixing and measurement and the errors resulting from interpolation between points on the calibration curve. In principle, these sources of error can be reduced to any desired level by more sophisticated measuring techniques and more points on the calibration curve. The two systems containing n-butyl bromide in Table II have the same relationship as that described above.

If many points are to be taken on the calibration curve, it may become tedious to construct a new curve each time there is an appreciable temperature change. The use of a constant-temperature room has the advantage in convenience over the use of a thermostatted bath. Even though heat of mixing causes temperature fluctuations, these effects will cancel between the unknown and the calibration curve (all other factors being constant). Sensitivity to temperature change varies considerably from one system to another.

The last two series in Table II show the effect of curve separation and end-point quality on accuracy.

In the penultimate determination, the difference in titres was about 11 ml, but in order to achieve that separation the composition line intersected the Type A solubility curves where they were very steep. We have seen[4] that most systems have the best end-point on the flat of their Type A solubility curves.

The final entry in Table II shows the same determination at a lower relative ethanol concentration. The difference between maximum and minimum titres has been reduced to 9·5 ml but the end-point has been improved and the error considerably reduced.

Acknowledgment—The authors gratefully acknowledge a grant by the Society of Sigma Xi in support of this research. We thank Tuğrul Yasar for help with the calculations.

Zusammenfassung—Ergebnisse der Phasentitration 27 neuer binärer Lösungen mit den wasserunlöslichen Komponenten Dichlormethan, Cyclohexan, Allylbromid, Benzol, Toluol und Xylol und den wasserlöslichen Komponenten Methanol, Äthanol, Isopropanol, Dioxan, Aceton und Essigsäure werden angegeben. Eine neue Methode für die Phasentitration binärer Lösungen chemisch ähnlicher Flüssigkeiten wird beschrieben. Ergebnisse werden für die Phasentitration binärer Lösungen der chemisch ähnlichen Flüssigkeitspaare Methylanilin-Anilin, Nitrobenzol-Anilin, Tetrachlorkohlenstoff-Chloroform, n-Butylbromid-n-Butylacetat und Cyclohexan-Benzol angegeben. Verfahren zur Probenahme und Fehlerquellen werden diskutiert.

Résumé—On donne les résultats de la détermination de la composition des phases de 27 nouveaux mélanges binaires de liquides non miscibles à l'eau: dichlorométhane, cyclohexane, bromure d'allyle, benzène, toluène et xylène combinés à des liquides miscibles à l'eau: méthanol éthanol, isopropanol, dioxanne, acétone et acide acétique. Une nouvelle méthode pour la détermination de la composition des phases de mélanges binaires de liquides qui sont chimiquement analogues est décrite. On donne les résultats de la détermination de la composition des phases de mélanges binaires de liquides chimiquement analogues: méthylaniline-aniline, nitrobenzène-aniline, tétrachlorure de carbone-chloroforme, bromure de n-butyle-acétate de n-butyle et cyclohexane-benzène. Les méthodes d'échantillonnage et les causes d'erreur sont discutées.

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LE TITRAGE ENTHALPIMETRIQUE DE QUELQUES REACTIFS ORGANIQUES SOUFRES UTILISES EN CHIMIE ANALYTIQUE

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Résumé—Dans le présent travail on a appliqué la méthode de titrage enthalpimétrique de deux réactifs organiques soufres, le 2-mercapto-5-anilino-1,3,4-thiodiazol et l'allylmonoamide de l'acide hydrazin-*N,N'*-bisthiocarbonique, qui ont un caractère très faiblement acide. On a appliqué une technique manuelle discontinue, et dans le cas de l'allyl-monoamide de l'acide hydrazin-*N,N'*-bisthiocarbonique on a procédé à une transformation des coordonnées droites en coordonnées obliques, afin d'écarter l'influence des processus secondaires sur l'effet thermique de la réaction de neutralisation. A partir des données expérimentales on a calculé aussi les chaleurs de neutralisation de ces réactifs par l'hydroxyde de sodium.

PRINCIPE DE LA MÉTHODE

TOUTE réaction chimique est accompagnée d'une variation de l'enthalpie du système, ainsi que l'attestent les effects thermiques qui ont lieu pendant la réaction. De ce fait, des renseignements précieux peuvent être obtenus sur une réaction chimique par la connaisance des échanges thermiques au cours de la réaction.

La méthode de titrage enthalpimétrique a été l'objet de modifications, tant en ce qui concerne la dénomination que la technique de travail. A l'origine, cette méthode était nommée "titrage thermique" ou "titrage thermométrique" et la quantité de chaleur dégagée était déterminée calorimétriquement.[1]

La détermination calorimétrique de la quantité de chaleur dégagée au cours d'une réaction chimique implique certaines difficultés. Dutoit et Grobet[2] ont remplacé la détermination calorimétrique de la quantité de chaleur par la mesure des variations de température. Par ailleurs, par la différence de titrage potentiométrique, on évalue l'énergie libre au moyen de la réaction:

$$\Delta F = -\varepsilon z Fy$$

(ε = f.e.m. de la pile, z = nombre d'équivalents qui participent au transport du courant électrique, Fy = constante de Faraday).[3]

Les titrages enthalpimétriques mettent en évidence d'une part l'énergie libre et d'autre part l'entropie du système, en vertu de la relation:

$$\Delta H = \Delta F + T\Delta S$$

(ΔH = variation de l'enthalpie, respectivement du contenu calorique, ΔF =variation de l'énergie libre, ΔS = variation de l'entropie, T = température absolue).

Il en résulte avec évidence pourquoi la notion de "titrage thermique" ou de "titrage thérmométrique" a été remplacée par celle de "titrage enthalpimétrique". En outre, cette notion rend mieux compte de la méthode.

TECHNIQUE DE TRAVAIL

Ainsi que nous le signalions, la technique de travail a subi elle aussi des modifications au long des années. C'est ainsi que de la détermination calorimétrique de la quantité de chaleur on est passé à la détermination de la variation de température. Cela est réalisable soit à l'aide d'un thermomètre différentiel Beckmann, soit d'un thermistor.

Il importe que ces titrages soient effectués dans des vases thermiquement isolés—Dewar—, avec des dispositifs de titrage également isolés, que l'on ajoute des quantités égales de réactif à des intervalles de temps égaux et que l'on mesure la température avec toute la précision possible. On représente graphiquement la variation de température, en fonction des ml. de réactif additionnés, tandis que la courbe obtenue représente le titrage enthalpimétrique, dans le processus donné.

Dans les installations modernes, réalisées par certains chercheurs,[4,5] on effectue les titrages enthalpimétriques à l'aide de burettes à écoulement constant, tandis que la variation de la température est enregistrée par un thermistor et la courbe de titrage se trace avec un enregistreur potentiométrique.

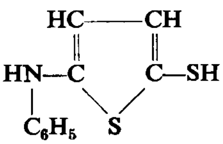
La technique utilisée par nous a été la suivante: un vase Dewar, isolé lui aussi par précaution, une burette Schelbach de grande précision introduite dans un manchon de verre, afin de réaliser l'isolation thermique par la couche d'air formée de la sorte, un thermomètre Beckmann, et pour l'agitation continue et constante un agitateur électromagnétique du type I.O.R. (R.P.R.). Pour la lecture des millièmes de degré nous avons utilisé une loupe. Avant la détermination on vérifie les températures des solutions contenues dans la burette et le vase Dewar à l'aide d'un thermomètre décimal. La différence entre les températures de la solution à titrer et la solution titrante ne doit pas être plus grande que 0,3°C. La pointe de la burette doit être effilée et isolée, et elle s'introduit dans le vase Dewar par un bouchon en liège, tout comme le thermomètre Beckmann.

Les déterminations doivent être faites dans une pièce où les variations de température soient minimales; les solutions y sont abandonnées pendant une heure environ pour permettre l'équilibre de la température avec celle du milieu ambiant.

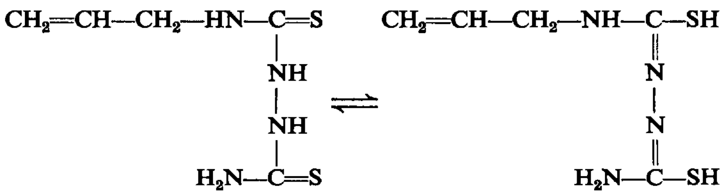
APPLICATION DE LA MÉTHODE

Cette méthode physico-chimique peut être appliquée à l'étude de beaucoup de réactions chimiques, parmi lesquelles nous signalons: la neutralisation des acides polybasiques, le déplacement des acides faibles de leurs sels avec des bases fortes, la précipitation des hydroxydes métalliques, la formation des hydroxydes amphotères, la formation des sels basiques, diverses précipitations analytiques, la formation de complexes, réactions d'oxydation-réduction, sulfonations, titrages[6] ainsi le titrage de certains alcaloides.[7] Contrairement aux méthodes de volumétrie physico-chimique, conductivités électriques et sauts de potentiel, comme indicateurs, cette méthode n'est pas assez précise pour un dosage analytique.

Dans le présent travail, nous rapportons une étude enthalpimétrique de la réaction de neutralisation de quelques réactifs organiques soufrés, à savoir le 2-mercapto-5-anilino-1,3,4,-thiodiazol (I) et l'allyl-monoamide de l'acide hydrazin-*N*,*N'*-bisthiocarbonique (II), par de l'hydroxyde de sodium:



(I)



(II)

la forme cétonique la forme énolique

Cette étude vient compléter celles effectuées avec ces réactifs en vue d'élaborer de nouvelles méthodes gravimétriques rapides, colorimétriques, etc.,[8] pour le dosage des divers cations, ainsi que les recherches tendant a remplacer l'hydrogène sulfuré comme réactif analytique.

Compte tenu du fait que ces réactifs ont un caractère faiblement acide, en raison de l'influence que l'atome de soufre exerce sur l'hydrogène qui lui est lié ou qui est voisin, nous avons cru utile de proceder au titrage enthalpimétrique, afin de déceler le comportement de ces réactifs dans certaines réactions. Cela est d'autant plus utile qu'il est bien connu que l'on titre difficilement les acides très faibles par la titrimétrie habituelle. Dans le cas des acides bibasiques très faibles, le second palier de dissociation ne peut pas même être mis en évidence. Or, on verra que, par cette méthode, dans le cas de L'allyl–amide on peut mettre en évidence le deuxieme palier de dissociation. On a calculé aussi la chaleur de neutralisation dans le cas des deux réactifs.

RÉSULTATS DES EXPERIENCES

A. *Détermination de la constante enthalpimétrique de la cellule*

Avant d'effectuer un titrage enthalpimétrique, il importe de déterminer expérimentalement la constante enthalpimétrique de la cellule où l'on fait le titrage, en utilisant la relation:

$$Q = Nm \frac{\Delta H}{\Delta T_Q}$$

où:

Q = la constante enthalpimétrique de la cellule,
Nm = nombre de mols du produit formé,
$\Delta H = \Delta H^\circ = 13{\cdot}4$ kcal/mol,

ΔT_Q = la variation totale de température, à la neutralisation de 250 ml de HCl. 0·01*M* par une solution d'hydroxyde de sodium 1*M*. Pratiquement, on place dans la cellule 250 ml de HCl 0·01*M* et on titré par de l'hydroxyde de sodium 0·1*M* en ajoutant un ml. de minute en minute. Cicontre (fig. 1) est représentée la courbe de titrage enthalpimétrique de l'acide chlorhydrique par de l'hydroxyde de sodium, qui permet de déterminer la constante enthalpimétrique de la cellule de titrage.

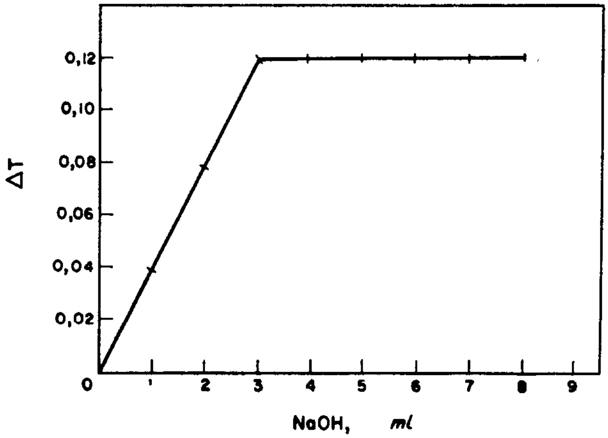


FIG. 1

Si $\Delta H = \Delta H^\circ = 13{\cdot}4$ kcal/mol, $\Delta T_Q = 0{\cdot}12$°C et $Nm = 0{\cdot}003063$, la constante enthalpimétrique a la valeur:

$$Q = Nm \frac{\Delta H}{\Delta T_Q} = 0{\cdot}003063 \frac{13{\cdot}4}{0{\cdot}12} = 0{\cdot}34205 \text{ kcal/°C.}$$

B. *Titrage enthalpimétrique du 2-mercapto-5-anilino-*1,3,4,*-thiodiazol*

Ce réactif a une fonction mercapto dont l'atome d'hydrogène peut être remplacé par des métaux. Comme nous venons de le dire, ce réactif a été employé pour le dosage pour divers cations (Ag^+, Pb^{2+}, Cu^{2+}, Hg^{2+}, Cd^{2+}, Bi^{3+}).

Ce réactif a été titré en solution *M*/334·4 par une solution 0·1*M* d'hydroxyde de sodium, en ajoutant à 300 ml de réactif, 2,5 ml d'hydroxyde de sodium par minute. Le réactif étant insoluble dans l'eau on a préparé aussi bien le réactif que l'hydroxyde en solutions alcooliques (50% alcool). Ce fait est particulièrement important parce que, lorsqu'on travaille avec une solution alcoolique de réactif et une solution aqueuse d'hydroxyde, l'effet thermique de la dilution de l'alcool est beaucoup plus grand que celui de la réaction. La courbe de titrage pour ce cas est représentée dans la fig. 2, où est consignée la variation de température ΔT, en fonction du volume de réactif ajouté. Il ressort du graphique, comme prenu que dans l'intervalle A-B la température varie de manière linéaire. Au point B, qui normalement devrait correspondre au point d'équivalence, la température demeure constante, et l'on obtient un palier horizontal parallèle à l'axe des abscisses.

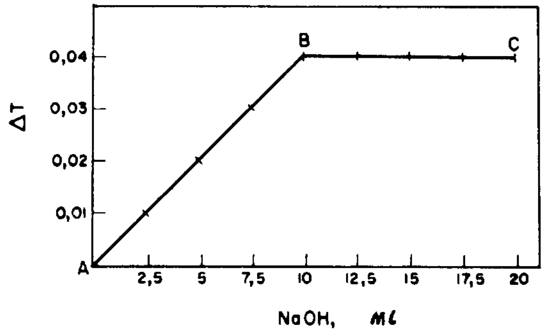


FIG. 2

Nous avons essayé d'appliquer la méthode à des dosages, mais pour de petits volumes d'hydroxide (0·5–1 ml) la variation de témperature est très petite, surtout autour du point d'équivalence, parce que ce réactif est un acide très faible.

Puisque dans ce cas ΔT = 0·04°C, Q = 0·34205 et Nm = 0·00099135, dans cette réaction la chaleur de neutralisation est:

$$\Delta H = \frac{Q}{Nm} \cdot \Delta T = \frac{0{\cdot}34205}{0{\cdot}00099135} \cdot 0{\cdot}04 = -13{\cdot}801 \text{ kcal/mol.}$$

C. *Titrage enthalpimétrique de l'allyl-monamide de l'acide hydrazin N,N'-bisthiocarbonique*

Avec ce réactif, le titrage enthalpimétrique est plus utile et plus intéressant parce que, ayant deux fonctions mercapto d'un caractère acide plus faible ($K_1 = 1{\cdot}437 \,.\, 10^{-11}$), la méthode offre la possibilité de mettre en évidence le second palier de dissociation.

Dans ce cas aussi nous avons travaillé avec des solutions alcooliques (50% alcool) de réactif et d'hydroxyde en plaçant dans la cellule 200 ml de réactif *M*/29·996, et ajoutant de minute en minute 2 ml NaOH env. 1*M*.

La courbe de titrage est consignée dans la fig. 3, où on a representé graphiquement les variations de température au cours du titrage (ΔT) en fonction du volume d'hydroxyde de sodium ajouté. Il ressort du graphique que la température varie de manière

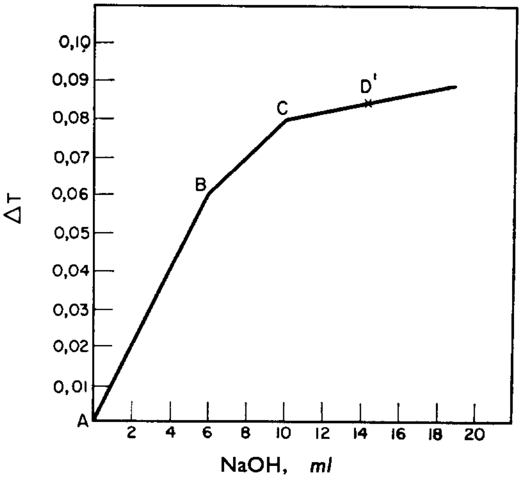


Fig. 3

linéaire dans l'intervalle A-B. Cette portion de la courbe correspond à la neutralisation du premier atome d'hydrogène. A partir du point B, la pente de la courbe se modifie brusquement, la température variant également de manière linéaire sur la portion B-C, qui correspond en réalité au titrage du deuxième atome d'hydrogène. A partir du point C, la pente de la courbe se modifie de nouveau, la température variant de manière linéaire lorsqu'on ajoute l'excès d'hydroxyde.

Afin d'écatrer l'effet thermique qui résulte du mélange de deux liquides à des température relativement différentes, un système de coordonnées obliques, *ayant les niveaux en* ordonnée inclinés avec la pente a été adojté:

$$p = \frac{\Delta T}{\Delta n}.$$

La courbe de titrage transposée sur les nouvelles coordonnées est représentée fig. 4. On remarque que cette représentation met en évidence seulement la variation de température déterminée par le procès de neutralisation, en éliminant l'influence des

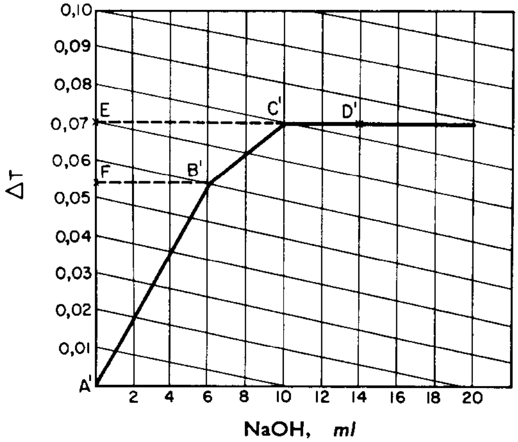


Fig. 4

phénomènes secondaires. Ce fait ressort avec évidence lorsqu'on prolonge le segment C'D' et que l'on trace une parallèle à l'abscisse par B', ce qui détermine sur l'ordonnée les points E et F correspondant à la variation de température due uniquement au processus de neutralisation.

On passe aux coordonnées obliques à l'aide des équations de transformation suivantes:

$$Y = y - px$$

$$X = x\sqrt{1 + p^2}$$

où:

X et Y sont les coordonnées du nouveau système de représentation, x et y les coordonnées de l'ancien système, et p la pente de la dernière portion de la courbe.

Les coordonnées des points B et C dans le système de coordonnées droites sont $x_B = 6$, $y_B = 0{\cdot}06$, la pente du segment CD, $p = \frac{\Delta T}{\Delta n} = \frac{0{\cdot}04}{4} = 0{\cdot}01$, et après la transformation en coordonnées obliques, les coordonnées des points B' et C' sont:

$$X_B' = 6\sqrt{1 + 0{\cdot}0001} = 6\varepsilon$$

$$Y_B' = 0{\cdot}060 - 0{\cdot}006 = 0{\cdot}054$$

$$X_C' = 10\sqrt{1 + 0{\cdot}0001} = 10\varepsilon$$

$$Y_C' = 0{\cdot}08 - 0{\cdot}01 = 0{\cdot}07.$$

Etant donné que l'accroissement ε a de X_B, et X_C, par la transposition en coordonnées obliques est très petit on le néglige, de sorte que ces coordonnées restent pratiquement les mêmes; en revanche, la diminution de Y_B, et Y_C, est sensible.

En ce qui concerne la chaleur de neutralisation, on la calcule comme dans le cas du titrage du 2-mercapto-5-anilino-1,3,4-thiodiazol au moyen de la relation:

$$\Delta H = \frac{Q}{Nm} . \Delta T .$$

Compte tenu du fait que la valeur de la constante enthalpimétrique de la cellule est $Q = 0{\cdot}34205$, $\Delta T_1 = 0{\cdot}054$, $\Delta T_2 = T - T_1 = 0{\cdot}07 - 0{\cdot}054 = 0{\cdot}016$ et que $Nm_1 = Nm_2 = 0{\cdot}00337$, les valeurs des chaleurs de neutralisation pour les deux paliers de la réaction sont:

$$\Delta H_1 = -5{\cdot}5403 \text{ kcal/mol}$$

$$\Delta H_2 = -1{\cdot}6417 \text{ kcal/mol}$$

CONCLUSIONS

1. Le titrage enthalpimétrique du 2-mercapto-5-anilino-1,3,4-thiodiazol et de l'allyl-monoamide de l'acide hydrazin-*N*,*N'*-bisthiocarbonique par de l'hydroxyde de sodium démontre l'allure des réactions de neutralisation, et dans le cas du dernier réactif permet de mettre en évidence le second palier de dissociation (par la transposition de la courbe en coordonnées obliques).

2. La méthode permet de calculer les chaleurs de neutralisation dans le cas des deux réactifs, après la détermination préalable de la constante enthalpimétrique de la cellule.

3. En dépit des essais que nous avons faits, la méthode n'a pas pu être utilisée pour des déterminations quantitatives; Nous pensons néanmoins y parvenir en modifiant la technique de travail.

4. Ce travail constitue le commencement d'une étude physico-chimique de ces réactifs qui ont été étudies et utilisés à des fins analytique. Nous aurons en vue, par suite, d'etudier le problème de la structure des combinations que ces réactifs forment avec les cations lourds.

5. En ce qui concerne l'établissement des équations de transformation en coordonnées obliques, les auteurs ont joui de l'aide précieuse que leur a accordée l'Institut de calcul de L'Académie de la R.P.R. Cluj, auquel ils adressent par cette voie leurs plus vifs remerciements.

Summary—Enthalpimetric titration has been applied to two organic sulphur compounds, 2-mercapto-5-anilino-1,3,4-thiodiazol and hydrazine-*N*,*N*′-bisthiocarbonic acid allyl-monoamide, which are weakly acidic. A discontinuous manual technique has been used, and in the case of the allyl-monoamide a transformation from rectangular to oblique co-ordinates allows for the influence of secondary processes on the thermal effect of the process of neutralisation. From the experimental results the heats of neutralisation of the compounds with sodium hydroxide have also been calculated.

Zusammenfassung—Die enthalpimetrische Titration wurde auf zwei schwach saure organische Schwefelverbindungen, 2-Mercapto-5-anilino-1,3,4-thiodiazol und Hydrazin-*N*,*N*′-bisthiocarbonsäure-allyl monoamid, angewandt. Es wurde mit diskontinuierlichem Handbetrieb gearbeitet. Im Falle des Allylmonoamids wird dem Einfluß von Sekundärprozessen auf den thermischen Effekt der Neutralisation durch Übergang von rechtwinkligen auf schiefwinklige Koordinaten Rechnung getragen. Aus den Versuchsergebnissen wurden auch die Neutralisationswärmen der Verbindungen mit Natriumhydroxyd berechnet.

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ANION-EXCHANGE BEHAVIOUR OF URANIUM AND OTHER ELEMENTS IN THE PRESENCE OF ALIPHATIC DI- AND TRICARBOXYLIC ACIDS

METHOD FOR THE SEPARATION OF URANIUM FROM THORIUM AND RARE EARTHS

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Summary—The exchange behaviour of uranium, thorium, the rare earths and some other elements towards the strongly basic anion exchanger Dowex 1 in aqueous and methanolic systems containing di- or tricarboxylic acids is described. Based on the measurement of the distribution coefficients in such media a method for the separation of uranium from thorium and the rare earths in an aqueous solution containing malonic acid has been developed.

INTRODUCTION

Investigations carried out by Zaki and Shakir[1] have shown that uranium can be separated from other elements on an anion exchanger by using buffered solutions of oxalic, succinic or adipic acid. Uranium, thorium and zirconium, as well as other elements, form with these acids negatively charged complexes which are strongly retained by the exchange resin.[1-3] Several other authors have also reported on the adsorption behaviour of uranium and various other elements from solutions containing organic acids, such as acetic[4-6] and ascorbic acid.[7-9]

Previous research work dealing with the anion-exchange behaviour of uranium and other elements in organic acid-organic solvent mixtures[10] showed that in such media many separation possibilities for uranium could be uncovered. For this reason we have now investigated the behaviour of some elements in the presence of polyfunctional organic acids, especially the homologous dicarboxylic acids of the aliphatic series.

EXPERIMENTAL

Reagents

Ion-exchange resin. The strongly basic anion exchanger Dowex 1, ×8 (100–200 mesh, chloride form) was used. For the equilibrium and separation experiments in the various media the corresponding organic acid forms of this resin were employed. The preparation of these forms was performed according to the directions previously given for the monocarboxylic acid forms.[10]

Standard solutions of uranium and other elements. Hydrochloric or nitric acid solutions of the chlorides or nitrates of precisely known element content were employed. For each experiment an aliquot corresponding to the desired amount of the element to be investigated was evaporated to dryness on a water bath. To the residue thus obtained, first the solid organic acid and then the solvent was added.

Organic acids and solvent. The following reagent-grade acids were employed: oxalic, malonic, succinic, glutaric, *d,l*-tartaric and citric. The methanol employed was also of reagent-grade purity.

Apparatus

The column operations were carried out in columns of the same type and dimensions as described earlier.[7] For the fluorimetric determination of uranium a Galvanek Morrison Mark V fluorimeter and for the spectrophotometric determination of the other elements a Beckman Model B spectrophotometer was employed.

Quantitative determination of elements investigated

The determination of uranium was performed fluorimetrically,[11] and that of thorium and the rare earths spectrophotometrically by employing the azo dye Solochromate Fast Red.[12,13] The other elements were determined quantitatively using photometric methods recommended by Sandell.[14]

Determination of distribution coefficients

The distribution coefficients of all elements were determined in the same manner as has earlier been described for the equilibrium experiments in mineral acid-organic solvent[15] and organic acid-organic solvent[10] mixtures. Twenty ml of solvent, containing a certain amount of the acid and 5 mg of the element in question, were equilibrated with 1 g of the resin. The results of the experiments shown in Figs. 1 and 2 were obtained by using varying amounts of acid whereas those recorded in Fig. 3 and in Table I were always performed in the presence of 1 g of acid.

Column operations

All separation experiments on resin columns were performed by employing the following working procedure.

Pretreatment of resin bed. In order to transform the chloride form of the resin into the malonate form the resin bed was treated with a 10% aqueous malonic acid solution which had been buffered to a pH of approximately 5 to 6 with aqueous ammonia. As soon as the effluent was free from chloride ions (which was usually the case after the passage of less than 50 ml of this solution), the resin was washed with 50 ml of a solution (washing solution) containing 50 g of malonic acid/1,000 ml of distilled water.

Adsorption of uranium. The sorption solution was prepared by dissolving the residue obtained by evaporation of certain amounts of the standard solutions of the elements in question, first by adding 5 g of malonic acid to the dry residue, followed by 100 ml of distilled water. This solution was passed through the column at a flow rate of 0·5–0·75 ml/min. During this operation uranium was strongly adsorbed whereas the other elements, *i.e.*, thorium, cerium and gadolinium, passed into the effluent.

Washing process. In order to remove the last traces of the other elements the resin bed was washed with 50 ml of the washing solution.

Elution. The uranium was eluted with 100 ml of 1*M* hydrochloric acid.

Further treatment of eluate and effluent. After evaporation of the eluate to dryness (water bath) the uranium was determined as previously described.[16] During this process as well as when evaporating the effluent, malonic acid was decarboxylated, whereby acetic acid was formed, so that very little organic matter was present in the residue. In the residues obtained after evaporation of the effluents, thorium and the rare earths were determined by previously described procedures.[12,13]

The results of a series of such column separations are recorded in Table II.

RESULTS

Effect of acid concentration on distribution coefficients of uranium and thorium

In Figs. 1 and 2 the results of the experiments performed in aqueous and methanolic solutions containing varying amounts of the organic acids are recorded.

Although the adsorption of uranium from oxalic acid solutions is higher than from all mixtures containing other acids, it did not seem practical to use this acid for further investigations because its solubility in water is rather low; furthermore, it forms insoluble precipitates with thorium, the rare earths and other elements in aqueous as well as in methanolic media. In malonic acid mixtures, however, both these adverse effects are not observed so that this acid was employed for the separation of uranium, thorium and rare earths on ion-exchange columns.

By comparing Fig. 1 with Fig. 2 it can clearly be seen that the difference existing between the adsorption of uranium in aqueous and methanolic solutions is rather large (especially at a higher acid concentration) in comparison with that of thorium, which shows in both solvents a practically identical adsorption behaviour. Besides,

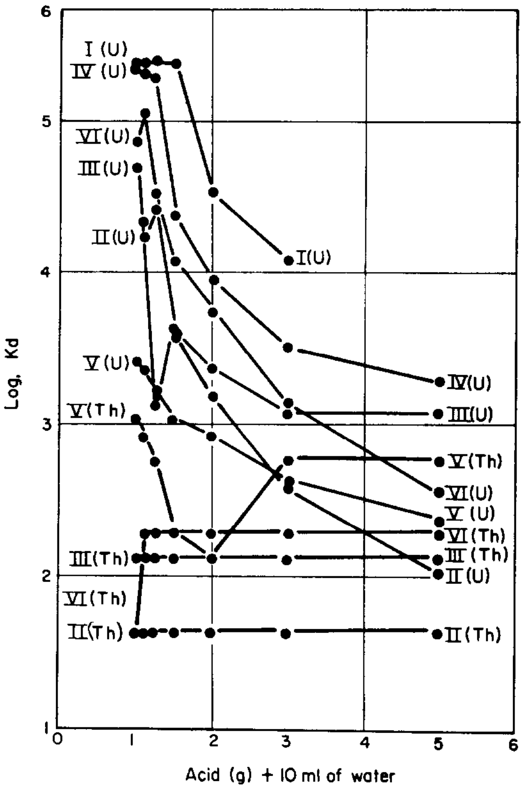

FIG. 1.—Adsorption of uranium and thorium from aqueous solutions containing di- and tricarboxylic acids:

I—oxalic acid, IV—glutaric acid,
II—malonic acid, V—tartaric acid,
III—succinic acid, VI—citric acid.

its solubility in methanolic solutions is rather limited. That is why in Fig. 2 only two curves for thorium could be established. Several experiments in other solvents, *e.g.*, ethanol, n-propanol, acetone, *etc.*, with some of the acids have shown that the adsorption of uranium from tartaric and citric acid media did not deviate appreciably from the results obtained in methanolic solutions, whereas in the presence of the other acids a decrease of uranium adsorption with increasing chain length of the alcohols could be observed[15] in the case of oxalic acid. Because of the low solubility of the acids, however, no systematic investigations as to the adsorption of uranium or other elements were conducted in solvents other than water and methanol.

Effect of water-methanol concentration

In Fig. 3 the variation of the distribution coefficients of uranium at different water to methanol ratios is shown. From the results it is seen that the Kd of uranium in the dicarboxylic acid-methanol-water mixtures does not vary as much with increasing percentage of methanol as in tartaric and citric acid media, where a sharp decline of the Kd occurs when increasing the methanol content of the mixtures from 80 to 100%. This is because the hydrophilic hydroxyl groups of these acids gradually lose their complex-forming tendencies by a decrease in the water content of the mixtures. In

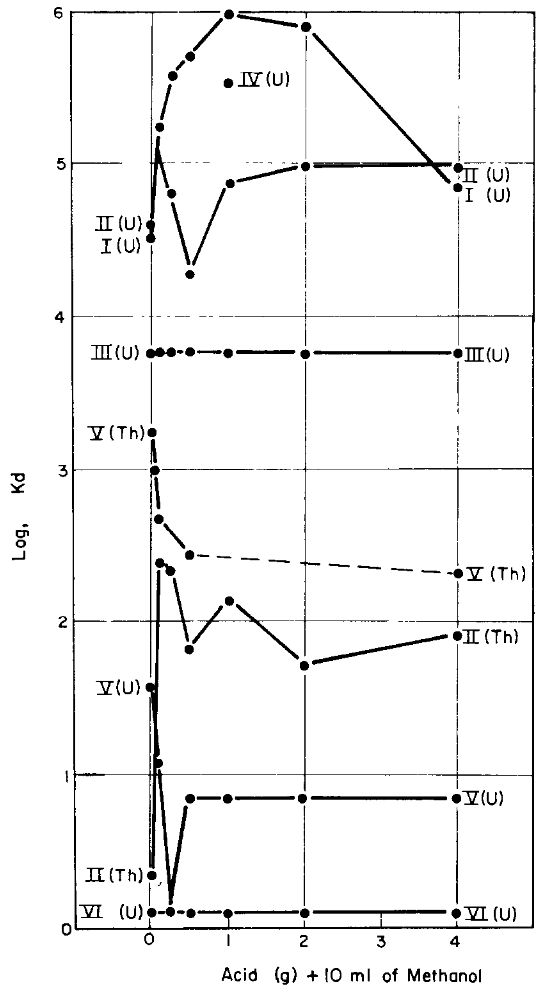

Fig. 2.—Adsorption of uranium and thorium from methanolic solutions containing di- and tricarboxylic acids:

I—oxalic acid,	IV—glutamic acid,
II—malonic acid,	V—tartaric acid,
III—succinic acid,	VI—citric acid,

- - - - region of insolubility.

the case of the dicarboxylic acids without hydroxyl groups, however, the adsorption of uranium in 100% aqueous solutions of the acids is less than in 100% methanol solutions of the acids, so that in the presence of these acids an increase of the methanol concentration increases the uranium adsorption.

Adsorption behaviour of other elements

In Table I the distribution coefficients of a series of other elements in aqueous and methanolic media containing malonic, succinic, glutaric, tartaric and citric acid are recorded.

For comparison purposes the distribution coefficients of uranium and thorium in the various media have also been included in this table.

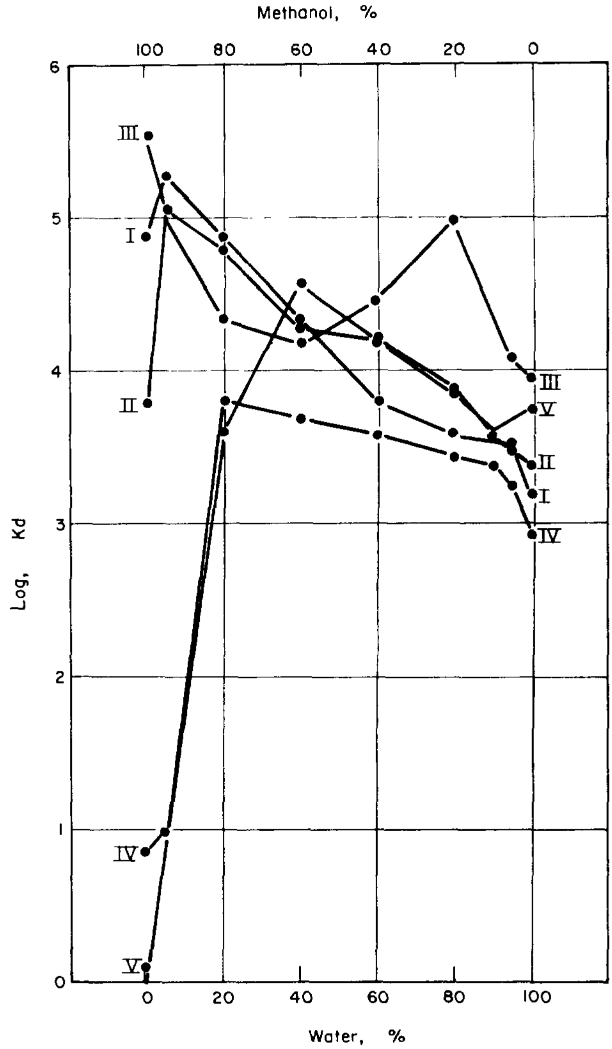

Fig. 3.—Effect of water-methanol concentration on uranium adsorption:
I—malonic acid, III—glutaric acid,
II—succinic acid, IV—tartaric acid,
V—citric acid.

From the results it is seen that malonic acid in methanol is superior to the other di- and tricarboxylic acids in-so-far as it shows the greatest solubility and sufficient acid strength to keep most of the investigated elements in solution without forming precipitates or causing hydrolysis. In aqueous solutions, however, all of the acids can be employed for the adsorption of uranium with nearly equal effect, irrespective of their chemical constitution. For the purpose of separating uranium from thorium and other elements (with the exception of iron, which could easily be separated from uranium in a water-succinic acid medium), the use of malonic acid seemed to be advantageous because most of the elements, except for iron and yttrium, show rather low distribution coefficients in aqueous malonic acid solutions.

TABLE I.—DISTRIBUTION COEFFICIENTS OF VARIOUS ELEMENTS

Element	Acid	Solvent	
		Water	Methanol
UO_2^{2+}	Malonic acid	1,540	77,000
Th^{4+}	Malonic acid	45	142
La^{3+}	Malonic acid	12	240
Ce^{3+}	Malonic acid	33	1,470
Pr^{3+}	Malonic acid	1·0	×
Nd^{3+}	Malonic acid	1·0	270
Sm^{3+}	Malonic acid	0·1	670
Eu^{3+}	Malonic acid	0·1	708
Gd^{3+}	Malonic acid	1·0	885
Tb^{3+}	Malonic acid	1·0	690
Dy^{3+}	Malonic acid	8·0	800
Ho^{3+}	Malonic acid	0·1	465
Er^{3+}	Malonic acid	1·0	550
Tm^{3+}	Malonic acid	1·0	505
Yb^{3+}	Malonic acid	1·0	650
Lu^{3+}	Malonic acid	1·0	670
Sc^{3+}	Malonic acid	100	×
Mg^{2+}	Malonic acid	1·0	8·0
Ca^{2+}	Malonic acid	0·5	×
Sr^{2+}	Malonic acid	10·0	10·0
Zn^{2+}	Malonic acid	1·0	170
Cd^{2+}	Malonic acid	1·0	15
Al^{3+}	Malonic acid	1·0	16,660
In^{3+}	Malonic acid	1·0	1,920
Cu^{2+}	Malonic acid	6·3	435
Pb^{2+}	Malonic acid	0·1	×
Bi^{3+}	Malonic acid	33·5	490
Mn^{2+}	Malonic acid	1·0	×
Fe^{3+}	Malonic acid	324	×
Co^{2+}	Malonic acid	0·1	0·1
Ni^{2+}	Malonic acid	3·2	12·0
UO_2^{2+}	Succinic acid	2,400	6,000
Th^{4+}	Succinic acid	84	×
Ce^{3+}	Succinic acid	×	×
Gd^{3+}	Succinic acid	40	×
Cu^{2+}	Succinic acid	7·0	×
Bi^{3+}	Succinic acid	65·0	×
Fe^{3+}	Succinic acid	1·0	×
Co^{2+}	Succinic acid	0·1	0·1
Ni^{2+}	Succinic acid	6·6	6·6
UO_2^{2+}	Glutaric acid	9,500	340,000
Pb^{2+}	Glutaric acid	0·1	×
Bi^{3+}	Glutaric acid	107	×
UO_2^{2+}	Tartaric acid	1,000	7·0
Th^{4+}	Tartaric acid	147	×
Ce^{3+}	Tartaric acid	40	×
Cu^{2+}	Tartaric acid	7·0	×
Bi^{3+}	Tartaric acid	507	×
Fe^{3+}	Tartaric acid	160	×
Co^{2+}	Tartaric acid	0·1	0·1
Ni^{2+}	Tartaric acid	17·2	6·6
UO_2^{2+}	Citric acid	5,900	1·0
Th^{4+}	Citric acid	200	×

TABLE I (*Continued*)

Element	Acid	Solvent	
		Water	Methanol
Ce^{3+}	Citric acid	11·5	×
Gd^{3+}	Citric acid	815	×
Cu^{2+}	Citric acid	48·5	×
Bi^{3+}	Citric acid	×	×
Fe^{3+}	Citric acid	203	×
Co^{2+}	Citric acid	0·1	0·1
Ni^{2+}	Citric acid	1·0	1·0

× In these media completely or partially insoluble.

In methanolic solutions of this acid, on the other hand, the possibility of co-adsorbing uranium together with thorium, the rare earths and other elements exists, so that malonic acid can be regarded as a more versatile complexing agent than the other acids, the element salts of which are also poorly soluble in methanol.

Separation procedure

Based on the results presented in Figs. 1 and 2 and in Table I a method of separating uranium from thorium, cerium and gadolinium (as representatives of the rare earth elements) in an aqueous medium was developed. The experimental steps involved in this ion-exchange procedure have been described above under *Column operations*.

In Table II the results of these resin column separations are recorded. It is seen that all separations of uranium from the other elements were practically quantitative. For this reason and because the break-through capacity for uranium under these conditions (2g of resin in column 15 cm high and 0·5 cm diameter) was found to be

TABLE II.—SEPARATION OF URANIUM FROM OTHER ELEMENTS IN AQUEOUS MALONIC ACID MIXTURES*

Uranium taken, μg	Element to be separated from uranium, μg	Uranium recovered, μg	Other element recovered, μg
10,000	Th: 5,000	9,950	4,960
5,000	Th: 1,000	4,975	985
5,000	Th: 100	4,937	100
5,000	Th: 50	4,950	48
5,000	Th: 20	5,010	21
10,000	Ce: 500	9,980	492
5,000	Ce: 100	4,978	95·8
5,000	Ce: 50	4,967	50
5,000	Ce: 25	5,000	24
5,000	Ce: 10	4,986	9·5
10,000	Gd: 500	10,013	497
5,000	Gd: 100	5,000	97
5,000	Gd: 50	4,980	48
5,000	Gd: 25	4,978	27
5,000	Gd: 10	5,000	11

* Each result is the average of 3 separations performed under the same experimental conditions.

60 mg of uranium, this procedure could be employed effectively for the removal of fission products like the rare earths, strontium, *etc.*, from uranium.

By this anion-exchange method not only the separation of these elements from uranium can be accomplished but also from a series of other elements (those having sufficiently low distribution coefficients, *viz.* <50). It is, therefore, of broad applicability, unlike the method described by Zaki and Shakir[1] which has only limited use for analytical purposes.

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Zusammenfassung—Es wurde das Ionenaustauschverhalten von Uran, Thorium, der seltenen Erden und einiger anderer Elemente gegenüber dem stark basischen Anionenaustauscher Dowex 1 in wäßrigen und methanolischen Systemen die Di- oder Tricarboxylsäuren enthalten untersucht. Auf Grund von Messungen der Verteilungskoeffizienten in derartigen Medien konnte eine Methode zur Trennung des Urans von Thorium und den seltenen Erden in malonsaurer wäßriger Lösung entwickelt werden.

Résumé—On décrit l'échange de l'uranium, du thorium, des éléments de terres rares et de quelques autres éléments en présence de l'échangeur d'anions fortement basique Dowex 1 dans des systémes aqueux ou méthanoliques contenant des acides di- ou tricarboxyliques. Dével-oppement d'une méthode basée sur la mesure des coefficients de distribution dans de tels milieux, pour séparer l'uranium du thorium et des éléments des terres rares en solution aqueuse contenant de l'acide malonique.

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CHEMICAL COMPOUNDS FORMED IN THE COPRECIPITATION OF CATIONS WITH SULPHIDES

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Summary—A study of the coprecipitation of thallium with As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 and In_2S_3, and of indium with CuS and Ag_2S by physicochemical analysis has shown that the process results from formation of the following compounds: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ and $AgInS_2$. A type of coprecipitation diagram characteristic for the case of the formation of chemical compounds has been established and the fields on it, corresponding to phases of definite composition, have been delimited. The formation in the coprecipitation of microdisperse systems of "colloidal" solid solutions of one sulphide in another has been shown.

VARIOUS views have been put forward to explain the reasons for the coprecipitation of cations with sulphides.[1,2] A number of authors consider that the entrainment of cations by sulphides results from formation of chemical compounds. Feigl explains the coprecipitation by the formation of heteropolymers or mixed sulphides of the type: $Me^{I}S\text{–}SMe^{II}$.[3–5] Okač also indicates the formation of heteropolysulphides $(MeS)_x$ $(Me'S)_y$.[6] He states that x and y may in special cases correspond to the stoichiometric figures for hypothetical complex compounds of the general formula $[Me(SMe')_x]S$. According to Hawley's results, in the simultaneous precipitation of Tl_2S and SnS_2 and also of Tl_2S and As_2S_5, compounds of the composition Tl_4SnS_4 and Tl_3AsS_4 are formed.[7,8] Bruner and Zawadzki mention the compound $Tl_2S{\cdot}4CuS$, which, in their opinion, is obtained in the coprecipitation of thallium with CuS.[9] Malfatti considers that the precipitation of FeS in the presence of the alkali and the alkaline-earth metals gives thiosalts of the composition $MeFeS_2$ and $Me(FeS_2)_2$, where Me is a uni- or bivalent cation.[10] The compounds $PbS{\cdot}Tl_2S$ and $GaS{\cdot}ZnS$, formed in the coprecipitation of thallium with PbS and of gallium with ZnS, respectively, are referred to by Nanobashvili *et al.*[11,12] In the precipitation of sulphides of copper and germanium, Davydov and Diyev obtained a precipitate with a composition close to that for the compound $CuS{\cdot}GeS_2$.[13]

In the papers discussed, only individual facts indicating the formation of chemical compounds under certain conditions are given. In the majority of them, however, only hypotheses, not confirmed by direct experiments, are put forward about their formation. No investigations exist with a general approach to the solution of the question of the possibility of the formation of chemical compounds in coprecipitation.

In an investigation of the coprecipitation of thallium and indium with sulphides of the second analytical group of the classical hydrogen sulphide scheme, we found that the phenomenon was clearly expressed where the sulphides in the system possessed opposite—basic and acidic—properties. This fact gave grounds for assuming the formation of chemical compounds. Consequently, we considered it desirable to carry out investigations of the coprecipitation of cations with sulphides starting from the positions of the elements in the Periodic Table. This study of the phenomenon was carried out on the basis of physicochemical analysis.

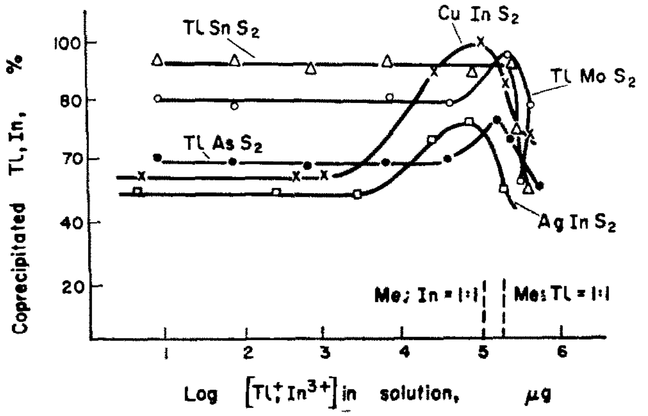

FIG. 1.—Coprecipitation diagrams of Tl with As_2S_3, SnS_2 and MoS_3, and of In with Ag_2S and CuS.

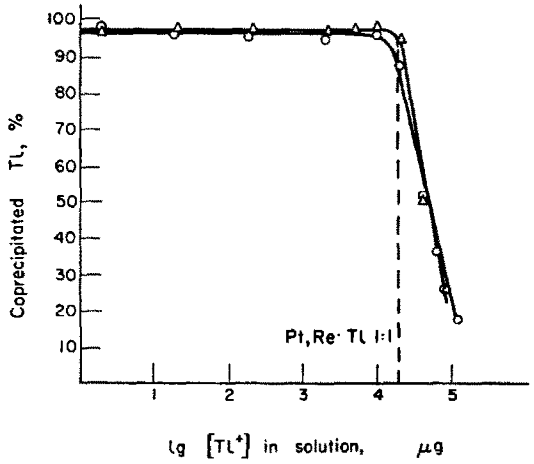

FIG. 2.—Coprecipitation diagrams of Tl with Re_2S_7 and PtS_2.

Physicochemical analysis with a constant concentration of one component and a variable concentration of the other was used. Construction of the coprecipitation diagrams was carried out by plotting as ordinates the amount of coprecipitation in per cent and as abscissae the logarithm of the concentration of the thallium or indium in the solution. The amount of coprecipitation was determined by a radioactive tracer method using the radioisotopes ^{204}Tl and ^{114}In.

EXPERIMENTAL

I. *Application of physicochemical analysis to the coprecipitation of thallium and indium with sulphide*

Below we give data on the coprecipitation in a series of systems for sulphides of the metals mentioned.

The systems Tl^+, H^+/AsO_3^{3-}, S^{2-}; Tl^+, H^+, Sn^{4+}/S^{2-}; Tl^+, H^+/MoO_4^{2-}, S^{2-}; and Tl^+, H^+/ReO_4^-, S^{2-}. From the breaks in the coprecipitation diagrams given in Figs. 1 and 2 may be deduced the formation of compounds having ratios of As, Sn, Mo and Re to Tl of 1:1.

The constancy of the distribution coefficient of thallium in the case of the coprecipitation of small concentrations of thallium is striking.*

Analysis of the compounds isolated showed that they had the following compositions: $TlSnS_2$, $TlAsS_2$, $TlMoS_3$ and $TlReS_4$.

An X-ray examination of Tl_2S, As_2S_3, SnS_2, MoS_3 and Re_2S_7, and also of $TlSnS_2$, $TlAsS_2$, $TlMoS_3$ and $TlReS_4$, gave amorphous pictures.

The systems Cu^{2+}, In^{3+}, H^+/S^{2-}; Ag^+, In^{3+}, H^+/S^{2-}. As follows from the coprecipitation diagrams given (Fig. 1), chemical compounds are also formed in these systems. The breaks in the diagrams correspond to a ratio in the precipitates of Cu or Ag to In of 1:1.

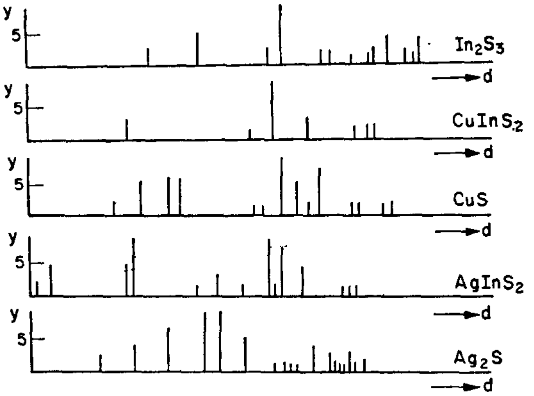

FIG. 3.—Results of calculation of the X-ray diagrams for CuS, In_2S_3, $CuInS_2$, Ag_2S and $AgInS_2$.

The behaviour of low concentrations of indium is analogous to the cases of the coprecipitation of thallium already considered.

From the results of analysis, the compositions of these compounds are as follows: $CuInS_2$ and $AgInS_2$.

X-ray investigation showed diffraction pictures for $CuInS_2$ and $AgInS_2$ different from those for the starting materials CuS, Ag_2S and In_2S_3, which is characteristic for the formation of chemical compounds (Fig. 3).

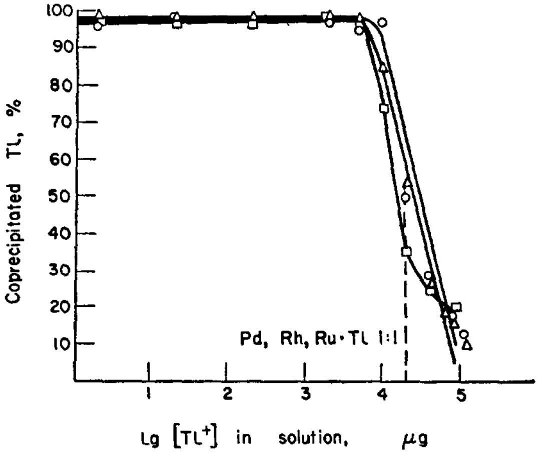

FIG. 4.—Coprecipitation diagrams of Tl with Rh_2S_3, Ru_2S_3 and PdS.

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* The distribution coefficient may be calculated from the formula $K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}$

The systems Tl^+, H^+ / Pt^{IV}, S^{2-}; Tl^+, H^+/Pd^{II}, S^{2-}; Tl^+, $H^+/Ru,^{III}$ S^{2-}; *and* Tl^+, H^+/Rh^{II}, S^{2-} Analogous results were also obtained in the coprecipitation of thallium with sulphides of the platinum metals. As can be seen from the diagrams given (Fig. 4), in contrast to those obtained previously the breaks in the curves correspond to a ratio of Pd, Ru and Rh to Tl of 2:1. In the case of the coprecipitation of Tl with PtS_2, the ratio of Tl and Pt in the compound formed is 1:1 (Fig. 2).

Analysis of the compounds obtained showed that they had the compositions: $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$ and $TlRh_2S_4$. The results of calculation of the X-ray diagrams for $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$ and $TlRh_2S_4$ are given in Fig. 5. For PtS_2, PdS, Ru_2S_3 and Rh_2S_3, amorphous X-ray pictures were obtained.

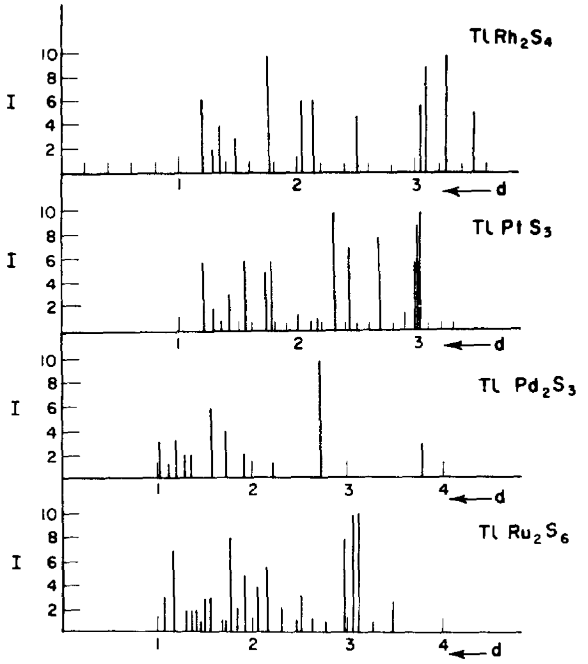

FIG. 5.—Results of the calculation of the X-ray diagrams for $TlRh_2S_4$, $TlPtS_3$, $TlPd_2S_3$ and $TlRu_2S_6$.

The systems Tl^+, H^+/Ir^{III}, S^{2-}; In^{3+}, Tl^+, H^+/S^{2-}. In a study of the coprecipitation of thallium with Ir_2S_3, a diagram somewhat different from those given above was obtained (Fig. 6). From the break in the curve, as in the diagrams given in Figs. 1, 2 and 4, it may be concluded that a compound with a Tl:Ir ratio of 1:1 is formed.

Analysis of the compound formed showed that it had the composition Tl_3Ir_3S, the unusual nature of which is striking.

The most interesting field in the diagram obtained is C, characterising a proportionality between the concentration of the cation in the solution and in the solid phase, which shows the formation of solid solutions (the distribution coefficient may be calculated from the formula $K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}$

The X-ray diagrams of Tl_3Ir_3S and Ir_2S_3 are given in Fig. 7. The difference in the position and intensity of the lines of the Tl_3Ir_3S X-ray diagram as compared with that for Ir_2S_3 confirms the formation of a chemical compound.

It follows from the results of our study of coprecipitation in the systems given above that the formation of chemical compounds is found in those cases where one of the sulphides of the given system possesses basic properties and the other acidic properties. The elements giving these compounds are located in different groups of the Periodic Table. The rule mentioned has been confirmed in many cases of the coprecipitation of thallium with sulphides of an acidic character and of indium with sulphides of a basic character. It is quite natural to assume that the coprecipitation of thallium with In_2S_3 will also lead to the formation of a chemical compound. The results obtained are given in Fig. 8. The break in the diagram corresponds to an In:Tl ratio in the precipitate of 1:0·5.

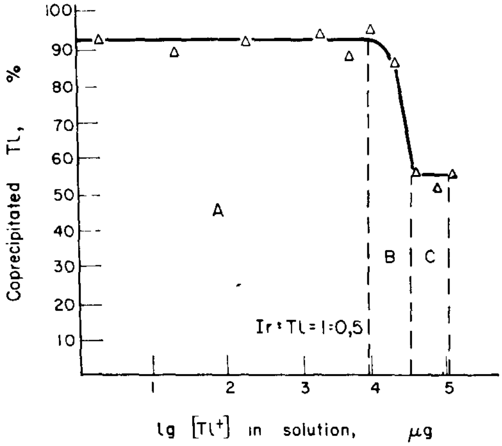

FIG. 6.—Coprecipitation diagram of Tl with Ir_2S_3.

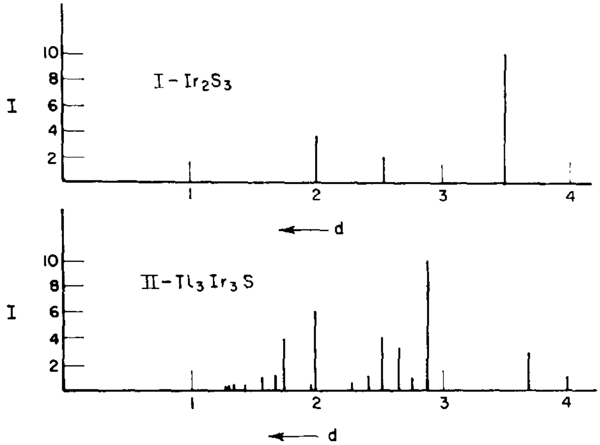

FIG. 7.—Results of the calculation of the X-ray diagrams for Tl_3Ir_3S and Ir_2S_3.

Of particular interest is the shape of the curve for ratios of In to Tl in the solution of 1:10, 1:12, 1:14 and 1:16, where there is a constant degree of coprecipitation of thallium with In_2S_3. On the diagram, this corresponds to the parallel course of the coprecipitation curve. The constancy of the distribution of thallium between the solution and the solid phase shows the formation of a solid solution of this composition with an excess of Tl_2S (field D).

Analysis of the precipitate showed that the compound obtained had the composition $TlIn_2S_3$. The X-ray diagrams of $TlIn_2S_3$ and In_2S_3 are given in Fig. 9. The difference in the position and intensity of the lines of the X-ray diagrams of $TlIn_2S_3$ and In_2S_3 is characteristic for a chemical compound.

Thus, in spite of the presence of indium and thallium in a single Sub-Group of the Periodic Table, in consequence of which the acidic—basic properties of In_2S_3 and Tl_2S differ less than for the sulphides of the elements mentioned above, the formation of a chemical compound also takes place in this case.

II. *X-ray investigation of the solid phases obtained in coprecipitation when a chemical compound is formed*

A more complete idea of the reactions in the solid phases for the investigated concentrations of the coprecipitating cation can be obtained by the use of X-ray analysis.

In the majority of the systems which we studied, the sulphides were amorphous to X-rays, which limited their application. The system Cu^{2+}, In^{3+}, H^+/S^{2-} proved to be suitable, because CuS, In_2S_3 and $CuInS_2$ give sharp X-ray diagrams.

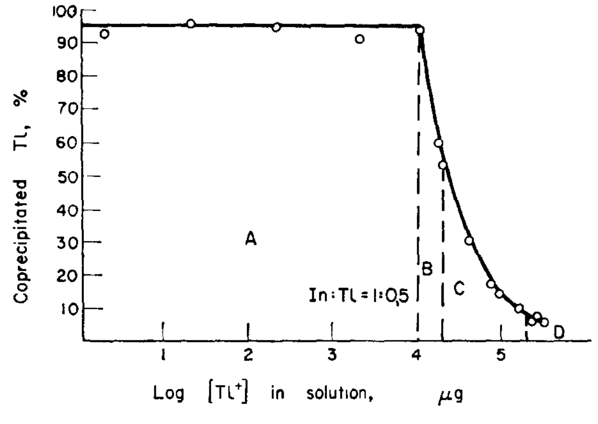

FIG. 8.—Coprecipitation diagram for Tl with In_2S_3.

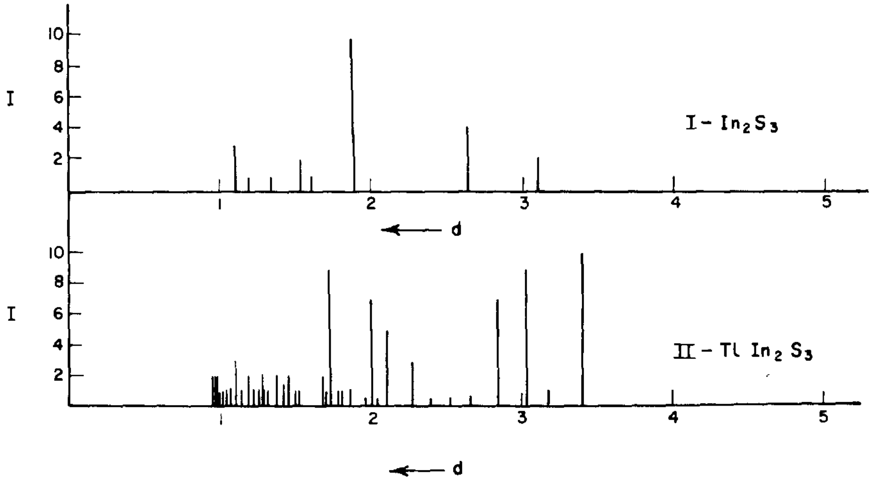

FIG. 9.—Results of the calculation of the X-ray diagrams of In_2S_3 and $TlIn_2S_3$.

The diagrams of coprecipitation of indium with CuS are given in Fig. 10.

The changes in the composition of the phases formed in the coprecipitation of various concentrations of In^{3+} with CuS are shown schematically in Fig. 11 on the basis of the results of the X-ray analysis.

In this diagram (Fig. 11) there are three regions: a single-phase region A′ (the pure CuS component), a two-phase region A (CuS + $CuInS_2$ in various proportions) and a single-phase region ($CuInS_2$).

Field A, where there is a constant distribution of indium between the solution and the solid phase, indicates the formation of solid solutions. However, it follows from the X-ray diagrams that this is a two-phase region. This contradiction can be resolved by assuming in our case the formation of a microdisperse system where the dispersion medium is CuS and the dispersed substance is $CuInS_2$. The structure, the particle size and the features of its formation are such that the uniform distribution of one phase in the other is possible. As can be seen from Fig. 11, from a certain ratio between CuS and $CuInS_2$ onwards, the latter will be the dispersion medium and the CuS will be the dispersoid.

The following facts favour this hypothesis. In the case of the coprecipitation of In^{3+} with CuS, because its molecules are being formed at the moment when the CuS produced passes through the colloidal stage, a uniform distribution of the compound formed, $CuInS_2$, throughout the volume of the CuS gel is quite natural. Entrainment of indium after the separation of the CuS in the form of a solid phase must also give a uniform distribution of $CuInS_2$ by virtue of the extremely high porosity of CuS and the possibility of the interaction of the In^{3+} ion practically throughout the mass of CuS, The exceptionally large specific surface of sulphide precipitates (600 m^2) follows from its determination

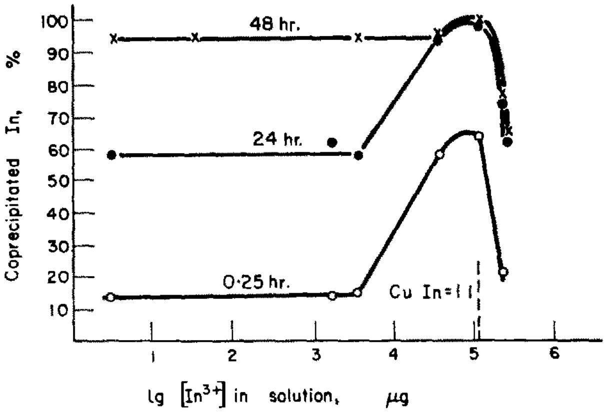

FIG. 10.—Coprecipitation diagram of In with CuS.

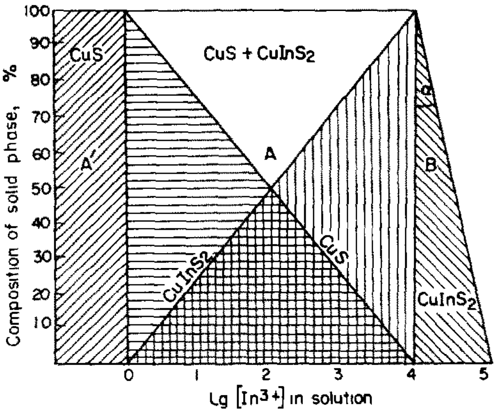

FIG. 11.—Change in the composition of the phases obtained in the coprecipitation of various concentrations of In^{3+} with CuS.

by the sorption of surface-active dyes[14] and by isotopic exchange between ions in the solution and the solid sulphide phase,[15] and also from electron-microscope pictures.[14,16]

The X-ray diagrams of the precipitates recorded were used to determine the particle dimensions of the phases of interest to us. Calculations of the mean effective grain size were carried out by Selyakov's formula.[17]

As the results showed, the mean effective grain size for CuS and $CuInS_2$ was *ca.* 3×10^{-6} cm. Consequently, the particles of $CuInS_2$, with a degree of dispersion of 3×10^{-6} cm, are distributed in a precipitate of CuS with a particle size of the same order.

According to the hypothesis being discussed, the constancy of the distribution coefficient is connected with the formation of solid solutions with a molecular degree of dispersion of the components. The results we obtained indicate the possibility of the compatibility of the constancy of the distribution of the coprecipitated cation and the absence of a molecularly dispersed distribution of one component in the other. In the present case, we encounter new facts requiring a revision of the hypotheses that have become established.

III. *Conditions of formation and properties of the compounds*

The compounds concerned are obtained as the result of coprecipitation, *i.e.*, under somewhat unusual conditions. Consequently, it was of interest to study these conditions and also the properties of the compounds arising. It is possible in this way to obtain a more profound insight into the coprecipitation process.

In view of the fact that the sulphide precipitates have an enormous surface with HS^- and S^{2-} ions present on it and giving to it a negative charge, it was essential to elucidate the role of adsorption in the formation of the compounds we were studying.

It was possible to elucidate the dependence of the coprecipitation on adsorption by studying the influence on the degree of coprecipitation of the conditions existing when the coprecipitating cation was added to a precipitate of previously separated sulphide and also when foreign ions were present in the solution.

The results obtained are given in Tables I and II.

TABLE I—COPRECIPITATION OF THALLIUM WITH Re_2S_7, PtS_2, PdS, Ru_2S_3 AND Ir_2S_3 UNDER VARIOUS CONDITIONS

	Coprecipitation of thallium, %			
		Addition to previously formed precipitate		
Metal sulphide	At the moment of formation of the precipitate	Unwashed	Washed with H_2O	Washed with H_2O, but on the addition of Tl H_2S–H_2O was introduced
Re_2S_7	51·7	40·7	6·5	15·8
PtS_2	49·9	21·6	2·6	10·1
PdS	49·6	37·9	7·9	16·4
Ru_2S_3	49·5	50·9	6·1	25·5
Ir_2S_3	56·7	24·2	1·6	—

TABLE II—INFLUENCE OF FOREIGN IONS ON THE COPRECIPITATION OF THALLIUM WITH Re_2S_7, PtS_2, PdS AND Ru_2S_3

	Coprecipitation of thallium, %			
Foreign electrolyte	For a Re:Tl ratio in the solution of 1:2	For a Pd:Tl ratio in the solution of 1:1	For a Ru:Tl ratio in the solution of 1:1	For a Pt:Tl ratio in the solution of 1:2
$MgSO_4$(4·9 mg of Mg)	54·2	51·1	50·1	52·8
$Al_2(SO_4)_3$(5·4 mg of Al)	52·4	48·8	50·9	49·1
$ZnSO_4$(6·5 mg of Zn)	50·1	50·0	51·2	51·9
In the absence of foreign electrolyte	51·7	49·6	49·5	49·9

As the results given show, the coprecipitation of thallium at the moment of formation of Ru_2S_3 is identical with that produced by a previously formed precipitate of this sulphide. In the case of Re_2S_7, PtS_2, PdS and Ir_2S_3, thallium is coprecipitated in considerably greater amount than when it is added to preformed precipitates of these sulphides. Precipitates of sulphides first washed free from H_2S with water entrain thallium to only a slight extent. However, if a washed sulphide is added to a sulphuric acid solution containing H_2S, then marked coprecipitation of the thallium is again found.

The presence of large amounts of foreign cations—Mg^{2+}, Al^{3+}, Zn^{2+}—does not affect the degree of coprecipitation of the thallium with Re_2S_7, PtS_2, Ru_2S_3 and PdS. It follows from this that the formation of these compounds is not associated with an ordinary adsorption process. In order to obtain a more detailed explanation of the role of hydrogen sulphide in the process under study, the sorption by PdS of H_2S in solution in different concentrations was determined. Experiments were carried out at the same time with Ag_2S. The latter coprecipitates the cations from all sulphides to the smallest extent. Consequently, we desired to establish whether there was a relationship between the amounts of sorbed H_2S and the degree of coprecipitation of thallium.

The experiments showed that PdS and Ag_2S sorb approximately the same amounts of H_2S. Nevertheless, thallium is not coprecipitated with Ag_2S, or else this phenomenon is not exhibited to an appreciable extent.

The precipitates previously washed free from H_2S with water also entrain thallium to an inconsiderable extent.

Consequently, we may conclude that the presence of H_2S on the surface of the sulphides is a necessary, but not sufficient, condition for coprecipitation of the cations.

The chemistry of the phenomenon is also confirmed by the maintenance of stoichiometric ratios between the elements in the precipitate on the partial separation of the main component.

The results obtained are given in Table III.

TABLE III—COPRECIPITATION OF THALLIUM WITH PARTIAL SEPARATION OF Re_2S_7

Re precipitated, %	Tl coprecipitated, %	Ratio of Re to Tl in the precipitate
100	52·4	1:1·04
75·0	37·0	1:0·96
50·0	24·2	1:0·97
25·0	10·0	1:0·80

As follows from the results given, the amount of thallium is equivalent to the Re_2S_7 which separated, which is characteristic for the formation of chemical compounds.

It was also of interest to determine the solubility of the compounds obtained. These compounds were obtained by coprecipitation, *i.e.*, by a somewhat unusual method. Nevertheless, a determination of their solubilities was important from the point of view of using these compounds for analytical purposes.

Solubility figures determined from the contents in aqueous solutions of the given compounds of the ions Tl, Ag and Cu, respectively, are given in Table IV.

TABLE IV—SOLUBILITY OF THE COMPOUNDS OBTAINED IN WATER AT $t° = 25 \pm 0·5$

Compound	Solubility, *mole/litre*
$TlReS_4$	$7·3 \times 10^{-5}$
$TlPd_2S_3$	$2·0 \times 10^{-5}$
$TlRu_2S_6$	$3·4 \times 10^{-5}$
$TlPtS_3$	$4·4 \times 10^{-5}$
Tl_3Ir_3S	$4·9 \times 10^{-5}$
$TlRh_2S_4$	$0·49 \times 10^{-5}$
$TlAsS_2$	$4·5 \times 10^{-6}$
$TlMoS_2$	$2·5 \times 10^{-5}$
$TlSnS_2$	$2·2 \times 10^{-5}$
$AgInS_2$	$4·7 \times 10^{-9}$
$CuInS_2$	$6·3 \times 10^{-8}$

The figures in Table IV clearly show that the magnitude of the solubility is not characteristic for the sulphides. Moreover, magnitudes of the same order are obtained for all of the compounds.

The experiments on the addition of thallium to a previously separated precipitate of Ru_2S_3 proved to be extremely fundamental. Under these conditions, thallium is entrained in the same amounts as at the moment of separation of the Ru_2S_3. Consequently, it was necessary to determine whether the compound $TlRu_2S_6$ is formed by the reaction of the Tl^+ ion with Ru_2S_3 or whether the thallium is present on the surface of the Ru_2S_3 in the form of Tl_2S. The identical X-ray diagrams for these compounds show that the first hypothesis is correct.

DISCUSSION

The experimental results presented show that chemical compounds are very important in the sulphide coprecipitation process. For the formation of chemical compounds to take place in the coprecipitation process, the presence in the sulphides of opposing properties—acidic and basic—is necessary. This condition is connected with the position of the elements forming the sulphides in the Periodic Table. Consequently, knowing the components of a given system, it is possible to predict the formation of chemical compounds and, consequently, the degree of coprecipitation, its course and the properties of the solid phase formed.

In the case of the formation of chemical compounds, the coprecipitation diagrams obtained are of a single type; the difference between them consists only in the position of the breaks corresponding to the ratio of the components in the solid phase.

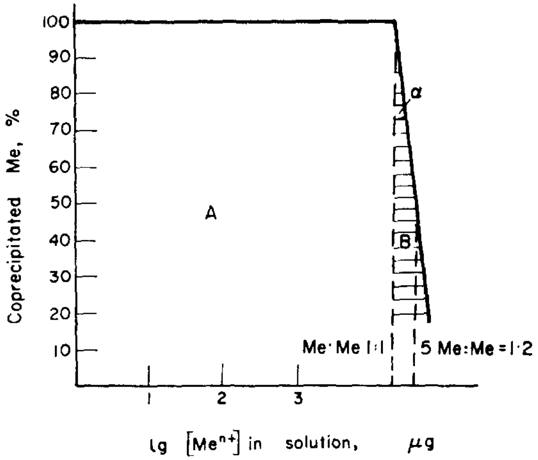

FIG. 12.—Theoretical coprecipitation diagram caused by formation of a chemical compound.

In the case of the coprecipitation of thallium with MoS_3, As_2S_3, SnS_2, Re_2S_7, PtS_2 and Ir_2S_3, and of In with CuS and Ag_2S, the ratio of Tl or In to Me is 1 : 1.

The coprecipitation of thallium with In_2S_3, PdS, Ru_2S_3 and Rh_2S_3 is characterised by curves with breaks at a Tl : Me ratio of 1 : 2.

It is important to note that at a ratio in the solution of Tl to Re, Pt or Ir of 1 : 1, the ratios in the solid phase are, respectively, 1 : 0·85, 1 : 0·95 and 1 : 0·87, and at ratios of Tl to Pd, Ru or Rh in the solutions of 1 : 2 these ratios are 1 : 0·42, 1 : 0·48 and 1 : 0·39, respectively.

We obtained an analogous picture for the coprecipitation of Tl with As_2S_3, SnS_2 and MoS_3, and also for In with CuS and Ag_2S.

Thus, the coprecipitation reaction, for example for the Tl^+ ion with Re_2S_7, takes place to the extent of only 85·4% by the equation

$$2Tl^+ + Re_2S_7 \cdot nH_2S \rightleftharpoons 2TlReS_4 \cdot (n-1)H_2S + 2H^+.$$

In order that the coprecipitation reactions mentioned should take place quantitatively, a two-fold excess of Tl^+ ion in the solution is necessary. The investigation of coprecipitation in the systems mentioned which has been carried out permits the theoretical coprecipitation diagram characteristic for the formation of chemical compounds to be given (Fig. 12). All of the systems that we have studied correspond to this type of diagram, in which coprecipitation is connected with the formation of chemical compounds.

In the case of the coprecipitation of Tl with As_2S_3, SnS_2 and MoS_3, and of In with CuS and Ag_2S, the coprecipitation diagrams should have a similar form. The displacement of part of the curve with respect to the abscissae apparently resulted from the fact that for low concentrations of Tl^+ and In^{3+} the equilibrium state was not attained (Fig. 10.).

In the diagrams of this type, field A (Fig. 12) is characterised by parallel coprecipitation curves indicating proportionality between the amount of coprecipitated cation and its concentration in the solution. As is well known, such a situation is characteristic for solid solutions.

As the results of X-ray analysis have shown, in the range of concentrations of the second component corresponding to field A, the formation of a microdisperse system—a "colloidal" solid solution—takes place.

When the concentration of the cation in the solution is increased, a new field B appears on the diagram (Fig. 11). For the case of the formation of chemical compounds, the break in the curve is found at multiple ratios between their components. The formation of chemical compounds for the range of concentrations corresponding to field B was confirmed by analysis of the precipitates and by their X-ray diagrams. The composition of the solid phase as the concentration of the second component is increased within the range AB remains constant. Graphically, this is determined by the angle of inclination α of the coprecipitation curve.

As the experiments show, with an excess of thallium in the solution (Me:Tl = 1 : 4 — 1 : 16) its content in the solid phase exceeds the stoichiometric amount. This is particularly clearly expressed in the case of the coprecipitation of thallium with In_2S_3 and Ir_2S_3.

The phenomenon observed is obviously connected with the general property of chemical compounds of giving solid solutions with an excess of their components. A confirmation of the hypothesis expressed is the invariability of the distribution constant of the second component between the solution and the solid phase formed under these conditions. The capacity of chemical compounds for giving solid solutions with an excess of the second component explains the appearance on the diagram for the coprecipitation of thallium with Ir_2S_3 (Fig. 6) of a new field C, and with In_2S_3 of field D (Fig. 8).

It follows from the results given that the coprecipitation diagram in association with X-ray analysis of the solid phases obtained permits a fairly complete picture of the phenomenon to be obtained.

In conclusion, we should like to mention that the experimental material presented shows the importance of chemical compounds in the coprecipitation of cations with sulphides. Construction of the coprecipitation diagram makes it possible to obtain a complete picture of this process.

Acknowledgment—The authors express their thanks to Corresponding Member of the U.S.S.R. Academy of Sciences, I. P. Alimarin, for valuable advice on the investigation.

Zusammenfassung—Eine Untersuchung der Mitfällung von Thallium mit As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 und In_2S_3 und von Indium mit CuS und Ag_2S mit physikochemischen Methoden zeigte, daß die Mitfällung auf der Bildung folgender

Verbindungen beruht: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ und $AgInS_2$. Eine für die Bildung von Verbindungen charakteristische Art von Mitfällungsdiagramm wurde aufgestellt und darauf die Phasen bestimmter Zusammensetzung entsprechenden Bereiche abgegrenzt. Es wurde gezeigt, daß sich bei der Mitfällung mikrodisperser Systeme "kolloide" feste Lösungen eines Sulfids im andern bilden.

Résumé—Une étude de la coprécipitation du thallium avec As_2S_3, SnS_2, MoS_3, Re_2S_7, PtS_2, PdS, Ru_2S_3, Rh_2S_3, Ir_2S_3 et In_2S_3, et de l'indium avec CuS et Ag_2S au moyen de l'analyse physico-chimique a montré que le phénomène est dû à la formation des composés suivants: $TlAsS_2$, $TlSnS_2$, $TlMoS_2$, $TlReS_4$, $TlPtS_3$, $TlPd_2S_3$, $TlRu_2S_6$, $TlRh_2S_4$, Tl_3Ir_3S, $TlIn_2S_3$, $CuInS_2$ et $AgInS_2$. On a établi un type de diagramme de coprécipitation caractéristique, pour le cas où il y a formation de composés chimiques, et on y a délimité les domaines correspondant aux phases de composition définie. On a montré qu'il se forme, lors de la coprécipitation, des systèmes microdispersés de solutions solides "colloïdales" d'un sulfure dans l'autre.

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A THERMOGRAVIMETRIC STUDY OF ALUMINIUM OXINATE

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Summary—A thermogravimetric study of aluminium oxinate obtained by three different procedures has confirmed the view generally held that 150° is a suitable drying temperature. It has also been shown that this temperature is satisfactory, irrespective of the original moisture content of the precipitate. That a temperature of 700° is sufficient to obtain aluminium oxide is also confirmed. On the other hand, the statement by some workers that aluminium oxinate can be dried at 375° has not been substantiated.

INTRODUCTION

THERE is some confusion in the literature regarding the drying and decomposition temperatures of aluminium oxinate. Dupuis and Duval[1] studied this complex thermogravimetrically and found that it achieved constant weight between 102 and 220°, thus concluding that the drying temperature of 110° recommended by many workers is correct but too restrictive. In addition, they found that total destruction of organic matter and conversion to the oxide was only complete above 1000°.

However, Borrel and Paris,[2] also from thermogravimetric data, found that anhydrous aluminium oxinate is not obtained until 135° and that 110° is too low a drying temperature to obtain the anhydrous material. They further claimed that the complex is stable up to 375°, but beyond this temperature there is gradual decomposition until 700° when the oxide is formed, with an unexplained and anomalous weight change at 520°. Unlike Dupuis and Duval, they consider it unnecessary to raise the temperature to 1000° in order to destroy organic matter and suggest that Dupuis and Duval used too rapid a heating rate to obtain complete decomposition at 700°.

In his authoritative text-book on oxine and its derivatives, Hollingshead[3] comments on the above divergence of opinion as to the drying temperature of aluminium oxinate that "in view of the fact that many other workers have obtained satisfactory gravimetric determinations by drying in this range (100–135°) it would appear that further substantive evidence is necessary before the lower drying temperatures are discarded".

It was in an attempt to clarify the situation that this present work was initiated.

EXPERIMENTAL

In thermogravimetric measurements, many parameters can influence the final shape of the thermogram[4] and in the present context, it was considered that the following factors merited investigation:

(1) *Heating Rate*

It is reasonable to assume that the heating rate employed by Dupuis and Duval of approximately 6°/min was too fast to obtain good resolution of a thermogram. Borrel and Paris used a heating rate

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of 3°/min, which is considered to be a reasonable increment in order to achieve good resolution of a thermolysis curve. In the present work a heating rate of 3°/min was employed.

(2) *Moisture Content of Precipitate*

It has been demonstrated[5] that the moisture content of a precipitate can considerably alter the position of the thermogram plateau. Dupuis and Duval give no details as to the moisture content of their samples, although the published thermogram indicates that it is considerable. On the other hand, Borrel and Paris dried their precipitates on the filter crucible by drawing air at room temperature through the precipitate for 24–48 hr. In view of these two widely differing procedures and their possible influence on the shape of the thermolysis curve, undried and air-dried precipitates were studied in the current investigation.

(3) *Mode of Precipitation*

It is well known that different methods of forming precipitates influence the shape of the thermogram[6] and it appears feasible that this observation could apply in the present context. Dupuis and Duval precipitated aluminium oxinate by Berg's method[7] whereas Borrel and Paris, although saying that the oxinate was precipitated by the usual method, used a procedure which differed in detail from Berg's technique. It would not, of course, be practicable to study aluminium oxinate precipitated by all of the numerous published methods, but in addition to the two procedures mentioned above, it was considered worthwhile including the technique currently in use in the author's laboratory[8] because, again, this differs in detail.

In order that a comparison can be made, the essential details of the precipitation methods used in the current investigations are given below.

Method of Berg[7]

To an aluminium solution containing less than 100 mg of aluminium/ml were added 3–5 g of sodium acetate followed by a slight excess of oxine solution (3 g of oxine dissolved in 3 ml of glacial acetic acid, diluted to 100 ml with water and neutralised with aqueous ammonia). The mixture was stirred vigorously, warmed to 60–70° and the precipitated complex filtered, then washed with water until the washings were colourless.

Method of Borrel and Paris[4]

To 100 ml of 0·0333*M* aluminium solution was added sufficient oxine solution (0·1*M* in 0·2*M* hydrochloric acid) to give a 10% excess and the mixture warmed to 70–80°. The solution was neutralised with 0·5*M* sodium carbonate, then buffered to about pH 7 with 15% w/v ammonium acetate solution. The mixture was boiled gently for 2–3 min, then maintained at 80° for 0·5 hr. The oxinate was filtered, washed twice by decantation with hot water, transferred to the filter crucible and washed further with hot water to remove the excess oxine.

Method of the British Ceramic Research Association[8]

To approximately 100 ml of neutralised aluminium solution, containing 15–35 mg of aluminium, were added 4 ml of 50% w/v hydroxylamine hydrochloride followed by 5 ml of freshly prepared 1% w/v *o*-phenanthroline [1g dissolved in 100 ml of acetic acid (1 + 1)]. The solution was heated to 40–50°, 20 ml of 5% w/v oxine solution added (5 g of oxine dissolved in 12 ml of glacial acetic acid and diluted to 100 ml with water) followed by 40 ml of 40% w/v ammonium acetate solution, added slowly and with stirring. The solution was heated to 70° with stirring and maintained at this temperature for 10 min, stirring periodically. After cooling for 30 min, the precipitate was filtered and washed thoroughly with warm water (40–50°).

Portions of the oxinate obtained by these three different procedures were removed from the filter crucible immediately after washing was complete and stored in well-stoppered containers. The remainder of the precipitate in each case was dried by drawing air through the filter crucible for 48 hr.

A sample of each preparation, weighing between 250 and 350 mg, was transferred to a prefired recrystallised alumina crucible and heated in air on a Stanton thermobalance, Model HT-SM, which was programmed for a linear temperature rise from room temperature to 1400° over 8 hr (3°/min nominal) and a chart speed of 6 in./hr. The thermograms obtained are given in Fig. 1.

DISCUSSION

From the thermograms, it is apparent that all of the samples have achieved constant weight at 160°. Thus it can be concluded that the drying temperature of 150° recommended by many workers is satisfactory, irrespective of the original

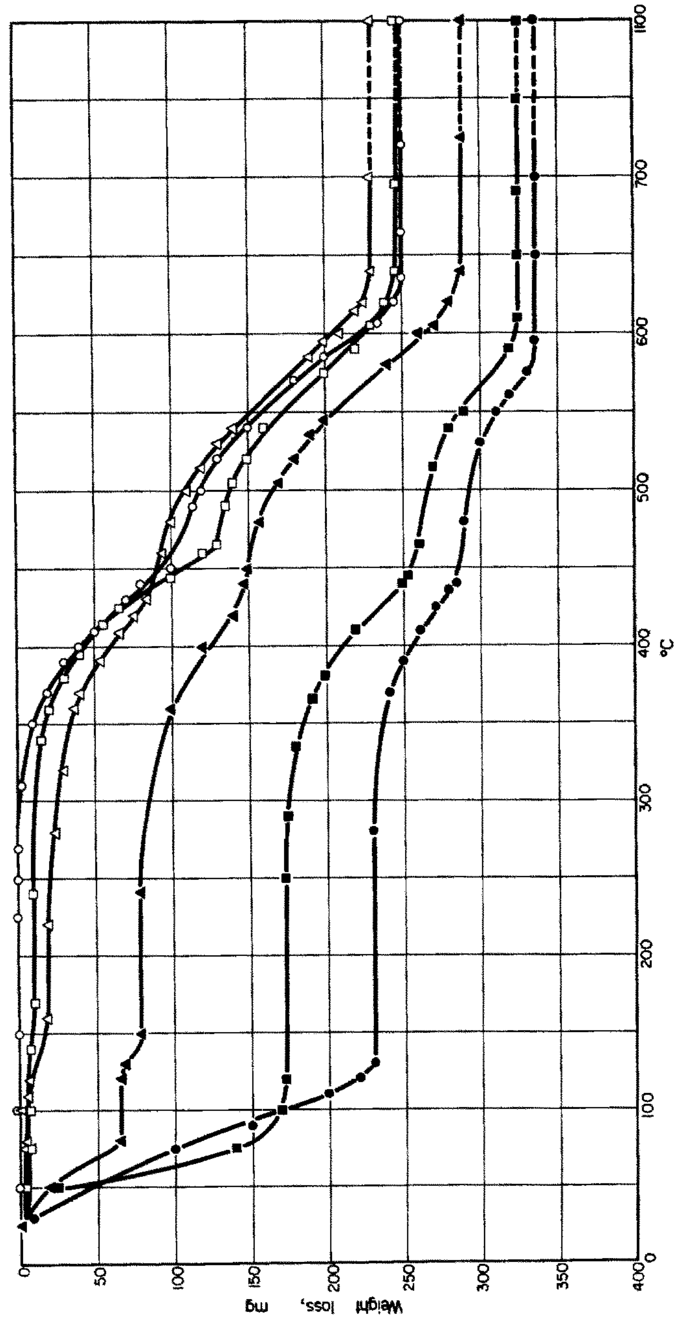

Fig. 1.—Thermograms of aluminium oxinate obtained by different precipitation procedures:

△—Brit. Ceram. Res. Assoc., air dried;
▲—Brit. Ceram. Res. Assoc., undried;
○—Borrel and Paris, air dried;
●—Borrel and Paris, undried;
□—Berg, air dried;
■—Berg, undried.

moisture content of the precipitate. Although only three different methods of precipitation have been investigated, it is reasonable to assume that 150° is a suitable drying temperature for aluminium oxinate precipitated by any published method.

The results also confirm the conclusion of Dupuis and Duval that a drying temperature of 110° is satisfactory, but too restrictive. However, contrary to the findings of Borrel and Paris, the thermograms of all of the samples demonstrate, quite conclusively, that the precipitate is not stable at 375° and independent attempts to dry aluminium oxinate at this temperature resulted in complete failure. On another point, the thermograms indicate that aluminium oxide is formed at approximately 600°. There is little doubt that, as Borrel and Paris remark, 700° is a sufficiently high temperature to obtain the oxide and that Dupuis and Duval used too high a heating rate to obtain complete decomposition at this temperature.

The anomalous weight change at 520° described by Borrel and Paris is manifest in the present work by a change in slope occurring at about 460°, which suggests the formation of an intermediate compound. It is doubtful whether it would be possible to isolate this intermediate, because it has been shown[9] that the decomposition of metal oxinates is a complicated process and the exact mechanism of decomposition is not known.

CONCLUSIONS

Using three different procedures for precipitating aluminium oxinate, it has been confirmed that a satisfactory drying temperature for the complex is 150°. It has been shown that this temperature can be used irrespective of the original moisture content. Contrary to the findings of Borrel and Paris, spurious results were obtained on drying the complex at 375°. Aluminium oxide is formed at temperatures above 600° and failure to obtain complete decomposition at temperatures much in excess of this value strongly indicates too high a heating rate.

Aluminium oxinate, prepared by precipitation from homogeneous solution (PFHS), has also been studied. The procedure used was according to Marec, Salesin and Gordon[10] except that the 8-acetoxyquinoline was purchased. (B. Newton Maine Ltd., Silsoe, Bedfordshire, England.)

As was to be expected, the thermolysis curves of both undried and air-dried samples were very similar to those depicted in Fig. 1. They confirm that 150° is a suitable drying temperature for aluminium oxinate precipitated by this technique but that drying at 375° results in decomposition.

The major difference in the thermolysis curves of aluminum oxinate prepared by PFHS is that aluminium oxide is not formed until a little over 700°. This is to be expected as PFHS results in denser crystals.

Acknowledgment—The author thanks the Directors of John Laing Research and Development Ltd., for permission to publish this paper.

Zusammenfassung—Eine thermogravimetrische Untersuchung an auf drei verschiedene Arten erhaltenem Aluminiumoxinat bestätigte die allgemeine Ansicht, daß 150° eine geeingete Trocknungstemperatur ist. Es wurde auch gezeigt, daß diese Temperatur unabhängig vom ursprünglichen Feuchtigkeitsgehalt des Niederschlags ausreicht. Es wurde auch bestätigt, daß 700° zur Bildung von Aluminiumoxyd ausreichen. Andererseits ließ sich nicht bestätigen, daß Aluminiumoxinat bei 375° getrocknet werden kann.

Résumé—Une étude thermogravimétrique de l'oxinate d'aluminium obtenu par trois procédés différents a confirmé l'opinion généralement admise que 150°C constitue une bonne température désséchante. Il a pu être montré que cette température est satisfaisante pour l'humidité du précipité. Le fait que 700°C soient suffisants pour obtenir l'oxyde d'aluminium a été également confirmé. D'autre part, les conclusions de certains chercheurs qui indiquent 375° comme température de dissociation de l'oxinate d'aluminium n'ont pu être confirmés.

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NEW STUDIES ON CALCIUM OXALATE MONOHYDRATE

A GUIDE TO THE INTERPRETATION OF THERMOGRAVIMETRIC MEASUREMENTS

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Summary—The pyrolysis of calcium oxalate monohydrate in air occupies a unique place in the literature of thermogravimetry. Not only was a thermogram for this reaction the first pyrolysis curve published by Duval and his collaborators, but Duval and others have suggested that it can be used as a reference substance for judging the performance of a thermobalance. However, the pyrolysis of calcium oxalate monohydrate under a variety of conditions gives rise to considerable differences in its thermograms. The effects of sample size, heating rate, atmosphere and container geometry are presented in a series of paired thermograms, and the differences are accounted for with the aid of additional evidence from differential thermal analysis and from combustion train experiments. Variations in atmosphere are particularly important, and the atmospheres studied are dry nitrogen, humidified nitrogen, dry air, humidified air, dry oxygen, dry carbon dioxide and dry carbon monoxide. Even subtle variations in the shape of a thermogram obtained on a reliable balance may reflect the complexity of the reactions that produce the more noticeable over-all weight changes. Results presented in this report thus delineate conditions for the use of calcium oxalate monohydrate as a thermogravimetric reference substance, and show that its behaviour under controlled conditions in a thermobalance can provide an unusually versatile guide to the interpretation of thermogravimetric measurements.

INTRODUCTION

THE pyrolysis of calcium oxalate monohydrate in air occupies a unique place in the literature of dynamic thermogravimetry. A thermogram for this reaction (Fig. 1) was the first pyrolysis curve published by Duval and his collaborators[42] in their comprehensive study of the thermogravimetric behaviour of analytical precipitates, and was

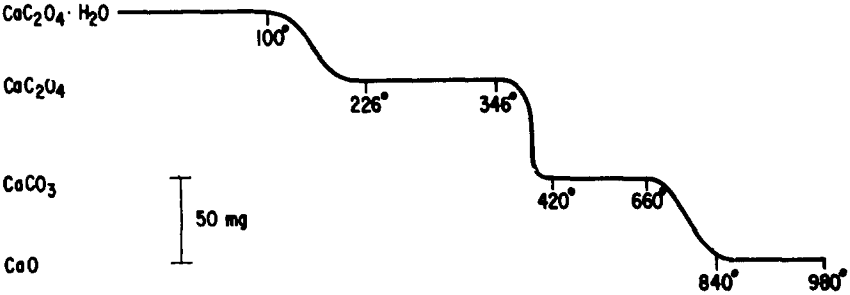

FIG. 1.—Pyrolysis curve of calcium oxalate monohydrate as published by Peltier and Duval.[42]

singled out by Duval for special mention in his book.[13] Because the thermogram's unusual sequence of consecutive reactions was characterised by four parallel, horizontal plateaux, corresponding successively to calcium oxalate monohydrate, calcium oxalate, calcium carbonate and calcium oxide, the material was used by Duval[12] "to adjust the thermobalances after they have been set up, cleaned, or repaired." He further claimed that the thermogravimetric measurements on this material with a photographic recording Chevenard thermobalance were accurate and reproducible enough to permit students to obtain reliable values for the atomic weight of carbon from the dimensions of thermograms obtained as an instructional exercise.[13] Subsequently, Barcia Goyanes[2] and Wilson[57] suggested that the extremities of the plateaux in this thermogram be used as temperature calibration points for a thermobalance, as if they were characteristic transition temperatures.

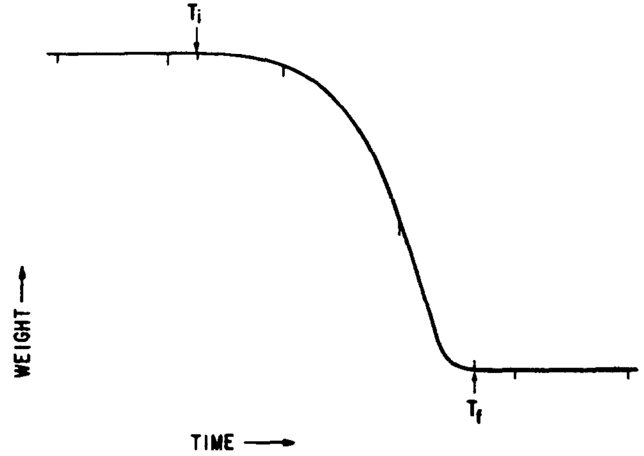

Fig. 2.—Schematic thermogram for general single-stage reaction: $A_{(solid)} = B_{(solid)} + C_{(gas)}$.

Previous work in this Laboratory has demonstrated that the accuracy and precision of measurements with a Chevenard pen-recording thermobalance (which has the same suspension and sensitivity as the photographic recording balance) are below the level required for atomic weight work[48] and that the temperature limits of a plateau are not a property of the sample alone.[36] This report presents thermograms for calcium oxalate monohydrate pyrolysed under a variety of conditions and attempts to provide a consistent explanation for all of the observed differences, using additional data from differential thermal analysis measurements and from combustion train experiments. The results of these studies show that if calcium oxalate monohydrate is pyrolysed under carefully controlled conditions in a thermobalance, it can serve as a yardstick for judging the performance of the instrument and can provide an unusually versatile guide to the interpretation of thermogravimetric measurements.

CHARACTERISTICS OF SINGLE-STAGE REACTIONS

The thermogram of Fig. 2 has been drawn to represent the general reaction

$$A_{(solid)} = B_{(solid)} + C_{(gas)}.$$

Two temperatures may be selected as characteristic of any single-stage non-isothermal reaction: T_i (initial temperature) is the temperature at which the cumulative weight-change reaches a magnitude that the thermobalance can detect, and T_f (final temperature) is the temperature at which the cumulative weight-change first reaches its maximum value, corresponding to complete reaction. Although T_i may be the lowest temperature at which the onset of a weight-change can be observed in a given experiment, it is neither a transition temperature in the phase rule sense,[35] nor is it a true decomposition temperature below which the reaction rate suddenly becomes zero.[20,21,24,25] Because the value of T_i depends upon the interaction of many variables, it shall be called the *procedural decomposition temperature*,[36] a term introduced by Doyle[10] in reporting his thermogravimetric studies of the pyrolysis of polymers. At a linear heating rate, T_f must be greater than T_i, and the difference $(T_f - T_i)$ will be called the *reaction interval.* For an endothermic decomposition, T_i and T_f both increase with increasing heating rate, the effect being greater for T_f than for T_i, as has been clearly shown by Richer[45] and others.[8,34,36]

SIGNIFICANCE OF TEMPERATURE IN DYNAMIC THERMOGRAVIMETRY

At this point it is advisible to comment upon the significance of temperature as a variable in dynamic thermogravimetry. The fundamental datum produced by a recording thermobalance is a record that shows the variation with time of some quantity whose changes may be related in magnitude to changes in the weight of the sample. The foundations of modern dynamic thermogravimetry were laid in the early 1920's by Guichard,[22,23] who proposed that the method of continuous weighing be applied to "the study of all reactions that cause the weight of any solid to vary in one way or another . . . in a selected atmosphere, while the temperature is raised at a rate nearly proportional to the time, and slowly enough." Although Guichard did not explicitly specify the temperature to be measured, it is apparent from his work and that of his students that he referred to the temperature of the furnace atmosphere and not to that of the sample.[11,53,54]

Guichard had insisted, since the beginning of his studies, "on the necessity of realising a very regular rise of temperature." He pointed out that "there is a risk that every irregularity in this increase may appear on the curve of weight *vs.* time and complicate its interpretation." Such regularity in heating rate can be achieved in the furnace atmosphere but not in the sample, whose rate of temperature rise changes with the onset of each exothermic or endothermic phase transition or chemical change. These internally generated changes in the rate of sample temperature rise, of course, provide the basis for the widely used method of differential thermal analysis. Both differential thermal analysis and dynamic thermogravimetric analysis require a linear furnace heating rate. In differential thermal analysis one detects the onset of reactions or transitions in a sample by observing the perturbations in what would otherwise be a regular rate of increase in sample temperature. In thermogravimetry one detects and measures those transformations that produce a change in the weight of a sample. The only independent temperature variable in either technique is the heating rate of the furnace. The changes in sample weight and temperature are both consequences of the chemical and physical changes produced in a sample when it is brought into contact with a given atmosphere whose temperature is changing at a predetermined rate.

In this investigation an independent record was kept of the furnace temperature as a function of time, which record also served to verify the linear heating rate that had been set on the furnace controller. The temperature markings on the thermograms were established by coupling the temperature and weight recorders so that a pip was automatically introduced into the pyrolysis curve at each integral 100-degree reading of the furnace temperature. The pips could also have been introduced after the run by juxtaposition of the weight-time curve with the separate record of furnace temperature as a function of time. Values of T_i and T_f were interpolated between 100-degree markings.

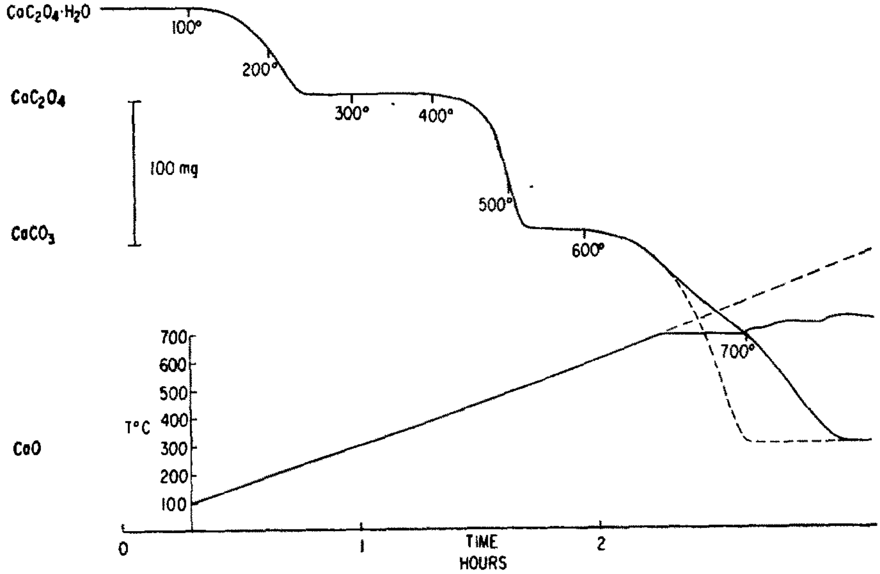

FIG. 3.—Effect of perturbation in rate of heating upon thermogram for calcium oxalate monohydrate (500 mg, platinum dish, flowing dry nitrogen):
- - - unperturbed rate of heating.

It is particularly risky to try to record a thermogram directly by feeding the weight and temperature signals to the two inputs of an X-Y recorder. Unexpected disturbances that sometimes occur in the heating rate or thermocouple response can produce artificial perturbations in the weight-temperature record. Only a separate temperature-time record can disclose these adventitious effects and permit effects caused solely by changes in sample weight to be distinguished from them.[27] Fig. 3 shows the thermobalance record of a pyrolysis of calcium oxalate monohydrate during which the temperature controller became stuck at 695°, for a period of time, after which it produced an irregular temperature rise up to about 750°. The dashed curve shows the course that the thermogram would have taken had the linear heating rate of 300 degree/hr been maintained above 695°. The perturbation in the recorded curve can be properly understood only in the light of the independent record of temperature as a function of time. Had an X-Y recorder been used for this run, the period of constant temperature would have been represented by a vertical line at 695°. Although such an abrupt change in the slope of the curve would probably have been suspect, more subtle, but nonetheless significant changes in heating rate could pass completely unnoticed in a direct recording of weight *vs.* temperature.

CHARACTERISTICS OF MULTI-STAGE REACTIONS

Successive, non-overlapping reactions

Under certain conditions, the thermogram for a sequence of successive decompositions, such as occurs during the pyrolysis of calcium oxalate monohydrate

$$CaC_2O_4{\cdot}H_2O = CaC_2O_4 + H_2O$$

$$A_{(s)} = B_{(s)} + \text{gas} \qquad (1)$$

$$CaC_2O_4 = CaCO_3 + CO$$

$$B_{(s)} = C_{(s)} + \text{gas} \qquad (2)$$

$$CaCO_3 = CaO + CO_2$$

$$C_{(s)} = D_{(s)} + \text{gas} \qquad (3)$$

can be considered as the composite of the thermograms for the individual stages. This is shown in Fig. 4, in which are superimposed the thermograms that were obtained on separate days by heating in air, at 300 degree/hr, 500 mg of calcium oxalate monohydrate and equivalent quantities of the anhydrous oxalate and of calcium carbonate, each in a porcelain crucible. The initial stages of the latter two curves are indicated by broken lines. Thermograms 4(B) and 4(C) are identical with 4(A) at temperatures above their intersections.

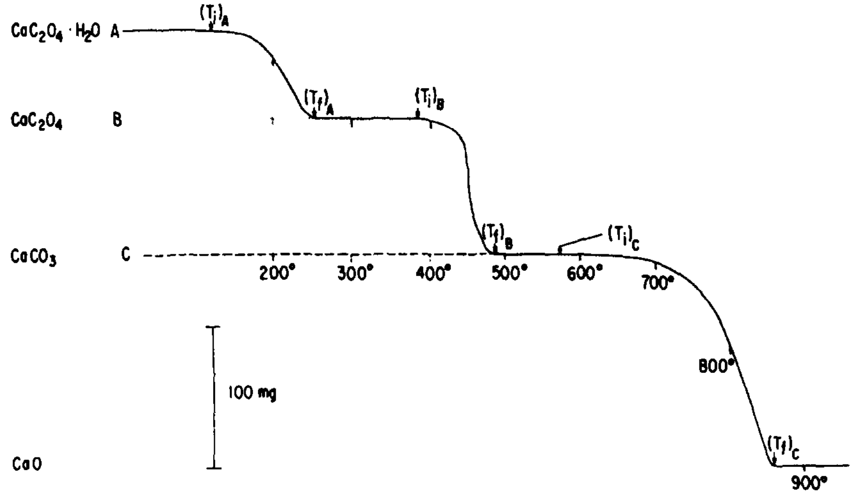

FIG. 4.—Thermograms for successive non-overlapping reactions (porcelain crucible, ambient air, 300 degree/hr):
——— 500 mg of calcium oxalate monohydrate,
...... 438 mg of calcium oxalate,
– – – – 343 mg of calcium carbonate.

It is not evident from this reproduction that the true value of $(T_i)_B$ is about 390°. The position of $(T_i)_B$ shown in this figure was chosen for illustrative purposes only.

Although temperature $(T_f)_A$ marks the beginning of the plateau for calcium oxalate, its value is determined by the interaction between the heating rate, the sample size and the rate of dehydration of calcium oxalate monohydrate; it cannot be interpreted as setting a lower limit to the thermal stability of the anhydrous salt. Temperature $(T_f)_A$ lies on the calcium oxalate plateau only because, under the conditions of the experiment, the dehydration reaction was complete before the temperature reached the value of $(T_i)_B$, the procedural decomposition temperature of the anhydrous salt. When calcium oxalate, previously dehydrated at 175°, was the starting material, the thermogram, beginning at level B, showed no perturbation as it passed through $(T_f)_A$. The calcium carbonate plateau, of course, bears the same relationship to its precursor as the calcium oxalate plateau bears to the monohydrate.

The exact superposition of the independently determined thermograms of Fig. 4 could have been achieved only if the reactions being studied were indeed successive and non-overlapping, and only if the characteristics of the thermobalance remained constant over the period of days covered by the experiments.

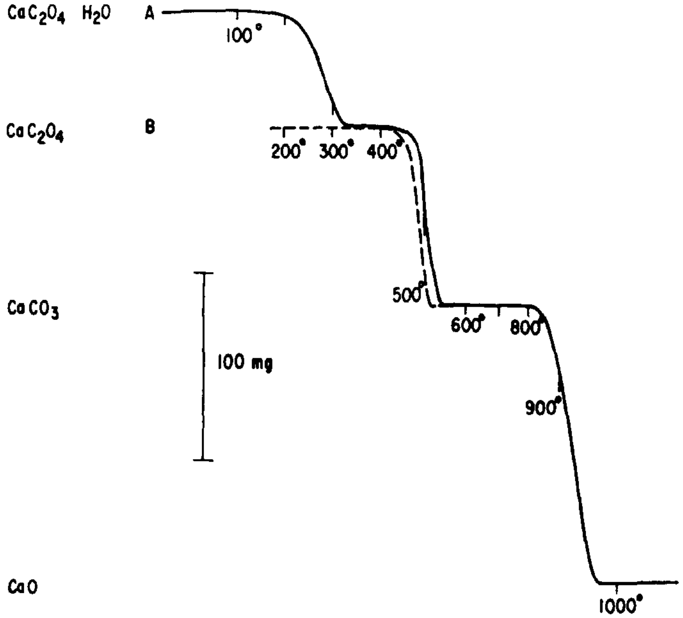

Fig. 5.—Thermograms for successive, partially overlapping reactions (porcelain crucible, ambient air, 600 degree/hr):
——— 500 mg of calcium oxalate monohydrate,
– – – – 438 mg of calcium oxalate.

Successive, partially overlapping reactions

The exact superposition of Fig. 4 is not characteristic of the pyrolysis of calcium oxalate monohydrate under all conditions. As noted earlier, both T_i and T_f for a given reaction rise as the heating rate is increased, the effect being more pronounced for T_f. The consequences of this are shown in Fig. 5, in which are superimposed the thermograms that were obtained by repeating two of the pyrolyses of Fig. 4, but at a heating rate of 600 degree/hr. The intermediate plateau for calcium carbonate is still clearly defined, but it begins at a higher temperature.[36] On the other hand, the formation of anhydrous calcium oxalate as an intermediate in the pyrolysis of the monohydrate is no longer marked by a true plateau, but simply by a change in the slope of the thermogram. At the higher heating rate the dehydration reaction on curve 5(A) was not complete by the time the furnace temperature had reached about 350°, which is the procedural decomposition temperature indicated for the anhydrous salt on curve 5(B). During the latter part of pyrolysis 5(A), therefore, water and carbon monoxide were being evolved simultaneously,[43] and at the point where the cumulative weight loss reached level B the sample crucible contained anhydrous calcium oxalate and a small amount of both the monohydrate and calcium carbonate.

A careful examination of the original thermograms discloses that curve 5(A) lies above curve 5(B) even in the region between 300° and 400°, and does not become coincident with it until the calcium carbonate plateau is reached. By increasing the heating rate from 300 to 600 degree/hr the initial sequence of two successive decompositions has been transformed to a sequence of two partially overlapping or simultaneous decompositions, the thermogram for which is not an exact composite of the individual stages.

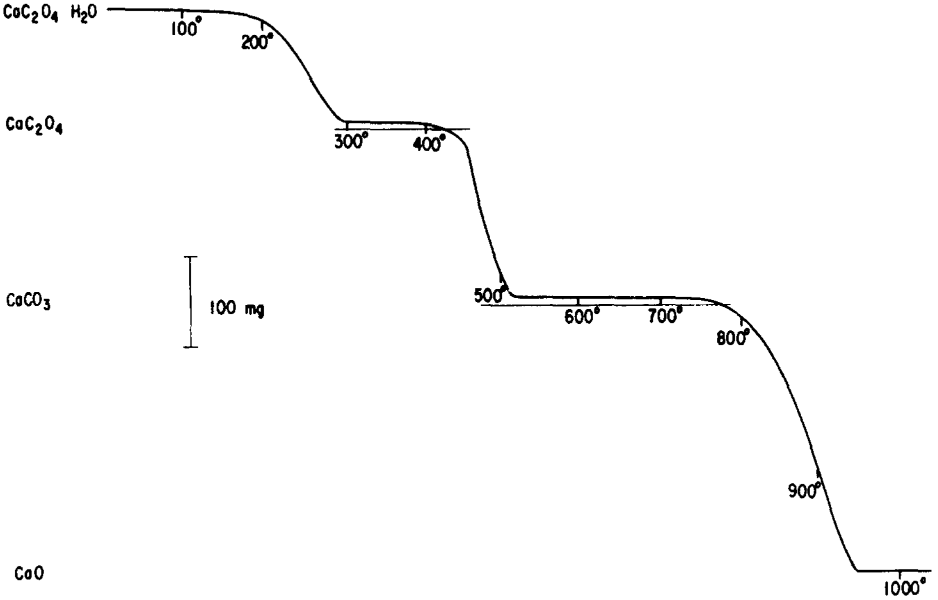

FIG. 6.—Thermogram for calcium oxalate monohydrate (1·019 g, porcelain crucible, ambient air, 300 degree/hr).

The transformation of a true plateau for anhydrous calcium oxalate into a curve like that of Fig. 5(A) was also produced by keeping the heating rate at 300 degree/hr, but increasing the sample weight from 0·5 g to approximately 1 g (Fig. 6). With more water in the initial sample, complete dehydration was not achieved before the procedural decomposition temperature for the anhydrous salt was reached, even at 300 degree/hr. This parallelism between the effects of heating rate and sample weight will be examined more closely in a subsequent section of this report.

At this point the following general conclusions may be drawn from the foregoing experiments on the multi-stage pyrolysis of calcium oxalate monohydrate:

1. *The appearance of a plateau for a compound on a dynamic thermogram does not necessarily imply that the compound is isothermally stable, either in a thermodynamic or practical sense, at all or any temperatures that lie on that plateau.* The temperature limits between which it extends apply only to the particular conditions of that pyrolysis.[5,20,44]

Certainly, none of the curves in Figs. 4, 5 or 6 can be used to set an upper limit to the isothermal stability of calcium carbonate in air. Similarly, anhydrous calcium oxalate undergoes slow isothermal decomposition in air at 300°, even though this temperature lies on the true plateau observed for that compound in Fig. 4.[43]

2. *If the thermogram obtained for a multi-stage reaction has no intermediate portion in which the sample weight remains constant with time over a range of temperature, one can make the reasonable inference that the reactions leading to the formation and to the subsequent decomposition of the intermediate are not independently sequential, but at least partly overlap.* The weight level at which a bend or change of slope occurs in the thermogram for such a pair of successive but overlapping reactions depends upon the relative amount of product B that has been formed by the time its procedural decomposition temperature has been reached and upon the relative rates of decomposition of A and B.

3. *In the absence of a true plateau, which can appear only if* $(T_f)_A \leqslant (T_i)_B$, *one cannot determine from a thermogram for successive reactions exact values for either* $(T_f)_A$, $(T_i)_B$, *or the stoichiometric weight level of B,*[4] *although a reasonable inference as to the latter can often be made.* There is little doubt, for example, that the gently sloping portion of Fig. 5 indicates the formation of anhydrous calcium oxalate.

CHARACTERISTICS OF INDIVIDUAL REACTIONS OF $CaC_2O_4 \cdot H_2O$

Among the factors that affect the thermogravimetric behaviour of calcium oxalate monohydrate are the reversibility of each stage of the pyrolysis and the enthalpy change that accompanies each of the individual reactions. The pertinent data are summarised in Table I.

TABLE I

Reaction	Heat of reaction ($\Delta H^\circ_{298^\circ K}$ kcal/mole)[47]	Reversibility
(1) $CaC_2O_4 \cdot H_2O = CaC_2O_4 + H_2O$	13·3*	Reversible[43]
(2) $CaC_2O_4 = CaCO_3 + CO$	15·5*	Irreversible[48,58]
(3) $CaCO_3 = CaO + CO_2$	42·5	Reversible

* Heat of formation of CaC_2O_4 estimated from tabulated values for the di- and monohydrates.

Reactions (1) *and* (3)

Both of these reactions are endothermic and reversible. In their thermogravimetric work, Peters and Wiedemann[43] showed that calcium oxalate monohydrate, after dehydration at about 280°, could be regenerated by allowing the anhydrous salt to cool to room temperature in humidified air. The effect of carbon dioxide in markedly raising the procedural decomposition temperature and decreasing the reaction interval for calcium carbonate has been clearly demonstrated by these workers and by Richer and Vallet.[44,45] For any given atmosphere containing carbon dioxide, the procedural decomposition temperature must be equal to or greater than the temperature at which the dissociation pressure of calcium carbonate reaches the partial pressure of carbon dioxide in that atmosphere.[28]

Reaction (2)

Thermal measurements by several investigators[14,41,49,56] have shown that the decomposition of anhydrous calcium oxalate is endothermic in an inert atmosphere, but becomes strongly exothermic in an oxidising atmosphere. These results have been confirmed in a Chevenard thermobalance. With the balance mechanism locked and a Pt-Pt, 10% Rh thermocouple inserted into the powdered sample, the difference between the sample temperature and the furnace temperature was recorded as a function of the furnace temperature, and the tracings shown in Fig. 7 were obtained from experiments made in flowing dry nitrogen and oxygen.

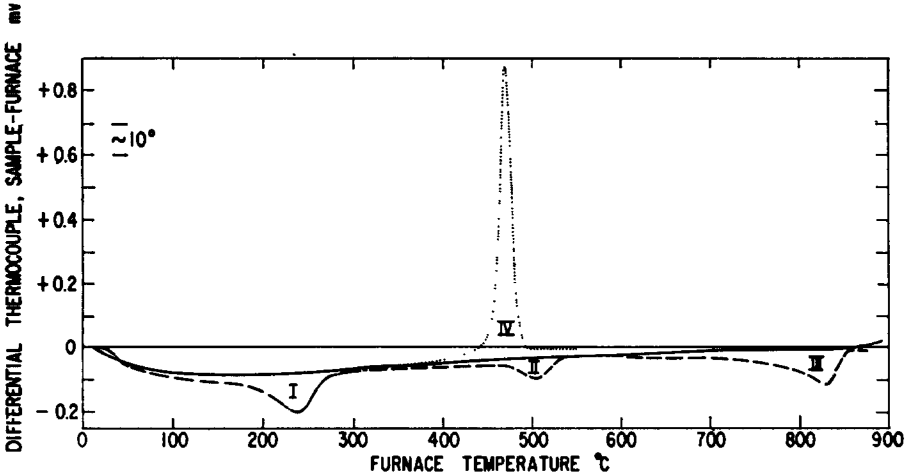

FIG. 7.—Differential thermal measurements on calcium oxalate monohydrate (500 mg):
——— inert sample (ignited calcium oxide),
– – – – calcium oxalate monohydrate in dry nitrogen,
...... calcium oxalate monohydrate in dry oxygen.

The exothermic peak observed in oxygen (and, with a more complex shape, in air) has been attributed by the investigators previously cited to the formation of carbon dioxide by oxidation of the carbon monoxide produced in the decomposition of the oxalate. The heat evolved/mole of carbon monoxide oxidised in the reaction

$$CO + 0{\cdot}5O_2 = CO_2 \qquad (4)$$

is 67·7 kcal at 700°K,[7] which is about four times larger than the heat absorbed by reaction (2). Reaction (4) has also been postulated to explain the exothermic effects noted when thorium oxalate was decomposed under oxidising conditions.[6,38]

The evidence to support the hypothesis that reaction (4) can also occur during the pyrolysis of calcium oxalate is presented in the following section.

DECOMPOSITION OF ANHYDROUS CALCIUM OXALATE

A weighed sample of calcium oxalate monohydrate in a platinum boat was loaded into a combustion tube and heated overnight at 125° in a stream of dry nitrogen to effect complete dehydration. Then, as in the method used by D'Eye and Sellman[9] for studying the thermal decomposition of thorium oxalate, the modified combustion train shown in Fig. 8 was assembled, and isothermal decompositions of the anhydrous salt were carried out for 3 hr at 420° with a stream of suitable carrier gas passing over the sample at a rate of 20 ml/min.

The gas, after leaving the pyrolysis chamber, passed through a series of tubes filled, successively, with Ascarite, hot copper oxide at 700° and Ascarite. Any carbon dioxide in the exit gas stream was trapped in the first Ascarite tube; any carbon monoxide in the exit gas stream was oxidised by the hot copper oxide and subsequently absorbed as carbon dioxide in the last absorption tube.

The results obtained with dry air and dry nitrogen as the carrier gases are given in Table II, to which the following comments are pertinent:

1. The dehydration of the samples was complete at 125°.

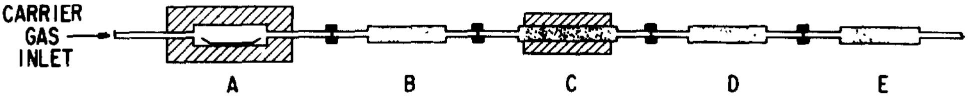

FIG. 8.—Schematic illustration of modified combustion train for experiments with dry nitrogen and dry oxygen:

A—furnace with combustion tube and platinum boat,
B—Ascarite absorption tube,
C—furnace with tube of copper oxide,
D—Ascarite absorption tube,
E—Ascarite tare tube.

2. The amount of calcium oxalate that decomposed in 3 hr at 420° was significantly greater in dry air than in dry nitrogen.

3. In dry air (run 1), the primary gaseous product of the decomposition of anhydrous calcium oxalate at 420° was carbon monoxide. Virtually all of this product had been oxidised to carbon dioxide by the time the gas stream reached the first Ascarite tube, and the total moles of carbon dioxide trapped by both Ascarite tubes is in excellent agreement with the weight loss of the sample, calculated as moles of carbon monoxide.

4. In dry nitrogen (run 2) most of the carbon monoxide produced during the decomposition of the anhydrous calcium oxalate left the reaction zone unchanged and appeared as carbon dioxide only after passing through the hot copper oxide tube. However, a significant amount of carbon dioxide was absorbed in the first Ascarite tube, between the pyrolysis furnace and the copper oxide furnace. In a nitrogen atmosphere, this carbon dioxide could not have been produced by oxidation of carbon monoxide, but must have arisen from the disproportionation reaction

$$CO = 0{\cdot}5CO_2 + 0{\cdot}5C \qquad \Delta H_{700^\circ K} = -20{\cdot}7 \text{ kcal}^{7} \qquad (5)$$

On this basis, the following material balance can be made:

CO (mmole) undergoing disproportionation = 2(0·36)	= 0·72
CO (mmole) undergoing oxidation by CuO	= 2·30
Total	= 3·02
CO (mmole) calculated from weight loss	= 2·90

Thus, in dry nitrogen as in dry air, the primary gaseous product of the decomposition of anhydrous calcium oxalate at 420° was carbon monoxide.

The disproportionation reaction has been observed by Glasner and Steinberg[17–19] in their studies of the thermal decomposition of rare earth oxalates in vacuum. Qualitative evidence for its role in the vacuum decomposition of sodium oxalate and of alkaline earth oxalates has been reported by Günther and Rehaag[26] and by Wöhler and Schuff,[58] and it has been observed by D'Eye and Sellman[9] when thorium oxalate was decomposed in a stream of nitrogen.

Further evidence for disproportionation in these experiments was the grey discoloration observed in the sample that had been partially decomposed in a stream of nitrogen; the residue from the air run was pure white. The intensity of the discoloration could be reduced by passing air over the hot residue. A greyish-brown discoloration was also observed in the residues from thermogravimetric runs made in dry nitrogen.

To confirm the reported irreversibility of the decomposition of anhydrous calcium oxalate,[43,58] runs were made at 420° in a stream of dry carbon monoxide; this

TABLE II.—PYROLYSIS OF $CaC_2O_4{\cdot}H_2O$ IN MODIFIED COMBUSTION TRAIN

Run no.	1	2	3(a)	3(b)
Atmosphere	Dry air	Dry N_2	Humid N_2	Dry O_2
Wt. $CaC_2O_4{\cdot}H_2O$, *mg*	1331·5 (9·11 mmole)	1105·1 (7·56 mmole)	1109·0 (7·59 mmole)	Run 3(b) was made on residue remaining from 3(a)
Wt. loss in N_2 at 125° (stoich. = 12·33%), *mg*	165·2 (12·40%)	139·0 (12·58%)	140·0 (12·62%)	
Wt. loss in carrier gas at 420° for 3 hr, *mg*	93·2 (≡ 3·33 mmole CO)	81·2 (≡ 2·90 mmole CO)	99·6 (≡ 3·56 mmole CO)	48·6 (≡ 1·74 mmole CO)
Wt. CO_2 absorbed in 1st Ascarite tube, *mg*	140·0 (≡ 3·18 mmole CO_2)	15·7 (≡ 0·36 mmole CO_2)	89·9 (≡ 2·04 mmole CO_2)	77·8 (≡ 1·77 mmole CO_2)
Wt. CO_2 absorbed in 2nd Ascarite tube, *mg*	1·7 (≡ 0·04 mmole CO_2)	101·2 (≡ 2.30 mmole CO_2)	39·5 (≡ 0·90 mmole CO_2)	0·0
Total CO_2 absorbed, *mg*	141·7 (≡ 3·22 mmole CO_2)	116·9 (≡ 2·66 mmole CO_2)	129·4 (≡ 2·94 mmole CO_2)	77·8 (≡ 1·77 mmole CO_2)
Wt. H_2O absorbed in Anhydrone tube, *mg*			12·8 (≡ 0·71 mmole H_2O)	0·7 (≡ 0·04 mmole H_2O)

atmosphere neither prevented the decomposition of the pure salt nor reversed the decomposition of a partially decomposed sample. This observation means, of course, only that if the reaction is reversible, its equilibrium pressure of carbon monoxide at 420° is greater than 1 atmos.

The following conclusions may be drawn from the foregoing combustion train experiments and from the thermal measurements described in the preceding section:

1. In both oxidising and inert atmospheres the primary endothermic formation of carbon monoxide from anhydrous calcium oxalate is accompanied, to varying degrees, by one or more secondary exothermic reactions that produce carbon dioxide from carbon monoxide.
2. The direct oxidation of carbon monoxide by oxygen occurs more readily than the disproportionation reaction.
3. The heat evolved during direct oxidation of carbon monoxide by oxygen raises the temperature of the remaining sample and solid product at a rate greater than the heating rate of the furnace, and, as a result, the decomposition is more rapid in dry air than in dry nitrogen.

EFFECT OF VARIABLES UPON A DYNAMIC THERMOGRAM

The characteristics of the separate stages in a multi-stage pyrolysis have an important bearing on the interpretation of thermogravimetric data. In particular, the pyrolysis of calcium oxalate monohydrate, with its sequence of alternating reversible and irreversible reactions, coupled with secondary reactions between components of the atmosphere and a primary decomposition product, provides an ideal vehicle for demonstrating the effects of many variables upon the shape of a dynamic thermogram. In the remainder of this report, a series of comparison thermograms is presented to show these effects.

Geometry of sample container

Several investigators have recommended that for thermogravimetric measurements the sample should be loosely packed in a shallow dish in order to facilitate gaseous exchange between the sample and the atmosphere that surrounds it.[3,8,16,37,41] Indeed, Garn and Kessler[16] have declared, "That the traditional crucibles are useless in thermogravimetry is essentially true. In a few cases crucibles are acceptable... In controlled atmosphere work, where the atmosphere is solely the gas involved in the reaction, the geometry of the container is immaterial."

As can now be shown with calcium oxalate, the geometry of the container is also immaterial if no interaction is possible between the solid phase and the gaseous atmosphere or products. The pyrolysis of 500 mg of calcium oxalate monohydrate was conducted in flowing dry carbon dioxide using both a porcelain crucible and a quartz dish as sample holders. The thermograms in Fig. 9 are identical above about 275°, which marks the completion of the dehydration reaction in the crucible. As expected, the loss of water occurred more readily from the shallow dish than from the crucible. On the other hand, the shape of the container had no effect upon the decomposition of anhydrous calcium oxalate because this reaction is not reversible, and in a carbon dioxide atmosphere no important diffusion-controlled secondary reactions can occur. The shape of the container also had no effect upon the dissociation of calcium carbonate because this reaction is reversible, and the atmosphere used was

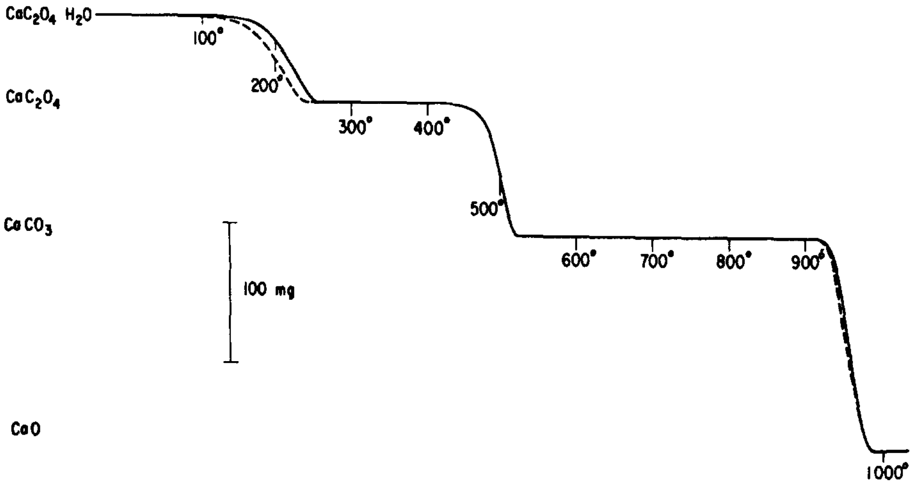

FIG. 9.—Effect of sample container upon thermogram for calcium oxalate monohydrate in flowing dry carbon dioxide (500 mg, 300 degree/hr):
- - - - quartz dish,
——— porcelain crucible.

solely the gas involved in the reaction. When the reversible pyrolysis of calcium carbonate was performed in a given container, the higher the pressure of carbon dioxide in the atmosphere, the higher the value of the procedural decomposition temperature and therefore, the smaller the reaction interval, ($T_f - T_i$). (Compare Fig. 9 with Figs. 5, 4, 6, and 10.)

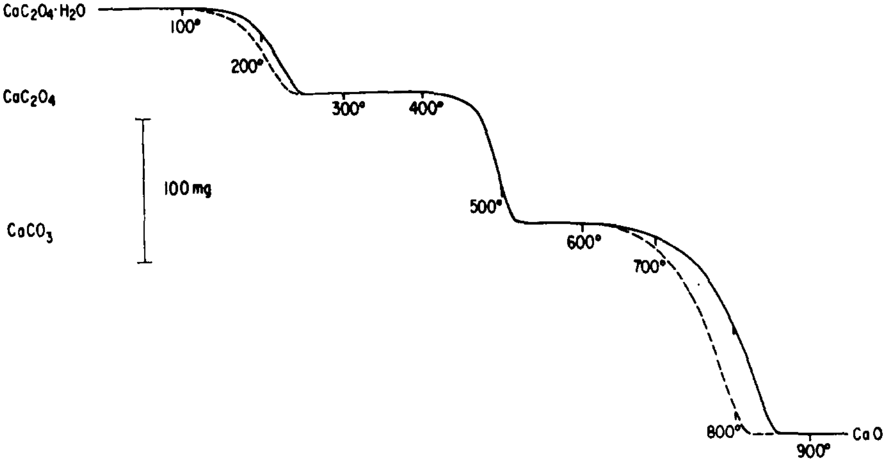

FIG. 10.—Effect of sample container upon thermogram for calcium oxalate monohydrate in flowing dry nitrogen (500 mg, 300 degree/hr):
- - - - quartz dish,
——— porcelain crucible.

When the pyrolysis was carried out in a flowing stream of dry nitrogen (Fig. 10), both the loss of water and the loss of carbon dioxide were affected by the shape of the container; the loss of carbon monoxide was unaffected. There is a thermodynamic possibility that the loss of carbon dioxide, illustrated by the dashed curve of Fig. 10, was caused by reaction between the calcium carbonate and the quartz dish. However, Longuet[59] has shown that this reaction becomes significant below 900° only if both the silica and the calcium carbonate are finely divided and intimately mixed. We have repeated the pyrolysis of Fig. 10 using a platinum-lined quartz dish, and the results were the same as those obtained with the unlined dish. Both curves shown in Fig. 10, therefore, represent only the thermal dissociation of calcium carbonate.

The marked effect of container shape that is illustrated in Figs. 9 and 10 provides evidence that a significant pressure of water vapour and carbon dioxide must have existed in the interior of the crucible during dissociation, even when the atmosphere that flowed over the crucible entered the thermobalance free from either water or carbon dioxide or both.

In the study of reversible reactions or of reactions in which a component of the atmosphere can react either with the original sample or with a solid or gaseous decomposition product, one must recognise the possible existence of such partial pressure gradients throughout a mass of powdered sample. These gradients can effect both the shape of thermogravimetric curves[31,51,52] and the magnitude of thermal effects that accompany the reactions.[30] They can be reduced by packing the powder loosely in a shallow dish,[16] by using crucibles with micro-porous[15,29] or macro-porous[1] walls, or by passing a controlled atmosphere through the bed of powdered sample. The effectiveness of the latter technique for differential thermal analysis has been vividly demonstrated by Stone,[50] who has also announced the development of thermogravimetric equipment to provide dynamic gas flow through the specimen under study.[46] Papailhau[39,40] has designed a crucible, for use with a null-type balance, that permits an externally generated atmosphere to be passed through the entire bed of powdered sample.

Except for the experiments of Figs. 9 and 10 that were made with a quartz dish, all differential thermal and thermogravimetric measurements described in this report were made with Coors high form-000 porcelain crucibles, in which both thermal gradients and partial pressure gradients undoubtedly existed. Reproducible results were obtained by careful control of experimental conditions, but, as illustrated by Fig. 10, these results would have been different with more efficient interaction between solid sample and gaseous atmosphere. The interpretation of the experiments has been made with this restriction in mind.

Comparison of dry nitrogen and dry oxygen

Thermograms that were obtained by heating calcium oxalate monohydrate in flowing atmospheres of dry nitrogen and of dry oxygen are shown in Fig. 11. The dehydration step is unaffected by the change in atmosphere, and the two curves are nearly identical in this region because both gases are equally effective in sweeping evolved water vapour away from the sample surface. On the other hand, the thermograms diverge at the intermediate stage because in oxygen or air the secondary oxidation of carbon monoxide raises the temperature of the unreacted solid at a rate greater than the heating rate of the furnace, producing a marked acceleration in the decomposition rate. The decomposition of calcium oxalate occurs more rapidly and is completed at a lower furnace temperature in an atmosphere of dry oxygen (or air) than in an atmosphere of dry nitrogen.

Although the product of this decomposition in either atmosphere is calcium carbonate, the procedural decomposition temperature for the subsequent loss of carbon dioxide was higher in the run made in an oxygen atmosphere than for that made in a nitrogen atmosphere (Fig. 11). This small difference is not an artifact of the instrument. Indeed, thermograms that we obtained by heating separate portions of the same sample of *calcium carbonate* in nitrogen and in air were identical in the region of weight loss because nitrogen and air were equally effective in sweeping away the evolved carbon dioxide. However, the calcium carbonate produced by the decomposition of a given sample of calcium oxalate in an oxygen atmosphere is *not* identical with that produced by decomposition of the same material in a nitrogen atmosphere.

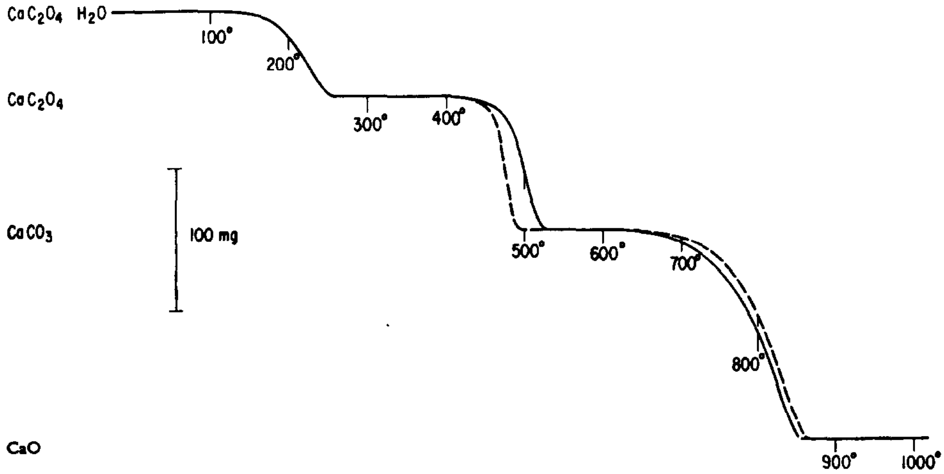

FIG. 11.—Effect of atmosphere upon thermogram for calcium oxalate monohydrate (500 mg, porcelain crucible, 300 degree/hr):

- - - - dry oxygen,
——— dry nitrogen.

The dry oxygen run shown in Fig. 11 was repeated, but at a temperature of about 450° the furnace was turned off and the flowing oxygen was replaced by flowing nitrogen. After the temperature had dropped to about 140°; the heating rate of 300 degree/hr was resumed. The resulting thermogram, although obtained in a nitrogen atmosphere, was identical above 500° with the dashed oxygen curve of Fig. 11. The thermogravimetric behaviour of the calcium carbonate in these experiments was determined by the atmosphere in which it had been formed and not by the atmosphere in which it was decomposed. Thermogravimetry cannot disclose whether this difference in pyrolytic behaviour is a reflection of differences in particle size, surface area, lattice imperfections, or some other characteristics, but these experiments and those shown in Fig. 10 do illustrate the usefulness of thermogravimetric measurements, made on a reliable balance, for quickly surveying a variety of experimental conditions and thus disclosing those areas in which more detailed studies should be made, possibly with other supplementary techniques. As will be shown later, the shape of even a single thermogram can indicate complexities in the reaction under study.

Sample weight

In the earlier discussion of successive, partially overlapping reactions, certain similarities were noted between the effects of heating rate and sample weight upon the shape of a dynamic thermogram. This parallelism cannot be carried too far. Unlike heating rate, sample weight is not a completely independent variable in thermogravimetry. For a given sample container a change in the weight of a powdered solid sample simultaneously changes the thickness of the sample bed, its total heat capacity, and its area of contact with the walls of the container, through which much of the heat transfer with the furnace atmosphere occurs.

Some of these factors can change during a pyrolysis, as illustrated by Fig. 12, in which are superimposed the thermograms obtained in ambient air with approximately 1 g of calcium oxalate monohydrate (Fig. 6) and those obtained with equivalent quantities of the anhydrous salt and calcium carbonate. The relationship between curve 12B and the second weight-loss section of curve 12A is the same as shown in Fig. 5 and arises from the overlap of the dehydration reaction and the loss of carbon monoxide. However, even though this second stage, the loss of carbon monoxide, was complete before the procedural decomposition temperature of calcium carbonate was reached (and therefore a true plateau was observed for this compound), the value of T_i for the loss of carbon dioxide is markedly lower for curve 12C than for curves 12A and B. Examination of the crucibles at the end of each pyrolysis showed that the residues of calcium oxide from runs 12A and B were more loosely packed than that from run 12C, and were separated by an air gap from the wall of the sample crucible. Although the final weight of calcium oxide was the same in each run, its volume represented a larger shrinkage from the initial sample volume in runs A and B than in run C. The gaps produced by this shrinkage undoubtedly reduced the flow of heat

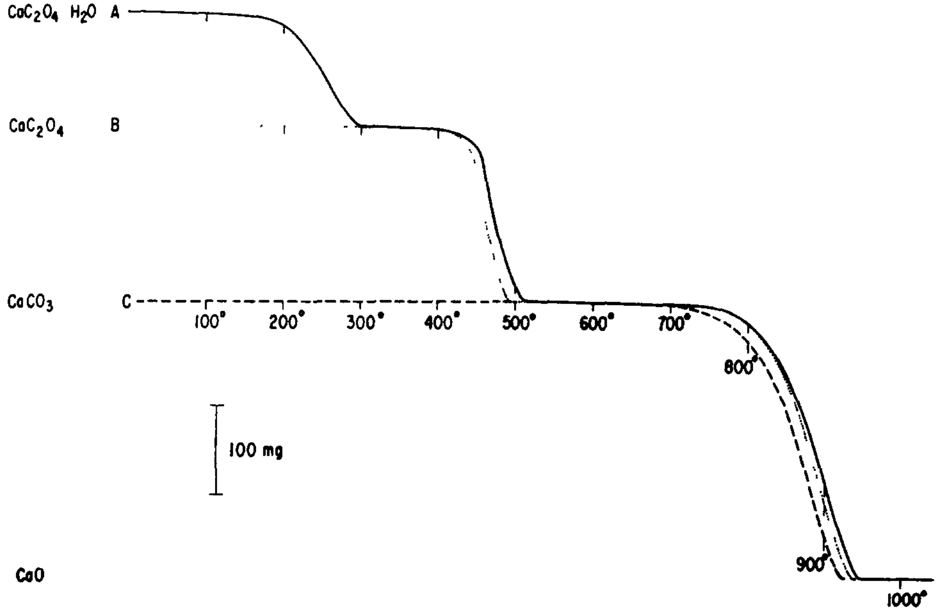

FIG. 12.—Thermogram for successive partially overlapping reactions (porcelain crucible, ambient air, 300 degree/hr; curve A as for Fig. 6):

——— 1·019 g of calcium oxalate monohydrate,
...... 0·893 g of calcium oxalate,
– – – – 0·699 g of calcium carbonate.

between the sample and furnace and thus contributed, at least in part, to the higher value of T_i in runs A and B.

Undoubtedly the effect of sample shrinkage observed with the 1-g (and equivalent) samples of Fig. 12 was also present during the runs made with 0·5-g (and equivalent) samples of Fig. 4, but because the sample was smaller the magnitude was much less.

Thus, although the thermograms of Fig. 4, demonstrate that under certain conditions the curve for a multi-stage pyrolysis can be considered as the exact summation of the curves for the individual stages, those of Figs. 11 and 12 emphasise that under other conditions the thermogravimetric behaviour of a given substance may depend upon whether it is the material initially loaded into the sample container or whether it is formed in the container by decomposition of a percursor.

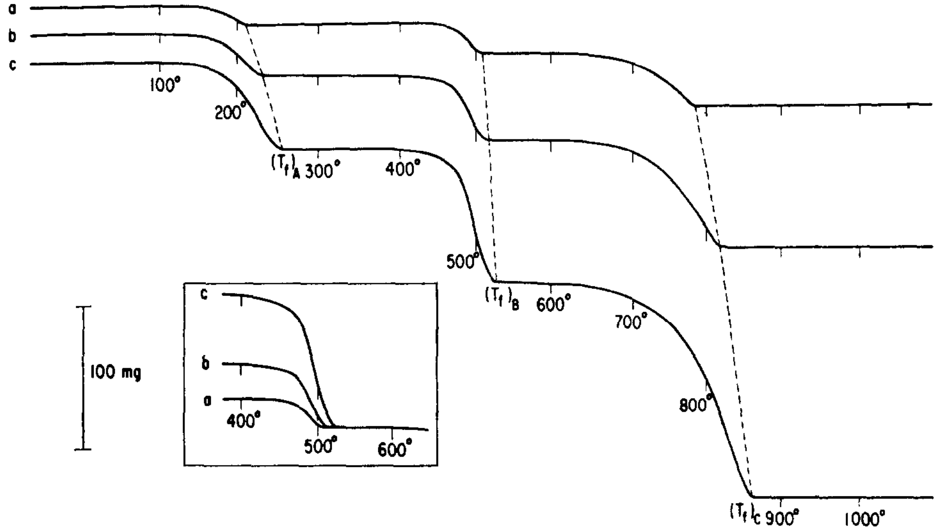

FIG. 13.—Effect of sample weight upon thermogram for calcium oxalate monohydrate in flowing dry nitrogen (porcelain crucible, 300 degree/hr):

a—126 mg of calcium oxalate monohydrate,
b—250 mg of calcium oxalate monohydrate,
c—500 mg of calcium oxalate monohydrate.

Insert shows three curves superimposed at calcium carbonate level to emphasise effect of sample weight on loss of carbon monoxide.

From the foregoing results it appears that no generalisations can be made about the effect of sample weight upon the procedural decomposition temperature, particularly for intermediate products. Even with powdered calcium carbonate as a starting material, Richer and Vallett^{44,45} found that T_i was virtually independent of sample weight in the range 0·25 to 1 g, both in nitrogen and carbon dioxide. At 100 degree/hr, T_i was 517° in nitrogen and 914° in carbon dioxide. On the other hand, once the decomposition of a powdered solid has begun, it generally does not occur uniformly in every particle throughout the entire mass of sample.^{31,51,52,55} Measurable temperature gradients exist even across relatively thin beds of powder.$^{32-34}$ Under such non-homogeneous conditions one would expect that the time required for complete decomposition of a powdered solid would increase with increase of sample weight. Because the furnace heating rate is linear there would be a resultant increase in the observed value of T_f. This expected increase was observed by Richer and

Vallet[44,45] for the pyrolysis of calcium carbonate and in this work for each stage in the pyrolysis of calcium oxalate monohydrate in nitrogen at 300 degree/hr (Fig. 13).

A perturbation in this generalisation can occur if the reaction is exothermic. The sample temperature then increases more rapidly than does the measured furnace temperature, and the resultant acceleration in specific reaction rate may compensate, at least in part, for the increase in sample weight. It has already been noted that in air the endothermic decomposition of calcium oxalate is accompanied by the highly exothermic oxidation of carbon monoxide, with a consequent acceleration of the reaction rate. As a result, as shown in Fig. 14, T_f for the decomposition of calcium oxalate in air is less than in nitrogen and is virtually independent of the starting weight of monohydrate, at least in the range 125 to 500 mg. A comparison between Figs. 14 and 6 shows the normally expected increase in T_f between 500 mg and 1 g and the pronounced increase in T_i for calcium carbonate that was noted in the discussion of Fig. 12.

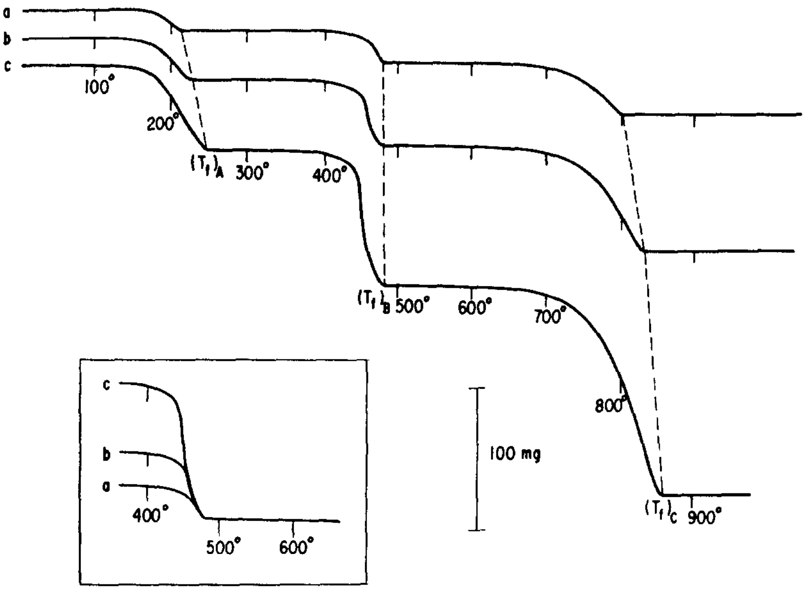

FIG. 14.—Effect of sample weight upon thermogram for calcium oxalate monohydrate in ambient air (porcelain crucible, 300 degree/hr):

a—126 mg of calcium oxalate monohydrate
b—250 mg of calcium oxalate monohydrate,
c—500 mg of calcium oxalate monohydrate.

Insert shows three curves superimposed at calcium carbonate level to emphasise that T_f for loss of carbon monoxide is independent of sample weight.

Water vapour

The value of a dynamic thermogram in the preliminary study of chemical reactions lies not just in its gross characteristics, such as plateaux or clearly marked changes of slope, from which one can draw inferences about the stoichiometry of the reaction, but also in the more subtle variations of shape that may reflect the complexity of the reactions that produce the more noticeable, over-all weight changes. This is illustrated by a re-examination of Fig. 4 for the pyrolysis of calcium oxalate monohydrate in ambient air. The over-all stoichiometry of the three distant stages is clearly defined by each of the plateaux. However, there is a significant qualitative difference between the shape of the curve that marks the loss of carbon monoxide and the shapes of the curves for the loss of water and of carbon dioxide. The latter curves are smooth and continuous between the two plateaux, but the loss of carbon monoxide is characterised by three rather abrupt changes in slope that have no apparent stoichiometric significance. This shape is reproducible and is not an artifact of the instrument, although it can be modified by using a platinum instead of a porcelain crucible. Clearly, the thermogram suggests that further investigation of this stage of the reaction is warranted.

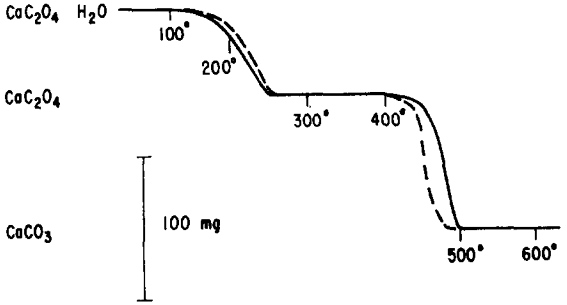

FIG. 15.—Effect of water vapour upon thermogram for calcium oxalate monohydrate in oxidising atmosphere (500 mg, porcelain crucible, 300 degree/hr):

——— dry air,

– – – – humid air.

In the region of carbon monoxide loss the curve obtained in ambient air (curve A of Fig. 4 and curve *c* of Fig. 14) is identical to the dashed curve in humid air.

Additional experiments were performed, which showed (Fig. 15) that the unusual shape, originally observed in ambient air, could be reproduced exactly in a flowing atmosphere of humidified air, but that in dry air the loss of carbon monoxide was characterised by the same smooth continuous shape noted in Fig. 11 for dry nitrogen and oxygen. Furthermore, the accelerating effect of water vapour upon the decomposition of CaC_2O_4 is clearly evident from the curves of Fig. 15. Finally, a comparison between thermograms obtained in dry air, dry nitrogen, and humid nitrogen (Fig. 16) shows that the loss of carbon monoxide begins more abruptly and at a lower furnace

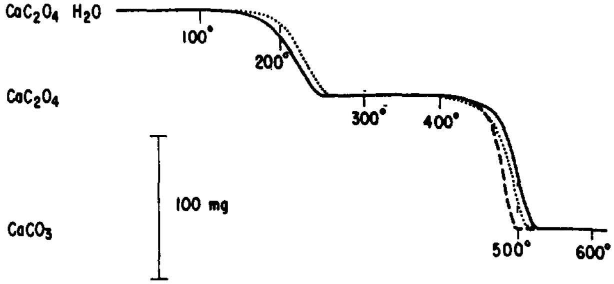

FIG. 16.—Effect of water vapour upon thermogram for calcium oxalate monohydrate in inert atmosphere (500 mg, porcelain crucible, 300 degree/hr):

——— dry nitrogen,

...... humid nitrogen,

– – – – dry air.

temperature in humid nitrogen than in dry air, although the total loss is completed at a lower furnace temperature in the latter gas.

That water vapour has a marked effect upon the decomposition of anhydrous calcium oxalate was confirmed by repeating the thermal experiments illustrated in Fig. 7 with humidified gases. The exotherm noted previously in dry oxygen was still present, but it had been shifted about 40° to a lower temperature. In humidified nitrogen, however, the magnitude of the endotherm for the oxalate decomposition was significantly reduced. The combustion train experiment was also repeated as a two-part experiment. During the first 3-hr period the carrier gas was humidified nitrogen; during the second 3-hr period it was dry oxygen. For the period in humidified nitrogen the combustion train was modified by inserting a large capacity water absorption tube at the exit end of the pyrolysis tube to ensure that no water vapour was present in the gas that entered the first Ascarite tube. In addition, an Anhydrone absorption tube was inserted in the train immediately after the copper oxide furnace. Any hydrogen in the gas stream leaving the reaction zone would be oxidised by the hot copper oxide and be absorbed as water in the Anhydrone tube.

The results are listed as runs 3(a) and 3(b) in Table II. The following comments are pertinent to the data:

1. The amount of calcium oxalate that decomposed during the first 3 hr at 420° was significantly greater in humid nitrogen than in dry nitrogen.

2. Unlike run 2 made in dry nitrogen, less than one-third of the total carbon dioxide that was absorbed by the Ascarite appeared in the tube that was mounted at the exit end of the copper oxide furnace, indicating that less than one-third of the evolved carbon monoxide left the reaction zone unchanged.

3. Part of the carbon monoxide evolved in the humidified nitrogen atmosphere was oxidised by the water vapour to carbon dioxide:

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H_{700^\circ K} = -9{\cdot}1 \text{ kcal}^7 \qquad (6)$$

The hydrogen that was simultaneously produced appeared as water after it had passed through the copper oxide furnace.

4. Not all of the evolved carbon monoxide ended up as carbon dioxide. Unlike runs made in dry air and dry nitrogen, the total mole of carbon dioxide absorbed during run 3(a) was significantly less than the weight loss of the sample, calculated as mole of carbon monoxide. During this run in humid nitrogen a yellow deposit appeared at the cool exit end of the combustion tube. Preliminary pyrolysis experiments in humid nitrogen with both calcium and magnesium oxalates had produced similar deposits, which were soluble in benzene and whose infrared spectra showed them to contain aliphatic C-H bonds. In addition to hydrogen, various hydrocarbon species are thermodynamically possible products of the reaction between carbon monoxide and water vapour. Depending upon their volatility, such species can condense out of the gas stream at various points in the train before the copper oxide furnace and therefore would not appear ultimately as carbon dioxide and water. More volatile hydrocarbons might reach the hot copper oxide tube but be incompletely oxidised in passing through it. Experience in this Laboratory has shown that at the recommended temperature of 700° for operation of the copper oxide furnace, even the oxidation of methane may be slow enough to permit small amounts of the gas to pass

through the reaction zone unchanged. For the foregoing reasons a reliable material balance was not possible in this experiment.

5. To confirm the reliable operation of the train itself, run 3(b) was made by passing dry oxygen over the residue remaining from 3(a). As seen from the results in Table II, all of the evolved carbon monoxide was oxidised in the reaction zone and was absorbed as carbon dioxide in the first Ascarite tube.

No further work has been performed to explore and understand the effect of water vapour upon this reaction, and certainly thermogravimetry alone will not provide the answers. Thermogravimetry has provided, however, as few other techniques could, simple and graphic evidence for the existence of an effect that might warrant further investigation.

CONCLUSION

Calcium oxalate monohydrate is ideally suited for demonstrating many of the factors that affect the quality of thermogravimetric measurements. It is particularly useful for showing the great variety of effects that may be produced by three common atmospheric constituents, carbon dioxide, oxygen and water vapour, as well as three common experimental variables, heating rate, shape of sample container and size of sample. These variables and the interaction between them will determine whether the thermogravimetric curve for the pyrolysis of calcium oxalate monohydrate will appear as a succession of independent reactions or as a sequence of partially overlapping and non-independent reactions. Calcium oxalate monohydrate can be used as a standard for judging the performance of a thermobalance only if it is pyrolysed under carefully controlled conditions.

Acknowledgments—The authors acknowledge the skilful assistance of Adrian Breitenstein, Harley W. Middleton and Mrs. Renette Vincelette, in performing some of the measurements described in this report. They are also indebted to Dr. Paul D. Garn, University of Akron, for suggesting both the interpretation of the calcium carbonate portion of Fig. 11 and the revised experiments described in the text.

Zusammenfassung—Die Pyrolyse von Calciumoxalat-Monohydrat an Luft nimmt in der Literatur über Thermogravimetrie einen hervorragenden Platz ein. Ein Thermogramm dieser Reaktion war die erste von Duval und Mitarbeitern publizierte Pyrolysenkurve und Duval und andere schlugen diese Substanz als Bezugssubstanz zur Beurteilung der Anzeige einer Thermowaage vor. Die Pyrolyse von Calciumoxalat-Monohydrat gibt aber unter verschiedenen Bedingungen beträchtliche Unterschiede in den Thermogrammen. Die Einflüsse von Probengröße, Aufheizgeschwindigkeit, Atmosphäre und Gefäßgeometrie werden in einer Reihe von Thermogrammpaaren vorgelegt und die Unterschiede mit zusätzlichen Informationen aus Differential thermoanalyse und Versuchen im Verbrennungs-schiffchen erklärt. Besonders wichtig sind Änderungen der Atmosphäre: untersucht wurden trockener und feuchter Stickstoff, trockene und feuchte Luft, trockener Sauerstoff, Kohlendioxyd und Kohlenmonoxyd. Selbst geringfügige Änderungen der Form eines Thermogramms von einer verläßlichen Waage können die Kompliziertheit der Reaktionen widerspiegeln, die die leichter bemerkbaren Gewichtsänderungen insgesamt hervorrufen. Die hier vorgelegten Ergebnisse grenzen auf diese Weise die Arbeitsbedingungen ab, unter denen Calciumoxzlat-Monohydrat als thermogravimetrische Bezugssubstanz verwendet werden kann, und sie zeigen, daß sein Verhalten in einer Thermowaage unter kontrollierten Bedingungen eine ungewöhnlich vielseitige Anleitun zur Interpretation thermogravimetrischer Messungen bieten kann.

Résumé—La pyrolyse dans l'air de l'oxalate de calcium monohydraté occupe une place unique dans la littérature de la thermogravimétrie. Non seulement la première courbe de pyrolyse publiée par Duval et ses collaborateurs a été un thermogramme de cette réaction, mais Duval et d'autres auteurs ont proposé ce composé comme substance de référence pour juger des possibilités d'une thermobalance. Toutefois, la pyrolyse de l'oxalate de calcium monohydraté dans des conditions variées conduit à des différences considérables dans les thermogrammes. Les influences de la taille de la prise d'essai, de la vitesse de chauffage, de l'atmosphère, et de la forme du récipient, sont présentées dans une série de thermogrammes comparatifs, et les différences sont confirmées au moyen de preuves supplementaires apportées par l'analyse thermique différentielle et des expériences de combustion en série. Des variations dans l'atmosphère sont particulièrement importantes, et les atmosphères étudiées sont l'azote sec, l'azote humide, l'air sec, l'air humide, l'oxygène sec, le gaz carbonique sec et l'oxyde de carbone sec. Même de très faibles variations dans la forme d'un thermogramme obtenu avec une balance fidèle peuvent refléter la complexité des réactions qui produisent les changements de poids globaux les plus remarquables. Les résultats présentés dans ce mémoire délimitent ainsi les conditions d'emploi de l'oxalate de calcium monohydraté comme substance de référence thermogravimétrique, et montrent que son comportement dans une thermobalance, dans des conditions contrôlées, peut constituer un exemple particulièrement souple pour l'interprétation des mesures thermogravimétriques.

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COLORIMETRIC DETERMINATION OF NICKEL WITH 2-MERCAPTOBENZOTHIAZOLE

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Summary—A colorimetric method has been developed for determining nickel with 2-mercaptobenzothiazole. At pH 7·7–8·1 in an ammoniacal medium nickel forms a yellow-brown complex, insoluble in water but soluble in chloroform. It is suitable for determining nickel in the concentration range 0·4–16 ppm with an average error of 0·5–2%. Cobalt, copper and iron interfere and have to be removed by an anion-exchange method before analysis. Bismuth and lead, if present, are removed with hydrogen sulphide, and complex formation of 2-mercaptobenzothiazole with alkali metals is prevented by fluoridation. No other metals were found to interfere.

This paper describes an investigation of 2-mercaptobenzothiazole as a colorimetric reagent in chloroform for the determination of nickel. In procedures involving the use of dimethylglyoxime,[1] manganese interferes and has to be removed before the colorimetric determination can be applied. A literature survey revealed that 2-mercaptobenzothiazole has not been reported previously for the colorimetric determination of nickel.

2-Mercaptobenzothiazole is not specific for nickel, but the reagent allows the determination of nickel in the presence of many other metal ions. It has already found use as a reagent for the gravimetric determination of a variety of metals too numerous to be listed here. Majumdar and Chakrabartty[2] have also investigated this reagent for the colorimetric determination of palladium.

EXPERIMENTAL

Reagents

2-Mercaptobenzothiazole. 1% w/v in chloroform; for purification of the commercial material see *Appendix.*

Standard nickel solution. A stock solution prepared from *Specpure* nickel sponge was suitably diluted, so that 1 ml contained 0·1 mg of nickel.

Hydrochloric acid. 0·5*M* solution prepared from A.R. reagent (Merck).

Aqueous ammonia. 0·5*M* solution prepared from A.R. reagent.

Hydrofluoric acid. Conc. (A.R.) and (1 + 20) solution prepared from A.R. reagent.

Chloroform. A.R.

Apparatus

Spekker absorptiometer (mercury vapour lamp), 2-cm and 4-cm cells and Hilger No. 1 violet-blue filters.

Procedure

Transfer 1·0, 2·0, 3·0 and 8·0-ml portions of the standard nickel solution from a micro burette into a series of beakers containing 10 ml of distilled water. Using a pH meter, adjust the pH of the solutions to 7·7–8·1 with 0·5*M* aqueous ammonia or 0·5*M* hydrochloric acid. Transfer the solutions quantitatively into 100-ml separating funnels and extract the nickel with 2 × 10 and 1 × 5 ml of

1% 2-mercaptobenzothiazole in chloroform. Shake gently for 2 min for each extraction and filter the organic phase into a 50-ml volumetric flask by means of a small funnel fitted with a cotton wool plug. After filtration, wash the cotton plug through with fresh chloroform and make the extracts up to the mark with chloroform. Measure the optical density of the yellow-brown solutions against a blank in chloroform using 2-cm cells. Plot a graph relating the optical density to the quantity of nickel present; it should be linear and pass through the origin.

Calibrations containing from 0·01–0·10 mg of nickel should be carried out in the same way but using 25-ml volumetric flasks and 4-cm cells. Extraction of nickel is established with 10 ml and 5 ml of 1% 2-mercaptobenzothiazole in chloroform.

DISCUSSION

The nickel-2-mercaptobenzothiazole complex in chloroform is yellow-brown whereas the reagent solution itself is almost colourless. The absorption spectrum for the coloured complex shows a maximum near 750 mμ.

FIG. 1.—Complex formation as a function of pH.

The complex formation is dependant on the pH of the aqueous solution and Fig. 1 indicates that a pH of 7·7–8·1 is critical for the quantitative formation of nickel-2-mercaptobenzothiazole. The optical density of the complex in chloroform showed no change after 24 hr.

Job's method of continuous variations[3] shows that every atom of nickel in the complex is bound to two molecules of 2-mercaptobenzothiazole and that a single complex species is formed in solution.

Various metal ions have been tested, after fluoridation, by the method described and their colour reactions are as follows:

Bi: yellow; Co: green; Cu: yellow; Fe: brown;
Ni: yellow-brown; Pb: yellow; Pd not tested.

Al, Ag, Au, Ba, Be, Ca, Cd, Ce, Cr, Hg, K, Li, Mg,
Mo, Mn, Na, Re, Se, Sr, Sn, Te, Ti, U, Zr, Zn:
no colour reaction

The interference from cobalt, copper, bismuth and iron is entirely removed by an anion exchange method* on a large column with a resin bed of 350-ml volume,† rejecting the first 100 ml of eluate, after which 500 ml are collected for the analysis of nickel in 8*M* hydrochloric acid as described by Liberman.[4] Lead, if present, passes

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* Permutit "De-Acidite" FF(SRA 65) anion-exchange resin, chloride form, 14–52 mesh.

† At the discretion of the analyst the size of the column may, of course, be adjusted in accordance with the size of the sample.

through the column but is removed by gassing with hydrogen sulphide for a period of 5 min at pH 1 either before or after the anion-exchange separation.

After removal of all interfering metal ions the hydrochloric acid eluate is evaporated and made up to a convenient volume. An aliquot which should contain 0·02–0·8 mg of nickel is pipetted into a platinum crucible and 2 drops of sulphuric acid added, followed by 1 ml of perchloric acid. The sample is evaporated to dryness preferably on a sand bath. After cooling, 0·5 ml of hydrofluoric is added and the sample is again evaporated to dryness. The sample residue in the platinum crucible is dissolved by the addition of 3·0 ml of (1 + 20) hydrofluoric acid whilst heating. The sample solution is transferred into a beaker and the pH adjusted to 7·7–8·1, then quantitatively transferred into a 100-ml separating funnel and analysed as described. The concentration of nickel in the sample is read from the calibration curve.

RESULTS

To verify the method, tests were carried out in which known amounts of nickel were added to synthetic solutions of various metal ions. The results obtained are shown in Tables I–V.

TABLE I.—SOLUTIONS ALL EVENTUALLY MADE TO 50 ml IN CHLOROFORM. ERROR IS THE DIFFERENCE BETWEEN THE 'EXPECTED' AND 'OBSERVED' NICKEL CONCENTRATIONS EXPRESSED AS A PERCENTAGE.

(A) A 50-ml aliquot was separated on the column. After evaporation of the hydrochloric acid eluate the volume was adjusted to 100 ml and 5-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·448	0·498	−0·5
0·450	0·500	0·0
0·450	0·500	0·0
0·445	0·496	−1·0
	Average:	−0·39

Co 25; Cu 5; Mn 2; Al 2; Na 1; K 1; Ca 1; Ni 0·20 g/l. Polarographic check on Ni: 0·19, 0·18, 0·20 g/l.

(B) A 10-ml aliquot was separated and the volume adjusted to 100 ml; 20-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·360	0·400	0·0
0·335	0·396	−1·0
0·335	0·396	−1·0
	Average:	−0·70

Co 25; Cu 5; Mn 2; Al 2; Fe 2; Ni 0·02 g/l.

TABLE I (contd.)

Direct Determination of Nickel in Manganese Solution

(C) A 50-ml aliquot was taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·448	0·498	−1·0
0·450	0·500	0·0
0·445	0·493	−2·0
	Average:	−1·0

Mn 30: Ni 0·01 g/l.

(D) A 2-ml aliquot was diluted to 100 ml and 20-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·273	0·304	−2·0
0·280	0·312	0·0
0·275	0·308	−1·3
	Average:	−1·1

Mn 5; Ni 0·78 g/l.

(E) A 10-ml aliquot was made up to 100 ml and 10-ml portions were taken for each analysis.

Absorbance	Ni found, *mg*	Error
0·345	0·385	−1·3
0·348	0·388	−0·6
0·350	0·390	0·0
	Average:	−0·6

Co 50; Mn 2; Ni 0·39 g/l.

TABLE II.—DETERMINATION OF NICKEL IN MILD STEEL (SAMPLES FROM MILD STEEL RESIDUAL SERIES OF BUREAU OF ANALYSED SAMPLES LTD., NEWHAM HALL, MIDDLESBOROUGH, ENGLAND). ERROR IS THE DIFFERENCE BETWEEN THE 'EXPECTED' AND 'OBSERVED' NICKEL CONCENTRATIONS EXPRESSED AS A PERCENTAGE

(A) Sample SS 11 (solutions made to 50 ml in chloroform)

Wt. of sample, *g*	Absorbance	Ni found, *mg*	Error
1·5887	0·145	0·160	+1·0
1·4852	0·135	0·150	+1·0
1·1239	0·105		+2·0
		Average:	+1·3

Ni 0·01; Cr 0·04; Mo 0·19; Cu 0·01; W 0·01; Co 0·01; Sn 0·11; V 0·005; Al 0·008; Zr 0·045; Pb 0·003; Ti 0·002%.

TABLE II (contd.)
(B) Sample SS 12 (solutions made to 50 ml in chloroform)

Wt. of sample, *g*	Absorbance	Ni found, *mg*	Error
1·1124	0·295	0·330	−1·0
1·3765	0·375	0·415	+1·0
0·7840	0.210	0·235	0·0
		Average:	0·0

Ni 0·03; Cr 0·02; Mo 0·17; Cu 0·01; W 0·01; Co 0·25; Sn 0·02; V 0·01; Al 0·006; Zr 0·031; Mg 0·003; Pb 0·004; Ti 0·013%.

(C) Sample SS 17 (The sample was made up to a volume of 25 ml; 1·0, 5·0 and 10·0-ml portions were taken for analysis; sample weight: 0·7634 g; solutions eventually made to 50 ml in chloroform, except last solution made to 25 ml*)

Wt. of sample in aliquot	Absorbance	Ni found, *mg*	Error
0·1527	0·310	0·346	−1·3
0·1527	0·305	0·340	−3·0
0·3054	0·660	0·738	+4·3
0·03054*	0·29	0·068	−4·3
		Average:	−1·1

Ni 0·23; Cr 0·03; Mo 0·01; Cu 0·10; W 0·12; Co 0·12; Sn 0·005; V 0·10; Al 0·01; Zr 0·02; Pb 0·015; Ti 0·029%.

TABLE III.—NICKEL CONTENT IN COBALT ELECTROLYTE SOLUTIONS

(A) Group II metals were gassed with hydrogen sulphide at pH 1–2 for a period of 5 min. After filtration of the samples through Whatman No. 31 filter paper they were evaporated to near dryness, dissolved in 8*M* hydrochloric acid and column separated. Aliquots of 25 ml were taken from each sample. They were made up to a volume of 50 ml and 5-ml portions were taken for analysis. Solutions were all eventually made up to 50 ml in chloroform.

Sample No.	Absorbance	Ni found, *mg*
1	0·395	0·44
2	0·396	0·45
3	0·41	0·458
4	0·50	0·558

(B) Samples 1–4 were repeated but gassing with hydrogen sulphide was undertaken after the column separation.

Sample No.	Absorbance	Ni found, *mg*
1	0·395	0·440
2	0·400	0·455
3	0·410	0·460
4	0·520	0·570

Co 30; Mn 0·01; Cu 2 g/l.
Samples 2 and 4 contained 1 g of Bi/l.

TABLE IV.—DETERMINATION OF NICKEL IN LEACH RESIDUES

Samples of 2 g were digested in nitric and hydrochloric acid, evaporated to dryness, dissolved in 8*M* hydrochloric acid and column separated. The eluate, after evaporation, was gassed with hydrogen sulphide at pH 1–2. The samples were made up to a volume of 50 ml and 10-ml portions were taken for analysis. Solutions were all eventually made to 25 ml in chloroform.

Sample No.	Absorbance	Ni found, *mg*
5[a]	0·200	0·047
	0·200	0·047
	0·200	0·047
6[b]	0·140	0·028
	0·140	0·028
	0·140	0·028

[a] Dimethylglyoxime method after removal of Mn = 0·010% Ni. Mn 0·10; Bi 0·02; Cu 1·0; Co 0·4; Fe 17% (Al, Ca, Mg, Si rest).

[b] Dimethylglyoxime method after removal of Mn = 0·007% Ni. Mn 0·10; Bi 0·02; Cu 1·0; Co 0·3; Fe 16% (Al, Ca, Mg, Si rest).

TABLE V.—DETERMINATION OF NICKEL IN COBALT METAL IN THE PRESENCE OF MANGANESE (SAMPLES MADE UP TO VOLUME OF 100 ml AND EVENTUALLY MADE TO 50 ml IN CHLOROFORM)

Wt. of sample, *g*	Aliquot, *ml*	Absorbance	Ni found, *mg*
4·1717[a]	5	0·438	0·488
0·9290[a]	20	0·365	0·410
0·6230	20	0·250	0·280

[a] Because of the high cobalt load the eluate was evaporated and re-introduced on a fresh column for the removal of cobalt.

APPENDIX

Purification of 2-mercaptobenzothiazole

2-Mercaptobenzothiazole, when pure, is a creamy-white crystalline powder with a melting point of 182·2°. The reagent is available commercially but further purification is necessary.

Dissolve 20 g of commercial 2-mercaptobenzothiazole in 100 ml of 5% sodium hydroxide solution. Add 20 g of activated charcoal powder and shake for 5 min. Filter the solution under vacuum through a Buchner funnel using Whatman No. 42 filter paper. To the filtrate add 50 ml of 1% magnesium chloride (A.R.) solution and dilute to an approximate volume of 2 litres. Precipitate sodium 2-mercaptobenzothiazole whilst stirring with an excess of a dilute hydrochloric acid solution. Filter the precipitate under vacuum. Repeat the above operation without the use of charcoal or magnesium chloride. Filter and wash the precipitate freely with distilled water. Dissolve the partially dry filter cake in 200–300 ml of A.R. acetone. Filter the acetone solution, under vacuum, through a column approximately (0·5 inch in diameter) which contains 10 inches of Whatman cellulose powder. On top of the cellulose powder is placed a 3 to 4-inch layer of activated charcoal powder. The column packing is changed when half of the acetone solution has passed through it. Receive the filtrate into a 1-litre Buchner flask which contains 500 ml of distilled water. Filter the purified crystalline 2-mercaptobenzothiazole through a clean No. 3 Gooch crucible and dry the powder under vacuum over sulphuric acid.

Zusammenfassung—Eine quantitative Farbenmethode wurde für die Bestimmung von Nickel mit 2-Mercaptobenzothiazole im Bereich von 0·4–16 p.p.m. und einer Genauigkeit von 0·5–2 percent ausgearbeitet. Der Nickel 2-Mercaptobenzothiazole Komplex wird mit Chloroform in einem ammoniakalischem medium extrahiert und ist kritisch im pH Bereich 7·7–8·1. Kobalt, Kupfer und Eisen stören in der Bestimmung und werden mit einem Anionvertauscher in 8N Salzsäure festgehalten. Wismuth und Blei stören auch und müssen durch ausgasen mit Schwefelwasserstoff bei pH 1 zuvor oder nach der Anionvertauschtrennung beseitigt werden. Keine anderen Metalle stören.

Résumé—On a développé une méthode quantitative colorimetrique pour le dosage de nickel avec 2-mercaptobenzothiazole dans la portée de 0·4–16 p.p.m. avec une precision de 0·5–2 pourcent. Le complexe coloré du nickel 2-mercaptobenzothiazole est extrait avec du chloroforme dans un agent ammoniacal et est critique á pH 7·7–8·1 On élimine l'intervention du cobalt, du cuivre, et du fer par une methode d'échange dans du 8N acide chlorhydrique. Le bismuth et le plomb interférent aussi mais on les enléve par le moyen de passage au gaz avec du hydrogéne sulphuré á pH 1 on avant on aprés la séparation par l'échange du anion. On constata qu'aucun autre métal n'interféra.

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DETERMINATION OF GASES IN METALS BY AN IMPROVED VACUUM FUSION METHOD

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Summary—An improved gas extraction, collection, pressure measurement and calculation apparatus is described for use in the vacuum fusion method. It is designed for routine analysis and versatility in research investigations. The time required for gas collection is 1–2 min, including 15–60 sec for gas extraction. The total time required for a complete analysis is 7–9 min. The operating blank is 0·01–0·03 ml/30 min at 1850°. Analysis of 20 or more samples can be made in 8 hr, including loading, outgassing and gas analysis. A description is given of a newly designed gas extraction recording system for studying the optimum conditions for determination of gases in metals of current interest.

INTRODUCTION

In recent years there has been an increasing demand for simple and rapid analytical methods that may be used under plant conditions for the determination of gases in metals and many such techniques have been successfully developed.[1–4] Particularly in the steel industry, more rapid and simple procedures have been required, and for the newer metals, such as titanium, uranium, hafnium, tantalum, *etc.*, more exacting demands are imposed on the analytical method.[5–8]

In this paper an improved vacuum fusion apparatus is described. The apparatus provides the following features:

1. A rapid gas extraction system.
2. A furnace assembly which is available for various kinds of sample and a wide range of sample weights.
3. A system in which the state of gas extraction can be simply and rapidly observed.
4. A simple and automatic pressure measurement system and minimisation of the use of mercury.
5. An automatic computer geared to the gas analysis system.

EXPERIMENTAL

Apparatus

The general appearance of the apparatus and the arrangement of the components are shown in Fig. 1. This apparatus differs from others which have been described in the fast gas extraction system, gas extraction recording system, gas collecting system and pressure measurement system. Some general considerations on these matters precede the detailed description of the various parts of the apparatus.

Gas extraction system

It is important that the gases evolved from a sample are removed from the furnace tube as rapidly as possible to minimise losses from chemisorption and reactions with evaporating metal vapours or evaporated metal films. This requirement has been met by connecting a newly designed, fast mercury diffusion pump[9] to the furnace tube by a wide-bore spherical joint (50-mm dia.) as shown in Fig. 4.

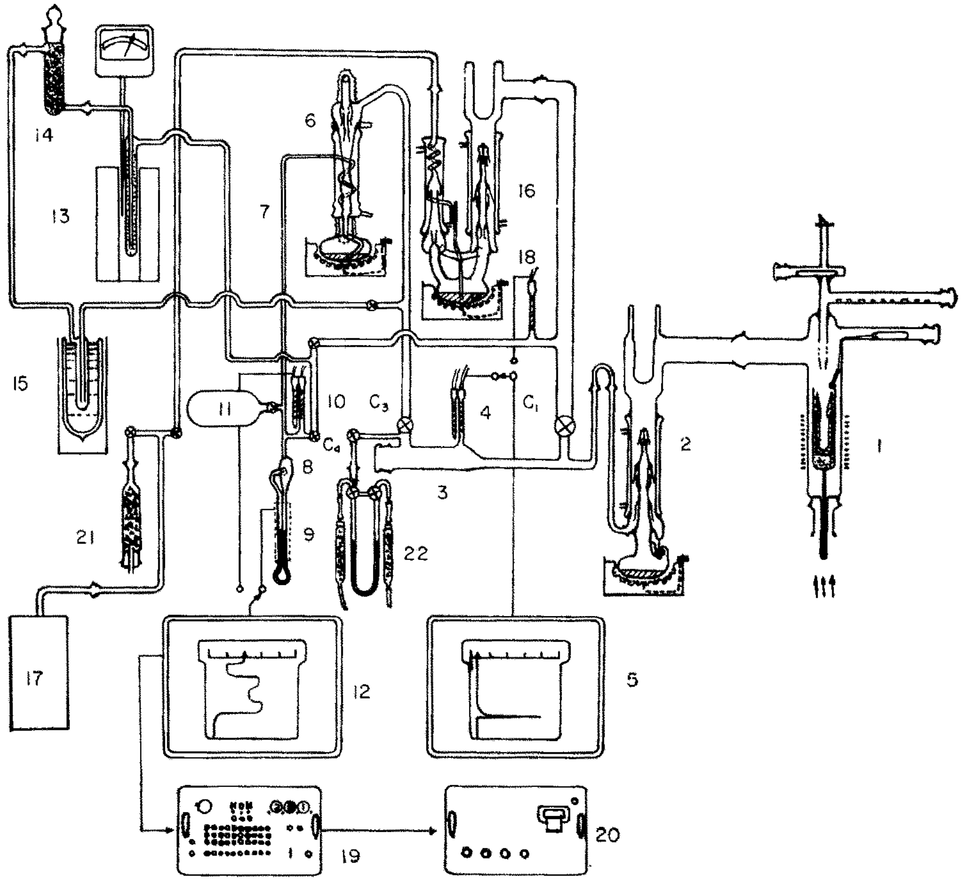


FIG. 1.—Schematic diagram of apparatus

1. Furnace assembly.
2. Extraction pump.
3. Intermediate gas collecting volume.
4. Pirani gauge P.G.2.
5. Automatic self-balancing recorder for gas extraction curve.
6. Collecting pump.
7. Gas collecting volume.
8. Oil manometer.
9. Photocells.
10. Pirani gauge P.G. 3.
11. Expansion volume.
12. Automatic self-balancing recorder for gas analysis.
13. CuO furnace.
14. Absorption tube (P_2O_5) for H_2O.
15. Cold trap for CO_2.
16. Exhaust pump.
17. Mechanical pump.
18. Pirani gauge P.G. 1.
19. Automatic computer for chemical analysis.
20. Digital printer.
21. Silica gel.
22. Silica gel.

C_1, C_3, C_4—stopcocks.

This transfer pump should have a reasonably high critical backing pressure because the pressure in the intermediate collecting volume (3 in Fig. 1) may occasionally build up to 0·1–0·3 mm of mercury. The pump used has, in fact, a speed of 70 litre/sec at 10^{-5}–10^{-2} mm of mercury and a critical backing pressure of 0·7 mm of mercury.

The spherical joint is sealed in place with synthetic rubber packing[10] as shown in Fig. 4, in place of grease, so that any blank caused by grease is reduced.

Gas extraction recording system

Pressure changes in the vacuum furnace chamber measured with an ionisation gauge attached directly to the high pressure side of the extraction pump do not follow accurately a pressure change at the beginning of gas evolution as shown in Fig. 2. Therefore pressure changes were measured indirectly with a Pirani gauge (4 in Fig. 1) attached to the intermediate collecting volume (about 400 ml) between the extraction pump and the collection pump. Pressure changes are recorded with an automatic self-balancing recorder to make gas extraction curves similar to the one illustrated in the right hand portion of Fig. 2. By partly closing the stopcock C_3 (Fig. 1), these curves can be run with greater sensitivity. Valuable information on gas extraction phenomena can be obtained from these recordings.

Stopcock C_3 is used to isolate the furnace system while the gas analysis is carried out. If gas extraction is incomplete, the residual gas evolved from the last sample can be collected during the following blank run in the intermediate collecting volume, and a check made to determine whether the gas extraction is complete or not.

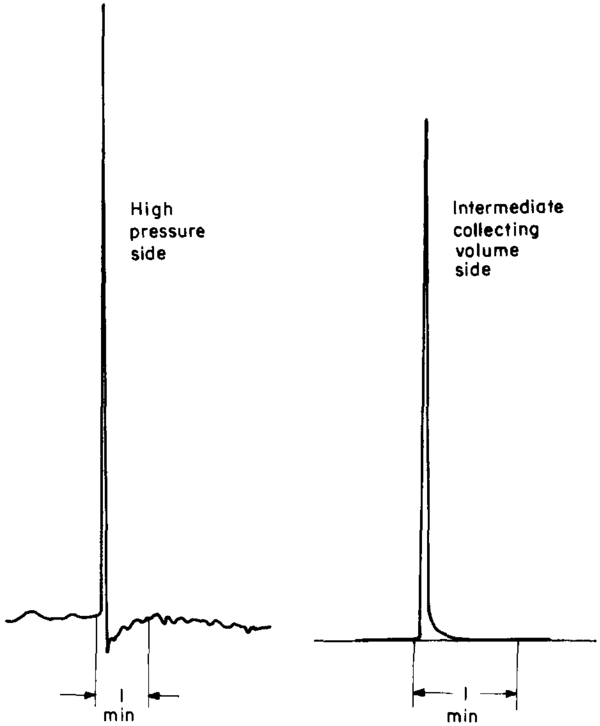


FIG. 2.—Comparison of pressure change between high vacuum side of extraction pump and intermediate collecting volume side.

Collection and circulation pump

The gas extracted is collected into a small collecting volume through the intermediate collecting volume with a newly designed vacuum pump. It is a two-stage mercury ejector pump (6 in Fig. 1),[9] capable of working against a high backing pressure. When the stopcock C_3 is closed, this pump can also be used to circulate the gas in the analysis system. Because the maximum backing pressure of this pump is 9 mm of mercury, the collecting volume can be made small, so that the pressure in it can be so high as to be easily measured.

The effective collecting volume is 75 ml, and the pressure in the collecting volume usually builds up to 3–5 mm of mercury. The speed of the pump is 5 litre/sec at 10^{-3}–1 mm of mercury.

Pressure measurement

Quantitative pressure measurements are made accurately, easily, continuously and rapidly by a newly designed oil manometer, as shown in Fig. 3, because the pressure in the collecting volume is comparatively high.

The oil used is No. 703 or 704 of Dow Corning Silicone. After redistilling and degassing, the oil is poured into the oil pool of the manometer. The manometer is attached to the collecting volume and turned upside down. Once more the oil is degassed by heating the oil pool with a weak flame. For the purpose of avoiding defects, such as absorption and release of gas, the volume of oil used should be a minimum and the contact area between oil and gas should also be a minimum.

An expansion volume of 400 ml (11 in Fig. 1) can be connected by opening a tap if the range of the oil manometer is exceeded by an unexpectedly large evolution of gas.

The volume in which the gases are collected is calibrated by means of a gas burette, and it can be determined with a precision of ±1 %. The temperature of the collecting volume should be held to within ±2° if a high precision measurement is desired. The electric current of the heater of the collection pump and the temperature of the cooling water should be controlled at the same condition as during calibration. The sensitivity (mg/mm of oil) for each gas is calculated, namely, 0·000670 for hydrogen, 0·00532 for oxygen and 0·00931 for nitrogen.

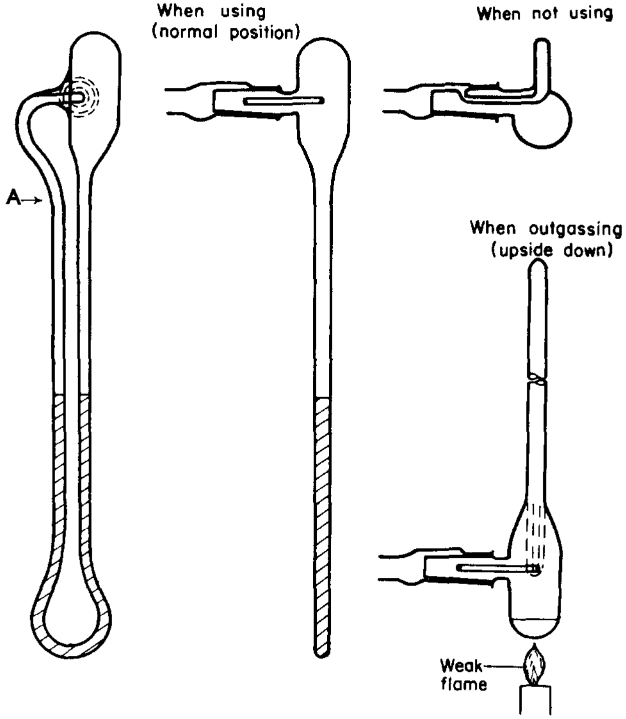


FIG. 3.—Oil manometer.
Below A the tubing is capillary.

The manometer reading is made automatically with photoelectric attachments and recorded on an automatic self-balancing recorder.

Induction heater

An induction heater of 3 kW nominal output at 400 kc/s is used. With the right combination of coil and crucible, a lower power, such as 0·6 kVA (plate voltage × plate current), is dissipated in the graphite to produce a temperature of 2300°. The 16-turn coil is 110 mm high with an internal diameter of 82 mm. The induction heater is provided with a control unit that gives a continuous change of temperature from about 800° to 2300°.

Furnace assembly

The furnace assembly developed by Guldner and Beach[11] has been modified. For the purpose of rapid gas extraction and collection, the dimensions of all parts of the assembly are changed as shown in Fig. 4. This section is an air-cooled Pyrex shell. A joint at the bottom is sealed in place with Dekhotinsky cement and acts as a support for a quartz thimble, which is positioned more uniformly and easily than when suspended by platinum wires from glass hooks. The thimble contains a graphite crucible surrounded by 200–250 mesh graphite powder.

The crucible with a renewable insert is of simple form. The insert, which makes a sliding fit with the crucible, is 75 mm high, 65 mm deep by 26 mm external diameter with a wall thickness of 3 mm, and has a working capacity of 50 g.

A large crucible assembly has the advantages of being able to treat a much greater total weight of metal per run, being more available for a wider range of sample weights, and having a lower rate of increase of bath viscosity, because of the reduction in the ratio of crucible-bath interface area to bath material. The disadvantage of having a somewhat larger blank than for a smaller crucible was a matter for consideration, but in practice the blank is usually as low as 0·01–0·03 ml/30 min at N.T.P.

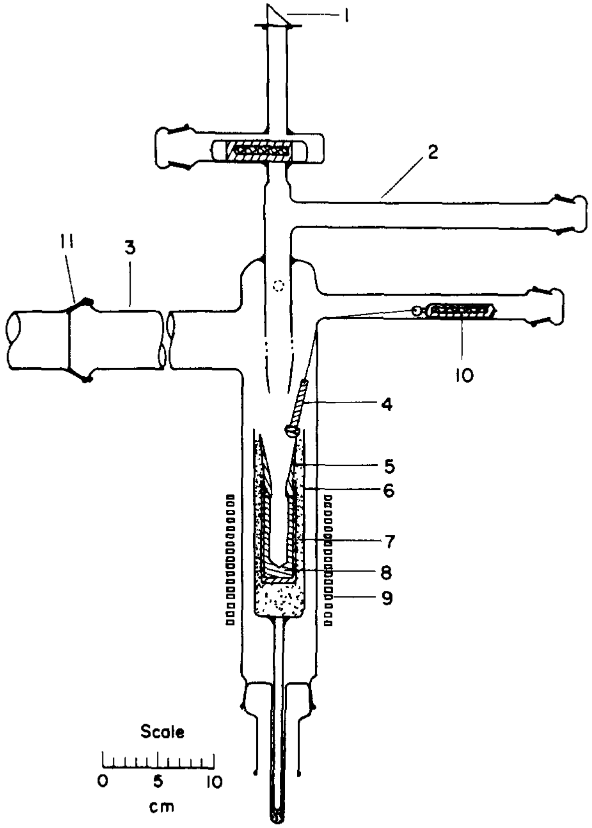


Fig. 4.—Furnace assembly:

1. Prism.
2. Side arm.
3. To diffusion pump.
4. Graphite lid.
5. Graphite funnel.
6. Quartz tube.
7. Graphite powder (200 mesh).
8. Graphite crucible.
9. Induction heater.
10. Magnetic plunger.
11. Rubber packing.

Gas analysis system

Low-pressure methods of gas analysis are rapid and accurate, and they have been used almost exclusively in the present work. Carbon monoxide and hydrogen are oxidised to carbon dioxide and water, respectively, by circulating the gas mixture over heated copper^{II} oxide. Water is absorbed with phosphorus pentoxide and carbon dioxide is frozen out in a liquid nitrogen trap. By measuring the pressure drop, each gas is determined. The residual gas is assumed to be nitrogen.

General vacuum system

The system is evacuated by a newly designed all-glass, two-stage mercury diffusion-ejector pump.[9] The speed is 30 to 50 litre/sec at 10^{-5}–10^{-3} mm of mercury, and the critical backing pressure is as high as 5 to 6 mm of mercury. By using this pump it is possible to shorten the outgassing time of the graphite crucible and also to simplify the apparatus on the low pressure side.

Calculation system

Analytical data can be automatically calculated and printed out with a digital electric computer[12] designed newly for chemical analysis. Briefly, if two resistances correspond with the sample weight and the sensitivity of the manometer, respectively, and a third resistance follows the response of the pressure change in the analytical system, and if these are used as three arms in the bridge circuit of the computer, the analytical data can be calculated by automatically matching the resistance of the fourth arm of the bridge circuit.

Safety devices

The most troublesome breakdowns in this apparatus were caused by failure of the cooling water, by breakage of glass parts or by the increase of leaks. The electric power to each part is automatically switched off by safety devices assembled with a pressure gauge or water level meter and meter relay. By these devices, any accident of interruption of the water supply or vacuum break can be avoided. Occasionally at the beginning of heating, a sudden rush of graphite powder used as a heat shield has been experienced. As a symptom of such a sudden rush, the vacuum becomes poorer. At this time a safety device switches off the induction heater automatically and then the sudden rush can be prevented.

Procedure

Sample preparation

A sample weight of 0·1–10 g, but below 10 mm in maximum dimension, is suitable for analysis. Samples are cut by a lathe or shaper without using cutting oil and should be stored in the side arm of the furnace chamber. Twenty or more samples can be placed in the side arm and released in turn by means of magnetic plungers.

Outgassing

Before a new crucible is placed in the apparatus, it is preheated to 400–500° in a stream of argon for about 1 hr. This reduces the time necessary for outgassing and also the crucible blank.

After evacuation of the system, the temperature of the crucible is raised to 2200–2300° and held at this temperature for 1·5–5 hr. The crucible assembly should not be outgassed at a higher temperature, otherwise the rate of evaporation of graphite becomes excessive.

When the outgassing of the graphite crucible is complete, the crucible is allowed to cool to below the extraction temperature. It is then desirable to outgas the bath material little by little because of the reduction of the time necessary for outgassing.

Blanks

The 'blank' gas is collected for 30 min and analysed. The composition normally consists of 30 to 100% of carbon monoxide, 0–70% of hydrogen and is free from nitrogen. The average value of the blank rate at 1850° is equivalent to 0·01–0·03 ml/30 min at N.T.P. This normally is only a small percentage of the gas collected from a sample during a collection time of 1 to 2 min.

The blank is always measured for the 3 min immediately following the collection of gas from a sample. Carbon monoxide and hydrogen blanks do not increase with the number of droppings of the sample but the nitrogen blank tends to increase gradually for some kinds of sample.

Dropping the sample

To obtain a rapid reduction of the oxide, it is generally desirable to introduce the sample into a molten metal bath containing dissolved graphite, except light metal samples. Even if the reaction between bath and sample is violent and a part of the sample or bath material is ejected from the crucible, or if the gas comes off in a rush from the crucible, our experience has shown that lower results are not obtained. It has been observed with the gas extraction curve that ejection of a sample does not happen before gas evolution but at the same time. The crucible lid has been provided but we have not used it, except when outgassing a crucible assembly. By this means, a prolonged stay of gas inside the crucible is avoided. Generally, it seems that high pressure causes incomplete extraction of the gas.

Gas extraction temperature

A gas extraction curve for every kind of sample is determined while the crucible temperature is increased from 800° to 2100°. The selected extraction temperature is 50°–100° higher than the temperature at which gas evolution stops.

Collection time

The observed gas extraction curves show that only 15–60 sec is required for the rate of evolution to become equal to that of the original blank rate. In this apparatus, the gas is usually collected for

1–2 min. If residual gas is found in the intermediate collecting volume during the following blank run, the gas is measured again and analysed.

Gas analysis

The analysis of the gas, the evacuation of the nitrogen and the transfer of the following blank gas into the system, can be completed in 5–7 min. It is undesirable to use anhydrous magnesium perchlorate as an absorber of water vapour in place of phosphorus pentoxide, possibly because of the higher water vapour pressure of the former.

Time required for analysis

The time required for determination of gases in a metal is as follows:

1. Setting furnace assembly, including crucible assembly and sample introduction	30 min
2. Pumping out furnace	5 min
3. Outgassing of crucible at 2200°–2300°	90–300 min
4. Cooling to extraction temperature	5–7 min
5. Blank run	3 min
6. Dropping of sample	0·05–0·2 min
7. Gas collection time	1–2 min
8. Gas analysis (for three elements)	7 min
(for oxygen only)	5 min
9. Calculation by automatic computer	0·1 min
10. Recording with digital printer	0·05 min
11. Evacuation of gas analysis system	0·5–1 min

The total time required for carrying out a complete extraction up to printed results is 7–9 min. If the time required for gas analysis is shortened, the total time may be reduced even more. Analysis of 20 or more samples can be made in 8 hr, including loading, outgassing and gas analysis.

APPLICATION OF GAS EXTRACTION CURVE

Much valuable information about gas extraction phenomena can be obtained from the gas extraction curves measured with a Pirani gauge (4 in Fig. 1).

Gas extraction curve at extraction temperature

From a curve recorded at the extraction temperature, information can be obtained on the following items: state of gas evolution, gas extraction time and gas collection time, successful dropping of sample, state of melting of sample and bath condition.

If dropping, melting and gas extraction are carried out under good conditions, the normal gas extraction curve has a shape similar to curve A in Fig. 5. In such a case, the gas extraction may be completed in as short a time as 15–60 sec.

A gas extraction curve also provides information on whether the results are reasonable or not. For example, when analysing hafnium metal samples, various shapes of gas extraction curve, as shown in Fig. 6, were obtained. The normal gas extraction curve shown in Fig. 6 (A) gives accurate results. Low results are obtained for extraction curves of the type shown in Fig. 6 (B).

When pieces of sample or bath material are dropped one by one into a new crucible, the shape of the gas extraction curve changes gradually and approaches the shape of a normal gas extraction curve as shown in Fig. 7. By this means the state of melting of a metal sample can be observed.

When unexpectedly large amounts of gas evolve from a sample, the curve obtained is similar to B in Fig. 5. In such a case, the tap of the expansion volume should be opened as soon as possible. If a sample is occasionally caught on an upper position of the crucible and does not drop directly into the bath, the curve obtained is as shown in Fig. 5 (C) or (D). Sometimes a similar curve is observed when the bath becomes viscous and a dropped sample floats on the bath.

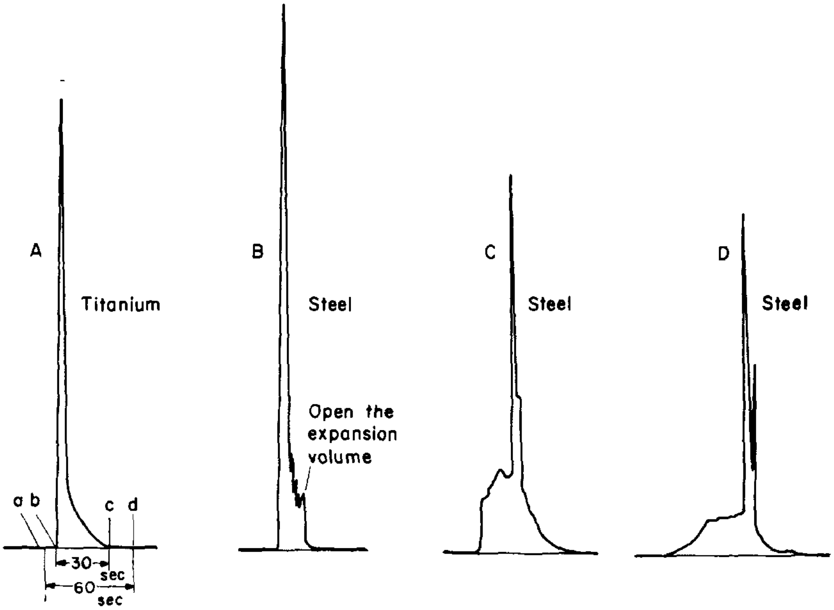
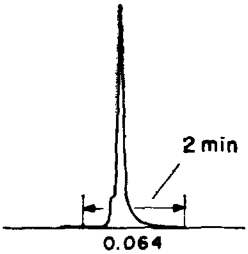
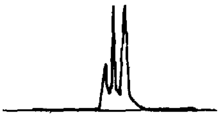


FIG. 5.—Gas extraction curves at extraction temperature:
a–d = collection time,
b–c = extraction time.



0.064
Oxygen, %
(a)



0.045
Oxygen, %
(b)

FIG. 6.—Extraction curves of gases in hafnium metal at 1900° (bath material: nickel).

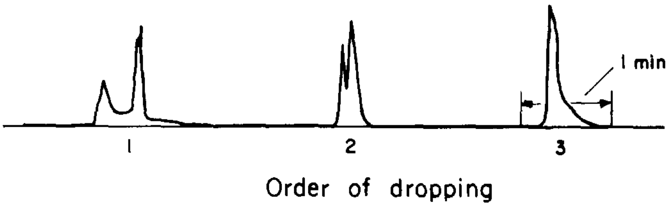


FIG. 7.—Change of gas extraction curve with order of dropping (sample: nickel; temperature: 1850°).

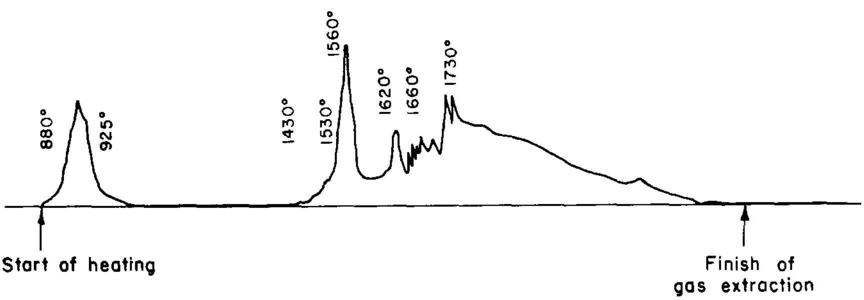


FIG. 8.—Extraction curve of gases in hafnium with increasing temperature.

Gas extraction curve with increasing temperature

From a curve recorded with increasing temperature, information can be obtained on the following items: gas extraction temperature, form of oxides or nitrides, *etc.*

It is very important to decide on a reasonable gas extraction temperature. That is, its temperature should be high enough to complete the extraction but conversely it should be as low as possible in order to avoid the evaporation of sample and bath material. A reasonable temperature can be decided by a gas extraction curve. For example, by this means, the extraction temperature of a sample of hafnium metal in a nickel bath could be decided easily and reasonably. Its extraction curve is shown in Fig. 8.

The total oxygen and nitrogen in a sample can only be obtained by the usual vacuum fusion method. If some information on the form in which the oxygen or nitrogen exists can be obtained, this will be very useful, particularly in the steel industry. By measuring a gas extraction curve with increasing temperature, some information on the form of the oxides or nitrides can be obtained. For example, gas extraction curves of some kinds of steel are shown in Fig. 9. The shape of the curves varies with the kind of sample and it seems that there is a possibility of inference of the form of oxide or nitride.

APPLICATION

Iron and steel

Samples of various kinds and various ranges of oxygen content from 10 ppm up to 650 ppm have been examined. The determinations were made at 1850° without employing a bath material, using sample weights up to 2 g and collecting the gas for 1 min. More reproducible results were obtained than with other types of apparatus and in spite of a very short collection time the analytical results coincided with those found by other investigators, as shown in Table I. The effect of manganese[14] on the determination of oxygen in steel was also studied. As shown in Table II, if a platinum or tin bath is used, the effect of manganese was negligible, but without such a bath more than about 1 % of manganese had a bad effect.

A number of difficulties in the determination of nitrogen by the vacuum fusion method have been reported.[13] Nitrogen results obtained with the old type of apparatus at our laboratory were 20–50 % lower than with the Kjeldahl method. By using the new apparatus the recovery of nitrogen increased, and the nitrogen values were lower by 0–15 % than those obtained by the Kjeldahl method. We think this is caused by the very fast gas extraction. If the same collection time as with oxygen is applied, the extraction of nitrogen is incomplete and the nitrogen content in a blank run gradually increases. Therefore, the amount of nitrogen in the following 26-min blank run was added to the nitrogen value of the last sample. Consequently, the reproducibility was relatively improved as shown in Fig. 10. Yet these results were a little lower than the Kjeldahl values. By using a platinum bath, however, the difference became smaller and in addition, if the collection time was reduced to only 3 min, the recovery of nitrogen was almost complete. Moreover, the effect of manganese on the determination of nitrogen almost disappeared. These results are shown in Table III.

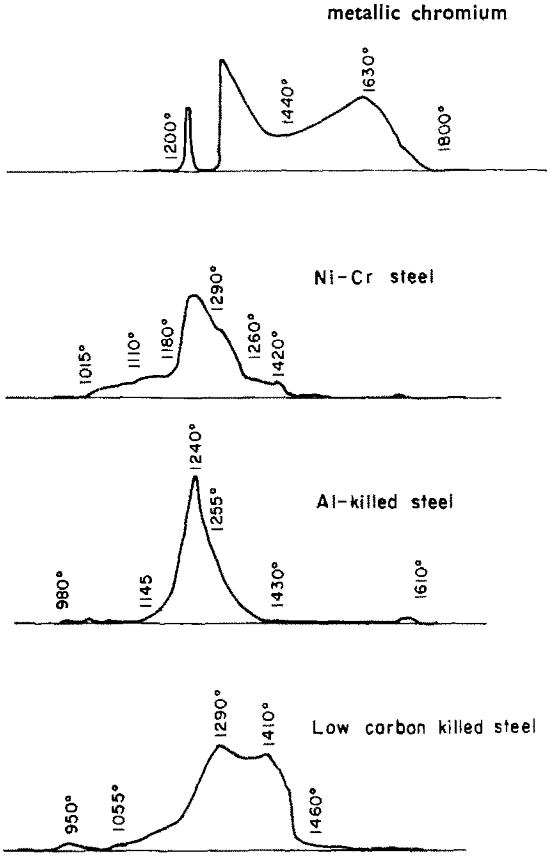


FIG. 9.—Gas extraction curve of various steels and metallic chromium with increasing temperature.

TABLE I.—COMPARISON OF OXYGEN DETERMINATION BETWEEN DIFFERENT LABORATORIES

	Our Laboratory		Gas Analysis[a] Committee		Japan Steel Works Ltd.
	Found, *ppm*[b]	σ,[c] *ppm*	Found, *ppm*[b]	σ,[c] *ppm*	Found, *ppm*
Ni-Cr steel	42	1·3	43	8	—
Low carbon killed steel	54	1·3	58	7	—
Nitriding steel	18	0·8	17	5	—
Carbon steel	79	2·6	—		78
Alloy steel	49	1·8	—		49
Pure iron	176	1·7	—		—
Electrolytic iron	640	10	—		—

[a] Gas Analysis Sub-committee of the 19th Committee in the Japan Society for the Promotion of Science. Collection time: 10–30 min.

[b] Average value.

[c] σ is the standard deviation of the analytical data.

TABLE II.—EFFECT OF MANGANESE ON DETERMINATION OF OXYGEN IN STEEL

Sample	Manganese, %	Oxygen, %		
		None	Pt-Bath	Sn-Bath
Carbon steel	0·35	0·020$_3$	0·020$_1$	0·019$_6$
18-Cr stainless steel	0·50	0·014$_0$	0·014$_5$	0·018$_5$
13-Cr stainless steel	0·65	0·016$_8$	—	0·018$_8$
Cr-Mo steel	0·79	0·005$_3$	0·005$_7$	—
Mn steel	1·02	0·002$_0$	0·006$_2$	0·006$_1$
18-Cr-8-Ni stainless steel	1·35	0·003$_7$	0·011$_0$	0·010$_6$

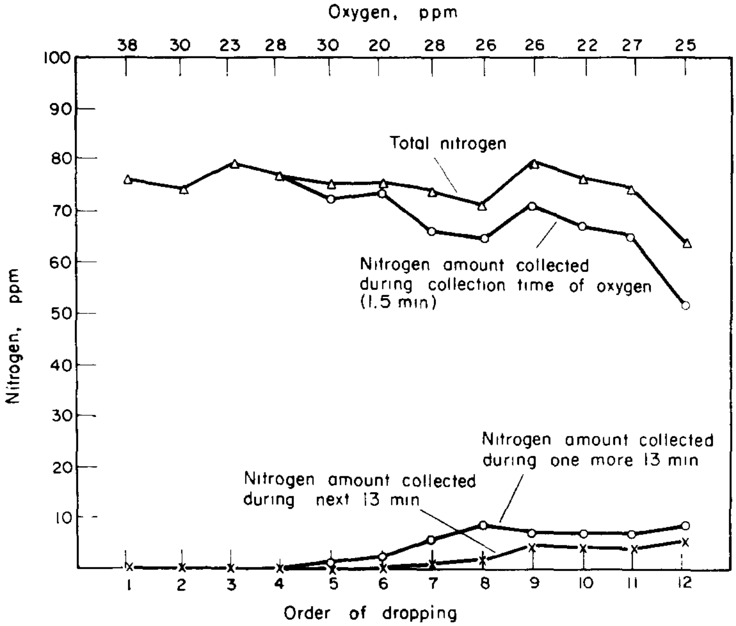


FIG. 10.—Relation between nitrogen recovery and order of dropping (sample: Mn steel; sample weight: 2–2·5 g).

TABLE III.—COMPARISON OF NITROGEN DETERMINATION BY VARIOUS METHODS

		Nitrogen, %		
Sample	Manganese, %	Vacuum fusion method		Kjeldahl method
		None[a]	Pt-Bath[b]	
18-Cr-8-Ni stainless steel	1·35	$0{\cdot}028_0$	$0{\cdot}030_4$	$0{\cdot}029_7$
Mn steel	1·02	$0{\cdot}007_9$	$0{\cdot}009_1$	$0{\cdot}009_6$
Cr-Mo steel	0·79	$0{\cdot}007_2$	$0{\cdot}008_1$	$0{\cdot}008_6$
18-Cr stainless steel	0·50	$0{\cdot}033_6$	$0{\cdot}034_3$	$0{\cdot}035_1$
Carbon steel	0·35	$0{\cdot}004_1$	$0{\cdot}004_4$	$0{\cdot}004_6$

[a] Collection time: 30 min.
[b] Collection time: 3 min.

Acknowledgement—The investigators were assisted by helpful discussions with Drs. H. Ishii and A. Ito and the staff of Industrial Analytical Chemistry, Faculty of Engineering, University of Tokyo.

Zusammenfassung—Eine verbesserte Anordnung für die Freisetzung und Sammlung von Gasen sowie für Messung und Berechnung des Druckes zum Gebrauch beim Vakuumschmelzverfahren wird beschrieben. Es ist für Routineanalyse und für Forschungsaufgaben mit vielseitigen Ansprüchen ausgelegt. Die Sammlung des Gases braucht 1–2 Minuten, einschließlich 15–60 Sekunden zur Freisetzung des Gases. Der gesamte Zeitaufwand für eine fertige Analyse beträgt 7–9 Minuten. Der Blindwert ist 0,01–0,03 ml in 30 Minuten bei 1850°. In 8 Stunden können 20 oder mehr Proben analysiert werden, Aufgeben der Probe, Entgasen und Gasanalyse inbegriffin. Ein neu entworfenes Registriersystem zur Gasextraktion wird beschrieben, mit dem man die günstigsten Bedingungen zur Bestimmung von Gasen in den gebräuchlichsten Metallen aufsuchen kann.

Résumé—On décrit un appareil amélioré pour extraire les gaz, les recueillir, effectuer les mesures de pression et les calculus, pour emploi dans la méthode de fusion sous vide. Il est conçu pour les analyses courantes et les recherches de caractère général. Le temps nécessaire pour recueillir les gaz est de 1–2 mm, y compris 15–60 sec. pour l'extraction des gaz. Le temps total nécessité pour une analyse complète est de 7–9 mn. L'essai à blanc est de 0,01–0,03 ml/30 mn à 1850°. On peut effectuer, en 8 h, l'analyse de 20 échantillons, ou davantage, en comprenant la charge, le dégazage et l'analyse des gaz. On décrit un système enregistreur d'extraction de gaz nouvellement conçu, pour étudier les conditions optimales de dosage des gaz dans les métaux d'intérêt courant.

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PIONIERE DER ELEKTROANALYSE

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Zusammenfassung—Es werden die Erfinder und die bedeutendsten Forscher der verschiedenen Zweige der Elektroanalyse, und zwar der Elektrogravimetrie, pH-Messung, potentiometrischern und konduktometrischern Titration, Coulombmetrie, Polarographie, Amperometrie und der verschiedenen üblichsten Elektroden besprochen. Von der Mehrzahl der erwähnten Persönlichkeiten werden auch die wichtigsten biographischen Daten gegeben.

IM Jahr 1800 begann das Zeitalter der Elektrizität, als Volta seine berühmte "Säule" erfand und damit der elektrische Strom "erfunden" war. Noch im selben Jahr hatten damit Carlisle und Nicholson das Wasser zersetzt,[1] und Cruikshanks beobachtete, dass wenn die Elektrizität der Voltaischen Säule durch eine Metallsalzlösung geleitet wird, daraus Metalle am negativen Pol abscheiden.[2] Das waren die Anfänge einer neuen Wissenschaft, der Elektrochemie, die dann besonders durch die Arbeit von Ritter, Davy und Faraday einen raschen Aufschwung nahm.

Merkwürdiger Weise liess aber die analytische Anwendung des elektrischen Stromes noch ziemlich lange auf sich warten, obzwar man annehmen würde, dass nach Cruikshanks Beobachtung die Elektrogravimetrie sich schnell entwickeln hätte müssen. Tatsächlich liest man aber in den folgenden Jahrzehnten höchstens über einzelne qualitative Nachweise mit Hilfe des elektrischen Stroms. Fischer wies 1812 das Arsen elektrolytisch nach,[3] Cozzi und Gaultier de Claubry empfahlen elektrischen Strom zum Nachweis von Metallen bei toxikologischen Analysen[4,5] während Despretz Blei und Kupfer nebeneinander elektrolytisch nachwies, indem das eine an der Anode, das andere an der Kathode abgeschieden wurde.[6]

DIE ELEKTROGRAVIMETRIE

Die Elektrogravimetrie wurde endlich im Jahr 1864 geboren, also mehr als ein halbes Jahrhundert später als die erste elektrische Batterie. Ihr Erfinder war Wolcott Gibbs. Er bestimmte Kupfer and Nickel in Platintiegeln mit Hilfe der Bunsenschen Batterie. Die Tiegelwand selbst diente als Kathode, während die Anode ein in den Tiegel reichender Platindraht war.[7]

Luckow veröffentlichte 1865 eine ähnliche Methode und behauptet darin sie seit 1860 schon benützt zu haben.[8]

Nun folgten rasch nacheinander Vorschriften zur elektrogravimetrischen Bestimmung weiterer Metalle.

Bedeutend war die Tätigkeit Classens, der zuerst die Rolle der Stromstärke untersuchte und Galvanometer in den Stromkreis schaltete. Er elektrolysierte zuerst unter Erwärmen der Lösung, wodurch die Abscheidung beschleunigt wurde. Ebenfalls Classen ist die erste Monographie über Elektrogravimetrie zu verdanken.[9] Lange Zeit diente der Platintiegel als Kathode, Paweck konstruierte die erste Netzelektrode.[10] Die Quecksilberkathode stammt von Gibbs selbst.[11]

Verwandt zur Elektrogravimetrie, weshalb hier zu erwähnen ist die sogenannte coulombmetrische Analyse, wo unmittelbar Faradays Gesetze zur Bestimmung verwertet werden. Diese verhältnismässig junge Methode wurde 1938 von Szebellédy und Somogyi in die Analyse eingeführt.[12]

ELEKTROMETRISCHE pH-MESSUNG UND ELEKTRODEN

Wie bekannt, gab Nernst die erste quantitative Beziehung für die elektromorische Kraft der galvanischen Ketten.[13] Die elektromotorische Kraft steht danach in Verhältnis mit der Konzentration der Elekrolytlösung. Somit war prinzipiell eine Möglichkeit gegeben zur elektrometrischen Konzentrationsbestimmung. Es fehlte aber die geeignete Elektrode um die Wasserstoffionenkonzentration, der nach der Arrheniusschen Dissoziationstheorie eine bevorzugte Rolle zukam, zu bestimmen. Le Blanc machte 1893 die Beobachtung, dass eine mit Wasserstoff von bekanntem Druck gefüllte Platinelektrode sich gegen Säurelösungen ebenso verhält wie eine Metallelektrode gegen eine entsprechende Metallsalzlösung.[14] Mit Hilfe von Konzentrationsketten unter Anwendung von Wasserstoffelektroden bestimmte dann Salessky die Wasserstoffionenkonzentration von solchen Säure- bzw. Basenlösungen in welchen verschiedene Indikatoren eben Übergangsfarbe zeigten.[15] Soerensen mass den pH-Wert seiner Pufferlösungen schon mit Hilfe von Wasserstoff und Kalomelelektroden.[16] (Kalomelelektrode soll aber Kohlrausch zu physikalischen Zwecken schon im vorigen Jahrhundert verwendet haben.) Cremer beobachtete 1906 bei seinen biologischen Versuchen,[17] dass eine Potentialdifferenz zwischen zwei durch Glasmembran getrennten Lösungen von verschiedenen Wasserstoffionenkonzentrationen auftritt, und stellte auch fest, dass dafür die Membran verantwortlich ist. Haber und Klemensiewicz untersuchten dann diese Frage weiter und fanden dass eine mit neutraler Salzlösung gefüllte dünnwandige Glaskugel ihr Potential ebenso in Funktion der Wasserstoffionenkonzentration ändert wie eine Wasserstoffelektrode. Sie konstruierten 1909 dann die erste Glaselektrode.[18] Obzwar Sie ihrer Elektrode in der Ersetzung der Platinwasserstoffelektroden grosse Zukunft voraussagten, liess diese ziemlich lange auf sich warten. Der grosse innere Widerstand der Elektrode verhinderte nämlich ihren Gebrauch bei der üblichen Kompensationsmethode, man konnte sie nur benützen, wenn mit Quadrantenelektrometer gemessen wurde, das jedoch wegen der Umbequemlichkeit nicht sehr beliebt war. Das richtige Zeitalter der Glaselektroden kam erst mit den Röhrevoltmetern in den dreissiger Jahren unseres Jahrhunderts.

Die Chinhydronelektrode entdeckte Biilmann 1920,[19] die Antimonelektrode Uhl und Kestranek 1923.[20]

POTENTIOMETRISCHE TITRATION

Die erste potentiometrische Titration unternahm Behrend 1893.[21] Er titrierte Quecksilber (I)nitrat mit Kaliumchloridlösung in einer Hg-n/10 $HgNO_3$-n/10 $HgNO_3$-Hg Kette: “Setzt man nun zu einer der Lösungen Chlorkalium, so fällt Quecksilberchlorür aus, der osmotische Druck der Quecksilberionen wird auf dieser Seite geringer und man erhält eine Potentialdifferenz in dem Sinne, dass das Quecksilber unter der mit Chlorkalium versetzten Lösung negativ wird gegen das unter der unveränderten Nitratlösung. Bei weiterem Zusatz von Chlorkalium wird die Potentialdifferenz grösser und zwar bei gleichen Zusätzen zuerst langsam dann immer schneller... Den stärksten Einfluss auf die Änderung der Potentialdifferenz übt der

Zusatz von Chlorkalium in dem Augenblick, in welchem der letzte Rest des Merkuronitrats ausgefällt wird... Weiterer Zusatz von Chlorkalium bewirkt alsdann ein verhältnismäasig langsames Steigen der Potentialdifferenz..." schrieb Behrend, woraus zu sehen ist, dass er den Vorgang auch theoretisch gut zu erklären vermochte.

Vier Jahre folgte dann nichts auf diesem Gebiet, bis dann 1897 Böttger zuerst eine Säure-Basetitration potentiometrisch unter Anwendung einer mit Palladium überzogenen Goldelektrode und der Kompensationsmethode unternahm.[22] Die Redoxtitration war die letzte, die potentiometrisch ausgeführt wurde. Crotogino titrierte 1900 Halogene mit Kaliumpermanganat unter Anwendung einer glatten Platinelektrode.[23]

Zur Messung diente im allgemeinen die Kompensationsmethode. Doch wurden bald auch andere Methoden geschaffen. Wenn man z.B. einen Artikel von Salomon aus 1897[24] aufmerksam durchliest, so findet man, dass dort eigentlich schon ganz genau die sogenannte "dead-stop" Methode beschrieben wurde, die allerdings dann 1926 neu entdeckt wurde.[25]

Unter Anwendung einer polarisierten Elektrode titrierten zuerst 1911 Dutoit und Weisse, die Titration auf Nullpotential wurde gleichzeitig von Pinkhof und Treadwell und Weiss entdeckt,[27] die Differenztitration stammt von Cox.[28]

KONDUKTOMETRISCHE TITRATION

Leitfähigheitsmessungen an Flüssigkeiten wurden für physikalische Zwecke seit Mitte des vorigen Jahrhunderts oft unternommen, sie trugen in hohem Mass zur Ausbildung der physikalischen Chemie bei. Die durch die Neutralisation oder Fällung verursachte Leitfähigkeitsverminderung einer Lösung nützten zu analytischen Zwecken jedoch erst im Jahr 1903 Küster und Grüters aus, die die erste konduktometrische Titration ausführten.[29] In ihrer sehr kurzen Mitteilung berichteten sie aber nichts näheres über die angewandte Einrichtung.

Die moderne Hochfrequenztitration beruht ebenfalls auf der Leitfähigkeitsänderrung der Lösung, sie wurde 1946 unabhängig voneinander von englischen und amerikanischen Forschern entdeckt.[30]

POLAROGRAPHIE

Heyrovský beobachtete 1922 dass das gleichmässig tropfende Quecksilber eine sehr geeignete Elektrode zum Studium von Elektrolysevorgängen bietet. An der sich ständig erneuernden Oberfläche besteht eine grosse Überspannung, man kann sie vollständig polarisieren. Er fand ferner, dass man aus den Potentialkurven die depolarisierenden Komponenten der Lösung qualitativ und quantitativ ermitteln kann.[31] Zur praktischen Vereinfachung dieses Prinzips konstruierten dann 1924 Heyrovský und Shikata den ersten Polarographen.[32] Die Weiterentwicklung der Polarographie, die Oscillopolarographie ist ebenfalls Heyrovský zu verdanken,[33] ebenso wie die sogenannte polarometrische (amperometrische) Titration (1927).[34]

BIOGRAPHISCHE DATEN

Behrend, Robert (1856–1926)

Schüler Ostwalds in Leipzig, von 1897 Professor der organischen Chemie an der Technischen Hochschule Hannover.

Biilmann, Einar (1873–1946)

Professor der Chemie an der Universität Koppenhagen.

Böttger, Wilhelm (1871–1949)

Schüler Ostwalds, von 1910 bis 1938 Professor der analytischen Chemie an der Universität Leipzig.

Carlisle, Anthony (1768–1840)

Arzt im Westminster Hospital, London.

Classen, Alexander (1843–1934)

Von 1883 Professor der analytischen Chemie an der Technischen Hochschule, Aachen.

Cozzi, Andrea (+1852)

Professor der Chemie an der Universität Florenz.

Cruikshanks, William (1745–1800)

Arzt, Professor der Anatomie in London und Chemiker der Artillerie.

Davy, Humphry (1778–1829)

Professor an der Royal Institution, einer der berühmtesten Chemiker, Entdecker der Alkalimetalle, des Bogenlichsts usw.

Despretz, César (1792–1863)

Professor der Physik an der Universität Paris.

Dutoit, Paul (1873–1944)

Von 1898 Professor der physikalischen, von 1918 der analytischen Chemie an der Universität Lausanne.

Faraday, Michael (1791–1867)

Laborant, später Mitarbeiter Davys, endlich Direktor der Royal Institution. Machte bedeutende Entdeckungen sowohl in der Physik (Indukton) wie in der Chemie (Gesetze der Elektrolyse, Benzol usw.)

Foulk, Charles William

Geboren 1869, von 1898 bis 1939 Professor der analytischen Chemie an der Ohio State University.

Gaultier de Claubry, Francois (1792–1878)

Professor der Chemie, später der Toxicologie an der École Supérieure de Pharmacie, Paris.

Gibbs, Wolcott (1822–1908)

Arzt. studierte in Europa neben Rose, Liebig und Dumas, dann Professor im

College of the New York City, später Professor der Chemie an der Harward University, U.S.A.

Haber, Fritz (1868–1934)

Professor der Chemie an der Technischen Hochschule Karlsruhe, von 1912 Direktor des Kaiser Wilhelm Institute für Chemie. Berühmt wegen seiner Arbeit hinsichtlich der Ammoniak-Synthese. Nobelpreisträger für Chemie 1916.

Heyrovský, Jaroslav

Geboren 1890, von 1926 Professor der physikalischen Chemie an der Karls Universität, Prag, seit 1950 Leiter des Polarographischen Instituts der Tschechoslowakischen Akademie. Nobelpreisträger für Chemie 1959.

Klemensiewicz, Zygmunt

Geboren 1886, bis 1939 Professor der Physik an der Technischen Hochschule Lemberg.

Kohlrausch, Friedrich (1840–1910)

Professor der Physik der Reihe nach an der Technischen Universität Zürich, an der Universität Würzburg, Strassburg und endlich Berlin.

Küster, Friedrich Wilhelm (1861–1917)

Schüler von Nernst, wurde 1899 Professor der Chemie an der Bergakademie Clausthal, zog sich 1904 zurück und lebte privatisierend weiter.

Le Blanc, Max (1865–1943)

Zuerst Professor der physikalischen Chemie an der Technischen Hochschule Karlsruhe, dann von 1906 bis 1934 an der Universität Leipzig.

Nernst, Walther (1864–1941)

Schüler Ostwalds, von 1894 bis 1904 Professor der physikalischen Chemie an der Universität Göttingen, von 1904 an der Universität Berlin. Von 1922 Direktor der Physikalisch-Technischen Reichsanstalt. Nobelpreisträger für Chemie 1920.

Nicholson, William (1753–1815)

Beamter des Ostindischen Gesellschaft, dann Schuldirektor in London, dann Privatingenieur, endlich Herausgeber einer wissenschaftlichen Zeitschrift.

Paweck, Heinrich (1870–1941)

Von 1907 Professor der Elektrochemie an der Technischen Hochschule, Wien.

Ritter, Johann Wilhelm (1776–1810)

Praktisierender Arzt in Jena und Gotha, von 1810 in München lebend als Mitglied der Bayrischen Akademie der Wissenschaften.

Shikata, Mazuro

1895 geboren, arbeitete 1923 in Prag, wurde 1924 Professor an der Universität Kyoto, nach 1953 Professor an der Universität Nagoya.

Soerensen, Soeren Paul Lauritz (1868–1939)

Direktor des Carlsberg Laboratoriums in Koppenhagen, Einführer der pH-Bezeichnung.

Somogyi, Zoltán

Assistent an der Universität Budapest. Gestorben durch Kriegsereignisse 1945.

Szebellédy, László (1901–1944)

Von 1938 Professor der anorganischen und analytischen Chemie an der Universität, Budapest.

Treadwell, William Dupré (1885–1959)

Bis 1955 Professor der analytischen Chemie an der Technischen Universität Zürich.

Uhl, Alfred

Geboren 1889, tätig in dem Oesterreichischen Forschungsinstitut für die Landwirtschaft, von 1942 bis 1947 Direktor ebendort.

Volta, Alessandro (1745–1827)

Von 1780 bis 1819 Professor der Physik an der Universität Pavia, Erfinder der ersten elektrischen Batterie (Voltaische Säule, 1800).

Über die im Artikel erwähnten Forscher die im biographischen Teil nicht aufgezählt sind, konnte ich leider überhaupt keine biographischen Daten erfahren.

Summary—The pioneers and the most outstanding research workers in the different branches of electro-analysis—electrodeposition, pH measurement, potentiometric and conductometric titration, coulometry, polarography and amperometry, and the inventors of the commoner types of electrodes are discussed. Brief biographies are given for most of the individuals mentioned.

Résumé—On donne des récapitulations des fondateurs et des chercheurs remarquables dans les différentes branches de l'électroanalyse, la galvanoplastie, la mesure de pH, dosages potentiométrique et conductimétrique, coulométrie, polarographie et ampérométrie, ainsi que des inventeurs des différents types d'électrodes. Brèves biographies sont données pour la plupart des chercheurs.

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LIQUID-LIQUID EXTRACTION OF TUNGSTEN^{VI} WITH TRIBUTYL PHOSPHATE

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Summary—A new method has been developed for the rapid extraction of tungsten^{VI} with tributyl phosphate (TBP). Quantitative extraction occurs from 8–10*M* hydrochloric acid using 100% TBP. Tungsten is finally determined spectrophotometrically as thiocyanate. The extractable species is probably $WO_2Cl_2.2TBP$. There are very few interferences. The method is shown to be applicable to an alloy steel.

IN this laboratory tributyl phosphate (TBP) has been used for the extraction of iron^{III} and vanadium^{V}.[1] The extraction studies with TBP have now been extended to tungsten^{VI}. The latter can be extracted from hydrochloric acid solution with TBP. It can then be stripped with water and treated with tin^{II} chloride plus thiocyanate to give a coloured product for spectrophotometric determination. This forms the basis of the method outlined in this paper for extraction and determination of tungsten^{VI} at the milligram level. The method has been successfully applied to an alloy steel.

The thiocyanate method for extraction of tungsten after reduction with tin^{II} chloride or any other suitable reducing agent is well known.[2] Dithiol[3] has been reported to be a good extractant for tungsten. Thenoyltrifluoroacetone[4] in n-butyl alcohol-acetophenone mixture in a strong hydrochloric acid medium has also been used to extract tungsten^{VI}. Other extractants for tungsten are α-benzoinoxime[5] and cupferron.[6]

Pfeifer[12] has previously reported the extraction of tungsten as thiocyanate complex by TBP from 3–6*M* hydrochloric acid. However, his method involves a time-consuming procedure of wet ashing after extraction for subsequent determination of tungsten by the hydroquinone method. The present technique is simple and more rapid.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were carried out with a Unicam SP600 spectrophotometer using matched 1-cm glass cells.

Reagents

Tributyl phosphate: The reagent (Matheson, Coleman and Bell, Cincinnati, Ohio, U.S.A.), b.p. 143–145° at 5 mm, was employed as extractant after purification according to the method of Peppard *et al.*,[13] *viz.*, washing first with 8*M* hydrochloric acid, then with 5% sodium carbonate and finally with water.

Stock solution of sodium tungstate: Prepared by dissolving about 9 g of sodium tungstate (Riedel De Haenag Seelze-Hanover, Germany) in 1 litre of water containing 4g of sodium hydroxide and 8 g of tartaric acid. The solution, standardised by the oxinate method, contained 4·42 mg of tungsten^{VI}/ml. Test solutions for extraction purposes were prepared by dilution of the stock solution so as to contain 188 μg of tungsten^{VI}/ml.

50% *Potassium thiocyanate solution*: Prepared from E. Merck reagent.

7% *Tin*^{II} *chloride solution:* Prepared from E. Merck reagent in 10*M* hydrochloric acid.

General procedure

A 2-ml aliquot of sodium tungstate solution containing 188 μg of tungsten^{VI}/ml was mixed in a 250-ml separatory funnel with the requisite volume of hydrochloric acid to give an acid concentration of 9*M*. In the experiments involving salting-out agents and diverse ions, the appropriate salting-out agents and foreign ions were added before the acid. The resultant aqueous solution was extracted with an equal volume of 100% TBP for 10 min. Where the effect of TBP concentration was studied, benzene was the diluent. At the end of the extraction, the two layers were allowed to separate. The aqueous phase was retained for measurement of acidity and also for determination of any residual tungsten. Tungsten was then stripped from the TBP layer by consecutive shaking for 10 min with 10 and 5 ml, respectively, of water. To remove any TBP dissolved in the aqueous layer, the back-extract was washed with 5 ml of benzene in a separatory funnel and transferred to a 25-ml volumetric flask. To this 1·5 ml of 50% potassium thiocyanate were added, mixed well and diluted to the mark with 7% tin^{II} chloride in 10*M* hydrochloric acid. The absorbance of the yellow coloured solution was measured at 420 mμ against water within 4 hr.

The optimum period of extraction is 10 min.

RESULTS AND DISCUSSION

Effect of acidity

The solvent extraction behaviour of tungsten^{VI} with respect to TBP was investigated at varying concentrations of hydrochloric acid from 2 to 11*M*. In moderately concentrated acid ($< 6M$), the precipitation of tungstic acid was prevented by the presence of tartaric acid. The distribution ratio (D) was computed from the ratio of the concentrations in the organic and aqueous phases (Table I, Fig. 1). The tungsten in the organic phase was determined as above and in the aqueous phase by the thiocyanate method.[2]

Table I shows that extraction with 100 % TBP (3·66*M*) starts from 2*M* hydrochloric acid and becomes quantitative ($>$ 99%) from 7*M* acid onwards, the aqueous phase after extraction being practically free from tungsten. In Fig. 1, a steep rise in

TABLE I.—DISTRIBUTION RATIO AS A FUNCTION OF ACID CONCENTRATION

TBP concentration, %	HCl, *M* (initial)	Distribution ratio, D^b
	2	0·08
100	3	0·42
(3·66*M*)	4	1·25
	5	2·9
	6	11·5
	7	61·6
	8·5–10^a	—
	4	1·2
75	6	6·36
(2·74*M*)	7	21·4
	9	230
	4	0·56
50	6	3·13
(1·83*M*)	7	4·7
	9	50·1
	4	0·21
25	6	1·32
(0·91*M*)	7	3·64
	9	10

[a] Aqueous phase does not contain any detectable tungsten.

[b] $D = \dfrac{[W^{VI}]_{org.phase}}{[W^{VI}]_{aq.phase}}$.

the extraction is observed at lower acidities. This is followed by a further rise at higher acidities. The effect is probably caused by salting-out from the aqueous phase by the chloride ion. For quantitative extraction the optimum acid concentration is 8–10*M*

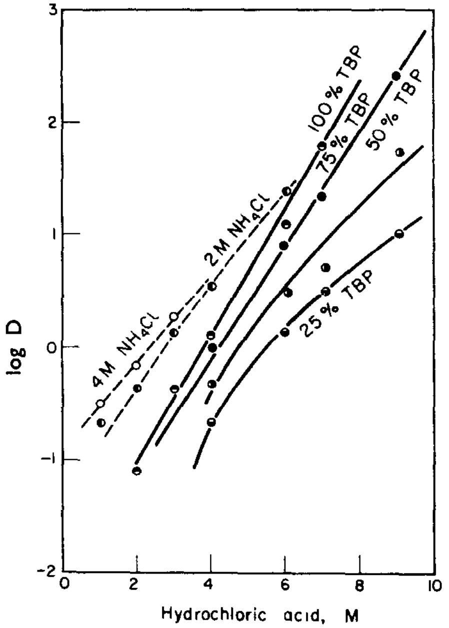

FIG. 1.—Extraction of tungsten^{VI} with TBP as a function of hydrochloric acid concentration in the aqueous phase.

hydrochloric acid (equilibrium acidity 6–7*M*). More concentrated acid is not recommended because of trouble in manipulation, although the extraction is quantitative.

TBP concentration

The concentration of TBP was varied from 25% (0·914*M*) to 100% (3·66*M*) with benzene as diluent. The effect on the extraction was noted at different acid concentrations (Table I). Dilution of the TBP lowers the extraction (Fig. 1). An attempt was made to determine the composition of the extractable tungsten-TBP species by means of a log D *vs.* log C_{TBP} plot.[7] For the plot at 9*M* hydrochloric acid (to obtain four points in all) an extra measurement was taken at a lower concentration of TBP, *i.e.*, 10% TBP (D = 1·3). Below a TBP concentration of 10% the extraction is very poor and the accuracy of measurement unsatisfactory; no further experiments were therefore attempted. The best lines through the points at 6 and 9*M* hydrochloric acid (Fig. 2) give slopes of 1·77 and 2·33, respectively, showing that the extractable species is most probably $WO_2Cl_2 \cdot 2TBP$. This is analogous to other solvated species, *e.g.*, $H[FeCl_4.(TBP)_2]$,[1] $ZrCl_4.2TBP$,[8] $Th(NO_3)_4.2TBP$[9] and $VOCl_3.2TBP$,[1] at high acidity. The optimum reagent concentration is 100% (3·66*M*).

A study of the extraction with 100% TBP from 9*M* hydrochloric acid as a function of tungsten concentration shows that the optimum analytical range is from 50 to

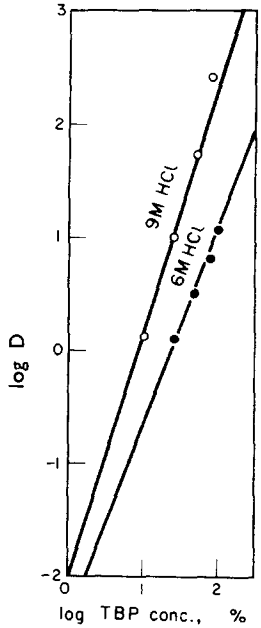

FIG. 2.—Distribution ratio as a function of TBP concentration.

TABLE II.—EFFECT OF AMMONIUM CHLORIDE AND MAGNESIUM CHLORIDE AS SALTING-OUT AGENTS
[376 μg of tungsten^{VI}; 100% TBP]

Salting-out agent	HCl, M (initial)	Distribution ratio
2M NH_4Cl	1	0·21
	2	0·38
	3	1·34
	4	3·37
	5	5·25
	6	22·5
4M NH_4Cl	1	0·32
	2	0·56
	3	1·77
1M $MgCl_2.6H_2O$	2	0·46
	3	1·17

470 μg of tungsten. For higher concentrations the relationship between percentage extraction and tungsten concentrations is not linear.

Salting-out agent

The presence of ammonium chloride in the aqueous phase serves to exert a salting-out effect leading to an increased extraction of tungsten^{VI} (Table II). Magnesium chloride in the aqueous phase increases the extraction to the same extent as ammonium chloride. The partition coefficients at lower acidity are found to increase by several orders of magnitude. Under this condition TBP is less combined with acid and so is more available for extraction. This occurs in conjunction with the salting-out function of chloride ion from the added salt. The extractant used was 100% TBP (3·66*M*).

Diverse ions

Nineteen representative ions were carried through the procedure and examined for interference. The tolerance limit for each, recorded in Table III, represents that concentration of the foreign ion in the presence of which tungsten^{VI} can be extracted and determined spectrophotometrically within ± 2%. It is interesting to note that chromium^{III} and nickel^{II} (10 mg) are not extracted; iron^{III} (10 mg) is co-extracted with tungsten^{VI} but does not interfere in the spectrophotometric determination; zirconium^{IV}, manganese^{II}, phosphate, borate, fluoride, EDTA (10 mg) and citrate, acetate, tartrate (1 g) do not interfere; thorium (1 mg) and uranium^{VI} (0·5 mg) can be tolerated; copper^{II}, molybdenum^{VI}, cobalt^{II}, titanium^{IV} and vanadium^{V} are co-extracted with tungsten and interfere but this can be eliminated by either their preliminary removal or by using suitable masking agents.

TABLE III.—EFFECT OF DIVERSE IONS
[376 μg of tungsten^{VI}; 100% TBP]

Foreign ion	Tolerance limit to ion, μg
Cu^{2+} ($CuSO_4.5H_2O$)	2×10^{3c}
Th^{4+} [$Th(NO_3)_4.4H_2O$]	10^3
Zr^{4+} ($ZrOCl_2$)	10^4
Ti^{4+} [$Ti(SO_4)_2$]	$2{\cdot}7 \times 10^{3a}$
V^{5+} ($VOCl_3$)	4×10^{2b}
Mo^{6+} [$(NH_4)_6Mo_7O_{24}.4H_2O$]	4×10^{2c}
U^{6+} [$UO_2(NO_3)_2.6H_2O$]	5×10^2
Cr^{3+} [$Cr_2(SO_4)_3.18H_2O$]	10^4
Mn^{2+} ($MnSO_4.5H_2O$)	10^4
Ni^{2+} ($NiSO_4.6H_2O$)	10^4
Co^{2+} ($CoSO_4.7H_2O$)	10^{3c}
Fe^{3+} ($FeCl_3.6H_2O$)	10^4
BO_3^{3-} (H_3BO_3)	10^4
PO_4^{3-} [$(NH_4)_2HPO_4$]	10^4
F^- (NaF)	10^4
EDTA (Disodium salt)	10^4
Citrate (Citric acid)	10^6
Acetate (Ammonium acetate)	10^6
Tartrate (Tartaric acid)	10^6

[a] Masked with hydrogen peroxide.
[b] In presence of tartaric acid.
[c] Foreign ion removed first.

Copper^{II} and cobalt^{II} are first removed by extracting with 0·15*M* TTA in benzene[10,11] at pH 4·5 and 6, respectively. The aqueous phase, after evaporation to small volume, is extracted from 9*M* hydrochloric acid as usual for tungsten.

Molybdenum^{VI} is extracted with 0·15*M* TTA in acetophenone from 0·5*M* hydrochloric acid.[4] Tungsten^{VI} remains in the aqueous phase which is then extracted with TBP.

It has already been shown[1] that tartaric acid reduces vanadium^{V} to vanadium^{IV}

and prevents its extraction with TBP. In order to remove the interference from vanadium^{V} 1 g of tartaric acid was used in the aqueous phase (vanadium$^{(V)}$ = 0·4 mg) during the extraction. Titanium^{IV} in 9*M* hydrochloric acid was masked with hydrogen peroxide (5 ml) and tungsten extracted with TBP.

APPLICATION TO AN ALLOY STEEL

A known weight (0·1 g) of alloy steel (No. 64a, Bureau of Analysed Samples, Ltd., Newham Hall, Yorks., U.K.) was dissolved in 9 ml of concentrated sulphuric acid and 50 ml of water. After the initial reaction was over, the solution was heated, oxidised carefully with 5 ml of nitric acid and evaporated to fumes. Finally, it was diluted with 80 ml of water, boiled to dissolve the salts, filtered to remove silica and washed with 1% sulphuric acid. The filtrate was evaporated to about 25 ml, then diluted to 100 ml in a 100-ml volumetric flask with water. A 4-ml aliquot of this solution was taken in a 250-ml separatory funnel, 0·5 g of tartaric acid added to remove interference from vanadium, followed by 10 ml of 9*M* hydrochloric acid. The solution was extracted twice with 12-ml portions of 100% TBP. Molybdenum^{VI}, tungsten^{VI} and iron^{III} were extracted. From the combined extracts, iron, molybdenum and tungsten were stripped with three 10-ml portions of water. The aqueous phase was evaporated to a small volume (about 2 ml) and transferred to a separatory funnel together with 10 ml of 0·5*M* hydrochloric acid plus 10 ml of 0·15*M* TTA in acetophenone[4] and extracted for 10 min. Molybdenum and some iron were extracted. The aqueous phase containing tungsten^{VI} and iron^{III} was transferred to a 25-ml volumetric flask and tungsten was determined as outlined before.

The results from triplicate analysis of this alloy steel were 5·55, 5·60 and 5·54% of tungsten (reported present: 5·66% of tungsten, 4·11% of molybdenum).

Zusammenfassung—Eine neue Methode zur schnellen Extraktion von Wolfram^{VI} mit Tributylphosphat (TBP) wurde entwickelt. Aus 8–10m Salzsäure ist die Extraktion mit 100% TBP quantitativ. Wolfram wird zuletzt als Rhodanid spektralphotometrisch bestimmt. Die extrahierte Spezies ist höchstwahrscheinlich WO_2Cl_2.2TBP. Es gibt nur wenige Störungen. Die Methode läßt sich auf legierte Stähle anwenden.

Résumé—Description d'une méthode d'extraction rapide du tungstène VI par le tributylphosphate-TBP. L'extraction quantitative est effectuée par l'acide chlorhydrique 8 à 10M, en utilisant 100% de TBP. Le tungstène est finalement dosé spectrophotométriquement sous forme de thiocyanate. Le produit extractible est probablement formé en grande partie de WO_2Cl_2.2TBP. Il y a très peu d'interférences. Application de la méthode aux alliages d'acier.

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INDIRECT DETERMINATION OF TRACES OF URANIUM USING 1-(2-PYRIDYLAZO-)2-NAPHTHOL

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Summary—In the determination of traces of uranium using 1-(2-pyridylazo)-2-naphthol (PAN), solvent extraction of the complex is replaced by the separation of the insoluble complex from homogeneous solution. This is followed by hydrolysis to give free PAN equivalent to the uranium present. An increase in sensitivity of almost 50% results, and the conditions for complex formation require less stringent control. A general method for the determination of uranium in impure liquors is described. Reversed-phase partition chromatography is used for the initial separation of uranium, followed by the use of complexing agents to prevent interference from any residual ions. The method is simple and rapid, and the precision compares favourably with other methods using PAN.

INTRODUCTION

THE use of 1-(2-pyridylazo)-2-naphthol (PAN) as a reagent for the determination of traces of uranium has been described by Cheng,[1] and this work has been extended by Shibata.[2] Cheng reports that the complex with uranium, formed under conditions of controlled pH in the presence of EDTA and cyanide ion to complex other cations, can be selectively extracted into *o*- or *m*-dichlorobenzene or bromobenzene and the absorption measured at 570 mμ. He gives the molar absorptivity as 23,000. Shibata's extension of the procedure permits the use of other solvents, such as chloroform and carbon tetrachloride, which Cheng had found unsuitable under the conditions of his work.

In attempting to adapt the procedure to the analysis of impure uranyl liquors some difficulty was experienced in achieving consistent behaviour. The reagent is largely precipitated in the aqueous medium prescribed, and it was considered possible that the heterogeneous reaction of uranyl ion and solid reagent in suspension could be a factor contributing to the difficulty.

The reagent PAN is readily soluble in a mixture of equal volumes of water and acetone and at approximately pH 9 the presence of a few μg of uranium results in the formation of an insoluble red compound. This precipitate can be separated quantitatively by filtration on asbestos fibre and washed free from excess PAN. If precipitation of the uranium complex is reproducible and a suitable solvent is available to dissolve the complex from the filter, an alternative procedure emerges. This avoids heterogeneous reaction conditions and enables the optical density of the solution of the uranium complex to be measured without interference from the excess PAN.

The non-specific nature of PAN as a reagent leads to interference in the determination of uranium by other metal ions. This effect can be overcome by the use of complexing agents, but where gross amounts of impurity are present a separation of the uranium is essential. A combination of a selective separation procedure, such as reversed-phase partition chromatography (RPPC)[3] with the use of complexing agents, can then be employed to obtain complete freedom from interference.

EXPERIMENTAL

Reagents[6]

All reagents are of analytical-grade quality unless otherwise stated.

1-(2-pyridylazo)-2-naphthol: Supplied by L. Light & Co., Ltd., England; 0·1% w/v solution in acetone.

Asbestos fibre: Powminco Grade A long fibre supplied by Hopkins and Williams Ltd., England.

Kel-F powder: Grade Kel-F 300 low density, supplied by the Minnesota Mining & Manufacturing Co., Ltd., England. Grind to powder with Drikold and liquid nitrogen. Retain the fraction B.S.S.44 to B.S.S.120 for use in preparing the column.

Tributyl phosphate (TBP): Purify the commercial product by refluxing with 0·5% w/v aqueous sodium hydroxide solution. Wash with cold 5% w/v aqueous sodium hydroxide solution until free from di- or monobutyl phosphate. To test this, neutralise a portion of the wash liquid to litmus with nitric acid and add a neutral solution of thorium nitrate. The formation of a precipitate indicates that di- and/or monobutyl phosphate is present and washing must be continued.

Ammonium acetate-aqueous ammonia buffer solution: Dissolve 60 g of ammonium acetate in 450 ml of cold water. Add aqueous ammonia solution to raise the pH to 9·5. Adjust the volume to 500 ml with cold water.

EDTA-ammonium tartrate complexing solution: Dissolve 7·5 g of tartaric acid in 200 ml of cold water. Neutralise to pH 9·0 with aqueous ammonia solution. Dissolve 18·75 g of EDTA (disodium salt) in 250 ml of water and mix with the tartrate solution. Adjust the volume to 500 ml with cold water.

Apparatus[6]

Preparation of asbestos fibre filter. The filter tube is shown in Fig. 1. Hold the perforated porcelain button in position and add a small quantity of a thin aqueous slurry of asbestos fibre to the tube. Apply gentle suction and press lightly with the flattened end of a glass rod to form a uniform pad about 3 mm deep. On removing the suction, water should pass through the filter at 1–2 ml/min; filters with faster rates should be rejected. Wash the pad with 10 ml of hydrochloric acid and finally with water until free from acid.

Shortly before use, wash twice with 5-ml portions of water-acetone solution (1 + 1). The pad may be used repeatedly if it is tamped lightly with the flattened end of a glass rod before re-use.

Preparation of the Kel-F column. The column tube is shown in Fig. 2. Fill the tube with water and press a small piece of cotton wool lightly into the junction with the side tube. Make a slurry of 5 g of Kel-F powder with 5 ml of TBP, set aside for 5 min, then add sufficient water to make a loose slurry. Transfer a small portion of this to the column tube and agitate with a glass rod to remove adherent air bubbles. Allow the Kel-F to settle under gravity while passing a constant stream of cold water through the tube. Repeat the addition of Kel-F several times until the tube is filled to within 1 cm of the reservoir. Insert a cotton wool plug to give a depth of about 1 cm. The rate of elution from the column should be 1·5–2 ml/min and visual inspection should reveal no voids.

Shortly before use, condition the column by passing 25 ml of nitric acid solution (7 + 13) through it. When not required further, wash the column with water until free from nitric acid, then close the outlet tube. Half fill the reservoir with cold water and cover with a watch glass to restrict evaporation.

The life of the column is about 15–20 separations before repacking is required.

Spectrophotometer. All absorption spectra and optical densities were measured using a Unicam S.P.600 spectrophotometer.

Dissolution of PAN-uranium complex following separation on an asbestos filter

Precipitates of the PAN-uranium complex, containing 40 μg of uranium, were formed in a water-acetone (1 + 1) medium buffered to approximately pH 9. The precipitates were separated by filtration on asbestos-fibre filters and washed with water-acetone solution (1 + 1) to remove excess PAN. The residues were extracted by washing with a variety of organic solvents. When solvents immiscible in water were used, the filter and precipitate was first washed with methanol. Methanol, distilled methylated spirit and carbon tetrachloride had no apparent effect. Acetone, chloroform, dichlorobenzene and trichlorethylene all dissolved the complex in varying degrees, giving red solutions, but

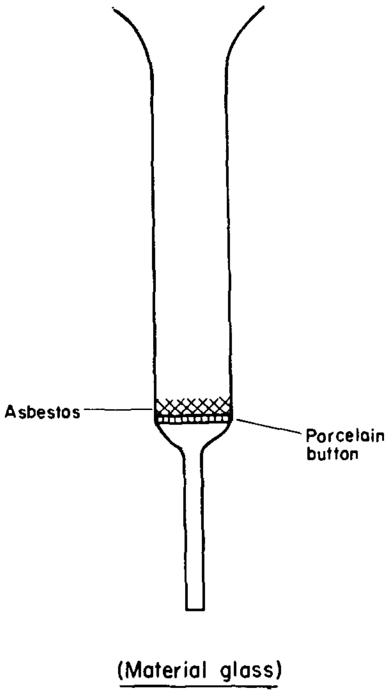

FIG. 1.—Tube for asbestos fibre filter. (Half scale)

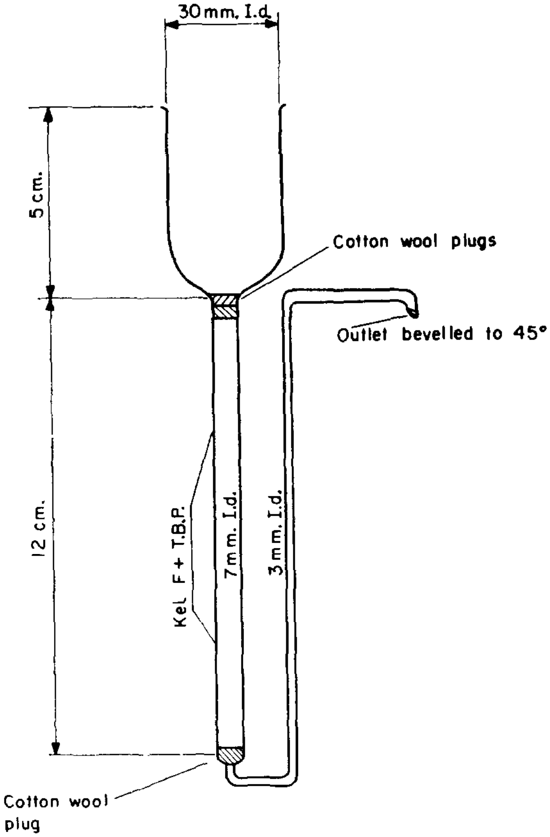

FIG. 2.—Chromatography column tube.

in each case an insoluble pink residue remained on the filter. Tetrahydroxysylvan gave a yellow-brown extract with a dark residual colour on the filter, which on drying showed a pink hue. Similar results were obtained when the complex was formed in a water-methanol medium.

Strong hydrochloric acid dissolved the PAN-uranium precipitates quickly and completely to give a yellow solution. This colour was considered to be that of free PAN resulting from the hydrolysis of the PAN-uranium complex, the optical density of which was found to be proportional to the uranium content of the precipitate. The stability of the PAN colour in hydrochloric acid solution appeared to be adequate and warranted further study of this method for determining the amount of PAN-uranium complex formed.

Absorptiometry

Visible absorption spectra. The visible absorption spectra of solutions of PAN and of PAN-uranium complex in 20% v/v hydrochloric acid solution were identical, both having an absorption maximum at 440 mμ (Fig. 3). Dissolution of the PAN-uranium complex in 20% v/v hydrochloric acid therefore results in complete hydrolysis to the free reagent.

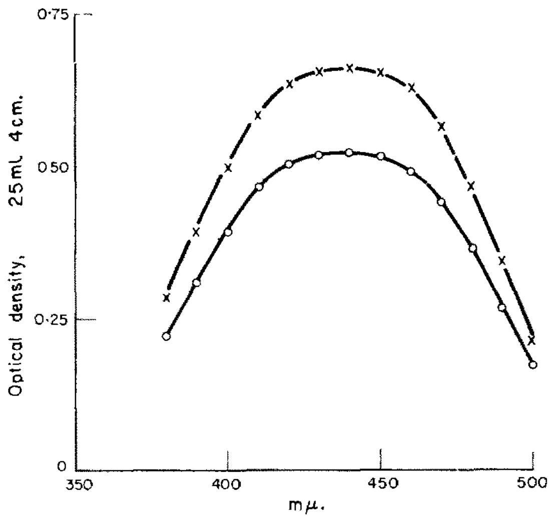

FIG. 3.—Visible absorption spectra of solutions of PAN-uranium complex and of PAN reagent in hydrochloric acid (1 + 4):
○—25 μg of uranium as hydrolysed PAN-uranium complex,
×—60 μg of PAN.

Effect of hydrochloric acid concentration. Aliquots of a solution of PAN-uranium complex in hydrochloric acid solution were diluted to standard volume with hydrochloric acid solutions of differing concentrations and the optical densities measured at 440 mμ. The optical densities were identical within experimental error over a range of concentrations of hydrochloric acid of 5–40%,v/v. At higher concentrations, acid fumes make measurements in the spectrophotometer difficult. In succeeding work, all optical densities were measured in 20% v/v hydrochloric acid solution unless otherwise stated.

Stability of the colour. To test the stability of the solution resulting from dissolution of the PAN-uranium complex in hydrochloric acid, precipitates were formed from varying known quantities of uranium, separated by filtration on asbestos fibre and dissolved in strong hydrochloric acid. The solutions were diluted to standard volume with water, and the optical densities measured at 440 mμ at timed intervals after this dilution. The results are shown in Table I.

The decrease in optical density with time is slow and less than a 1% error results if measurements are made within 1 hr of the dissolution of the precipitate.

Formation of PAN-uranium complex

Solution conditions. PAN-uranium precipitates were formed, using 50 μg of uranium in water-acetone solution (1 + 1) containing ammonium acetate, by adding dilute ammonia solution until a desired pH value was obtained. The precipitates were separated by filtration on asbestos fibre,

TABLE I—STABILITY OF THE COLOUR RESULTING FROM THE HYDROLYSIS OF THE PAN-URANIUM COMPLEX

Time, *hr*	Optical density			
	0 μg U	10 μg U	25 μg U	40 μg U
0	0·013	0·203	0·592	1·005
1	0·013	0·202	0·587	0·990
2·5	0·010	0·196	0·573	0·975
6	0·010	0·196	0·565	0·955
72	0·005	0·155	0·425	0·717

dissolved in hydrochloric acid and the optical densities measured at 440 mμ. The results are shown in Table II.

It is necessary to adjust the solution to at least pH 8 in order to achieve maximum precipitation of the PAN-uranium complex. Over the range pH 8 to pH 10 there is no further effect. Cheng[1] states that in an aqueous medium containing EDTA no significant complex between uranium and the dye is formed below pH 5 and above pH 12. His conditions give maximum complex formation at pH 10 and this is critical, the extent of complex formation falling rapidly above and below this value. The use of an acetone-water medium therefore results in a shift to higher pH for complex formation, but requires much less stringent control. An ammonium acetate-aqueous ammonia buffer adjusted to pH 9·5 was found to give adequate control.

Time required for complex formation. The time taken to complete the reaction between uranium and PAN at room temperature, was measured. The reagents were added to a series of solutions which were then set aside for various time intervals before separation of the complex by filtration. No significant difference in optical density of the final solutions was observed for reaction times in the range 5 to 20 min. The experiment was duplicated at both 40- and 100-μg levels of uranium.

Effect of other ions and limiting of interferences

Cheng and Bray[4] reported that a number of metal ions form coloured chelates and that some of these may be extracted into organic solvents. They also state that EDTA prevents all of the metal ions tested, from reacting with PAN.

A series of experiments was carried out taking 40 μg of uranium, an equal amount of each of 12 other metal ions, and a lower PAN concentration (1 mg), the object of the diminished PAN concentration being to emphasise any interference effects.

These experiments showed that:—

(a) Magnesium and molybdenum are virtually without effect.

(b) Iron, in the bivalent and tervalent states, and nickel form insoluble complexes with PAN and therefore interfere in the determination of uranium.

(c) Copper, lead, chromium, zirconium, thorium, manganese and vanadium capture PAN to the exclusion of uranium, or otherwise affect the precipitation of the PAN-uranium complex forming complexes which are soluble in the buffered acetone-water medium.

Further experiments, using EDTA at the maximum concentration which could be tolerated without affecting the determination of 40 μg of uranium (in the absence of other metal ions), showed that EDTA was not entirely effective in preventing interference from manganese, vanadium, copper, chromium and zirconium. Tartaric acid used together with EDTA eliminated these interferences to a large extent. In conjunction with the full concentration of PAN contemplated (10 mg), up to 190 mg of EDTA or 60 mg of tartaric acid could be tolerated without reducing the recovery of 40 μg of uranium. In admixture the maximum concentrations tolerable were 93 mg of EDTA and 37 mg of tartaric acid. These were reduced to 75 mg and 30 mg, respectively, to allow a margin of safety.

TABLE II

pH	Optical density
6	0·031
7	0·069
8	1·21
9	1·16
10	1·12

Determinations of 40-μg quantities of uranium in the presence of other metal ions using the mixed complexing reagent and 10 mg of PAN are shown in Table III.

A similar experiment was undertaken to show the effect of some anions. The results are shown in Table IV.

TABLE III—EFFECT OF OTHER METAL IONS ON THE DETERMINATION OF 40 μg OF URANIUM

Metal ion	Quantity, μg	Uranium found, μg
Pb	1000	41
Cu	1000	43
Mo	1000	41
Al	1000	42
Fe^{II}	1000	90
	760	45
	500	41
Th	1000	41
V	1000	41
Cr	500	39
Zr	500	34
	300	36
	150	39
Mn	1000	40
Mg	1000	41
Ni	1000	41
Fe^{III}	1000	41

TABLE IV—EFFECT OF SULPHATE, FLUORIDE AND PHOSPHATE ION ON THE DETERMINATION OF 100 μg OF URANIUM

Anion	Quantity, μg	Uranium found, μg
SO_4	10,000	99
	100,000	99
F	100	100
	1,000	98
	10,000	28
PO_4	100	99
	1,000	82
	10,000	NIL

Calibration procedure for the spectrophotometer[6]

Evaporate to dryness aliquots of a standard uranium nitrate solution (1 ml ≡ 40 μg of uranium) covering the range 0–200 μg of uranium. Dissolve each residue in 3 ml of hydrochloric acid solution (1 + 49). Add, with stirring, 2 ml of EDTA-tartrate solution followed by 10 ml of PAN solution and 5 ml of buffer solution in that order. Set aside for 20–25 min at room temperature, then separate the precipitate by filtration on an asbestos fibre filter. Wash the beaker five times with 5-ml portions of water-acetone solution (1 + 1), using each wash to rinse down the tube supporting the filter and allowing each portion to drain through the filter before adding the next. Wash the outside of the filter tube stem to remove crystallised reagent. Finally, wash the beaker and filter with two 5-ml portions of water and allow to drain completely. Dissolve the precipitate from the filter by adding 10 ml of hydrochloric acid (sp. gr. 1·18) in portions, followed by small portions of water, using about 15 ml in all. Collect the eluate in a graduated cylinder containing about 20 ml of water and finally adjust the volume to 50 ml. Measure the optical density of each solution using a 2-cm cell at 440 mμ and correct for the reagent blank value.

Fig. 4 shows a typical calibration curve over a range of 20–175 μg of uranium.

The calibration curve was studied in more detail below 20 μg of uranium, employing standard conditions, but a reduced final volume and increased light path to enhance the sensitivity of the measurements. The results are shown in Fig. 5.

The non-linear behaviour below 18 μg of uranium may result either from a kinetic effect or a solubility effect. The latter is unlikely because the normal calibration curve from 20 μg of uranium upwards passes through the origin.

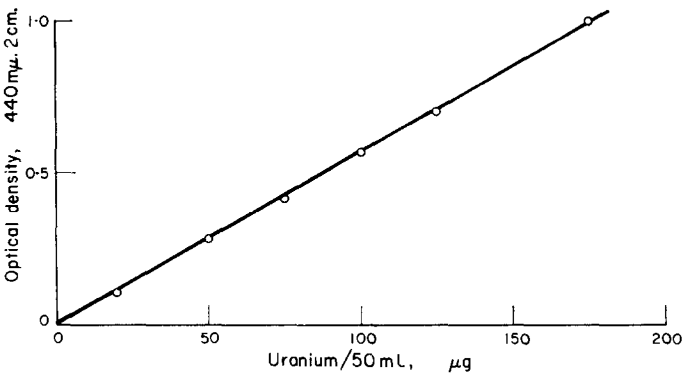

FIG. 4.—Calibration of Unicam SP 600 spectrophotometer for the determination of uranium.

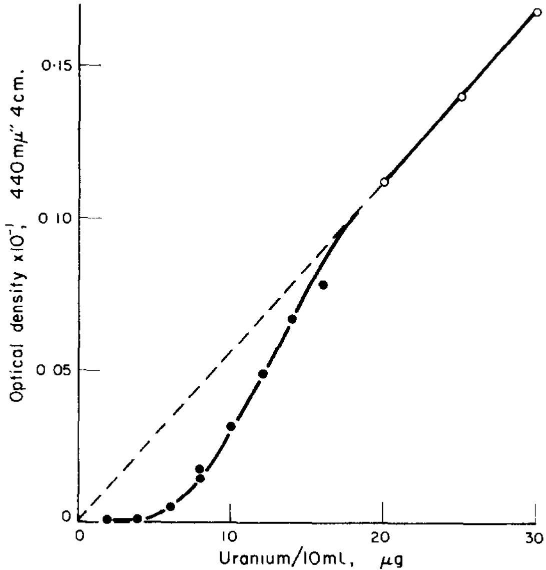

FIG. 5.—Calibration for 0–20 μg of uranium (10-ml volume; 4-cm cell; 440 mμ):

○—○—Calibration between 20 and 175 μg of uranium (see Fig. 4);

●—●—Calibration for 0–16 μg of uranium using stated conditions.

The deviation from linearity confines the lower limit of the method to 20 μg of uranium for normal operation and will cause some error in reagent blank determinations when these fall in the range 4–16 μg of uranium. Because a reagent blank was, however, subtracted from the optical density values used in constructing Fig. 4 and this curve passes through the origin, the effect is apparently not significant. Several more calibrations failed to reveal any effect.

Application of procedure to impure liquors[6]

Procedure. Evaporate a suitable volume of the sample to dryness with a mixture of 1 ml each of nitric and perchloric acids. Dissolve the residue in 5 ml of nitric acid solution (7 + 13) and transfer this solution to a prepared Kel-F tributyl phosphate column. Elute at not more than 2 ml/min. Wash the beaker with four 5-ml portions of nitric acid solution (7 + 13), adding each portion to the column and allowing it to elute at the specified rate before adding the next. Reject the eluate.

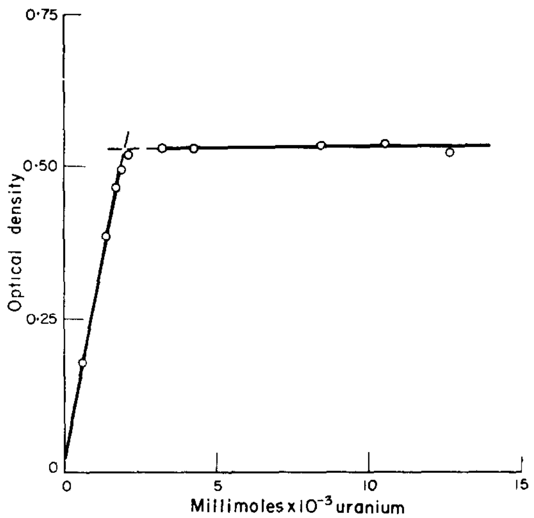

FIG. 6.—Mole ratio of uranium to PAN (separation of uranium using 4·00 × 10^{-3} mmole of PAN).

TABLE V—DETERMINATION OF URANIUM IN IMPURE LIQUORS

Sample no.	Vol. taken, *ml*	Aliquot after RPPC	Uranium found, *μg/ml* (PAN)	Recovery of 50 *μg* of uranium added to sample, %	Uranium by alternative method, *μg/ml*	Alternative method used
1	150	—	0·1	112	0·2	Ether extn./H_2O_2 colour[5]
2	250	—	0·29	108	0·29	Ether extn./H_2O_2 colour[5]
3	25	—	2·6	98	2·5	Ether extn./H_2O_2 colour[5]
4	100	—	0·30	100	0·30	Fluorimetry
5	25	—	3·0	106	2·5	Ether extn./H_2O_2 colour[5]
6	25	$\frac{1}{100}$	840	—	620	Ether extn./H_2O_2 colour[5]
6	2	$\frac{1}{10}$	800	—		
7	25	$\frac{2}{25}$	103	—	85	Ether extn./H_2O_2 colour[5]
8	10	—	12·6	104	10	Ether extn./H_2O_2 colour[5]
8	10	—	12·7	—		
9	25	$\frac{2}{25}$	40	—	36	Ether extn./H_2O_2 colour[5]
10	25	$\frac{3}{50}$	46	110	45	TBP extn./thioglycollate colour
10	2	$\frac{3}{4}$	46	—		

Wash the column with 20 ml of cold water added in two equal portions. Collect the eluate in a 50-ml beaker. Aliquoting may be undertaken at this stage. Evaporate to dryness and continue as described in the procedure for calibration. Carry out a reagent blank determination as above, omitting the sample.

Results on impure sample liquors. The above procedure was applied to a representative selection of samples of impure uranic liquors in which the uranium had been determined by alternative methods. The results are shown in Table V in which the aliquoting of samples after the RPPC separation is indicated

In sample No. 10 a clear yellow band formed at the top of the Kel-F column and was ultimately eluted in the water wash with the uranium. The colour was found to be from cerium^{IV} ion. Because the tolerance of cerium in the PAN determination is not more than 100 μg, 100 mg of sodium nitrite were added to the nitric acid solution of the sample before transferring to the Kel-F column. This served to reduce the cerium to the tervalent state in which it was no longer retained on the column.

Precision test

A number of equal volumes of two samples of impure liquor containing 65–75 μg of uranium were analysed by the procedure given. The results of 19 determinations gave a standard deviation of $\pm 0{\cdot}96$ μg of uranium.

Mole ratio of uranium to PAN in complex and the sensitivity of procedure

The mole ratio of uranium to PAN was determined by making a series of precipitations of the complex from a constant concentration of PAN with varying quantities of uranyl ion. The precipitated complex was then treated as described in the calibration procedure. The results, shown in Fig. 6, indicate a mole ratio of uranium: PAN of 1·0:2·0.

The calibration data shown in Fig. 4 give a molar extinction coefficient of 33,000.

DISCUSSION

In the procedures of Cheng and Shibata the PAN reagent is virtually insoluble in the test solution. This leads to heterogeneous reaction conditions during the formation of the PAN-uranium complex in which the concentration of reagent in solution is very low. Possibly as a result of this, these procedures are extremely sensitive to pH change.

Working in a mixed aqueous/organic solvent, homogeneous reaction conditions apply, and it was found that the PAN-uranium complex forms over a wide pH range, the complex being insoluble. This leads to the possibility of either solvent extraction of the complex or separation followed by dissolution, before colour measurement. Our experience with the PAN-uranium complex has shown that its solution properties in the usual solvents recommended are rather unpredictable. For this reason, separation of the insoluble PAN-uranium complex, followed by hydrolysis to give free PAN equivalent to the uranium, has been used. This gives a molar extinction coefficient of 33,000, an increase in sensitivity of almost 50% over procedures based on solvent extraction of the complex (23,000 and 21,000 by the procedures described by Cheng and Shibata, respectively).

Using the homogeneous reaction conditions a PAN-uranium complex in the molar ratio 2:1 is formed; this is the same as reported by Cheng. The complex is very insoluble, although a possible solubility effect can be detected at concentrations below $4 \times 10^{-6}M$ uranium. This is, however, insufficient to give rise to any significant effect over the normal working range of the method (20–180 μg of uranium). Complexing agents can be tolerated in moderate amounts during the PAN-uranium complex formation but, as with other methods using this reagent, there is some competition for the uranium and a fairly high concentration of reagent must be employed to offset this effect.

In applying the procedure as a general method for the determination of uranium, reversed phase partition chormatography (RPPC) has been used to effect an initial separation of the uranium from other metal ions. An EDTA-tartrate complexing medium is then used to eliminate any possible interference from traces of impurity which pass the initial separation stage. Under the conditions used for the RPPC, thorium, cerium^{IV} and zirconium will be eluted from the column together with the uranium. The amount of these which can be tolerated in the sample solution is therefore limited to that which is effectively complexed, namely, 1000, 100 and 150 μg, respectively. Interference from cerium^{IV} is readily removed by reduction to cerium^{III} with nitrite before RPPC.

Omitting the RPPC stage it was found that 100 mg of sulphate, 1 mg of fluoride and 100 μg of phosphate could be tolerated in the determination of 100 μg of uranium.

The method is applicable to a wide range of impure sample liquors, and is easy and relatively economical to operate. Although the sensitivity is 50% higher than other methods using this reagent, the precision, measured on impure samples, compares very favourably. No evidence of bias has been obtained over the normal working range of the method.

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Zusammenfassung—Bei der Bestimmung von Uranspuren mit 1-(2-Pyridylazo)-2-naphthol (PAN) wird die Extraktion des Komplexes durch Abtrennung des unlöslichen Komplexes aus homogener Lösung ersetzt. Die anschließende Hydrolyse liefert eine der anwesenden Uranmenge äquivalente Menge PAN. Die Empfindlichkeit steigt um fast 50% und die Bedingungen für die Komplexbildung erfordern nicht mehr die selbe genaue Kontrolle. Eine allgemein anwendbare Methode zur Bestimmung von Uran in verunreinigten Flüssigkeiten wird beschrieben. Die erste Abtrennung von Uran erfolgt durch Verteilungschromatographie mit umgekehrten Phasen, anschließend werden Komplexbildner zugesetzt, um Störungen durch andere Ionen zu vermeiden. Die Methode ist einfach, geht schnell, und ihre Genauigkeit ist mit anderen Methoden vergleichbar, die PAN verwerden.

Résumé—Dans le dosage des traces d'uranium au moyen du (pyridil-2-azo)-1-naphtol-2 (P.A.N.), le solvant d'extraction du complexe est remplacé par la séparation du complexe insoluble dans la solution homogène. La séparation est suivie d'une hydrolyse redonnant le P.A.N. équivalent à l'uranium présent. Une augmentation dans la sensibilité de presque 50% des résultats et les conditions de formation du complexe nécessitent un controle moins rigoureux. Description d'une méthode générale pour le dosage de l'uranium dans les solutions non pures; une chromatographie de partage par inversion de phase est utilisé pour une première séparation de l'uranium; on traite par un agent complexant pour éviter les interférences dues aux ions résiduels. Cette méthode est simple, rapide et la précision est comparable à celle que l'on obtient avec les autres méthodes utilisant le P.A.N.

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APPLICATION OF CATIONIC-SENSITIVE GLASS ELECTRODES TO THE STUDY OF ALKALI METAL COMPLEXES—I

THE SODIUM-MALATE SYSTEM

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Summary—Cationic-sensitive glass electrodes are used to study the weak complex formed by sodium ion and malic acid in aqueous media. The best value of 1·1 ± 0·3 for the calculated formation constant agrees well with literature values. Methods of measurements and calculation are described and evaluated.

INTRODUCTION

SINCE the recent commercial introduction of cationic-sensitive glass electrodes, a number of useful applications of these electrodes to analytical problems have been reported.[1] Palaty[2] has suggested that such electrodes might also be valuable in the study of complex equilibria, and particularly in the evaluation of formation constants for the alkali metal chelates. Attempts to extend this technique to the study of weak complexes of the alkali metal cations in aqueous solution are reported here.

The sodium-malate system was chosen for consideration because it has recently been studied by neutralisation[3] and nuclear magnetic resonance methods.[4] A value of 2·0 ± 0·3 for the formation constant of the 1:1 sodium-malate complex was reported. Because of certain assumptions concerning the effect of ionic strength and the dissociation of malic acid, however, the absolute value of this constant is probably meaningful only for the specific solution conditions for which the formation of the complex was studied. The principal attractiveness of the cationic-sensitive glass electrode is, in fact, that such restrictive assumptions might be avoided by direct measurements of alkali metal activities.

EXPERIMENTAL

All potentiometric measurements were made using a Beckman Model 76 pH meter on the expanded scale. The Beckman 78137V cationic-sensitive glass electrode and the 39170 fibre-junction calomel reference electrode were employed. In a few cases, a salt bridge containing a portion of the test solution was used, to eliminate the minute leakage of potassium chloride from the reference electrode. During the potentiometric measurements, the temperature was maintained at 30·0° ± 0·1° in the sample vessel by means of a circulating thermostat. Solutions were prepared from reagent-grade chemicals without further purification.

Because the cationic-sensitive glass electrode responds to hydrogen ion, and to ensure complete dissociation of the malic acid, it was desirable to work in alkaline media. Below pH 5, the potential developed by the electrode has been found to be a function of both hydrogen ion concentration and the concentrations of other univalent cations.[1] As a general rule, the hydrogen ion concentration should be 10^3 times less than the concentration of univalent cation under investigation. Tris-(hydroxymethyl)aminomethane was found to be an excellent reagent for pH control. When necessary, ionic strength was controlled with tetramethylammonium chloride.

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Preconditioning of the glass electrode is essential if reproducible potentials are to be obtained. The electrodes employed here were soaked for a minimum of 48 hr in neutral 0·1M sodium chloride solutions. To avoid transfer of interfering species to the sample, the electrode may be rinsed with portions of the test solution before measurement, but wiping or drying of the electrode leads to erratic potentials.

RESULTS AND DISCUSSION

General considerations

A serious limitation to the determination of formation constants by a direct potentiometric measurement arises at once out of the logarithmic relationship between potential and concentration. Because of the nature of this relationship, an error of only 2 mv corresponds to an apparent relative concentration error of about 8·5%. This is particularly serious in the study of weak complexes where the formation of a 1:1 complex with $K = 2$ results only in a 14% decrease in metal ion concentration if the total concentrations of metal ion and ligand are both 0·1M initially. Unfortunately, errors of 1 or 2 mv are still to be expected when working with these electrodes. In principle, at least, this problem could be minimised by working with high concentrations of the complexing species, but, apart from solubility considerations, changes in ionic strength and activity coefficient more than nullify any gain in relative measuring accuracy. Table I shows the pronounced effect of ionic strength on the measured potential in sodium chloride solutions.

TABLE I.—EFFECT OF IONIC STRENGTH ON POTENTIAL

Solution	Ionic strength (Adjusted with Mg SO_4)	Potential *vs.* S.C.E., *mv*
0·1M NaCl	0·1	152·0
	0·3	149·2
	0·5	147·9
	2·1	146·2
0·01M NaCl	0·05	92·3
	0·21	89·2

Methods of attack

All potentiometric methods of determining stability constants are based on the Nernst equation and the mass action laws, but three specific procedures have been employed here:

(1) *Titration method:* A plot of glass electrode potential *vs.* log sodium ion concentration is prepared as a calibration curve in the absence of complexing ligand. A known initial concentration of sodium chloride is then titrated with a standard solution of the ligand, and a plot of potential *vs.* log apparent concentration is prepared. With appropriate correction for dilution effects, the complex formation constant may then be calculated from the original metal ion concentration, the amount of complexing agent added, and the apparent decrease in metal ion concentration at each point along the titration curve. This method of calculating formation constants gives acceptable internal agreement for values calculated at different points along the titration curve, but yields considerable variation in values calculated from separate sets of experiments, probably because of "drifting" of the glass electrode potentials and changes in the slope of the calibration curve which accompany ageing of the electrode.

(2) *Single-point-calibration method:* The apparent formal potential is calculated *via* the Nernst equation from measurements performed on standard solutions of metal ion in the absence of complexing agent. Using this apparent formal potential and the appropriate Nernst slope, the metal ion concentrations in the presence of complexing agent are then calculated directly from the Nernst equation. This method has the advantage over the titration technique of permitting rapid successive measurements on pairs of solutions—one containing a known concentration of metal ion and the other containing metal ion plus ligand in known initial concentrations. The time-dependent effects noted in the titration method can thus be largely eliminated. The necessity of assuming or calculating an appropriate Nernst slope still remains as a significant source of error, however, unless measurements are made on pairs of solutions nearly identical in effective metal ion concentration.

(3) *Emf-difference method:* If it is assumed that in a series of solutions differing only slightly in total metal ion concentration but identical with regard to ligand concentration, pH, *etc.*, the numerical values for the various terms of the Nernst equation remain unchanged, apart from the term in metal ion concentration, then we can write for any such pair of solutions:

$$\mathrm{E}_1 - \mathrm{E}_2 = (\text{slope}) \log \frac{C_{\mathrm{M}_1^+}}{C_{\mathrm{M}_2^+}} \tag{1}$$

Combining equation (1) with the mass action expression for a 1:1 complex, one can derive:

$$\mathrm{E}_1 - \mathrm{E}_2 = (\text{slope}) \log \\ \times \frac{C^0_{\mathrm{M}^+1} - \left[C^0_{\mathrm{M}^+1} + C^0_{\mathrm{A}^{-n}1} + \frac{1}{K}\right] - \sqrt{\left[C^0_{\mathrm{M}^+1} + C^0_{\mathrm{A}^{-n}1} + \frac{1}{K}\right]^2 - 4C^0_{\mathrm{M}^+1}\,C^0_{\mathrm{A}^{-n}1}}}{C^0_{\mathrm{M}^+2} - \left[C^0_{\mathrm{M}^+2} + C^0_{\mathrm{A}^{-n}2} + \frac{1}{K}\right] - \sqrt{\left[C^0_{\mathrm{M}^+2} + C^0_{\mathrm{A}^{-n}2} + \frac{1}{K}\right]^2 - 4C^0_{\mathrm{M}^+2}\,C^0_{\mathrm{A}^{-n}2}}} \tag{2}$$

where K is the formation constant of the complex and $C^0_{\mathrm{M}^+}$ and $C^0_{\mathrm{A}^{-n}}$ denote initial concentrations of metal ion and ligand, respectively. Because all initial concentrations are known, equation (2) can be solved for K using the difference of the potentials determined in rapid succession on two similar solutions. This method has the advantage of not requiring a knowledge of the formal potentials involved, and circumvents the difficulties resulting from changes in activity coefficients with drastic alteration in solution composition. The major disadvantage of the method is its relative insensitivity to small changes in K.

A summary of the results obtained using the single-point-calibration and emf-difference methods is given in Table II.

It is immediately apparent that the emf-difference method yields values most nearly corresponding to the formation constants previously reported,[3,4] while the results obtained by the single-point-calibration method are difficult to interpret because of experimental variations. The relatively large variation in calculated values is not surprising, however, when one considers that an emf change of only 0·6 mv will change the calculated formation constant from 0·8 to 1·0 in a typical experiment. That pick-up of carbon dioxide from the atmosphere by the alkaline test solution cannot be of significance here is seen from the similarity of results obtained in runs

TABLE II.—FORMATION CONSTANTS OF SODIUM-MALATE SYSTEM

System	pH	Emf, *mv*	Nernst slope	Formation constant	Method
NaOH+ malic acid	7·0	158·9	55	4·4	(2)
	7·0	154·7	55	4·6	(2)
	6·4	137·6	55	7·0	(2)
				Mean = 5·3	
	8·49	178·0	57	1·0	(3)
	8·50	182·0	57	0·8	(3)
	8·51	176·0	57	1·5	
				Mean = 1·1	(3)
Na_2CO_3+ malic acid	7·7	83·3	55	5·3	(2)
	6·8	80·0	55	6·5	(2)
	8·9	85·6	55	7·7	(2)
	8·3	97·9	55	2·8	(2)
				Mean = 5·5	

using either sodium chloride and sodium carbonate as sources of metal ion. Variations in pH of the test solutions from 7 to 9·8 also produced no significant trends in calculated formation constants. Most of the observed uncertainties must, therefore, be attributed to limitations of the measuring techniques; work is currently in progress to improve these measurements by the use of null-balance potentiometry and will be described in a future report.

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Zusammenfassung—Kationenempfindliche Glaselektroden werden zur Untersuchung des schwachen Komplexes aus Na^+ und Äpfelsäure in wäßrigen Medien verwendet. Der Bestwert von 1,1 ± 0,3 für die berechnete Bildungskonstante stimmt gut mit den Literaturwerten überein. Meß- und Berechnungsmethoden werden beschrieben und bewertet.

Résumé—Les électrodes de verre sensibles aux cations sont utilisées pour étudier les complexes peu stables formés par l'ion sodium et l'acide malique en milieu aqueux. La valeur la meilleure de la constante de formation (1,1 ± 0,3) déterminée par le calcul est en bon accord avec les valeurs indiquées dans la littérature. Des méthodes de mesure et de calcul sont décrites et leur précision évaluée.

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INVESTIGATION OF REAGENTS FOR THE COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF CYANIDE—II*

A PROPOSED METHOD FOR TRACE CYANIDE IN WATERS

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Summary—*p*-Phenylenediamine is used in a König-type reaction for the determination of trace amounts of cyanide in waters. With slight variation in procedure, the method is applicable over the range 0·005–100 ppm.

THE present main methods for the determination of trace amounts of cyanide ion are based on the formation of a dyestuff by the reaction of cyanogen bromide[1] or chloride[2] with an aromatic amine in the presence of pyridine hydrochloride. The fundamental reaction involved is that of the König synthesis[3] of pyridine dyestuffs. A critical consideration of the amines capable of giving dyestuffs suitable for use in the colorimetric determination of cyanide,[4] revealed that only three amines, *p*-aminodiphenylamine, benzidine and *p*-phenylenediamine, formed coloured compounds of any significance. Although benzidine is in use in the United Kingdom standard method (Aldridge method), the range of concentrations that may be determined on the *raw* sample is very limited; furthermore, benzidine itself is a well known and active carcinogen and its use is deprecated by many authorities. It is possible to extend the range of the Aldridge method by suitable modifications,[5] but it is not possible to alter the physiological activity of benzidine.

Of the two other amines, *p*-aminodiphenylamine and *p*-phenylenediamine, the latter compound is more suitable as the dyestuff precursor for the following reasons:

1. It is easily soluble in dilute hydrochloric acid (0·5*M*), whereas *p*-aminodiphenylamine is fairly insoluble. (Prolonged boiling, cooling and filtering is required to produce even a 0·2% solution of *p*-aminodiphenylamine.).
2. When stored in a dark bottle, a 0·2% solution of *p*-phenylenediamine in 0·5*M* hydrochloric acid is stable for at least 6 weeks without noticeable discoloration; *p*-aminodiphenylamine turns blue-purple in less than 1 day.
3. The colour intensity of the pyridine dyestuff with *p*-phenylenediamine is much greater than that with *p*-aminodiphenylamine.[4]
4. With regard to the physiological properties of the two amines, whilst neither has been reported as causing cancer of any type, *p*-phenylenediamine, being a simple mononuclear compound, is more likely to be non-carcinogenic than is *p*-aminodiphenylamine.

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* Part I: see reference 4.

Factors which may affect the formation of a coloured compound of the pyridine dyestuff type, the intensity of its absorbance and the optimum wavelength to be used in any determination, are:

(i) The treatment of the *raw* sample before colour development;
(ii) The concentration of the reagents used;
(iii) The time allowed for colour development;
(iv) The treatment of the solution after colour development;
(v) The presence of interfering substances in the *raw* sample;

A factor which is of great practical importance is the stability of the reagent.

Treatment of Raw Sample and Colour Development

The initial treatment involves acidification to liberate hydrocyanic acid; this then reacts with added bromine to give cyanogen bromide which is the active species in the König reaction. The acid used in all recommended procedures is glacial acetic acid. A standard volume of glacial acetic acid was used throughout our previous work,[4] and the possible effect of varying the amount of acid used was now investigated.

Reagents

p-Phenylenediamine solution. Dissolve 0·1 g of solid in 50 ml of 0·5M hydrochloric acid.

Bromine water. Saturate cyanide-free water with liquid bromine.

Arsenious acid solution. Reflux 2 g of arsenious oxide with 100 ml of cyanide-free water until solution is complete.

Pyridine reagent. Add 3 ml of concentrated hydrochloric acid to a mixture of 18 ml of freshly distilled pyridine and 12 ml of cyanide-free water.

Standard cyanide solutions. Prepared by suitable dilution, with cyanide-free water, of a standardised stock solution.[4]

Procedure

To 4·0 ml of standard cyanide solution, 0·2 ml of bromine water and either 0·1, 0·2 or 0·6 ml of glacial acetic acid were added. The differences in volume were adjusted with cyanide-free water. To each solution 0·2 ml of arsenious acid solution was added; after mixing, the excess bromine vapour in the tube was removed by aeration. To this mixture were added 4 ml of freshly mixed pyridine reagent/*p*-phenylenediamine solution (3·0 ml of pyridine reagent + 1·0 ml of *p*-phenylenediamine solution). The two amines are mixed immediately before use. They must not be added singly because erratic and erroneous results are then obtained.

After thorough mixing the spectra of these solutions were examined using a recording spectrophotometer to establish the best wavelength (isosbestic point) for measurement of the developed colour. This wavelength (515 mμ) was then used to measure the absorbances of the solution compared to water,* with a manually-operated instrument (see Table I).

The effect of varying the amount of acetic acid used is very large. In our previous work regarding the König synthesis[4] the effect of glacial acetic acid was minimised by dilution of the standard cyanogen bromide solutions and the use of an aliquot therefrom, *i.e.*, 0·6 ml of glacial acetic acid was used for acidification of the slightly alkaline cyanide solutions before the formation of cyanogen bromide; then after arsenious acid solution addition, the volumes of the resultant solutions were adjusted to 50 ml. Aliquots of 1·0 or 5·0 ml of these solutions were used, *i.e.*, the equivalent amount of glacial acetic acid used was 0·06 ml in a 5-ml aliquot.

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* Because we have been particularly concerned with the stability of the aromatic amine reagent employed, we have always preferred to measure absorbances against water of both samples and blanks. With *p*-phenylenediamine the absorbance of a sample may be measured directly against a blank, especially if the amine reagent is reasonably fresh. In the case of a large number of samples, however, the absorbance of the blank may change significantly by the time the final sample is measured against it. Under these conditions measurement of both samples and blank against water is recommended.

TABLE I

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)		
		Glacial acetic acid, *ml*		
		0·1	0·2	0·6
0·1	15	0·055	0·028	0·004
	40	0·055	0·028	0·004
0·2	15	0·100	0·061	0·011
	40	0·099	0·059	0·014
0·3	15	0·148	0·088	0·013
	40	0·145	0·087	0·016
0·4	15	0·191	0·114	0·015
	40	0·192	0·116	0·018
2·0	15	1·114	0·630	0·043
	40	1·066	0·590	0·040

TABLE II[a]

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)			
		Acetic acid	Bromine water	Hydrochloric acid	Phosphoric acid
0·1	20	0·034	0·095	0·100	0·052
	25	0·033	0·098	0·101	0·052
	30	0·031	0·098	0·101	0·052
	35	0·029	0·097	0·100	0·050
	40	0·028	0·097	0·099	0·050
0·25	20	0·082	0·246	0·247	0·144
	25	0·077	0·254	0·255	0·142
	30	0·075	0·257	0·255	0·142
	35	0·074	0·255	0·255	0·142
	40	0·071	0·253	0·255	0·142
0·5	20	0·160	0·503	0·503	0·287
	25	0·154	0·511	0·510	0·285
	30	0·150	0·513	0·511	0·284
	35	0·146	0·510	0·509	0·284
	40	0·142	0·509	0·509	0·282
1·0	20	0·319	1·006	1·001	0·575
	25	0·309	1·030	1·020	0·573
	30	0·304	0·065	1·041	0·571
	35	0·300	1·080	1·050	0·569
	40	0·295	1·097	1·057	0·566

[a] All measurements at 515 mμ.

Because the amount of acetic acid used altered the absorbance of the colour developed, it was decided to investigate the effect of other acids. The acids chosen were concentrated hydrochloric acid, phosphoric acid and the acidity from the addition of saturated bromine water alone. The results were compared with those obtained using acetic acid. Because slight variations in absorbances with time were noted in the work with glacial acetic acid, the absorbances were measured at various fixed time intervals under standard conditions.

The procedure followed was as before, except that to the standard cyanide solution (4·0 ml) and bromine water (0·2 ml) one of the following was added:

(a) 0·2 ml of glacial acetic acid,
(b) 0·2 ml of cyanide-free water (acidity from bromine water alone),
(c) 0·2 ml of concentrated hydrochloric acid (sp. gr. 1·18),
(d) 0·2 ml of concentrated phosphoric acid (sp. gr. 1·75).

Calibration curves obtained from these results (Table II) are shown in Fig. 1.

The colour developed in the presence of all of the acids investigated obeys Beer's Law. Hydrochloric acid does not alter the absorbance of the solution from that when acidified only with bromine water, but both acetic acid and phosphoric acid greatly decrease the absorbance at all times.

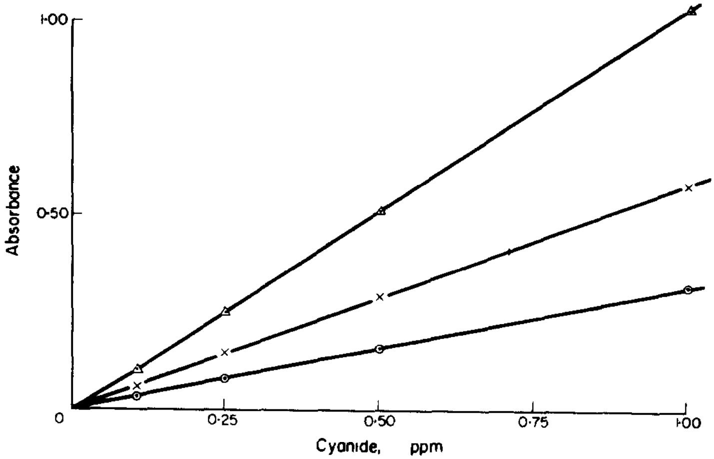

FIG. 1.—Absorbance with various acids (after 25 min; 515 mμ):
—△— water or concentrated hydrochloric acid,
—×— phosphoric acid,
—○— glacial acetic acid.

In order to show the effectiveness of *p*-phenylenediamine compared to benzidine, which is at present accepted as the standard reagent for determination of cyanide, the two were compared under conditions employed with the standard reagent (Aldridge procedure), except that the sample solution was acidified with bromine water alone, with bromine water plus concentrated hydrochloric acid or with bromine water plus glacial acetic acid.

The results are presented in Table III; the curves obtained from (a) and (d) are shown in Fig. 2. On the same scale, the curves from (a), (b), (c) and (f) are coincident for much of the range. Thus, neither glacial acetic acid nor hydrochloric acid has any appreciable effect on the absorbances produced when using benzidine. In the presence of acetic acid, the absorbances developed with *p*-phenylenediamine and benzidine are similar. When using conditions where no decrease in absorbance of the *p*-phenylenediamine colour occurs, this reagent gives a much greater absorbance than does the same concentration of benzidine.

Because the type of acid used has a significant effect, the possible effects of varying amounts of reagents were investigated for both *p*-phenylenediamine and benzidine. Increasing the amount of bromine water from 0·2 ml to 2·0 ml had no effect.

Using a 10-ml or a 5-ml *raw* sample and equal amounts of the other reagents had

TABLE III

Cyanide, *ppm*	Absorbance[a] after 30 min (corrected for blank)					
	Benzidine			*p*-Phenylenediamine		
	Bromine water	Hydrochloric acid	Acetic acid	Bromine water	Hydrochloric acid	Acetic acid
0·1	0·011	0·011	0·014	0·018	0·018	0·007
0·2	0·027	0·028	0·030	0·090	0·090	0·020
0·5	0·067	0·065	0·072	0·280	0·281	0·063
1·0	0·131	0·130	0·136	0·561	0·560	0·128
1·5	0·182	0·180	0·185	0·840	0·840	0·190
2·0	0·237	0·240	0·247	1·160	1·162	0·251
	(a)	(b)	(c)	(d)	(e)	(f)

[a] 515 mμ for *p*-phenylenediamine, and at 522 mμ for benzidine;[5] 0·2% solutions of the two amines in 0·5*M* hydrochloric acid were used.

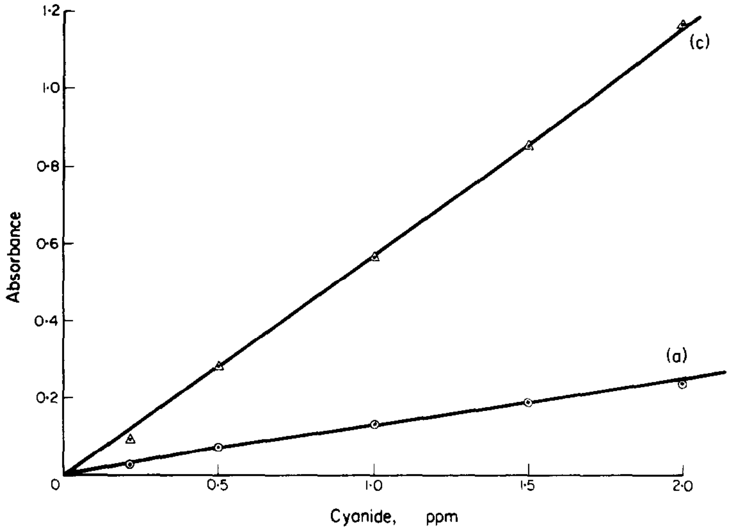

FIG. 2.—Absorbance obtained with 0·2% w/v solutions of:
(a) benzidine (522 mμ),
(c) *p*-phenylenediamine (515 mμ).

no significant effect. Less than a 0·4% difference in the absorbances of the two solutions was noted over a range of concentrations of cyanide.

Treatment of Solution After Colour Development

For samples containing cyanide at concentrations greater than 2·0 ppm, the procedure must be altered because the absorbance becomes so great as to make measurement by normal methods impracticable. In earlier work[5] we have shown that the upper range of the Aldridge method using benzidine could be extended by a modification of the method of Baker *et al.*,[6] using aqueous alcohol to dilute the developed colour. The present method was investigated using a similar dilution technique.

To 2·0-ml samples containing 0·0, 0·5, 1·0, 4·0, 5·0 and 10·0 ppm of cyanide in 25-ml volumetric flasks, 2·0 ml of bromine water and 0·1 ml of concentrated hydrochloric acid were added. After 5 min, 0·4 ml of arsenious acid solution was added and 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. After 1 min, 5 ml of ethyl alcohol were added and cyanide-free water to make each volume 25 ml. The best wavelength for measurement was ascertained, then the absorbance of the solutions was measured in 1-cm cells, compared to water, at this wavelength, using a manually operated spectrophotometer.

The results are shown in Tables IV(a) and IV(b). The isobestic point for solutions processed by the above dilution technique was at 520 mμ. This shift of wavelength from 515 mμ (isosbestic point for 2·0-, 4·0- or 5·0-ml sample is 515 mμ and for 10·0-ml sample 512 mμ, both using the non-dilution technique) must be caused by a concentration effect.

Table IV(a).—Absorbance of reagent blank solution

Time after mixing, *min*	Absorbance compared with water
20	0·018
30	0·017
40	0·018
50	0·020
60	0·020

Table IV(b).—Absorbance of solutions containing cyanide

Time after mixing, *min*	Absorbance (Corrected for blank)				
	Cyanide, *ppm*				
	0·5	1·0	4·0	5·0	10·0
20	0·035	0·078	0·366	0·486	1·010
30	0·034	0·077	0·365	0·485	1·005
40	0·033	0·076	0·367	0·487	1·006
50	0·033	0·075	0·363	0·482	0·999
60	0·033	0·074	0·362	0·477	0·995

The dilution procedure is fairly satisfactory when using *p*-phenylenediamine solution as reagent but offers no advantage over dilution of the *raw* sample before the addition of bromine and amine.

For samples containing trace amounts of cyanide and using benzidine as the dye precursor, Nusbaum and Skupeko[7] extended the lower range of the Aldridge method by extracting the pyridine dyestuff into n-butanol. The procedure of Nusbaum and Skupeko was followed, except that *p*-phenylenediamine solution (0·2% w/v) was used in place of benzidine. The developed colour was extracted using 10 ml of n-butanol. The absorption spectrum shows a maximum at 480 mμ. Some typical results are included in Table V.

Small bubbles occasionally form in the butanolic extract in the optical cell. These are water bubbles forming from a slightly supersaturated water/butanol solution; they may be removed by using a 5% solution of disodium phosphate to break any emulsion formed and centrifuging the butanol extract for 2–3 min. The phosphate does not have any appreciable effect on the actual absorbances. However, the extraction procedure involves one or two more steps in the over-all procedure and this is

TABLE V

Cyanide, *ppm*	Absorbances (corrected for blank) Solvent extraction (480 mμ)	Without extraction (515 mμ)
0·01	0·018	0·009
0·02	0·032	0·021
0·05	0·065	0·049
0·10	0·167	0·101
0·20	0·323	0·201
0·30	0·496	0·298
0·50	0·838	0·509

an obvious disadvantage. Although there is a 50% increase in the absorbance, at the lower end of the range the reproducibility using solvent extraction is not as good as without extraction. With a very low concentration of cyanide, more than one extraction is necessary and the resultant volume errors tend to remove the advantage of increased colour absorbance. The method is not recommended.

Thus, the procedure as so far envisaged is:

Using a 4·0-ml *raw* sample, add 0·2-ml of bromine water and 0·1 ml of concentrated hydrochloric acid. Mix well, add 0·2 ml of arsenious acid solution followed by 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. The absorbance is measured against water in 1-cm cells, at 515 mμ, after 30 min.

The results are as described (Fig. 1). It is possible to use the method down to 0·005 ppm with an accuracy of 1–2%, the main source of error being the measurement of the small volumes of reagents.* However, because industrial samples of cyanide (effluents, *etc.*) are relatively unlimited, these sources of error can be minimised by using a larger sample size. To ensure an adequate excess of bromine in the sample, the amount of this reagent used must, of course, be increased. The following procedure was adopted for samples of "unlimited" size:

Treat 40 ml of the *raw* sample in a 50-ml volumetric flask with 2·0 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid, then thoroughly mix. After 5 min, 0·4 ml of arsenious acid solution is added and the total volume adjusted to 50 ml with cyanide-free water. A 5·0-ml aliquot of this mixture is treated with 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. The solutions are thoroughly mixed and the absorbance of the resulting solution is compared to that of water at 515 mμ, at various times after mixing.

The results obtained showed that the colour obeys Beer's Law. To extend the upper range of the method, dilution of the sample before addition of reagents enables the method to be used from 0·001–100 ppm. Some typical results using this procedure are given in Table VI.

The absorbances after 30 min obtained from 5·0-ml of the treated mixture are shown graphically on Fig. 3.

For small concentrations of cyanide this procedure has no advantage over the original procedure other than that of increasing the accuracy by decreasing the relative volume errors in the sample size. For relatively large concentrations of cyanide (10 ppm or greater), however, the use of a 1·0-ml sample and dilution to 40·0 ml reduces the concentration of other material present by a factor of 10. This may reduce interferences (see later) to a tolerable level in some instances.

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* For 4-ml samples a 4-ml grade A pipette was used, and for volumes of reagents of less than 1-ml a 1-ml pipette (graduated into 0·01 ml) was used.

TABLE VI

	Cyanide in "raw" sample, *ppm*	Cyanide *µg/5 ml*	Absorbances (corrected for blank)		
			Time after mixing, *min*		
			20	30	40
a	0·001	0·004	0·002	0·003	0·003
a	0·005	0·02	0·005	0·004	0·004
a	0·025	0·1	0·027	0·026	0·026
a	0·050	0·2	0·048	0·047	0·047
a	0·100	0·4	0·096	0·102	0·104
a	0·250	1·0	0·218	0·248	0·246
b	20·0	2·0	0·425	0·448	0·451
b	40·0	4·0	0·933	0·990	0·995
b	100·0	10·0	2·32	2·55	2·45

a: 40·0-ml *raw* sample.
b: 1·00-ml *raw* sample.

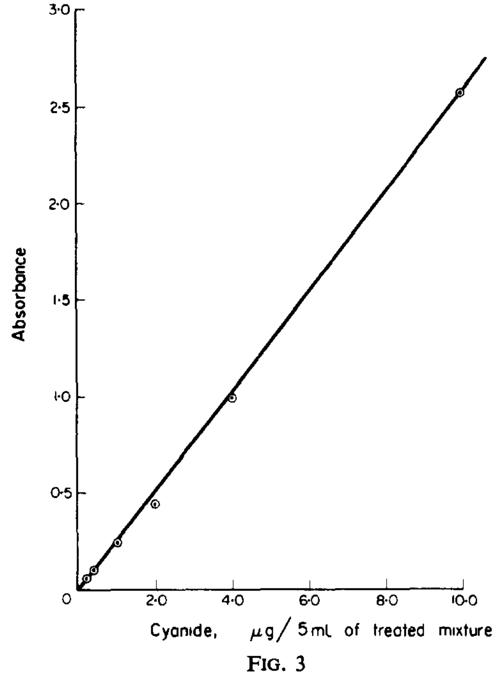

FIG. 3

Interferences

Interfering substances may be divided into:

(i) Those which react with bromine and form cyanogen bromide under the conditions of the reaction; these substances give high values for the cyanide present.

(ii) Those which prevent the cyanide ion from forming cyanogen bromide and hence give low results.

In the first class of substances, the most important is the thiocyanate ion, which reacts with bromine to produce cyanogen bromide. Both methods developed, employing *p*-phenylenediamine, may be used to determine the amount of thiocyanate present. The difference in reaction weights of the cyanide and thiocyanate ions is reflected in the absorbances produced, *viz.*

0·2 ppm of cyanide gives, on reaction, an absorbance of 0·200,

0·2 ppm of thiocyanate gives, on reaction, an absorbance of 0·100.

It is possible to determine the two ions in admixture, using the following procedure based on the non-volatility of thiocyanic acid. The total cyanogen bromide-producing substances in one aliquot of the sample are determined in the proposed manner. A second aliquot of the sample is acidified with either trichloracetic acid or boric acid, heated to 90–100° and aerated by a slow stream of air bubbles for 10–15 min. The evolved hydrocyanic acid is collected in 0·1*M* sodium hydroxide solution and the cyanide content of the resulting solution determined as previously described. The residual thiocyanate in the acidified solution may also be determined (like hydrochloric acid, trichloracetic acid and boric acid have no effect on the absorbance produced by bromine water alone).

Cyanates, hexacyanoferrate (II) and hexacyanoferrate (III) are without effect. Cyano-complexes of zinc and copper, however, yield cyanogen bromide when treated with bromine water, and it is necessary to remove free (uncomplexed) cyanide ion by the aeration procedure described.

Iron^{II}, nickel^{II} and copper^{II}, in quantities of 100 ppm, produce a ten-fold, three-fold and two-fold decrease in the concentration of cyanide found, respectively.

Of the other metal ions probable in effluents, manganese, lead, zinc, mercury^{II} and silver do not interfere in amounts up to at least 100 ppm in the solution as tested.

Reducing and/or oxidising agents present do not interfere except by consuming the bromine water or arsenious oxide solution, respectively.

Free chlorine which is often present in trade effluents, does not interfere; the cyanogen chloride formed has the same effect as cyanogen bromide.

Non-oxidising or non-reducing ions present, such as borate, bromide, carbonate, chloride, nitrate, phosphate and sulphate, do not interfere in amounts up to at least 100 ppm.

It is to be noted that using the dilution technique a ten-fold decrease of any interfering substances is obtained (on a 1·0-ml sample), and it is thus possible that relatively high concentrations of ions in a *raw* sample may be tolerated without any noticeable loss in accuracy.

Procedures for the decomposition of complex cyanides to give hydrogen cyanide for determination have been previously reviewed[8,9] and any of the recommended methods are applicable to the determination of cyanide by *p*-phenylenediamine.

Stability of the Reagent

The stability of the reagent was investigated using standard solutions of cyanide (4-ml samples) and a 0·2% w/v solution of *p*-phenylenediamine in 0·5*M* hydrochloric acid:

(1) freshly prepared (less than 1 hr)

(2) solution kept in a 'dark' bottle for 6 weeks.

TABLE VII(a).—ABSORBANCE OF REAGENT BLANK SOLUTION

Time after mixing, *min*	15	25	30
Absorbance (fresh solution)	0·019	0·020	0·022
Absorbance (6-weeks old solution)	0·021	0·020	0·023

TABLE VII(b).—ABSORBANCE OF SOLUTIONS CONTAINING CYANIDE

Cyanide, *ppm*	Time after mixing, *min*	Absorbance (corrected for blank)	
		Aged reagent	Fresh reagent
0·2	15	0·200	0·196
	25	0·203	0·201
	30	0·203	0·201
0·4	15	0·398	0·396
	25	0·406	0·404
	30	0·406	0·404
2·0	15	2·01	2·01
	25	2·01	2·02
	30	2·02	2·03

From the results in Tables VII(a) and VII(b), the reagent solution is stable for at least 6 weeks when stored in a dark bottle, and the reproducibility of the results at 30 min after mixing is $\pm 1\%$.

CONCLUSION

The procedure to be used depends on the expected concentration of cyanide to be determined, the size of the sample available and the contaminants. The following procedures are recommended.

Unlimited sample ($\nless$ 40 ml)

For a concentration of cyanide between 0·005 and 0·25 ppm, the sample is obtained free from interferences (if necessary) by distillation, aeration, *etc.* Forty ml of the sample are then treated with 2·0 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid and the solutions thoroughly mixed. After 5 min, 0·4 ml of arsenious acid solution is added and the total volume adjusted to 50·0 ml. A 5·0-ml aliquot of the mixture is then treated with 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine (3·0 ml of pyridine reagent + 1·0 ml of *p*-phenylenediamine solution). After thorough mixing and standing for 30 min at room temperature, the absorbance of the resulting solution is compared to that of water at 515 mμ.

The absorbance of a blank solution should be determined under the same conditions and the absolute absorbance used to calculate the concentration of cyanide present, from a previously determined calibration curve.

For samples containing 0·25—100 ppm of cyanide, a suitable aliquot should first be diluted to 40·0 ml with cyanide-free water, then processed as above.

Limited Sample

If the sample size is limited and dilution to 40·0 ml would decrease the concentration below 0·005 ppm, then 4·0 ml of the sample are mixed well with 0·2 ml of saturated bromine water and 0·1 ml of concentrated hydrochloric acid. After 5 min, 0·2 ml of arsenious acid solution is added, followed by 4·0 ml of freshly mixed pyridine/*p*-phenylenediamine. After 30 min at room temperature, the absorbance is measured at 515 mμ.

A separate calibration curve should be determined. If necessary, the sample may be obtained free from interferences as above.

Zusammenfassung—Zur Bestimmung von Cyanidspuren in Wässern wird p-Phenylendiamin in einer Reaktion vom Typ der König-Reaktion verwendet. Mit geringfügigen methodischen Änderungen läßt sich die Methode im Bereich von 0,005 bis 100 ppm anwenden.

Résumé—Pour doser le cyanure à l'état de traces dans les eaux, on utilise la p-phénylènediamine, dans une réaction du type König. Avec une légère modification de technique, la méthode est applicable dans l'intervalle de 0,005 à 100 p.p.m.

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WET OXIDATION OF ORGANIC COMPOSITIONS

MIXED NITRIC AND HYDROCHLORIC ACIDS WITH AMMONIUM PERCHLORATE AS OXYGEN DONORS

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Summary—The wet oxidation of organic compositions as introductory manipulation in the determination of micro- and macrogram metallic and non-metallic elements is described. The principal oxygen donor in this procedure is perchloric acid generated *in situ*. Mixed nitric and hydrochloric acids are employed to convert ammonium perchlorate to perchloric acid. The three mixed acids then serve as superior solvent for the organic matter to be oxidised. Conditions are particularly suited for the oxidation of large samples. Reaction rates are repressively controlled to give assurance against violent oxidation. Applications include organic compositions, essentially of cellulose, sugars and polyhydric alcohols, or proteins. Conditions prevail in the leisurely application of reaction time to provide maximum effects from nitric acid. This provision is the key to slowly advancing oxidation potential. The final high potential provided by perchloric acid over the temperature range 150° to 203°, stepwise increasing, completes oxidations with no accompanying menacing carbonisations. Reaction times involve 50 to 60-min digestions.

INTRODUCTION

THE oxidation of organic compositions by dry ignition has been shown[1] to be frequently accompanied by a serious loss of residual elements from high temperature volatilisation. By exhaustive test, wet oxidations employing perchloric, sulphuric and nitric acids involve no loss under easily adjusted reaction conditions. There appears to be general acceptance that the use of perchloric acid as oxygen donor in wet oxidation of organic compositions provides the most valuable reaction medium.

Wet oxidation digestions in the elimination of organic matter, with retention of metallic and non-metallic accompanying elements, fall into five general categories according to the reagents involved:

(1) Nitric plus perchloric acids: "The Liquid Fire Reaction."[2]

(2) Perchloric acid alone. This procedure applies static oxidation potential magnitudes of predetermined values.[3]

(3) Perchloric and sulphuric acid mixtures. This application applies high redox potentials.[4]

(4) Sulphuric acid at 350° followed by a perchloric acid finishing reaction at 190–195°.[5] Used with fuel oils and samples rich in fat.

(5) Periodic acid and perchloric acid: "The Periodic Acid Liquid Fire Reaction."[6]

The last listed method provides general oxidation at the lowest possible temperatures and shortest reaction times.

Employing one or more of these five reaction procedures, a wide range of organic compositions may be expeditiously oxidised. Samples include fuels (such as coal or oils), carbon (such as gas-mask canister materials), fats, synthetic fabrics (such as nylon, orlon or dacron), foods and feeds, leather and wool, syrups, conserves, fruits and cellulose-rich products. Method (5) has been applied to the determination of amino nitrogen.[7] Many published works involving one or more of the five procedures have been documented, but these are too numerous to cite in the interests of brevity.

EXPERIMENTAL

Reagents

Concentrated (67–68 %) *nitric and* (37–38 %) *hydrochloric acids*

Ammonium perchlorate (99·5 %). As produced in multiple tonnage for use in the solid rocket fuel programme. Recrystallisation purification is recommended.

Apparatus

The Bethge apparatus[8] is requisite. By its use reaction conditions are best controlled. Heat is provided using a ring burner and modified nichrome wire gauze. A modified Rogers ring burner with micro control of gas-fuel intake[9] is preferred. An electric hot plate or a glass fabric heating mantle with voltage control may be substituted. Rate of energy input should be of such magnitude as to bring the reaction temperature to no more than 100° during the first 5 min. The Bethge apparatus assembled is shown in Fig. 1. Adjustment of the thermometer insert is provided by a teflon adapter as shown.

RESULTS AND DISCUSSION

Reaction characteristics

The reactions involved fall under three stages:

(A) Initial conversion of ammonium perchlorate to perchloric acid. The reaction with mixed hydrochloric and nitric acid converts the ammonium ion to nitrous oxide and water. An amount of water approximately equal to the combined mixed acid volumes is added to the sampling mixture. Reaction time is 10 min at a maximum of 110°. Heat is applied at such magnitude to attain 90° to 100° in not less than 5 min. Reaction conditions involve a mildly exothermic condition and the reaction is conducted under reflux of the condensed vapour phase. In general, the organic compositions being oxidised are dissolved by the three mixed acids present during stage (A).

(B) Adjustment is provided to retain condensate during the remainder of the digestion. The hydrochloric acid has been consumed. The dilute solution of mixed nitric and perchloric acids gradually concentrates over the temperature range 110° to 150°. The reaction is exothermic to a greater or less extent depending upon the nature of the organic matter being oxidised. During this stage the nitric acid undergoes gradual uniform increase in concentration. The oxidation potential of the nitric acid increases gradually to its maximum value at 150°. All organic matter capable of destruction by nitric acid has been reacted upon and excess nitric acid has been collected in the condensate. Little reactivity from perchloric acid has, as yet, been applied. Stage (B) requires from 30 to 40 min at the same application of heat applied throughout the three stages (A), (B) and (C). Variation in time during stage (B) is governed by the exothermic reaction provided by nitric acid oxidation.

(C) The final stage completes the oxidation following the limited destruction of organic matter provided by nitric acid and elimination of its excess at 140° to 150°. At 150° the first influence of perchloric acid as oxygen donor becomes effective. As the temperature advances because of concentration increase, the oxidation potential steadily and uniformly increases from approximately 0·8 to 2·0 V. The perchloric acid concentration increases from 50 % at 150° to 72·5 % at 203°. The reaction over this range becomes increasingly exothermic. At 203° the distillate and residual acid

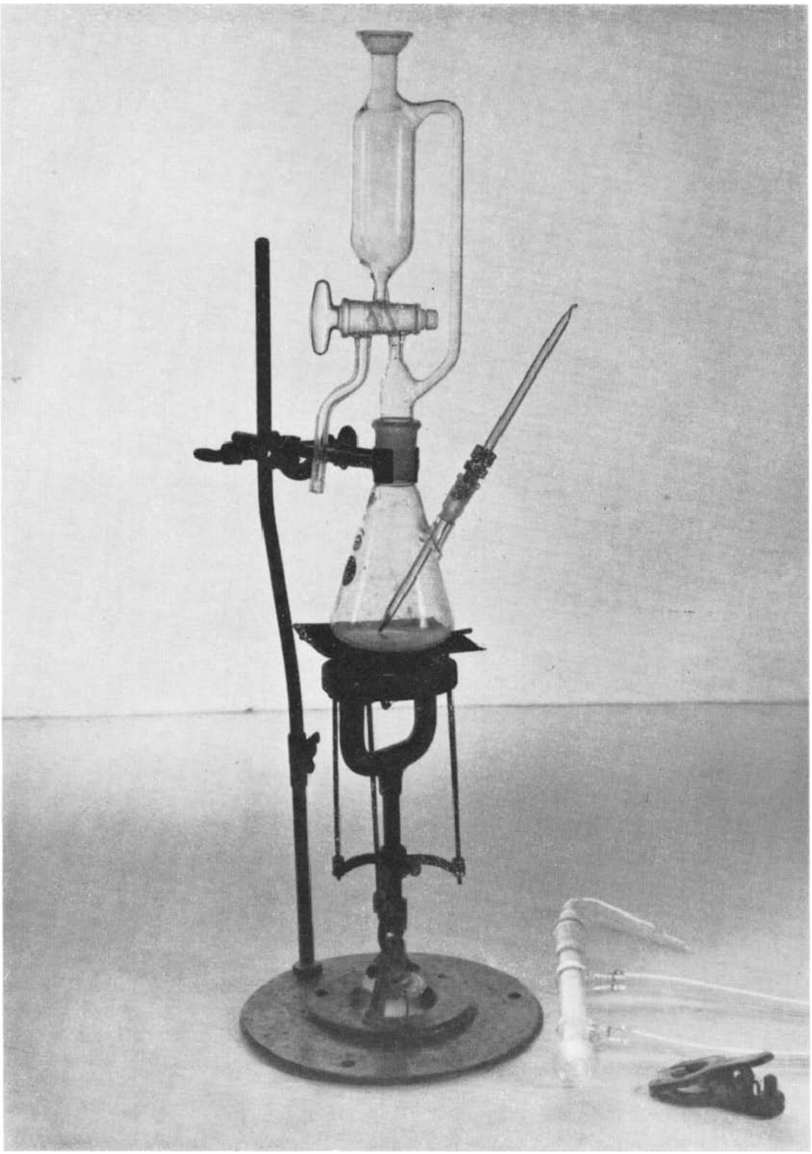

FIG. 1.—Bethge apparatus (water condenser disengaged) and modified Rogers ring burner.

in the reaction flask is at the water-perchloric acid azeotropic composition. The extent of the exothermic reaction depends upon the nature of the organic material being oxidised. Stage (C) requires 10 min, in general. Total reaction time, over-all, is approximately 60 min.

Reaction advantages

Previously described wet oxidation procedures[2-6] have one common objective, that of controlled oxidation at minimum time intervals. All types of organic compositions may be oxidised by one to three of the various applicable procedures. In general, the products oxidised involve little or no carbonisation. Degradation products, as well as the original compositions, are usually all in homogeneous solution throughout the entire digestion. Such reactions, if accompanied by the formation of dark brown or black reaction products, are still reaction rate controlled. However, in general, sample weights are limited to the 1 to 2 g magnitude.

The present work involves no reactions resulting in dark or black reaction media. Samples of 5 g are applicable. Conditions are adjusted to require longer reaction periods. Accordingly, the full possible effect of nitric acid as oxygen donor is provided. The oxidation of organic matter is thus as complete as possible before the perchloric acid oxidation begins. By following the reaction temperature during stage (b), the mildly exothermic nitric acid oxidation indicates the extent to which the removal of organic matter is progressing. Adjustment in the volume of nitric acid employed may then be made. Perchloric acid reaction in stage (c) may thus be favourably minimised.

The entire new procedure requires little operator attention. The apparatus involved is readily assembled and dismantled. It does not require a fume hood. The use of the new procedure encourages those reluctant to apply perchloric acid in wet oxidations, in fear of uncontrolled reaction intensities, to adopt the procedure in routine operations. In the present studies, no protective reaction screen was employed in any test oxidation.

Graphical representation of data

Three distinct types of organic compositions for wet oxidation include those which are predominantly cellulose, sugars or proteins. The time-temperature recording of the progress of the oxidation is the most informative technique serving to characterise each type of reaction. Employing the Bethge apparatus (Fig. 1), the oxidation of 2 g of tuna fish is characterised in Fig. 2. Because of the small weight of sample the reaction flask employed is 250 ml in volume. The oxidation is, for this reason, complete in 26 min. Stage (A) in Fig. 2 is complete in 6 min, and from 4 to 6 min no temperature rise indicates the conversion of ammonium perchlorate to perchloric acid. The sample during this period has been completely dissolved. At this point the return of reflux to the reaction flask is discontinued. For the following 16 min the stage (B) reaction of nitric acid is operative. Over the period 6 to 14 min the temperature elevation is slow and uniform indicating no appreciable exothermic nitric acid oxidation. Over the reaction period 15 to 22 min the oxidation is progressing at an increased tempo, as shown by the materially increased slope of the time-temperature plot. At 22 min the temperature has advanced to 150°. All excess nitric acid has now left the reaction flask to be collected in the condenser system. The effective oxidation period, 22 to 26 min, involves the reaction of perchloric acid as oxygen donor, stage (C). At 150° the perchloric acid concentration is approximately 50%. Here there comes into play a gradual increase in oxidation potential accompanied by a material exothermic reaction complete in 4 min. The completion of oxidation (as indicated by the oxidation of the chromium indicator,* Cr^{III} to Cr^{VI}, at 202°) indicates a perchloric acid concentration of 72·5%. During the entire reaction [stages (A), (B) and (C)] no alteration of heat applied has been made. Stage (C) owes its temperature rise almost entirely to its exothermic properties.

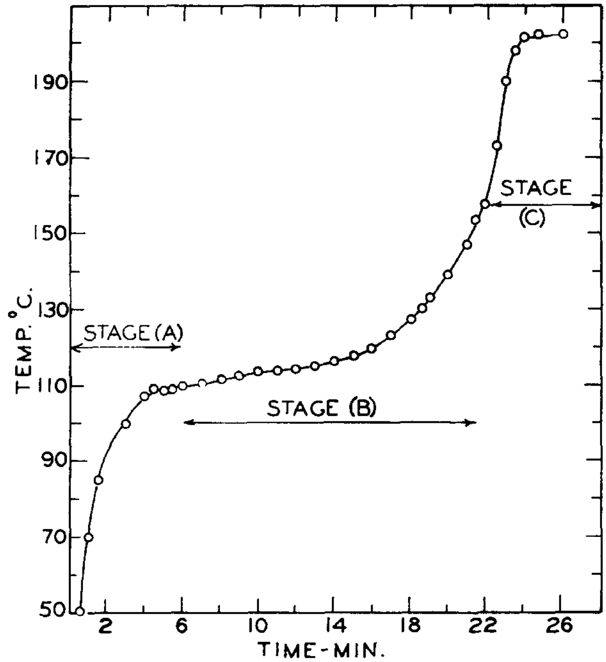

FIG. 2.—Oxidation of tuna fish [2 g of sample; 250-ml reaction flask; 10 ml of HCl; 17·6 ml of HNO_3; 21·5 g of NH_4ClO_4; 26 ml of H_2O; chromium indicator; 43 ml of distillate; 21·75 g (13 ml) of residue in $HClO_4$ flask].

At the completion of the oxidation the condensate may be removed, the air and water-cooled condenser rinsed and the distillation continued with elevation of temperature input. By this means excess perchloric acid can be removed from the reaction flask. Any silica originally present in the sample is now dehydrated and insoluble. The reaction flask can now be diluted with water, filtered and made ready for determination of metallic and non-metallic minor or major components originally present in the organic compositions of the sample. The flask contents, after completion of the oxidation covered by the results of Fig. 2, weighed 21·75 g or approximately 13 ml of perchloric acid. The distillate was 43 ml.

Non-condensed volatile products may be conducted from the top of the water-cooled condenser by flexible tubing into the sink drain, thus avoiding, by the use of the Bethge apparatus, the need for a fume hood in which to perform the oxidation.

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* 1–2 mg of potassium dichromate are included in the reaction mixture. As long as any organic matter is present, the chromium is held in the green tervalent state. When all traces of organic matter are oxidised, the chromium is immediately oxidised to the orange hexavalent state.

Oxidation of 5-g samples of organic compositions

The oxidation of 5 g of dried beef is characterised in Fig. 3. A 1000-ml Bethge apparatus was employed. As well as using a 5-g sample, the reactants were augmented and a resultant 60-min reaction time was required. As could be predicted, the general profile of the graphical recording of data duplicates that of Fig. 2 for the reason that both organic compositions oxidised are proteins (distillate: 67 ml; perchloric acid remaining in the reaction flask: 33·6 g or 20 ml).

The oxidation of 5 g of vegetable tanned leather is graphically recorded in Fig. 4. The reaction time is shown as 41 min under the same conditions as for an equal sample of dried beef. In the case of leather it is observed that the oxidation is less in

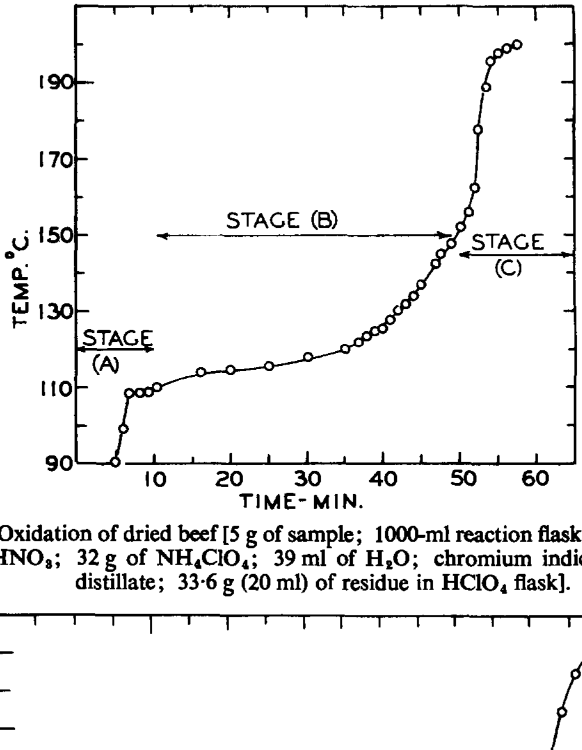

FIG. 3.—Oxidation of dried beef [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 26·5 ml HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 67 ml of distillate; 33·6 g (20 ml) of residue in $HClO_4$ flask].

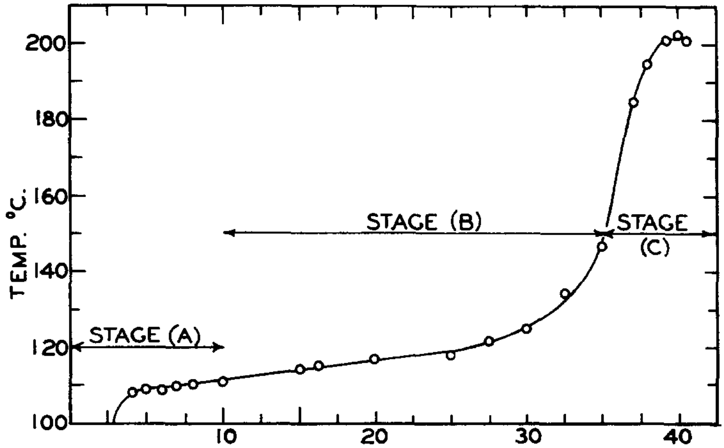

FIG. 4.—Oxidation of leather [5 g of sample; 500 or 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml H_2O; chromium indicator; 71 ml of distillate; 29 g (17·4 ml) of residue in $HClO_4$ flask].

the nitric acid stage (B) and the burden of reactivity is placed upon the perchloric acid stage (C). With the same sample weight, the distillate was 71 ml and the perchloric acid in the reaction flask 29 g or 17·4 ml. The same amounts of mixed reactants were employed in the reactions shown in Figs. 3 and 4. An additional 2·6 ml of perchloric acid were consumed.

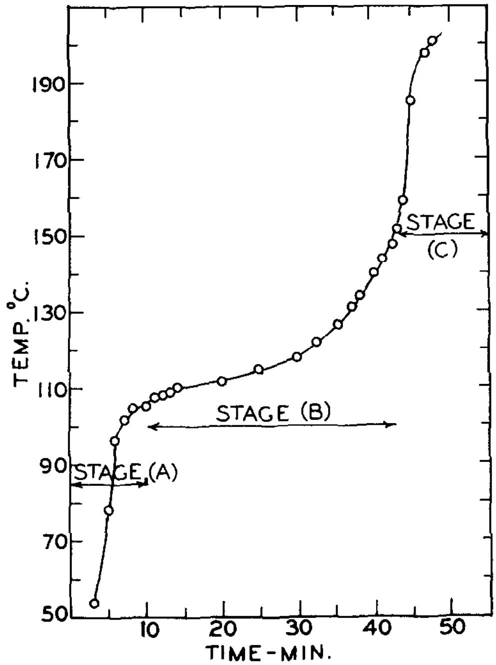

FIG. 5.—Oxidation of sugar [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 70 ml of distillate; 35·3 g (21·1 ml) of residue in $HClO_4$ flask].

The oxidation of 5 g of cane sugar is shown in the graph of results in Fig. 5. The results indicate that the oxygen donor contribution of both nitric acid and perchloric acid are approximately equal.

The oxidation of 5 g of raffia and 5 g of cinnamon bark (principally both cellulose) is depicted in Figs. 6 and 7. As would be predicted, the results indicate almost duplicate reaction characteristics. Subsequent to the reaction with nitric acid in stage (B), the exothermic nature of the perchloric acid oxidation is more pronounced than that of either the oxidation of samples essentially sugar or protein in composition.

Reaction commentary

Nitrous oxide formed in reaction stage (A), being soluble in water and many organic compositions, especially in the case of cellulose-laden materials, promotes foam formation. Such foams are very light and can be counteracted by increasing the flask volume of the Bethge apparatus.

The oxidations described in Figs. 2 to 7 may be well conditioned by employing modified amounts of reactants to suit any particular type of routine plant control oxidation samples. By trial, for example, the volume of nitric acid may be reduced to such favourable volume, provided there results no dark brown or black degradation reaction products. The time required may thus be favourably reduced for a given application.

Sufficient perchloric acid should be obtained to prevent dry spots from forming on the inside bottom of the reaction flask. By withdrawing distillate from the apparatus condenser system, and rinsing with distilled water at the completion of oxidations, one may collect by further distillation the bulk of the perchloric acid formed previously.

Organic compositions containing siliceous materials, in boiling 72·5% perchloric acid, precipitate insoluble SiO_2 quantitatively. In general, perchloric acid is a preferred medium for final determination of metallic and non-metallic residual isolated

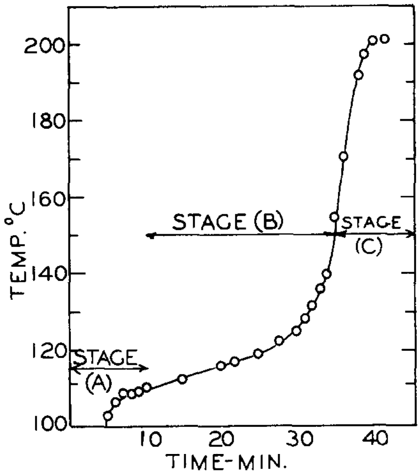

Fig. 6.—Oxidation of raffia [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 71 ml of distillate; 29 g (17·4 ml) of residue in $HClO_4$ flask].

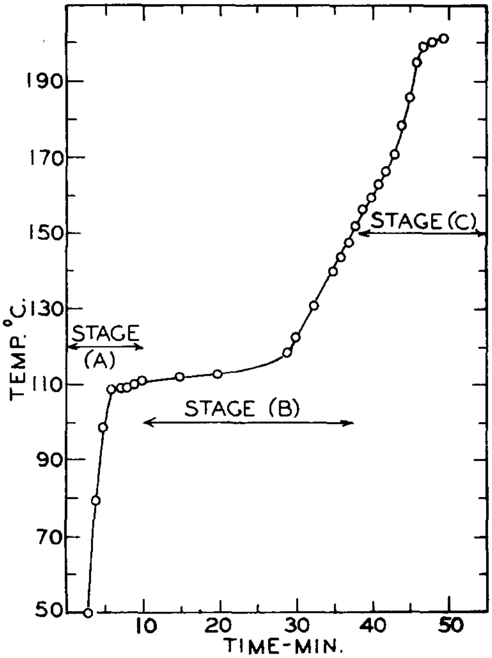

Fig. 7.—Oxidation of cinnamon bark [5 g of sample; 1000-ml reaction flask; 15 ml of HCl; 35 ml of HNO_3; 32 g of NH_4ClO_4; 39 ml of H_2O; chromium indicator; 73 ml of distillate].

and retained elements. If for any reason a sulphuric acid solution is preferred, it may be added to the perchloric acid solution and the latter displaced by volatilisation upon fuming at 180–190°.

Forty test oxidations of a wide variety of organic compositions have been carried out. Analysts, formerly apprehensive of methods 2 to 6, may well make "assurance doubly sure" through the use of the present disclosures.

Zusammenfassung—Die nasse Oxydation organischer Mischungen als erste Operation bei der Bestimmung von Mikro- und Makromengen metallischer und nicht-metallischer Elemente wird beschrieben. Bei diesem Vorgang dient in situ erzeugte Überchlorsäure in erster Linie als Sauerstoffquelle. Mit Salpetersäure-Salzsäure-Gemisch wird Ammoniumperchlorat zu Überchlorsäure umgesetzt. Das Dreisäurengemisch dient dann als ausgezeichnetes Lösungsmittel für das zu oxydierende organische Material. Die Bedingungen sind besonders zur Oxydation großer Proben geeignet. Die Reaktionsgeschwindigkeit wird zum Schutz gegen zu heftige Oxydation unter Kontrolle gehalten. Die Anwendungen schließen hauptsächlich Mischungen von Cellulose, Zuckern, mehrwertigen Alkoholen oder Proteinen ein. Hauptsächlich kommt es darauf an, daß man der Reaktion Zeit läßt, damit die Salpetersäure optimal ausgenutzt wird. So kann man das Oxydationspotential langsam steigern. Das zum Schluß von Überchlorsäure bei stufenweise ansteigender Temperatur von 150° bis 203° gelieferte hohe Potential beendet, die Reaktion, ohne daß Verkohlung droht. Der Aufschluß dauert 50–60 Minuten.

Résumé—On décrit l'oxydation humide de mélanges organiques, en tant que manipulation initiale dans le dosage d'éléments métalliques et non métalliques aux échelles du microgramme et du macrogramme. Le principe donneur d'oxygène est, dans cette technique, l'acide perchlorique généré "in situ". On utilise un mélange d'acides nitrique et chlorhydrique pour convertir le perchlorate d'ammonium en acide perchlorique. Le mélange des trois acides sert alors de solvant principal pour la matière organique à oxyder. Les conditions sont particulièrement appropriées à l'oxydation de grosses prises d'essai. Les vitesses de réaction sont très étroitement controlées, afin que l'on soit assuré d'éviter une oxydation violente. Les applications comprennent des mélanges organiques constitués essentiellement de cellulose, de sucres et polyols, ou de protéines. Les conditions reposent essentiellement sur un temps de réaction suffisamment long pour obtenir les effets maximaux de l'acide nitrique. Cette précaution est la clef qui autorise un potentiel d'oxydation lentement progressif. Le haut potentiel final apporté par l'acide perchlorique, pour les températures s'échelonnant de 150° à 203°, et croissant graduellement, complète les oxydations sans que celles-ci soient accompagnées d'une menace de carbonisation. Les temps de réaction comprennent des digestions de 50–60 minutes.

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[8] Reference 6 above: photo reproduction in Fig. 1.
[9] Illustrated in Fig. 1.

Talanta, 1964, Vol. 11, pp. 641 to 646. Pergamon Press Ltd. Printed in Northern Ireland

5-(8-HYDROXY-5-QUINOLYLMETHYL)-8-HYDROXY-1-METHYLQUINOLINIUM SALTS AS SOLVATOCHROMIC CHELATING AGENTS

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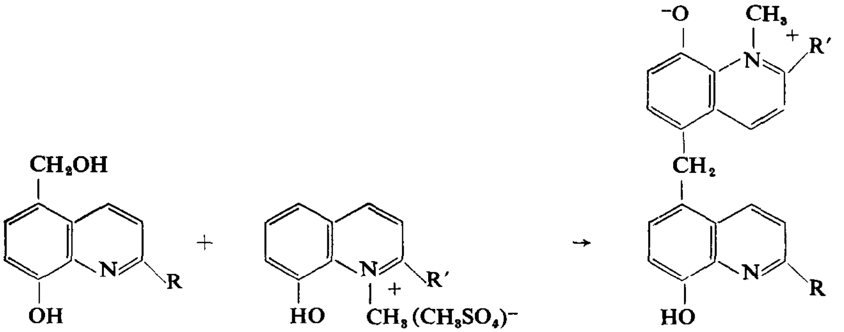
Summary—The title compounds and related substances were prepared, characterised and tested as solvatochromic chelating agents. These reagents show large color changes with solvent, and the chelates, though insoluble in most common solvents, are also solvatochromic. Reagents with a 2-methyl group adjacent to the chelating centre do not precipitate aluminium, and this effect can be used as a colour test for aluminium.

In continuation of studies of chelating agents that undergo large colour changes with solvent polarity (solvatochromism),[1] we have prepared four reagents of general formula I (R and R′ are H or CH_3). In these compounds the solvatochromism is conferred by the betaine function in one quinoline ring, and this is isolated by a methylene bridge from an 8-quinolinol (or 8-hydroxyquinaldine) moiety that can form chelates with metal ions. The chelates as well as the reagents can thus be solvatochromic, and it was anticipated that the two functions should be independent.

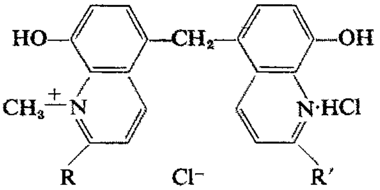
It was not possible to obtain the compounds by direct methylation of available bis(8-hydroxy-5-quinolyl)methanes[2,3] because dimethyl sulphate methylated both nitrogen atoms (see *Experimental*); though these products are solvatochromic they obviously are not chelating agents. The desired monomethylated compounds were obtained by rather tedious condensation reactions of 5-hydroxymethyl-8-quinolinol[4] or 5-hydroxymethyl-8-hydroxyquinaldine[5] with either 1-methyl-8-hydroxyquinolinium methosulphate or its 2-methyl derivative as shown in the following equation:



I
(R = R′ = H)
(II–IV; R or R′ is H or Me)

A similar condensation of 1-methyl-5-hydroxymethyl-8-hydroxyquinolinium methosulphate with 8-quinolinol also gave I, identical in m.p. and ultraviolet-visible spectra with a sample of the same compound prepared by the above reaction. All four of the compounds were isolated as the dark red inner salt represented by formula I and were also converted to the dihydrochlorides, yellow solids of high decomposition point. It is noteworthy (Table I) that all products were hydrated, a demonstration of the affinity of these substances for solvent molecules.

Table I.—5-(8-hydroxy-5-quinolylmethyl)-8-hydroxy-1-methylquinolinium salts



Substituents in formula						Nitrogen	
No.	R	R′	Formula	M.P.,[a] °C	Yield, %	Calcd., %	Found, %
I	H	H	$C_{20}H_{18}Cl_2N_2O_2{\cdot}H_2O$	c320	—	6·87	6·81
IB[b]			$C_{20}H_{16}N_2O_2{\cdot}H_2O$	185	88	8·38	8·38
II	CH_3	CH_3	$C_{22}H_{22}Cl_2N_2O_2{\cdot}H_2O$	238	—	6·44	6·41
IIB[b]			$C_{22}H_{20}N_2O_2{\cdot}H_2O$	187–189	94	7·73	7·57
III	H	CH_3	$C_{21}H_{20}Cl_2N_2O_2{\cdot}H_2O$	233	—	6·65	6·68
IIIB[b]			$C_{21}H_{18}N_2O_2{\cdot}H_2O$	225	93	8·04	8·24
IV	CH_3	H	$C_{21}H_{20}Cl_2N_2O_2{\cdot}H_2O$	207–209	—	6·65	6·50
IVB[b]			$C_{21}H_{18}N_2O_2{\cdot}H_2O$	155	61	8·04	8·42

[a] All compounds melt with decomposition.

[b] B = Betaine, which refers to the neutral molecule formed by the loss of two HCl molecules from the salt (see equation).

Spectra of basic I in a variety of solvents showed a considerable negative solvatochromism in the visible (Table II), with a change in the wavelength of principal maximum by over 100 mμ from water to chloroform as solvent. [For comparative purposes maxima for the inner salt (V) of *N*-methyl-8-hydroxyquinaldinium hydroxide are listed too.] The spectrophotometric determination of ionisation constants of these compounds gave the results of Table III, with the three ionisation constants representing transitions, respectively, from diprotonated to neutral (zwitter-ionic) to anion forms as the pH increases. Thus, the first pKa is for the N-H$^+$ dissociation and the second and third for the phenolic hydrogen atoms. Comparative figures for some related compounds are also listed.

Infrared spectra of potassium bromide pellets of the compounds were also obtained.

Because all four reagents have a pK$_2$ of about 6·7 they would be expected to exist primarily in the cationic form at pH values of 5 or less, and chelates formed at pH 5 or less should not be solvatochromic. All reagents gave yellow solutions at pH 5 with copper, nickel, zinc and aluminium ions and a green solution with iron^{III} ion. In concentrated solutions precipitates of these chelates, presumably as salts with anions in the solution, could be obtained, but lack of knowledge of the anions incorporated prevented successful analysis.

At pH 9 orange to red precipitates from aqueous solution were obtained with copper, cobalt, nickel, zinc, magnesium and iron^{III} ions using reagents I–IV and with aluminium using reagents I and IV. The reagents are soluble in chloroform, but the chelates

TABLE II.—ABSORPTION MAXIMA IN THE VISIBLE SPECTRA OF I AND V

Solvent[a]	Dielectric constant[b] (and Z values[c])	Maximum, $m\mu$ (log ε)	
		I	I
Water	80·4 (94·6)	458 (3·30)	428 (3.18)
90% MeOH	37·9 (85·8)	496 (3·26)	456 (3·06)
90% 1-Propanol	29·8	504 (3·25)	465 (3·13)
90% 2-Propanol	23·5 (83·20)	507 (3·24)	470 (3·09)
90% Acetone	25·9 (77·7)	516 (3·24)	479 (3·09)
Benzyl alcohol	13·1	495 (3·29)	462 (3·18)
Chloroform	4·8 (63·2)	575 (3·39)	529 (3·09)
80% 2-Propanol[d]	29·7	499 (3·25)	463 (3·12)
60% 2-Propanol[d]	45·6	487 (3·27)	456 (3·13)
40% 2-Propanol[d]	57·3	481 (3·28)	449 (3·14)
20% 2-Propanol[d]	68·1	472 (3·30)	438 (3·16)

[a] All aqueous solutions were also 0·01*M* in ammonia. Percentages are volume percentages at 30°, the temperature of measurement.

[b] Dielectric constants of aqueous solutions were interpolated from the values of G. Akerloeff, *J. Amer. Chem. Soc.*, 1932, **54,** 4125; 1936, **58,** 1241.

[c] These measures of solvent polarity were interpolated from the values of E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80,** 3253.

[d] Results at 10% intervals for 2-propanol-water mixtures were recorded; there is a uniform negative solvatochromic effect in this series as a function of dielectric constant.

TABLE III.—ACID DISSOCIATION CONSTANTS OF 5-(8-HYDROXY-5-QUINOLYLMETHYL)-8-HYDROXY-1-METHYLQUINOLINIUM COMPOUNDS

Compound No.	pK_1	pK_2	pK_3
8-Quinolinol[a]	5·13	—	9·89
I	4·6	6·70	9·85
III	4·7	6·62	10·2
V	—	6·83	—

[a] S. F. Mason, *J. Chem. Soc.*, 1958, 674.

TABLE IV.—ULTRAVIOLET-VISIBLE ABSORPTION MAXIMA

Compound	0·1*M* HCl	0·1*M* KOH	pH 7·9[a]
I	257 (4·81), 380 (3·70)	258 (4·57), 275 (4·53) 357 (3·74), 458s (3·32)	462 (3·29)
II	261 (4·97), 370 (3·73)	262 (4·58), 281 (4·55), 440s (3·31)[b]	441 (3·28)
III	260 (4·95), 377 (3·72)	263 (4·64), 275s (4·60), 355 (3·81), 464 (3·34)	465 (3·34)
IV	358 (4·87), 371 (3·75)	257 (4·53), 281 (4·48), 445s (3·30)[b]	447 (3·22)
V	258 (4·73), 357 (3·41)	277 (4·66), 432 (3·25)	

[a] Visible maxima only.

[b] An additional maximum is present near 355 mμ; this maximum appears to be caused by the chelating function.

are not. This lack of solubility of the chelates extended to most organic solvents, though aqueous pyridine mixtures did dissolve them well enough to allow solvatochromism to be observed, the chelates ranging from orange to violet with increasing pyridine content. In water the chelates were somewhat more soluble than is suitable for quantitative precipitations.

It would appear that the solvatochromism of the reagent determines in large part the colour of the chelates. Chelates prepared in alcohols and other non-aqueous solvents showed colours generally close to that of the reagent in each solvent, but upon filtration and loss of solvent the chelates changed to the red colour usually observed in the samples prepared from water solutions.

Any utility of these reagents must rest on the colours produced by extraction of the reagent. A novel colour test for aluminium, for example, is afforded by adding III to an aqueous solution containing metal ions to chelate all except aluminium; after addition of base, chloroform then extracts any excess III. Addition of a drop of dilute I to the aqueous phase and extraction again with chloroform will give a blue-violet chloroform layer if no aluminium is present but will leave the chloroform colourless if aluminium is present, because the aluminium chelate of I is not soluble in chloroform. There is no chelate of III with aluminium.

EXPERIMENTAL

Preparation of Compounds

1-Methyl-8-hydroxyquinolinium methosulphate was obtained by heating 0·1 mole of 8-quinolinol until liquid, then adding 0·1 mole of dimethyl sulphate and heating the mixture with stirring in a steam bath for 10 min. The solid product was washed with ether, dissolved in 2-propanol and precipitated with ether, and finally recrystallised from 2-propanol as yellow needles of m.p. 156° (52% yield). (Literature[6] gives m.p. 145–6°.)

1-Methyl-8-hydroxyquinaldinium methosulphate (m.p. 169–70°) was prepared similarly in 53% yield from 8-hydroxyquinaldine. (*Analysis.* Calcd. for $C_{12}H_{15}NO_5S$: C, 50·51; H, 53·0; N, 4·91. Found: C, 50·56; H; 4·89; N, 4·78.)

An aqueous solution of the methosulphate was converted to the chloride by passage through Dowex 2X-8 in the chloride form, evaporation of the effluent and recrystallization from 90% 2-propanol in the form of yellow needles melting at 231°. (*Analysis.* Calcd. for $C_{11}H_{12}ClNO{\cdot}2H_2O$: N, 5·48. Found: N, 5·48.)

1-Methyl-5-hydroxymethyl-8-hydroxyquinolinium methosulphate was similarly obtained from 5-hydroxymethyl-8-quinolinol[4] and dimethylsulphate in 73% yield by heating a nitrobenzene solution of the reactants for 1 hr on the steam bath. After three recrystallisations from 90% 2-propanol the product melted at 128°. (*Analysis.* Calcd. for $C_{12}H_{15}NO_6S{\cdot}H_2O$: N, 4·39. Found: N, 4·35.) In 0·1*M* hydrochloric acid the compound had λ_{max} 376 mμ; in 0·1*M* potassium hydroxide, 470 mμ (log ε 2·8).

5,5′-Methylenebis(8-hydroxy-1-methylquinolinium) dimethosulphate, decomposing 211–215°, was prepared in 47% yield by heating bis(8-hydroxy-5-quinolyl)-methane in excess dimethyl sulphate for 1 hr on the steam bath, precipitating the product by addition of 1:1 acetone-ether and recrystallising from 2-propanol. (*Analysis.* Calcd. for $C_{23}H_{26}N_2O_{10}S_2$: C, 49·81; H, 4·73; N, 5·05. Found: C, 49·78; H, 4·98; N, 5·02.)

This compound was converted to the dichloride, decomposing at 300°, by extracting an ammoniacal solution (pH 10) with amyl alcohol, adding ether and extracting the resulting solution with 0·1*M* hydrochloric acid. Evaporation of the aqueous extract and recrystallisation from ethanol gave the dichloride. (*Analysis.* Calcd. for $C_{21}H_{20}Cl_2N_2O_2{\cdot}2H_2O$: N, 6·38. Found: N, 6·31.)

In a similar way bis(8-hydroxy-5-quinaldyl)methane[3] was converted to the dimethylated derivative, isolated only as the chloride (m.p. 250°), because the methosulphate was hygroscopic. (*Analysis.* Calcd. for $C_{23}H_{24}Cl_2N_2O_2$: N, 6·46. Found: N, 6·43.)

5-(8-*Hydroxy*-5-*quinolylmethyl*)-8-*hydroxy*-1-*methylquinolinium salts*

Either 0·01 mole of 5-hydroxymethyl-8-quinolinol (1·75 g) or 5-hydroxymethyl-8-quinaldinol (1·89 g) or 5-hydroxymethyl-8-quinaldinol (1·89 g) and 0·02 mole of 1-methyl-8-hydroxy-quinolinium methosulphate (5·43 g) or 1-methyl-8-hydroxyquinaldinium methosulphate (5·71 g) were dissolved in 20 ml of glacial acetic acid. After the dropwise addition of 6 ml of concentrated sulphuric acid, the reaction mixture was allowed to stand for 2 days at room temperature, then was heated to 60° for an additional 2 hr. The mixture was poured over ice and diluted to approximately 200 ml. An aqueous solution of 2·5 g of $CuSO_4{\cdot}5H_2O$ was added and the solution neutralised with 20% sodium hydroxide solution until the formation of the olive copper chelate began. The pH of the solution was then adjusted to 9 by the addition of dilute ammonia solution. Warming the solution on a steam bath for 1 hr coagulated the precipitate, which was filtered and washed with dilute aqueous ammonia and water.

The chelate was dissolved in approximately 250 ml of $2M$ hydrochloric acid and the copper removed by precipitation with hydrogen sulphide. After coagulation of the copper^{II} sulphide by warming the solution, the sulphide was separated by filtration. The filtrate was neutralised with 20% aqueous sodium hydroxide, then saturated with carbon dioxide. After standing several hr, the precipitate was collected, washed with water and dried. The crude product was taken up in methanol and recovered by evaporation or alternatively, by precipitation with ether. The pure hydrated betaines were obtained as small dark red needles after two recrystallisations from 90% ethanol. Upon drying the betaines turned to a dark purple.

The chloride-hydrochloride is obtained by saturation of a methanolic solution of the betaine with hydrogen chloride, precipitation of the salt with a 1:1 acetone-ether mixture, and recrystallisation from 90% ethanol, to which several drops of hydrochloric acid had been added to prevent dissociation.

5-(8-*Hydroxy*-5-*quinolylmethyl*)-8-*hydroxy*-1-*methylquinolinium chloride* (*I in Table I*)
(*alternate method*)

A solution of 0·005 mole of 5-hydroxymethyl-8-hydroxy-1-methyl-quinolinium methosulphate (1·5 g) (XIV) and 0·01 mole of 8-quinolinol (1·5 g) in 10 ml of glacial acetic acid was prepared and 6 ml of concentrated sulphuric acid added dropwise. The mixture was allowed to stand at room temperature for 2 days, then heated at 60° for 2 hr. The mixture was poured over ice and neutralised with 20% sodium hydroxide and steam distilled. The pH of the remaining aqueous solution was adjusted to approximately 8·5 and the solution extracted with benzyl or amyl alcohol. An equal volume of ether is added to the combined alcoholic extracts and the resulting solution extracted with $0{\cdot}1M$ hydrochloric acid. This acidic extract was treated with ether to remove the remaining alcohol and evaporated to yield 0·3 g (15%) of I, melting at 319–322° (dec.).

Determination of Spectra and Ionisation Constants

Ultraviolet and visible spectra were recorded with a Beckman DK-2 Spectrophotometer using 1·004-cm matched silica cells for most measurements and 10-cm cells for very dilute solutions. Visible spectra as a function of pH for a large number of equimolar solutions of I were recorded in order to calculate the ionisation constants by standard procedures.[7]

Distribution coefficients for I between an aqueous buffer and chloroform or benzyl alcohol were estimated by recording the spectrum of the buffered solution (pH 8) before and after extraction of a known volume of solution with a known volume of the solvent. The ratio of absorbance at a given wavelength is the fraction of reagent remaining in the aqueous phase. These measurements were only approximate, but indicated coefficients of 2 and 46 for I extracted into chloroform and benzyl alcohol, respectively.

Infrared spectra were recorded on potassium bromide pellets using a Baird AB-2 spectrophotometer. Spectra of I-IV were very similar showing broad absorption in the 3-μ region for the bonded hydroxyl as well as broad absorption from about 3·2 to 5 μ indicative of quaternary nitrogen. The presence of the methyl group on the carbon adjacent to methylated nitrogen in II and IV apparently gave a double maximum at 6·17 and 6·23 μ, while the other two compounds (I and III) had only a single peak at 6·20 μ. Other bands were not assigned.

Formation of Chelates

Qualitative tests at pH 5 and 9 were run in accordance with previous procedures.[2] Results are described before *Experimental.*

A number of chelates of I with metals were precipitated at pH 9, filtered, washed, dried and weighed. Analysis of these for metal content by ashing to the corresponding metal oxide gave the following results:

Cu^{II}—Calcd. for $Cu(C_{20}H_{15}N_2O_2)_2{\cdot}2H_2O$: Cu, 8·7; found: Cu, 8·7.
Fe^{III}—Calcd. for $Fe(C_{20}H_{15}N_2O_2)_3$: Fe, 5·6; found: Fe, 5·7.
Zn^{II}—Calcd. for $Zn(C_{20}H_{15}N_2O_2)_2$: Zn, 9·4; found: Zn, 9·4.
Al^{III}—Calcd. for $Al(C_{20}H_{15}N_2O_2)_3$: Al, 2·8; found: Al, 3·1.

Acknowledgement—This work was supported by a National Science Foundation Grant.

Zusammenfassung—Die in der Überschrift genannten Verbindungen sowie verwandte Substanzen wurden dargestellt, charakterisiert und als solvatochrome chelatbildende Reagentien geprüft. Diese Reagentien zeigen große Farbänderungen je nach Lösungsmittel und die Chelate sind ebenfalls solvatochrom, obwohl sie in den meisten gebräuchlichen Lösungsmitteln unlöslich sind. Reagentien mit einer 2-Methylgruppe neben dem chelatbildenden Zentrum fällen kein Aluminium; dieser Effekt kann als Farbreaktion auf Aluminium verwendet werden.

Résumé—On a préparé, caractérisé, et essayé les composés du titre et des substances apparentées comme agents chélatants donnant des solvats colorés. Ces réactifs présentent d'importantes variations de couleur en fonction du solvant, et les chélates, quoique insolubles dans les solvants les plus usuels, sont également "solvatochromes." Les réactifs qui ont un groupement 2-méthyl adjacent au centre chélatant ne précipitent pas l'aluminium, et ce fait peut être mis à profit pour un essai coloré de l'aluminium.

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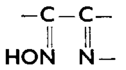
SHORT COMMUNICATIONS

Bisbiacetylmonoxime-ethylenedi-imine and bisbiacetylmonoxime-*o*-phenylenedi-imine as new gravimetric reagents for nickel and palladium

(*Received* 14 *March* 1963. *Accepted* 19 *November* 1963)

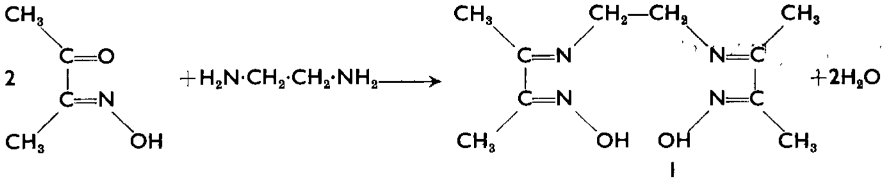
Vicinal diketone dioximes are among the most important organic reagents used in inorganic analysis. Dimethylglyoxime was the first dioxime to be used, as a reagent for nickel and palladium by Tschugaeff,[1] and since then a large number of dioximes have been prepared and tested as analytical reagents.[2-7]

It has been well established that the tautomeric form of the oximes (nitrone form) is responsible for the formation of metal complexes[8] and that the metal involved forms four nitrogen-metal bonds in the dioxime complex. Pfeiffer[8] has shown that if one of the oxime groups is replaced by the imino or methyl-imino group, complex formation occurs in the same fashion. Certain other reagents giving rise to a five-membered chelate ring with the nickel ion and having two co-ordinating nitrogen atoms have a highly selective action towards nickel, the group responsible for the formation of such complexes being



$$\begin{array}{c}-\mathrm{C}-\mathrm{C}-\\ \|\qquad\| \\ \mathrm{HON}\quad\mathrm{N}-\end{array}$$

A possibility exists of condensing diketone monoximes, such as biacetylmonoxime, with certain diamines, such as ethylenediamine and *o*-phenylenediamine, giving rise to the corresponding di-imines.



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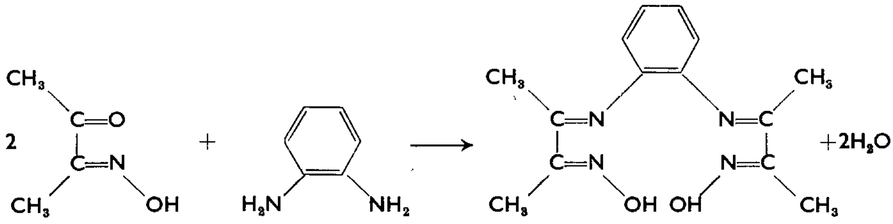


II

These compounds should have two salt-forming and two co-ordinating nitrogen atoms and give rise to tetradentate ligands.

The above possibility has now been verified experimentally and the new reagents, bisbiacetylmonoxime-ethylenedi-imine(I) and bisbiacetylmonoxime-*o*-phenylenedi-imine(II), form precipitates with nickel and palladium ions in which the metal and the reagent are present in the ratio of 1:1. As with other dioximes, such precipitates can be used for the gravimetric determination of these metal ions.

EXPERIMENTAL

Synthesis of the reagents

Ten g of biacetylmonoxime[9] were dissolved in 100 ml of water, 3·5 g of ethylenediamine or 5 g of *o*-phenylenediamine were added and the mixture was refluxed for about 1 hr. On cooling in ice, colourless crystals separated in the former case and pale yellow crystals in the latter case. Both compounds were recrystallised from ethanol:—

Compound I: m.p. 242° (with decomposition); 23·8% of N found, $C_{10}H_{18}O_2N_4$ requires 24·8% of N.

Compound II: m.p. 179°; 20·0% of N found, $C_{14}H_{18}O_2N_4$ requires 20·4% of N.

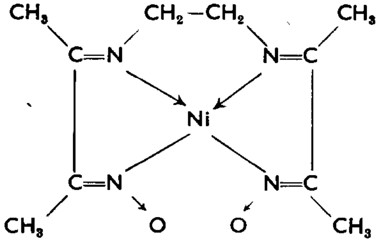
Gravimetric determination of nickel and palladium with the proposed reagents

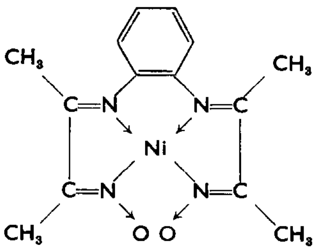
Reagents. One percent solutions of the reagents (I and II) were prepared in aqueous ethanol. A nickel solution was prepared by dissolving 19·735 g of AnalaR ammonium nickel sulphate in 1 litre of water, and a palladium solution by dissolving 1 g of palladium chloride in 500 ml of water. The strengths of the nickel and palladium solutions were checked gravimetrically using dimethylglyoxime.[2]

Procedures. To an aliquot of the nickel solution containing hydrochloric acid an excess of the reagent (I or II) was added, followed by aqueous ammonia till the solution became slightly ammoniacal. The red precipitate of the nickel complex obtained with both reagents was filtered using sintered glass crucibles and dried at 110° for 1 hour.

In the case of palladium a yellow precipitate was formed with both reagents in the presence of hydrochloric acid and it was determined in a similar way to that with the usual dioximes.[2]

By analogy with the dioxime complexes of nickel and palladium, the following structures have been assigned to the complexes with I and II:





Some typical results of determinations with the new reagents are given in Table I. Compound II has a more favourable conversion factor than dimethylglyoxime.

TABLE I

Determination of Nickel

	Ppt., *mg*	Ni, *mg* Found	Ni, *mg* Taken	Error, %
Compound I	211·7	43·95	43·87	0·18
	175·5	36·43	36·35	0·22
Compound II	177·4	31·49	31·42	0·23
	185·5	32·92	32·90	0·10

Determination of Palladium

	Ppt., *mg*	Pd, *mg* Found	Pd, *mg* Taken	Error, %
Compound I	205·8	76·26	76·18	0·10
	185·9	59·99	60·12	0·21
Compound II	223·0	62·84	62·95	0·18
	212·5	59·87	59·75	0·20

TABLE II

Metal ion	Mole ratio of Ni:other metal	Masking agent	Remarks
Fe^{II}	1:1	Acetate	Any Fe^{III} first reduced
Fe^{III}	1:1	Tartrate	Any Fe^{II} first oxidised
Co^{II}	1:1	Cyanide	—
Cu^{II}	1:1	Acetate	—
Ca^{II}, Mg^{II}	1:2	—	—
Zn^{II}	1:2	Acetate	—
Bi^{III}	1:0·5	Unsatisfactory	Prior separation necessary

Effect of foreign ions. Although the proposed reagents are highly selective for nickel, some metals interfere in its quantitative determination. These should either be removed by a prior separation or masked by suitable agents (see Table II). Because the precipitation of palladium takes place in an acidic medium, most of the common metals do not interfere.

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Summary—The condensation products of diketone monoximes with diamines have been shown to form precipitates with nickel which contain metal and reagent in the ratio 1:1, and can be used for the gravimetric determination of nickel.

Zusammenfassussung—Es ist gezeignet worden, dass die aus Diketonmonoximen und Diaminen entstehenden Kondensationsprodukte mit Nickel Niederschläge bilden, welche Metall und Reagens in Verhältnis 1:1 enthalten. Diese können zur gravimetrische Nickelbestimmung dienen.

Résumé—Les monoximes de dicétones réagissent avec les diamines en produisant des composées qui donnent avec le nickel des complexes dont la composition metal:nickel égal est à 1:1. Ces complexes peuvent être utilisées pour le dosage du nickel.

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Amperometric determination of lanthanum as molybdate

(*Received* 19 *April* 1963. *Accepted* 25 *November* 1963)

IN an earlier publication[1] the authors studied the reaction of lanthanum nitrate with sodium molybdate and some of its analytical applications by e.m.f. measurements. The present investigation was undertaken with a view to substantiating the earlier results and to studying the possibility of developing the reaction as an analytical method for the determination of lanthanum.

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Metal ion	Mole ratio of Ni: other metal	Masking agent	Remarks
Fe^{II}	1:1	Acetate	Any Fe^{III} first reduced
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Zn^{II}	1:2	Acetate	—
Bi^{III}	1:0·5	Unsatisfactory	Prior separation necessary

Effect of foreign ions. Although the proposed reagents are highly selective for nickel, some metals interfere in its quantitative determination. These should either be removed by a prior separation or masked by suitable agents (see Table II). Because the precipitation of palladium takes place in an acidic medium, most of the common metals do not interfere.

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EXPERIMENTAL

Reagents

Merck's guaranteed extra pure lanthanum nitrate and sodium molybdate were used and their solutions prepared in air-free conductivity water. The lanthanum solution was standardised potentiometrically as oxalate[2] and the molybdate solution as the 8-hydroxyquinoline complex.[3] The pH of the lanthanum and molybdate solutions, measured by means of a glass electrode, was 5·3 and 7·4, respectively.

Apparatus

A manual polarograph with scalamp galvanometer as a current recorder was used for the amperometric titrations; the dropping mercury cathode was used in conjunction with a saturated calomel electrode connected to the electrolysis cell by a low resistance salt bridge. The drop time in general was 3–3·5 sec. Both direct and reverse amperometric titrations were carried out at an applied potential of $-1·5$ V (*vs.* S.C.E.). At this potential the lanthanum ion yields a diffusion current proportional to its concentration, while the molybdate ion does not produce any wave in neutral or alkaline medium except the residual current of the sodium ion. Twenty ml of either lanthanum or molybdate solution containing 0·01% of gelatine were taken in the electrolysis cell and the dissolved oxygen removed by bubbling nitrogen through the solution for 10–15 min. After each addition of the titrant, the galvanometer deflection was read and the corresponding current calculated (corrected for the dilution effect[4]), then plotted against the volume of titrant added (Figs. 1 and 2). The titrations were also performed in the presence of ethanol. The presence of an indifferent electrolyte was not found necessary because the sodium nitrate formed during the reaction was quite sufficient to eliminate the effect of migration current. The end-point was obtained graphically making allowance for the volume change during the titration. The results are recorded in Table I.

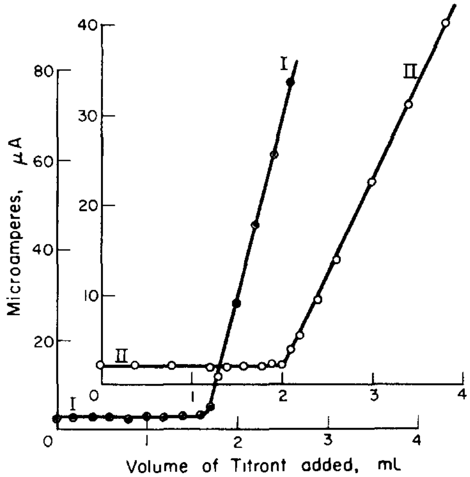

FIG. 1.—Direct amperometric titrations at an applied potential of $-1·5$ V (*vs.* S.C.E.):
I—0·1000M $La(NO_3)_3$ added to 20·0 ml of 0·0125M Na_2MoO_4,
II—0·0333M $La(NO_3)_3$ added to 20·0 ml of 0·0050M Na_2MoO_4.

TABLE I.—AMPEROMETRIC DETERMINATION OF LANTHANUM BY DIRECT AND REVERSE METHODS AT AN APPLIED POTENTIAL OF $-1·5$ V (*vs.* S.C.E.)

Direct titration			Reverse titration		
Lanthanum			Lanthanum		
Present, *g/litre*	Found, *g/litre*	Error, %	Present, *g/litre*	Found, *g/litre*	Error, %
13·900	13·900	0	0·695	0·695	0
4·633	4·5766	1·22	0·278	0·2795	0·54
3·089	3·0482	1·33	0·1853	0·1824	1·56

DISCUSSION

Figs. 1 and 2 represent direct and reverse amperometric titrations between lanthanum nitrate and sodium molybdate in an aqueous medium in the absence of any supporting electrolyte. In the direct titrations (Fig. 1) when lanthanum nitrate is the 'titrant,' at an applied potential of $-1{\cdot}5$ V molybdate ions do not produce any measurable diffusion current and hence no change in the value of current is observed on the addition of the lanthanum salt till the stoichiometric end-point, where a molecular ratio for $La^{3+}:MoO_4^{2-}$ of 2:3 is reached, after which the diffusion current from the lanthanum ions increases with the addition of the latter.

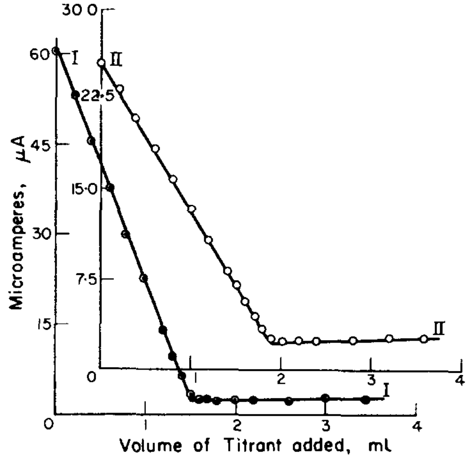

FIG. 2.—Reverse amperometric titrations at an applied potential of $-1{\cdot}5$ V (*vs.* S.C.E.):
I—0·1000*M* Na_2MoO_4 added to 20·0 ml of 0·0050*M* $La(NO_3)_3$,
II—0·0333*M* Na_2MoO_4 added to 20·0 ml of 0·0020*M* $La(NO_3)_3$.

In the reverse titrations (Fig. 2), addition of the molybdate solution causes a decrease in diffusion current which is proportional to the decrease in the concentration of lanthanum ions. Beyond the end-point when the lanthanum ion concentration becomes zero, the current almost remains constant. The amperometric titration curves indicate a sharp break at the point where the molecular ratio of $La^{3+}:MoO_4^{2-}$ is 2:3, corresponding to the formation and precipitation of normal lanthanum molybdate, $La_2O_3{\cdot}3MoO_3$, at pH 5–6 (this pH results from the reactants themselves—see *Experimental*). The accuracy and reproducibility of the titrations has been found to be excellent, even at low concentrations of lanthanum salt ($1 \times 10^{-3}M$). The presence of ethanol improves the end-point slightly because it reduces the solubility of the precipitated compound.

The quantitative precipitation of lanthanum as molybdate at pH 5–6 can be used for the amperometric determination of this metal at an applied potential of $-1{\cdot}5$ V (*vs.* S.C.E.). The method is simple, rapid, accurate and permits the determination of small quantities of lanthanum. Cations which form precipitates with alkali molybdate, *e.g.*, silver, cadmium, $cerium^{III}$, $thorium^{IV}$, $mercury^{I}$ and $mercury^{II}$, and anions which react with lanthanum, *e.g.*, vanadate, tungstate and chromate, interfere and must be absent. The formation of normal lanthanum molybdate as obtained from electrometric results[1] has now been confirmed by amperometric titrations.

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Summary—The reaction between lanthanum and molybdate ions has been followed by means of direct and reverse amperometric titration in aqueous and aqueous-alcoholic media at an applied potential of $-1{\cdot}5$ V (*vs.* S.C.E.). The amperometric end-point obtained from the sharp break in the titration curves occurs when the molecular ratio of $La^{3+}:MoO_4^{2-}$ is 2:3 and corresponds to the formation and precipitation of normal lanthanum molybdate, $La_2O_3.3MoO_3$, at pH 5–6. Amperometric titrations yield very accurate and reproducible results and offer a simple and rapid method for the determination of lanthanum as molybdate even at low concentrations ($1 \times 10^{-3}M$ lanthanum nitrate).

Zusammenfassung—Die Reaktion zwischen Lanthan und Molybdat wurde mittels direkter und umgekehrter amperometrischer Titration in wäßrigen und wäßrig-alkoholischen Medien verfolgt. Ein Potential von −1,5 V gegen die gesättigte Kalomelelektrode wurde angelegt. Der als scharfer Knick in der Titrationskurve sichtbare amperometrische Endpunkt liegt beim Molverhältnis $La^{3+}:MoO_4^{2-} = 2:3$, entsprechend der Bildung und Ausfällung von normalem Lanthanmolybdat $La_2O_3.3MoO_3$ bei pH 5–6. Die apperometrische Titration liefert sehr genaue und reproduzierbare Ergebnisse und bietet eine einfache und schnelle Methode zur Bestimmung von Lanthan als Molybdat selbst bei niedrigen Konzentrationen ($1 \cdot 10^{-3}$ M Lanthannitrat).

Résumé—On a suivi la réaction entre les ions lanthane et molybdate au moyen de dosages ampérométriques direct et inverse en milieux aqueux et hydroalcoolique, à u potentiel appliqué de −1.5 V (par rapport à une électrode de référence). Le point équivalent ampérométrique, obtenu à partir de la brisure nette des courbes de dosage, apparaît lorsque le rapport moléculaire $La^{3+}:MoO_4^{2-}$ est 2:3 et correspond à la formation et à la précipitation du molybdate de lanthane normal, La_2O_3, $3MoO_3$, à pH 5–6. Les titrages ampérométriques donnent des résultats très précis et reproductibles et offrent une méthode simple et rapide de dosage du lanthane à l'état de molybdate, même à de faibles concentrations (1×10^{-3} M de nitrate de lanthane).

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Phase titrations—IV:* New applications including the assay of water in pyridine

(*Received* 7 *May* 1963. *Accepted* 19 *June* 1963)

Recently Barreto and Barreto have described a convenient spectrophotometric method for the assay of water in organic solvents.[1] It is based on the development of a purple colour when an organic solvent containing a small amount of water is added to a solution of chloranilic acid in absolute ethanol.

The authors point out that the new method cannot be used for the assay of water in nitrogen-containing solvents, such as pyridine, because they react with chloranilic acid. We therefore suggest the use of phase titrations to supplement the chloranilic acid method, because these are applicable to problems to which the latter method is not. The assay of water in pyridine is given below as an example of the application of phase titration to nitrogen-containing solvents.

The theory, optimum titration conditions and pertinent references are given in the previous papers in this series,[2,3]

Results for 18 new binary solutions of organic solvents which have been analysed by phase titration with water are also included.

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Results for 18 new binary solutions of organic solvents which have been analysed by phase titration with water are also included.

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EXPERIMENTAL

Reagents

Reagent-grade *methanol*, *acetic acid* (96%) and *acetone*, were obtained from E. Merck A.G., Darmstadt. Reagent-grade *dioxan* and 1,2-*dibromoethane* were obtained from Fischer, Fair Lawn, New Jersey, U.S.A. *Bromobenzene* was a Fischer purified laboratory chemical. *Chloroform puriss.*, was obtained from Hoechst, Frankfurt (M.). Chemically pure *pyridine* and *isopropanol* of unspecified grade were obtained from Riedel De Haën A.G., Seelze-Hannover. *Ethanol* (96·6%) was obtained from Tekel Idaresi, Istanbul. *Distilled water* was used throughout.

Procedure

Six known binary solutions of pyridine and water were titrated with chloroform to obtain a calibration curve of the titre as a function of the volume per cent of the water in pyridine. Synthetic unknown solutions were analysed by comparison with it. Details of the procedure are given in the first paper of this series.[3]

RESULTS AND DISCUSSION

Preliminary tests were made on a number of solvents to determine which would be the best titrant. Chloroform was selected and proved to be excellent although benzene, nitrobenzene and dichloroethane were also promising; bromobenzene, carbon tetrachloride, acetophenone and cyclohexane were not.

A typical end-point (20% water–80% pyridine) was investigated with a Zeiss PMQ II spectrophotometer. Plotting absorbancy, *i.e.*, turbidity, as a function of ml of titrant gave the curve shown in Fig. 1. The earliest phase separation is not easy to observe and takes place before the solution becomes definitely turbid. Hence all solutions were titrated beyond the point of first phase separation to a point at which the increase in turbidity is greater and correspondingly more reproducible.

Eighteen samples, containing 10–40% of water in pyridine were titrated with chloroform. The average error was 0·07 absolute %; the maximum error was 0·2 absolute %. The end-point was good to excellent throughout the optimum titration range of 8–45% water in pyridine.

The accuracy is considerably better than with the chloranilic acid method (relative mean deviation 1·5%, maximum deviation 2·5%) but the present method suffers from the drawback that a suitable titrant must be found for each new system. A less suitable titrant would have given a less distinct end-point and a corresponding reduction in accuracy. The criteria for suitable titrants have been discussed.[3]

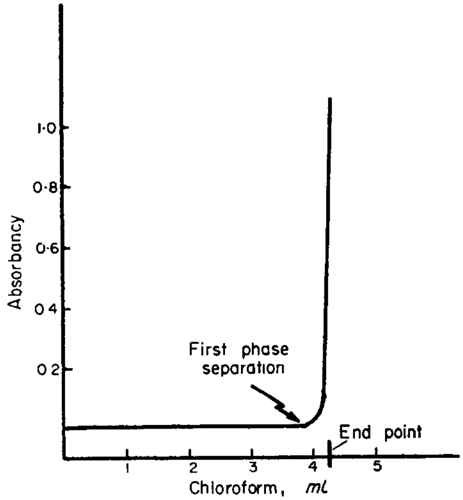

Fig. 1.—Absorbancy at 500 mμ, resulting from turbidity, of a solution of water in pyridine titrated with chloroform.

The assay of water in solvents by phase titration is based on the same principle as the well known cloud-point method.[4,5] In the cloud-point method, a standard amount of an insoluble component is added to a binary mixture of water and some solvent. The temperature at which opalescence appears is then compared with a calibration curve of the temperature of opalescence as a function of composition. We believe that phase titration has the advantage over the cloud-point technique in simplicity and speed because it is easier to carry out a titration than to control and adjust the temperature of a system.

If only a few samples are to be analysed, however, the cloud-point technique has the advantage that the calibration curve need not be made anew, provided that the chemical composition of the insoluble component can be reproduced exactly.[5] Reported results for the cloud-point technique show greater accuracy (0·01–0·02% error) than those for phase titration.

TABLE I.—RESULTS FOR THE TITRATION OF 18 HOMOGENEOUS BINARY SYSTEMS WITH WATER

Sample	Optimum range, %	Number of titrations	Average absolute error, %
Bromobenzene-methanol	2–25	12	0·09
Bromobenzene-ethanol	3–33	12	0·04
Bromobenzene-isopropanol	7–45	12	0·12
Bromobenzene-dioxan	2–20	12	0·07
Bromobenzene-acetone	2–25	12	0·05
Bromobenzene-acetic acid	2–23	10	0·10
Chloroform-methanol	8–60	15	0·13
Chloroform-ethanol	11–50	12	0·12
Chloroform-isopropanol	12–40	12	0·06
Chloroform-dioxan	4–20	9	0·16
Chloroform-acetone	4–30	12	0·09
Chloroform-acetic acid	10–50	11	0·13
1,2-Dibromoethane-methanol	2–25	12	0·06
1,2-Dibromoethane-ethanol	2–20	12	0·07
1,2-Dibromoethane-isopropanol	5–25	12	0·09
1,2-Dibromoethane-dioxan	2–15	12	0·06
1,2-Dibromoethane-acetone	3–20	12	0·04
1,2-Dibromoethane-acetic acid	3–25	12	0·13

The end-point was indicated by the appearance of a distinct permanent turbidity. Titrations and determination of the calibration curve were carried out on the same day.

Table I shows the results for the phase titration of 18 new binary solutions of organic solvents using water as the titrant. The optimum titration range varies slightly with ambient temperature. Binary solutions in which dibromoethane was one component showed good end-points; those with bromobenzene showed excellent end-points; those with chloroform were good in the middle but fair to poor at the extreme ends of the optimum titration range. The end-point appears somewhat more slowly (0·5-min pause) in isopropanol solutions, probably because of the relatively high viscosity of isopropanol.

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Summary—The assay of water in organic solvents by means of phase titration has been discussed in relation to the chloranilic acid method of Barreto and Barreto (*Analyt. Chim. Acta*, 1962, **26**, 494) and the older cloud-point technique. Results are given for the titration of water-pyridine solutions with chloroform, as representative of the phase titration of a nitrogen-containing compound to which the chloranilic acid method is inapplicable. In addition, results are given for the phase titration of 18 new binary solutions using water as the titrant. They are bromobenzene, chloroform and 1,2-dibromoethane, each in binary solution with methanol, ethanol, isopropanol, dioxan, acetone and acetic acid.

Zusammenfassung—Die Bestimmung von Wasser in organischen Lösungsnitteln durch Phasentitration wird im Vergleich zur Chloranilsäure-methode von Baretto und Baretto und der älteren Trübungsmethode diskutiert. Daten werden angegeben für die Titration von Wasser-Pyridin-Mischungen mit Chloroform als Beispiel für die Phasentitration einer stickstoffhaltigen Verbindung, auf die die Chloranilsäuremethode nicht anwendbar ist. Ferner werden Ergebnisse von Phasentitrationen mit Wasser als Titrant an 18 neuen binären Mischungen angegeben. Es handelt sich um Brombenzol, Chloroform und 1,2-Dibromäthan in Mischungen mit Methanol, Äthanol, Isopropanol, Dioxan, Aceton und Essigsäure.

Résumé—La détermination de l'eau dans les solvants organiques au moyen du dosage de phase a été discutée en relation avec la méthode à l'acide chloranilique de Baretto et Baretto et la méthode ancienne du point de trouble. Les résultats ont été donnés pour des solutions eau-pyridine avec le chloroforme comme exemple de dosage de phase des composés contenant de l'azote, et pour lesquels la méthode à l'acide chloranilique est inaplicable. De plus, les résultats concernant le dosage de phase de 18 nouvelles solutions binaires utilisant l'eau comme agent titrant sont données; ce sont: le bromobenzène, le chloroforme, le dibromo-1,2-éthane en binaire respectivement avec le méthanol, l'éthanol, l'isopropanol, le dioxane, l'acétone et l'acide acétique.

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INTRODUCTION

On account of their high thermal conductivity, metal density and melting point, and temperature stability, carbides of uranium and plutonium have been considered as potential fuels for nuclear reactors. It is often necessary to find the carbon content of these carbides; this may be present as both combined carbon and free carbon. The total carbon is determined by combustion at a high temperature in a stream of oxygen, and the carbon dioxide thus evolved is measured either manometrically,[1–3] gravimetrically by absorption in soda asbestos,[4] conductometrically[5,6] or titrimetrically by absorption in standard barium hydroxide solution.[7,8] The free carbon is separated from the sample by dissolving it in hydrochloric acid; the insoluble part, being free carbon, is determined in a similar way.[4,8]

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phase titration of a nitrogen-containing compound to which the chloranilic acid method is inapplicable. In addition, results are given for the phase titration of 18 new binary solutions using water as the titrant. They are bromobenzene, chloroform and 1,2-dibromoethane, each in binary solution with methanol, ethanol, isopropanol, dioxan, acetone and acetic acid.

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The present paper describes a simple method in which both combined and free carbon are determined in the same sample by taking advantage of their combustion at different temperatures.

PREPARATION OF THE CARBIDES

Well-powdered mixtures of U_3O_8 and graphite were heated in an atmosphere of argon in a high-current graphite-resistor furnace to 1600° for the formation of mainly uranium monocarbide, and to 2400° for the formation of mainly uranium dicarbide. Carbides of plutonium were likewise prepared by heating, at 2400°, a well-powdered mixture of PuO_2 and graphite. The carbide pellets were powdered in an argon atmosphere, and were stored dry in ground-glass stoppered tubes filled with argon.

THERMOGRAVIMETRIC ANALYSIS

Ten mg of the carbide under investigation were loaded on to the pan of a silica spring thermobalance,[9] and the weight changes in air were observed as a function of temperature; the rate of heating of the furnace being 5°/min. Uranium carbides started to decompose at 250°; for plutonium carbides the temperature was 300° (Fig. 1). The weight of the sample increased, showing the formation of oxide from the carbide. There was no change in weight for either carbide between 500 and 600°, which showed that the carbides are oxidised below 500°. Above 600° there was a loss of weight from the oxidation of free carbon; and at 800° there was complete combustion of carbon, leaving the metal oxides. This behaviour clearly showed the possibility of determining combined carbon in a combustion tube heated at 500°, and free carbon by heating the same sample above 800°, in each case determining the carbon dioxide evolved.

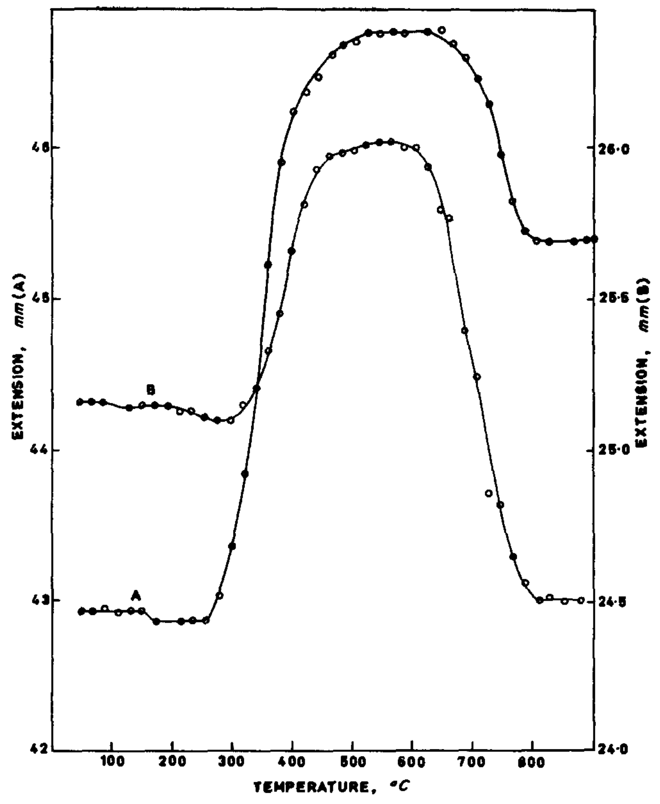

FIG. 1

DETERMINATION OF CARBON

The carbide sample (2–10 mg), weighed in a platinum microcombustion boat, was placed in a quartz combustion tube and heated at 500° for 45 min, passing a current of oxygen, purified by a

U-tube packed with "Carbosorb" (soda asbestos) and Anhydrone, through the combustion tube at the rate of a few bubbles per sec as counted by a sulphuric acid bubbler. The liberated carbon dioxide was absorbed in two conical flasks, each containing 10 ml of ~0·05*N* barium hydroxide solution. The carbon dioxide was determined by titrating the excess barium hydroxide against standard hydrochloric acid solution from an Agla microsyringe, using phenolphthalein as indicator. The same sample was thereafter heated at 900° for 45 min, and the liberated carbon dioxide was again determined. All titrations were performed in a nitrogen atmosphere to prevent absorption of any atmospheric carbon dioxide. The results are given in Tables I and II.

TABLE I.—ANALYSIS OF URANIUM CARBIDES

No.	Wt. of sample, *mg*	Combined carbon* *mg*	Combined carbon* %	Free carbon *mg*	Free carbon %
1.	10·66	0·8868	8·32	0·1128	1·06
2.	15·32	1·2852	8·39	0·1488	0·97
3.	7·13	0·5940	8·33	0·0756	1·06
4.	8·71	0·6948	8·00	0·0864	0·99
5.	7·36	0·6000	8·17	0·0756	1·03
6.	11·93	0·9720	8·15	0·1236	1·04
7.	12·37	1·0200	8·25	0·1260	1·02
8.	12·20	1·0080	8·26	0·1200	0·98
	Average		8·23		1·02
	Standard deviation		1·6%		3·2%

TABLE II.—ANALYSIS OF PLUTONIUM CARBIDES

No.	Wt. of sample, *mg*	Combined carbon* *mg*	Combined carbon* %	Free carbon *mg*	Free carbon %
1.	4·93	0·4464	9·05	0·2376	4·82
2.	3·85	0·3504	9·10	0·2076	5·39
3.	3·59	0·3300	9·19	0·1776	4·95
4.	2·81	0·2580	9·18	0·1500	5·34
5.	2·505	0·2244	8·96	0·1284	5·13
6.	2·595	0·2364	9·11	0·1332	5·13
	Average		9·10		5·13
	Standard deviation		0·3%		3·9%

TABLE III.—URANIUM CARBIDES

Wt. of sample, *mg*	Differential temperature method: Combined carbon*, %	Differential temperature method: Free carbon, %	Conventional method: Free carbon, %
10·230	4·52	9·36	
6·470	4·30	9·16	
5·075	4·47	9·15	
6·395			8·88
7·420			9·12

* Based on the total weight of sample.

COMPARISON WITH CONVENTIONAL METHOD

To test the reliability of this method, samples of uranium and plutonium carbides were analysed by the new and the conventional methods, and the results were compared. In the conventional method, the weighed sample was heated with 5*M* hydrochloric acid for 2 hr to decompose the carbide. The free carbon, which remains unaffected, was centrifuged, washed thoroughly with water, alcohol, acetone and ether to remove the solid and liquid hydrocarbons, and determined as described earlier. The results are given in Tables III and IV.

TABLE IV.—PLUTONIUM CARBIDES

Wt. of sample, *mg*	Differential temperature method		Conventional method
	Combined carbon,* %	Free carbon, %	Free carbon, %
3·200	9·04	8·25	
4·120	8·62	8·27	
3·760	9·00	8·04	
2·25			8·27
2·05			8·20

* Based on the total weight of the sample.

CONCLUSION

The conventional method for the determination of combined carbon and free carbon requires two samples, and the value for combined carbon is obtained by taking the difference between the total carbon present and the free carbon determined separately. The error in this method is, therefore, likely to be greater. In the present method, both combined and free carbon are determined separately in the same sample, thus saving time and reducing the error.

Summary—A simple method for the determination of combined and free carbon in the carbides of uranium and plutonium is based on the examination of the oxidation of carbide and free carbon thermogravimetrically. The combined carbon (carbide) oxidises to carbon dioxide in air below 500° while the free carbon oxidises above 600°. This allows the determination of both combined and free carbon in a single sample, using a furnace tube and a conventional method for carbon dioxide.

Zusammenfassung—Eine einfache Methode zur Bestimmung von gebundenem und freiem Kohlenstoff in den Carbiden von Uran und Plutonium wird beschrieben, die auf der thermogravimetrischen Untersuchung der Oxydation von Carbid und Kohlenstoff beruht. In Carbiden gebundener Kohlenstoff verbrennt an der Luft unter 500°C zu Kohlendioxyd, der freie Kohlenstoff erst über 600°C. Dies erlaubt die Bestimmung von gebundenem und freiem Kohlenstoff in einer Probe in einem Röhrenofen mit einer gebräuchlichen Bestimmungsmethode für Kohlendioxyd.

Résumé—On décrit une méthode simple pour le dosage du carbone combiné et libre dans les carbures d'uranium et de plutonium, basée sur l'observation de l'oxydation du carbure et du carbone libre au moyen de la méthode thermogravimétrique. Le carbone combiné (carbures) est oxydé à l'air en gaz carbonique en dessous de 500°C cependant que le carbone libre s'oxyde au-dessus de 600°C. Ceci rend possible les dosages du carbone combiné et du carbone libre dans un seul échantillon, par l'emploi d'un four tubulaire et d'une méthode usuelle de dosage du gaz carbonique.

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Possibility of automation of potentiometric EDTA titrations

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In many laboratories automatic and semi-automatic apparatus is in use for the simpler types of titration, *e.g.*, of acids, bases and halides. Because there are also many examples of metal titrations which have to be carried out daily, it was considered worthwhile to investigate the possibilities of automation in this field. Very little has been reported on this subject, so far. Haslam *et al.*[1] described an automatic titration of the hardness of water using an amalgamated silver rod as the indicator electrode. Lacy[2] recently published a photometric titration for the semi-automatic determination of hardness in water.

We have investigated the possibility of automation of the complexometric titration of some 20—mostly common—metals for which well-established titration curves were available from earlier work on manual titrations. These examples include direct and back-titrations—the latter with a copper solution as the titrant—in three different pH ranges that are easy to establish. The work is certainly not exhaustive in the sense that many other possibilities undoubtedly exist.

EXPERIMENTAL

Apparatus

Experiments have been carried out with the aid of the well-known Beckman model K titrator, which could be used without modification. An amalgamated gold wire served as indicator electrode, and a saturated potassium chloride calomel electrode as reference. The amalgamated gold wire was prepared by immersing 3 cm of the top part of a pure gold wire (24 carat, length 10 cm, diameter 1·5 mm) for some min in pure mercury. The electrode had to be cleaned frequently with fine emery paper and re-covered. The calomel electrode was connected with the solution by means of a potassium nitrate/agar bridge. pH values were checked by means of a pH meter, but a good grade of pH paper would have been satisfactory in most cases.

The model K titrator is equipped with an "anticipation circuit" which smooths the approach to the end-point of a titration. The number of titration increments is regulated by a dial, the correct setting of which has to be determined for each kind of titration. This is especially important for electrochemical reactions at the mercury electrode which do not proceed instantaneously.[3]

Reagents

The titrants for direct and back-titrations were 0·01*M* standard solutions of EDTA and of copper nitrate, respectively. The buffers were (a) 10 g of sodium hydroxide with 28 ml of glacial acetic acid diluted to 500 ml with water (acetate buffer), and (b) 8 g of ammonium nitrate with 55 ml of 25% aqueous ammonia diluted to 1 litre with water (ammonium buffer). Nitric acid and potassium hydroxide were used to adjust the pH when necessary. A 0·005*M* solution of mercury-EDTA was prepared by mixing a 0·01*M* solution of mercury$^{\mathrm{II}}$ nitrate with an equal amount of 0·01*M* EDTA and then adjusting to pH 4. All reagents were analytical grade.

Procedure

Titrations were carried out in 250-ml beakers in which 20 ml of an approximately 0·01*M* metal solution† were diluted with water to 100 ml. Four drops of 0·005*M* mercury-EDTA solution were

† Chlorides and sulphates must be absent because they interfere with potentiometric determinations using the mercury electrode.

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added and the pH established at the values given in Table I. For the lower pH range this was effected with nitric acid, for the pH range 4 to 6 with 10 to 15 ml of acetate buffer and for the higher range with 10 to 15 ml of the ammonium buffer. The correct end-point was derived from curves obtained by manual potentiometric titrations using the same electrochemical system; the values are given in Table I. The "anticipation" used is also given in the table. In the case of back-titrations (*B* in Table I), an excess of 0·01*M* EDTA was added to the beaker before titration with copper nitrate solution.

RESULTS AND DISCUSSIONS

Table I contains data on the accuracy of the 18 automatic titrations that were investigated. The standard deviations are calculated from seven-fold titrations in pure single metal-ion solutions. The accuracy has been determined at optimum and carefully controlled pH values.

TABLE I.—ACCURACY OF AUTOMATIC EDTA TITRATIONS WITH THE BECKMAN MODEL K TITRATOR

Metal	Direct (D) or back (B) titration	Setting of end-point, *mV*[a]	Setting of anticipation[b]	Optimum pH value	Standard deviation, *ml*[c]
Bi	D	+360	1·5	1·7	0·01
Fe	D	+360	2·5	1·8	0·05
Hg	D	+385	2·5	1·9	0·03
In	D	+360	2·5	1·5	0·03
Th	D	+340	2·5	1·6	0·06
Cd	D	+210	3·5	4·5	0·01
Cu	D	+220	3·0	4·6	0·04
Pb	D	+230	3·0	4·5	0·02
Zn	D	+220	3·0	4·6	0·03
Al	B	+220	6·0	4·8	0·03
Ni	B	+230	6·0	4·7	0·08
Ba	D	−72	2·0	10·0	0·10
Ca	D	−50	2·0	10·2	0·05
Mg	D	−55	2·0	9·9	0·13
Sr	D	−65	2·0	10·0	0·09
Co	B	−40	3·0	10·2	0·04
Cr	B	−40	3·0	10·0	0·04
Mn	B	−35	3·0	10·1	0·07

[a] *Vs.* saturated potassium chloride calomel electrode.

[b] These figures refer to our instrument. It may be necessary to alter them for other apparatus.

[c] Ml of 0·01*M* titrant, *viz.* EDTA solution for direct and copper nitrate solution for back-titrations, calculated from a seven-fold titration.

Table II compares the accuracies of automatic titrations with those of manual titrations found in earlier work. In the case of zinc there is only a negligible difference in accuracy; for magnesium the difference is a little larger. The automatic procedure might have been expected to be less accurate,

TABLE II

Metal	Standard deviation, *ml*	
	Automatic	Manual
Zn	0·03	0·02
Mg	0·13	0·035

but the difference actually found is surprisingly small and proves the feasibility of the automatic method. Even in the case of magnesium the relative error is less than 1% when 20 to 25 ml are titrated.

In general it can be said—and this is illustrated by the figures in Table 1—that if the titration curve shows a slight jump, the automatic titration is least accurate. Such curves occur, for instance, when the apparent stability of the metal-EDTA complex to be formed is lower than, say 10^9. At the pH applied this is the case for barium ($K^* = 10^7$), magnesium ($K^* = 10^8$) and strontium ($K^* = 10^8$). Also a curve with a flat top part (*e.g.*, that for thorium) is unfavourable for automatic indication of the end-point. Finally, back-titrations will tend to be somewhat less accurate, because two measurements of volume are necessary.

For work of a routine character, *e.g.*, plant control, it is important to know how far variations in the prescribed titration conditions (dial settings, pH, salt concentration) will affect the accuracy. It has been found that the end-point potential must be set precisely because even small deviations may cause the titration result to be very inaccurate. This is caused by the steep fall or rise of the curves in the region of the equivalence point and their sometimes peculiar shape. This effect can, to a certain extent, be compensated by a high "anticipation", but then titrations become very slow. A low setting of the "anticipation" may lead to overshooting of the end-point and it sometimes renders titration impossible because the apparatus does not stop at all.

It is evident that a lower pH value than prescribed will cause errors because this leads to a lowering of the apparent stability of the metal-EDTA complex concerned, which degrades the titration curves. It has been found that for the medium pH range errors will in the majority of cases not exceed ±0·2 ml of titrant when the pH is maintained between 4·0 and 6·0. Especially for the alkaline range, however, large errors must be expected when the pH deviates only a few tenths from the prescribed value.

The quantity of neutral salt in the titration solution was found not to be very critical. A high concentration leads to a slight shift of the titration curves because of a change in activity coefficients. Titration errors were serious only in the case of the poorest curves. In titrating 100 ml of a 0·002*M* solution of calcium ions to which 5 g of potassium nitrate had been added the result was 6% low (1·21 ml of 0·01*M* EDTA). For many other metals the difference was less than 0·2 ml.

The possibility of applying the automatic technique to samples that contain more than one metal will have to be studied for each individual case. An example is the determination of the hardness of water which essentially is the titration of the sum of calcium and magnesium. In a four-fold automatic titration of the hardness of tap water we found: 15·59, 15·56, 15·68 and 15·52°G.H., respectively. The extreme values differ by only 1%, which is very reasonable.

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Summary—Experiments are described which show that many metals can be determined in a simple way with the aid of the Beckman model K automatic titrator. As regards accuracy, the method is in many cases practically on a par with manual titrations.

Zusammenfassung—Es wird experimentell nachgewiesen, dass sich viele Metalle mit Hilfe eines automatischen Titrationsapparates (Beckmann, Modell K) einfach bestimmen lassen. In vielen Fällen ist die erzielte Genauigkeit der bei manuellen Titrationen erreichten praktisch gleich.

Résumé—Des expériences démontrent que nombre de métaux peuvent être dosés d'une manière simple à l'aide de l'appareil de titration automatique Beckman, modèle K. La précision atteinte est en beaucoup de cas équivalente à celle obtenue dans les titrations manuelles

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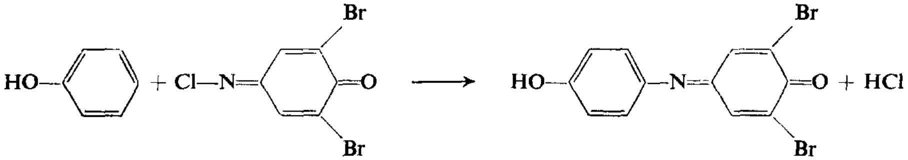
Zur Kenntnis der Gibbs'schen Farbreaktion auf Phenole

(*Eingegangen am* 13 *November* 1963. *Angenommen am* 18 *November* 1963)

DER von Gibbs[1] entdeckte Nachweis von Phenol mit 2,6-Dibrom-*p*-benzochinon-4-chlorimin beruht auf der Kondensation:



wobei durch gleichzeitige oder nachträgliche Alkalisierung (Natronlauge, Natriumcarbonat, Natriumbicarbonat, Ammoniak, Borax oder Pufferlösungen) ein tiefblaues Produkt entsteht. Gemäß obiger Umsetzung sollte die Farbreaktion mit allen Derivaten des Phenols eintreten, die eine freie *p*-Stellung besitzen. Daß dies jedoch nicht ausnahmslos der Fall ist, hat zuerst Bohdanecký[2] bei der Salicylsäure festgestellt, die nicht reagiert. Da auch bei einigen anderen *o*-substituierten Phenolen mit freier *p*-Stellung die Farbreaktion ausbleibt und somit kein allgemeiner Phenolnachweis möglich ist, mußte die Anwendung des Gibbs'schen Reagens in der Tüpfelanalyse auf bestimmte Fälle beschränkt bleiben. In Betracht kommt der Nachweis von bei Erwärmung flüchtigem Phenol, *o*-Kresol, Thymol, Brenzkatechin, Resorcin und Oxin.[3] Des weiteren ermöglicht der empfindliche Nachweis von Phenoldämpfen den tüpfelanalytischen Nachweis solcher Verbindungen, die bei trockener Erhitzung oder durch den Eintritt in chemische Umsetzungen Phenol abspalten.[4] Schließlich ist noch der Nachweis von Vitamin B_6 (Adermin) mittels des Gibbs'schen Reagens zu erwähnen.[5]

Es wurde festgestellt, daß im Gegensatz zur Salicylsäure das Salicylamid die Gibbs'sche Phenolreaktion zeigt. Dieses verschiedene Verhalten ließ es wünschenswert erscheinen, den Einfluß von *o*- und *m*-ständigen Substituenten auf den Eintritt der Gibbs'schen Phenolreaktion zu ermitteln. Diesbezügliche Versuche wurden mit 2%igen Lösungen hierhergehöriger Verbindungen nach folgenden Arbeitsvorschriften durchgeführt:

Test 1: Auf Filtrierpapier wurde je ein Tropfen der Probelösung, enthaltend 1 mg Probe, und ein Tropfen der benzolischen Lösung von 2,6-Dibrom-*p*-benzochinon-4-chlorimin bzw. des entrsprechenden 2,6-Dichlorderivates so aufgebracht, daß die beiden Tropfen sich auf dem Papier überschneiden. Dann wurde das Papier über Ammoniak geräuchert, wobei bei positiven Ausfall die spindelförmige Überlappung der durch die zwei Tropfen auf dem Filtrierpapier entstandenen Kreise gefärbt wurde. Ein Blindversuch wurde mit dem Reagens und dem Lösungsmittel der Probe angestellt.

Test 2: Wie oben, nur wurde nicht über Ammoniak geräuchert, sondern mit Sodalösung angetüpfelt.

Die Überprüfung von neun *m*-substituierten Phenolen mit freier *p*-Stellung (in Tabelle I) hat

TABELLE I

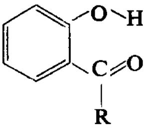
Phenol	Test 1	Test 2
o-Kresol	+ blau	+ blau
m-Kresol	+ blau	+ blau
p-Kresol	keine Rk.	keine Rk.
Salicylaldehyd	+ blau	keine Rk.
m-Hydroxybenzaldehyd	+ blau	+ blau
p-Hydroxybenzaldehyd	keine Rk.	keine Rk.
o-Nitrophenol	keine Rk.	keine Rk.
m-Nitrophenol	+ blau	+ blau
p-Nitrophenol	keine Rk.	keine Rk.
Chromotropsäure	+ blau	+ blau
H-Säure	+ blaugrau	+ blaugrau
K-Säure	+ blaugrün	+ blaugrün
Resorcin	+ violett	+ violett
Orcin	+ braunviolett	+ braunviolett
Naphthoresorcin	+ braunviolett	+ braunviolett

ergeben, daß diese ausnahmslos die Gibbs'sche Farbreaktion zeigen. Abweichungen scheinen demnach lediglich bei *o*-Derivaten zu bestehen, wie folgende Gegenüberstellung in Tabelle II zeigt.

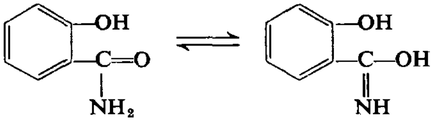
Aus Tabelle I und II geht hervor, daß die Gibbs'sche Farbreaktion bei solchen o-substituierten Phenolen ausbleibt, die im Substituenten ein am C-Atom bzw. N-Atom doppelt gebundenes Sauerstoffatom enthalten. Diese Konstitution ermöglicht eine Chelatisierung des Wasserstoffs der phenolischen Hydroxylgruppe zwischen zwei Sauerstoffatomen, und dies dürfte die Ursache für das Ausbleiben der Reaktion sein, da in diesen Fällen gar keine phenolische Hydroxylgruppe mehr vorliegt:

TABELLE II

Phenole	mit positiver Rk.	mit negativer Rk.
Phenol	blau	Salicylsäure
o-Kresol	blau	Salicylsäuremethylester
Thymol	blau	Salicylsäureisoamylester
o-Phenylphenol	blau	Salicylsäurehydrazid
Brenzkatechin	blau	*o*-Nitrophenol
Guajakol	blau	Salicylaldehyd (mit NH_3 positiv)
o-Aminophenol	blau	Orthovanillin (mit NH_3 positiv)
Glyoxal-bis-(2-hydroxyanil)	blau	
8-Hydroxychinolin	blau	
Salicylaldoxim	blau	
Salicylalhydrazon	grünblau	
Salicylsäureamid	blau	
Orthoeugenol	blau	
Salicylalanilin	blau	



Der Eintritt der Gibbs'schen Farbreaktion bei Salicylamid und Salicylanilid ist offenbar dadurch su erklären, daß in diesen Fällen der Substituent auch in einer tautomeren Imidform vorliegt, die keinen am Kohlenstoff doppelt gebundenen Sauerstoff enthält:



Die Tatsache, daß Salicylsäurehydrazid die Gibbs'sche Reaktion nicht zeigt, deutet darauf hin, daß bei dieser Verbindung eine dem Salicylamid analoge Tautomerie nicht vorliegt, zumindest nicht in dem für die Kondensation erforderlichem Ausmaß.

Daß doppelt gebundener Stickstoff die phenolische OH-Gruppe gegenüber der Gibbs'schen Reaktion nicht maskiert, zeigt die Reaktionsfähigkeit von Salicylaldoxim, Salicylalhydrazon und 8-Hydroxychinolin. Im Einklang damit kann die Reaktionsunfähigkeit von Salicylaldehyd durch Einwirkung von Ammoniakdampf aufgehoben werden, weil hierbei Salicylaldimin entsteht, das kein zur Chelatisierung erforderliches Sauerstoffatom besitzt.

Die Tatsache, daß bei Phenolen mit zur Chelatbildung befähigten Substituenten in *o*-Stellung die Gibbs'sche Farbreaktion ausbleibt, ist zur Charakterisierung von Phenolen von Bedeutung. Der positive Ausfall der Farbreaktion beweist das Vorliegen von Phenolen mit freier *p*-Stellung ohne o-ständige —CHO,COOH oder —COOR Gruppen. Die Anwesenheit solcher Gruppen ist demnach erwiesen, wenn bei positiven Ausfall anderer Nachweisreaktionen auf Phenole mit freier *p*-Stellung die Gibbs'sche Farbreaktion ausbleibt. Von Interesse ist auch die Anwendung der Gibbs'schen

Reaktion zur Unterscheidung von gewissen isomeren Derivaten des Phenols. Von Phenolcarbonsäuren und deren Estern sowie von Hydroxybenzaldehyd gibt es jeweils drei Isomere, von denen lediglich das *m*-Isomere die Gibbs'sche Reaktion zeigt.

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Zusammenfassung—Es wurde der Einfluss von Substituenten auf die Reaktionsfähigkeit von Phenolen gegenüber 2,6-Dibromchinon-4-chlorimin bzw. dessen Chloranalogem untersucht. Es zeigte sich, dass Substituenten in *m*-Stellung wenig Einfluss haben, hingegen in Orthostellung Substituenten mit einer C=O bzw. N=O Gruppe den Eintritt der Reaktion verhindern.

Summary—The influence of substituents on the reactivity of phenols towards 2,6-dibromoquinone-4-chlorimine and its chloro analogue has been investigated. It has been shown that substituents in the *m*-position have little influence, whereas *o*-substituents with a C=O or N=O group prevent the reaction taking place.

Résumé—On a étudie l'influence des substituants sur la réactivité des phénols vis-à-vis de la 2,6-dibromoquinone-4-chlorimine et de son analogue chloré. On a montré que les substituants en méta ont peu d'influence, mais que les substituants en ortho, avec un groupe C = O ou N = O empêchent la réaction.

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LETTERS TO THE EDITOR

Use of "dead-stop" indication of the end-point in chelometric titrations

SIR,

For indicating the end-point of the titration of iron^{III} salt with EDTA, we have used the change of current in a system of two stationary Pt-microelectrodes at a constant applied potential (dead-stop indication).* During the titration of iron^{III} in acidic unbuffered medium at pH 1–1·5, the current changes were found to be maximum 0·1 (μA) at an applied potential of 1–1·4v. The nature of the corresponding titration curves depends on the value of the applied potential, as will be discussed later.

Because indication of the end-point in the titration of iron^{III} with EDTA is possible even in a medium of 0·2*M* HCl, the determination is quite selective. Also, the stabilisation of the current after each addition of the titrant is very rapid, in comparison with the same titration carried out under potentiometric control.[1] This titration with two Pt electrodes can be used for the indirect determination of a series of metals by the back-titration of the excess of EDTA with iron^{III} solution. Preliminary results have shown also the possibility of a direct titration of Cu^{II}, Tl^{III} or U^{IV} with EDTA; and in the presence of small amounts of Fe^{III} with some traces of Fe^{II} it is possible to use dead-stop indication for the direct titrimetric determination of metals forming very stable complexes with EDTA (Th, Zr, *etc.*)

Details of this indication, and methods for the determination of some metals will be published in this Journal at a later date.

F. VYDRA
J. VORLÍČEK

* (NOTE ADDED IN PROOF: The course of this titration can also be followed using dead-stop indication and two graphite electrodes.)

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10 *December* 1963

[1] R. Přibil, Z. Koudela and B. Matyska, *Chem. Listy*, 1950, **44**, 222.

Rapid chemical analysis of silicate rocks

SIR:

IN recent years, numerous schemes for the rapid chemical analysis of silicate rocks and minerals have been proposed, and some of these are in widespread use throughout the world.

One of the greatest problems in devising such rapid schemes is that of obtaining a clear homogenous solution of the sample from which aliquot portions may be measured for the various determinations. In particular, the preparation of a solution for the colorimetric determination of silica is somewhat troublesome.

It has been found that a clear aqueous solution of most silicate samples may be quickly and conveniently prepared by the following simple procedure. No element likely to cause serious interference in any of the common determinations is added, and it should be possible to adapt existing methods for use with this method of solution. The procedure is as follows:

Weigh 0·1000 g of the 200-mesh sample into a 55-ml flat-bottom platinum dish, and add 0·50 g of anhydrous lithium metaborate ($LiBO_2$). Mix, and heat over a Meker burner (in an oxidising flame) for 5–10 min.

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After fusion is complete, remove the dish from the flame, and drop it (preferably while still red hot) into 125 ml of 2% v/v nitric acid in a 250-ml beaker. Pour 2% nitric acid into the dish until the latter sinks to the bottom of the beaker, and immediately add a Teflon covered stirring bar. Stir at moderate speed (without heating) until solution is complete. This will take about 10 min.

Transfer to a 200-ml flask, dilute to the mark with water and mix. The solution is now ready for use. Aliquot portions may be removed for the determination of silica, alumina, iron, titania, magnesia and the alkaline earths. Because lithium does not interfere seriously with the flame photometry of sodium and potassium, the alkali metals may also be determined.

The solution may also be used for spectrochemical analysis using spark-solution techniques. If this is intended, internal standard may conveniently be added to the dilute nitric acid before the sample fusion.

Lithium metaborate is an extremely active flux, and readily dissolves most of the minor refractory minerals (chromite, ilmenite, *etc.*) commonly found in silicate rocks. The suggested solution procedure is thus not only very much faster than those using hydrofluoric acid, but much more efficient as well. Hydrofluoric acid mixtures do not adequately attack all of the mineral constituents of rocks. The suggestion that the sample be ground to pass a 200-mesh screen is made because of sampling considerations, and not because the fine grinding is necessary for attack by the flux.

Detailed procedures for rapid silicate analysis based on this and other solution methods are at present being developed in this laboratory.

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12 *December* 1963

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PRECIPITATION FROM MIXED SOLVENTS—V*

URANIUM 8-HYDROXYQUINOLATE

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(*Received* 21 *June* 1963. *Accepted* 16 *January* 1964)

Summary—The technique of precipitation from homogeneous solutions of mixed solvents has been applied to the case of uranium 8-hydroxyquinolate. Precipitation from a water-acetone solution results in the formation of well-defined crystals of high purity. The separation of uranium from magnesium is easily accomplished and separations from thorium and lead may be achieved in the presence of EDTA.

THE use of 8-hydroxyquinoline as a gravimetric precipitant for uranium offers the advantages of forming a highly insoluble material and yielding a very favourable gravimetric factor. However, the direct addition of the reagent to a solution of uranyl ion results in the formation of a very finely divided material that is difficult to filter and wash. Bordner, Salesin and Gordon[1] have reported the use of 8-acetoxyquinoline as a reagent for the *in situ* generation of the precipitant as a means of improving the physical properties of the crystals. It has been reported earlier that the 8-hydroxyquinolates of aluminium, nickel, magnesium and copper are precipitated as well-defined, highly pure crystals by the volatilisation of the organic component of a water-organic solvent mixture.[2–6] A similar method has now been developed for the precipitation of uranium and excellent results are obtained.

EXPERIMENTAL

Reagents

Uranium: A uranium solution was prepared from reagent-grade $UO_2(CH_3COO)_2 \cdot 2H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) containing approximately 10 mg of uranium per 10 ml of solution. This solution was standardised by evaporating an aliquot sample in a porcelain crucible under an infrared lamp, igniting the dry residue at 700–800° for 5 hr, and weighing the product as U_3O_8. The results of the analysis of twelve 25-ml aliquots resulted in an average value of 24·94 mg of uranium, with a standard deviation of 0·19. The rather large standard deviation, and reported discrepencies in the stoichiometry of the final product,[7] prompted the verification of this value by an alternative method. For this purpose an aliquot of the uranyl solution was reduced by metallic lead, treated with excess iron^{III} alum, and the iron^{II} ions produced were titrated with a standard cerium^{IV} solution. The results thus obtained were in agreement with those reported above and no increase in precision was obtained.

Magnesium: Reagent-grade $Mg(NO_3)_2 \cdot 6H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution which contained 5·0 mg of magnesium per ml of solution.

Lead: Reagent-grade $Pb(NO_3)_2$ (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used to prepare a solution containing 5·0 mg of lead per ml of solution.

Thorium: Reagent-grade $Th(NO_3)_4 \cdot 4H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution containing 5·0 mg of thorium per ml of solution.

8-*Hydroxyquinoline:* A 1% acetonic solution of 8-hydroxyquinoline (reagent-grade, J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A., or Fisher Scientific Company, Fair Lawn,

---

* Part IV: See reference 6.

New Jersey, U.S.A.) was prepared by dissolving 1·0 g of the reagent in 100 ml of reagent-grade acetone. A fresh solution was prepared at least once a week.

EDTA solution: A 0·01*M* solution of disodium ethylenediaminetetra-acetate (reagent-grade, Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.) was prepared by dissolving 3·72 g of the reagent in 1 litre of distilled water.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreaux column using all-glass apparatus. This precaution was necessary to remove an unidentified, water-insoluble material.

All other chemicals used were reagent-grade.

Apparatus

A Beckman Model G pH meter equipped with glass and calomel electrodes was used for all pH measurements.

Procedure

Preliminary experiments involving adjustments in the experimental parameters of pH, evaporation, temperature and acetone-water ratio led to the following recommended procedure:

A sample of about 25 mg of uranium is prepared in approximately 75 ml of nearly neutral solution. To this are added 50 ml of acetone, 10 ml of 1% 8-hydroxyquinoline solution and 10 ml of 0·5*M* ammonium acetate. The reaction mixture is placed on a water-bath at 70–75° and left uncovered for 2·5 to 3 hr. Visible precipitation occurs within the first hour of heating. At the end of the evaporation period, the samples are cooled to room temperature and filtered through medium-porosity sintered-glass crucibles. The precipitates are washed 4 times with 10 ml of distilled water and dried at 135° for at least 4 hr or overnight. The red product is weighed as $UO_2(C_9H_6ON)_2{\cdot}C_9H_7ON$. The gravimetric conversion factor is 0·33840. In all cases the filtrate pH was found to be between 5·8 and 6·0.

Coprecipitation

The studies in the presence of magnesium were performed by the above procedure, the magnesium being introduced into the original uranium solution. In the case of the lead and thorium coprecipitation studies it was found desirable to alter the order of the addition of the reagents. For these studies a three-fold excess of EDTA over that required to form a 1:1 complex with the diverse ion was added to the buffered solution containing the uranium and diverse ion. The acetone and reagent solution were then added and the analysis completed as above.

RESULTS AND DISCUSSION

Following the above procedure a well-formed, crystalline precipitate was obtained which was easily filtered and displayed no tendency to creep. The analysis of fifteen 25-ml aliquots yielded an average value of 24·84 mg of uranium with a standard deviation of 0·05. These figures may be compared to the value of 24·94, with a standard deviation of 0·19, that was obtained by the evaporation and ignition to U_3O_8. Particularly striking is the four-fold increase in precision.

During the preliminary experiments it was noted that precipitations at a pH of 5 or in the presence of increased amounts of ammonium acetate resulted in low values. However, in all cases the reported composition appeared to be the only one obtained and agreed with that generally found.[8] No evidence for the precipitation of excess reagent was noted, though this may arise from the fact that at the drying temperature of 135° any excess reagent would be decomposed.[9,10]

Table I reports the results of the coprecipitation studies. The ability of this technique to increase the separation from magnesium is obvious from the results in this table. In the case of lead and thorium the proposed method still fails to yield good separation; however, the addition of EDTA to the reaction mixture results in practically complete separation from these two important uranium decay products.

CONCLUSIONS

The precipitation of uranium 8-hydroxyquinolate from homogeneous mixtures of water and acetone is a convenient and practical method of achieving the formation

TABLE I.—EFFECT OF DIVERSE IONS UPON THE PRECIPITATION OF 24·96 MG OF URANIUM[e]

		Classical method	Present method	
Diverse ion added	Weight of diverse ions, *mg*	Apparent weight of uranium, *mg*	Apparent weight of uranium, *mg*	Difference, *mg*
—		24·82 ± 0·06[d]		−0·12
Mg	25·0		24·82 ± 0·08[b]	−0·12
Mg	50·0		24·81 ± 0·06[d]	−0·13
Mg	100·0		24·90 ± 0·05[c]	−0·04
Mg	250·0		24·94 ± 0·05[c]	0·00
Mg	250·0	34·4 ± 2·7[b]		+9·46
Pb	10·0		27·65 ± 0·30[b]	+2·71
Pb	25·0		24·81 ± 0·02[a,d]	−0·13
Th	25·0		30 ± 3[b]	+5
Th	25·0		24·84 ± 0·03[a,d]	−0·10

[a] Present method containing an excess of EDTA.
[b] Average of 2 determinations.
[c] Average of 3 determinations.
[d] Average of 4 determinations.
[e] Errors shown are standard deviations.

of this precipitate. The product is produced in a highly pure form and the method is particularly advantageous for use in the presence of large amounts of magnesium, or of at least equal weights of lead or thorium when excess EDTA is present.

Acknowledgement—The authors wish to acknowledge the support given to this work by the U.S. Atomic Energy Commission under research contract AT(40-1) 2954.

Zusammenfassung—Die Methode der Fällung aus homogener Lösung eines Lösungsmittelgemisches wurde nun auf Uranoxinat angewandt. Gut ausgebildete Kristalle von hoher Reinheit werden erhalten bei der Fällung des Oxinats aus einer Wasser-Acetonlösung. Die Abtrennung des Urans von Magnesium ist leicht durchführbar, und eine Trennung von Blei and Thorium kann durch Zusatz von ADTE erreicht werden.

Résumé—Les auteurs décrivent une méthode pour le dosage de l'uranium, en précipitant l'oxinate en solution homogène, contenant un mélange d'eau et d'acétone comme solvants. En appliquant cette technique, les cristaux précipités sont bien formés, et très purs. Le magnésium est séparé aisément de l'uranium; de même, la séparation du thorium et du plomb est possible en présence d'EDTA.

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AMPEROMETRISCHE BESTIMMUNG DER METALLE UNTER DER ANWENDUNG VON THIOACETAMID—V*

UNTERSUCHUNGEN ÜBER PbS-BILDUNGSGESCHWINDIGKEIT IN AMMONIAKALISCHEN Pb^{2+}-IONENLÖSUNGEN MITTELS THIOACETAMID

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Szczecin, Polen.

(*Eingegangen am* 3 *September* 1963. *Angenommen am* 30 *September* 1963)

Zusammenfassung—Auf Grund der polarographisch durchgeführten Untersuchungen über PbS-Fällungsgeschwindigkeit mittels Thioacetamid (TAA) wurden folgende Gleichungen für Reaktionsgeschwindigkeit zwischen Pb^{2+}-Ionen und TAA in ammoniakalischen Lösungen abgeleitet:

$$-\frac{d[Pb^{II}]}{dt} = k_1 . \frac{[Pb^{II}][CH_3CSNH_2][NH_3H_2O]}{[H^+]^{\frac{1}{2}}} . \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{2}}} \qquad (1)$$

$$-\frac{d[Pb^{II}]}{dt} = k_2 . \frac{[Pb^{II}][CH_3CSNH_2][NH_3H_2O]}{[H^+]^{1/3}} . \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{3}}} \qquad (2)$$

Der Wert der Geschwindigkeitskonstante k_1 beträgt für Temp. 25°C: $3{,}67 \cdot 10^{-4} \pm 0{,}65 \cdot 10^{-4}$ $Mol^{-\frac{3}{2}} . L^{\frac{3}{2}} . Min^{-1}$. Der Wert der Konstante. k_2 für dieselbe Temperatur beträgt: $2{,}00 \cdot 10^{-2} \pm 0{,}30 \cdot 10^{-2}$ $Mol^{-5/3} . L^{5/3}$ Min^{-1}. Die Geltung der Gleichung (1) wurde für NH_3H_2O-Konzentrationsgebiet vom 1,12 Mol/L bis 2,25 Mol/L im c_H-Intervall: $2{,}09 \cdot 10^{-12} \leqslant c_H \leqslant 4{,}17 \cdot 10^{-11}$ überprüft. Die Überprüfung der Gleichung (2) wurde im NH_3H_2O-Konzentrationsgebiet vom 2,25 Mol/L bis 4,5 Mol/L im c_H-Intervall: $1{,}26 \cdot 10^{-12} \leqslant c_H \leqslant 8{,}31 \cdot 10^{-11}$ durchgeführt.

EINLEITUNG

UNTERSUCHUNGEN über die Geschwindigkeit der Reaktion zwischen dem Thioacetamid und Metallionen bilden den Grund für die Arbeit über das eigentliche Problem der Anwendbarkeit des TAA zu der elektrometrischen Bestimmung der Metalle der H_2S- und $(NH_4)_2S$-Gruppe.

Die Untersuchüng über die Geschwindigkeit der Reaktion zwischen TAA und Cd^{2+}-Ionen sowie Tl^+-Ionen ist bereits früher[1,2] durchgeführt worden.

Die vorliegende Arbeit über die Reaktionsgeschwindigkeit der Pb^{2+}-Ionen mit TAA in ammoniakalischen Lösungen ist die Fortsetzung dieser Untersuchungen.

Die Kinetik der Reaktion der Pb^{2+}-Ionen mit TAA in erhöhter Temperatur und in saurem pH-Intervall wurde bereits früher von Swift und Butler[3] untersucht. Die Ergebnisse der Untersuchungen dieser Autoren lieferten neues Material, wertvolles sowohl für die Anwendung des TAA in der systematischen qualitativen Analyse der Kationen als auch für das Problem des Mechanismus der Reaktionen zwischen TAA und Metallionen. Für die Arbeit über die Bestimmungsmethode der Pb^{2+}-Ionen in alkalischem pH-Gebiet sind sie jedoch nicht anwendbar, da ihre Geltung auf saures pH-Intervall begrenzt ist.

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* IV Mitteilung: Literatur Punkt 2.

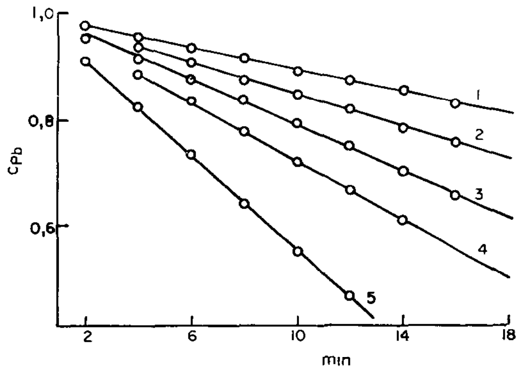

ABB. 1.—Reaktionsgeschwindigkeit der PbS-Fällung als pH-Funktion.
Temp. 25°: Pot. −1,0 v
$[NH_3H_2O] = c_{Am} = 2{,}25$: Mol/L: $[CH_3CSNH_2] = c_T = 6{,}00 \,.\, 10^{-4}$ Mol/L.
$[Pb(NO_3)_2] = c_{Pb} = 8{,}10 \,.\, 10^{-4}$ Mol/L
a_{H^+}: 1 — $3{,}93 \,.\, 10^{-11}$: 2 — $1{,}95 \,.\, 10^{-11}$: 3 — $9{,}75 \,.\, 10^{-12}$:
4—$5{,}92 \,.\, 10^{-12}$: 5—$1{,}95 \,.\, 10^{-12}$

DER EXPERIMENTALE TEIL

Apparatur

Polarograph „Radiometr PO3 m" (Dänemark). Tropfende Quecksilberelektrode als Kathode und gesättigte Kalomelelektrode als Anode.

Generator zur elektrolytischen Gewinnung des Wasserstoffs.

Termostat nach Wobser.

Automatische 1-ml Mikrobürette (zur Dosierung des TAA).

Lösungen

$Pb(NO_3)_2$-Lösung wurde aus analytisch reinem Handelspräparat vorbereitet und komplexometrisch bestimmt.[4]

Thioacetamidlösung aus dem „reinen" Handelspräparat nach dreimaliger Kristallisation vorbereitet und amperometrisch bestimmt.[5]

$AgNO_3$, $NaNO_3$, NH_4NO_3 wurden aus „analytisch reinen" Handelspräparaten nach zweimaliger Kristallisation angewandt. $NaNO_3$ wurde als Grundelektrolyt und zugleich als Ionenenstärkestabilisator angewandt. Die Ionenstärke aller untersuchten Lösungen war dieselbe.

Der pH-Wert der Lösungen wurde mittels Ammoniakpuffer ($NH_3H_2O + NH_4NO_3$) konstant gehalten.

Zugabe der Tartrat-Ionen ermöglichte die Pb-Ionen in der Lösung zu erhalten.

Prozedur

Die experimentale Bestimmung der Sulfidbildungsgeschwindigkeit wurde polarographisch so wie vorher[1,2] durchgeführt.

ERGEBNISSE UND DISKUSSION

Alle Untersuchungen über die Geschwindigkeit der Reaktionen des TAA mit Pb^{2+}-Ionen wurden in ammoniakalischen, mit NH_4NO_3 gepufferten Lösungen dieser Ionen von der gleichen Ionenstärke durchgeführt.

Schon im Laufe der Anfangsuntersuchungen wurde die proportionale Abhängigkeit der Sulfidbildungsgeschwindigkeit sowohl von der Konzentration der Metallionen wie auch von der Konzentration des TAA festgestellt, mit der Beschränkung auf ziemlich kleine Werte der Geschwindigkeit (also auch kleine Werte der Bleiionen- und TAA-Konzentration).

Die Untersuchungen über den Einfluss der H^+-Ionenkonzentration auf die PbS-Fällungsgeschwindigkeit, welche den Hauptteil der vorliegenden Arbeit bilden, wurden in Serien von Lösungen durchgeführt von dem gleichen NH_3H_2O-, TAA- und $Pb(NO_3)_2$-Konzentrationswert aber verschiedenem pH-Wert.

Die H^+-Ionenkonzentration jeder untersuchten Lösung dieser Serien wurde rechnungsweise bestimmt. Der f_{H^+}-Wert und f_{Pb}-Wert wurde nach Kolthoff[6] berechnet.

Es erwies sich, dass die Reaktionsgeschwindigkeit mit dem Steigen der H^+-Ionenkonzentration—in sonst gleichen Bedingungen—immer geringere Werte annimmt, dass also die PbS-Bildungsgeschwindigkeit eine absteigende Funktion der H^+-Ionenkonzentration ist (Abb. 1).

Als mögliche Form dieser Funktion wurden drei Gleichungen berücksichtigt:*

$$-\frac{dc_{Pb}}{dt} = k' \frac{c_{Pb} \cdot c_T}{c_H} \cdot \frac{f_{Pb}}{f_H} \qquad (1,V)$$

$$-\frac{dc_{Pb}}{dt} = k'' \frac{c_{Pb} \cdot c_T}{c_H^{\frac{1}{2}}} \cdot \frac{f_{Pb}}{f_H^{\frac{1}{2}}} \qquad (2,V)$$

$$-\frac{dc_{Pb}}{dt} = k''' \frac{c_{Pb} \cdot c_T}{c_H^{\frac{1}{3}}} \cdot \frac{f_{Pb}}{f_H^{\frac{1}{3}}} \qquad (3,V)$$

Die Werte von k', k'', k''' aus den obigen Gleichungen wurden für jeden untersuchten Fall auf Grund der experimentalen Daten berechnet.

Die Ergebnisse der Untersuchungen vier solcher Serien sind in den Tabellen I bis IV zusammengestellt. Bei allen Lösungen solcher Serien wie die aus der Tabelle I und II (vom c_{Am}-Wert 1,12 Mol/L bis 2,25 Mol/L) mit Steigen des pH-Wertes verändert sich stufenweise der k'-Wert wie auch der k'''-Wert, während der k''-Wert dabei annähernd konstant bleibt.

TABELLE I. REAKTIONGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+}-FUNKTION

Temp. = 25°
Pot. = −1,0v
$\mu = 0,9$
$f_{H^+} = 0,94$
$f_{Pb^{2+}} = 0,15$

$[NH_3H_2O] = c_{Am} = 1,12$ Mol/L
$[Pb(NO_3)_2] = c_{Pb} = 8,10 . 10^{-4}$ Mol/L
$[CH_3CSNH_2] = c_T = 6,00 . 10^{-4}$ Mol/L

Nr	a_{H^+} $(= c_H \cdot f_H)$	k' $\left(= -\frac{dc_{Pb}}{dt} \cdot \frac{c_H}{c_{Pb}c_T} \cdot \frac{f_H}{f_{Pb}}\right)$	k'' $\left(= -\frac{dc_{Pb}}{dt} \cdot \frac{c_H{}^{1/2}}{c_{Pb}c_T} \cdot \frac{f_H{}^{1/2}}{f_{Pb}}\right)$	k''' $\left(= -\frac{dc_{Pb}}{dt} \cdot \frac{c_H{}^{1/3}}{c_{Pb}c_T} \cdot \frac{f_H{}^{1/3}}{f_{Pb}}\right)$	k''/c_{Am}
1	$7,80 . 10^{-11}$	$3,80 . 10^{-9}$	$4,35 . 10^{-4}$	$2,13 . 10^{-2}$	$3,89 . 10^{-4}$
2	$3 92 . 10^{-11}$	$2,89 . 10^{-9}$	$4,55 . 10^{-4}$	$2,45 . 10^{-2}$	$4,09 . 10^{-4}$
3	$1,95 . 10^{-11}$	$2,15 . 10^{-9}$	$4,84 . 10^{-4}$	$2,98 . 10^{-2}$	$4,31 . 10^{-4}$
4	$3,92 . 10^{-12}$	$9,65 . 10^{-10}$	$4,87 . 10^{-4}$	$3,96 . 10^{-2}$	$4,35 . 10^{-4}$
5	$1,95 . 10^{-12}$	$6,06 . 10^{-10}$	$4,80 . 10^{-4}$	$3,93 . 10^{-2}$	$3,84 . 10^{-4}$

Im Fall der Lösungen solcher Serien wie die aus der Tabelle III und IV (vom c_{Am}-Wert 3,37 Mol/L bis 4,50 Mol/L) mit Steigen des pH-Wertes verändert sich stufenweise der k'-Wert so wie der k''-Wert, der k'''-Wert dagegen annähernd konstant bleibt.

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* Im folgenden werden in Gleichungen, Tabellen und im Text nachstehende Abkürzungen gebraucht:

c_T statt TAA-Konzentration
c_{Pb} statt $Pb(NO_3)_2$-Konzentration
c_H statt H^+-Ionenkonzentration
f_{Pb} statt $f_{Pb^{2+}}$
f_H statt f_{H^+}

TABELLE II.—REAKTIONSGESCHWINDIGKEITT DER PbS-FÄLLUNG ALS a_{H^+}-FUNKTION

Temp. = 25°
Pot. = −1,0 v
$\mu = 0{,}9$
$f_{H^+} = 0{,}94$
$f_{Pb^{2+}} = 0{,}15$

$[NH_3H_2O] = c_{Am} = 2{,}25$ Mol/L
$[Pb(NO_3)_2] = c_{Pb} = 8{,}10 \,.\, 10^{-4}$ Mol/L
$[CH_3CSNH_2] = c_T = 6{,}00 \,.\, 10^{-4}$ Mol/L

Nr	a_{H^+}	k'	k''	k'''	k''/c_{Am}
1	$3{,}93 \,.\, 10^{-11}$	$4{,}84 \,.\, 10^{-9}$	$7{,}45 \,.\, 10^{-4}$	$4{,}13 \,.\, 10^{-2}$	$3{,}31 \,.\, 10^{-4}$
2	$1{,}95 \,.\, 10^{-11}$	$3{,}33 \,.\, 10^{-9}$	$7{,}35 \,.\, 10^{-4}$	$4{,}50 \,.\, 10^{-2}$	$3{,}27 \,.\, 10^{-4}$
3	$9{,}75 \,.\, 10^{-12}$	$2{,}37 \,.\, 10^{-9}$	$7{,}40 \,.\, 10^{-4}$	$5{,}10 \,.\, 10^{-2}$	$3{,}30 \,.\, 10^{-4}$
4	$5{,}92 \,.\, 10^{-12}$	$1{,}84 \,.\, 10^{-9}$	$7{,}35 \,.\, 10^{-4}$	$5{,}52 \,.\, 10^{-2}$	$3{,}27 \,.\, 10^{-4}$
5	$1{,}95 \,.\, 10^{-12}$	$1{,}61 \,.\, 10^{-9}$	$7{,}00 \,.\, 10^{-4}$	$6{,}30 \,.\, 10^{-2}$	$3{,}10 \,.\, 10^{-4}$

TABELLE III.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+}-FUNKTION

Temp. = 25°
Pot. = −1,0 v
$\mu = 0{,}9$
$f_{H^+} = 0{,}94$
$f_{Pb^{2+}} = 0{,}15$

$[NH_3H_2O] = c_{Am} = 3{,}37$ Mol/L
$[Pb(NO_3)_2] = c_{Pb} = 8{,}10 \,.\, 10^{-4}$ Mol/L
$[CH_3CSNH_2] = c_T = 6{,}00 \,.\, 10^{-4}$ Mol/L

Nr	a_{H^+}	k'	k''	k'''	k'''/c_{Am}
1	$3{,}93 \,.\, 10^{-11}$	$7{,}55 \,.\, 10^{-9}$	$1{,}22 \,.\, 10^{-3}$	$6{,}70 \,.\, 10^{-2}$	$1{,}98 \,.\, 10^{-2}$
2	$2{,}60 \,.\, 10^{-11}$	$6{,}29 \,.\, 10^{-9}$	$1{,}22 \,.\, 10^{-3}$	$7{,}10 \,.\, 10^{-2}$	$2{,}10 \,.\, 10^{-2}$
3	$6{,}50 \,.\, 10^{-12}$	$2{,}30 \,.\, 10^{-9}$	$9{,}00 \,.\, 10^{-4}$	$6{,}40 \,.\, 10^{-2}$	$1{,}92 \,.\, 10^{-2}$
4	$3{,}93 \,.\, 10^{-12}$	$1{,}77 \,.\, 10^{-9}$	$8{,}95 \,.\, 10^{-4}$	$7{,}22 \,.\, 10^{-2}$	$2{,}18 \,.\, 10^{-2}$
5	$1{,}30 \,.\, 10^{-12}$	$7{,}27 \,.\, 10^{-10}$	$6{,}45 \,.\, 10^{-4}$	$6{,}20 \,.\, 10^{-2}$	$1{,}86 \,.\, 10^{-2}$

TABELLE IV.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS a_{H^+}-FUNKTION

Temp. = 25°
Pot. = −1,0 v
$\mu = 0{,}9$
$f_{H^+} = 0{,}94$
$f_{Pb^{2+}} = 0{,}15$

$[NH_3H_2O] = c_{Am} = 4{,}50$ Mol/L
$[Pb(NO_3)_2] = c_{Pb} = 8{,}10 \,.\, 10^{-4}$ Mol/L
$[CH_3CSNH_2] = c_T = 5{,}82 \,.\, 10^{-4}$ Mol/L

Nr	a_{H^+}	k'	k''	k'''	k'''/c_{Am}
1	$2{,}95 \,.\, 10^{-11}$	$9{,}60 \,.\, 10^{-9}$	$1{,}76 \,.\, 10^{-3}$	$1{,}00 \,.\, 10^{-1}$	$2{,}23 \,.\, 10^{-2}$
2	$1{,}97 \,.\, 10^{-11}$	$7{,}16 \,.\, 10^{-9}$	$1{,}55 \,.\, 10^{-3}$	$0{,}99 \,.\, 10^{-1}$	$2{,}21 \,.\, 10^{-2}$
3	$4{,}94 \,.\, 10^{-12}$	$2{,}65 \,.\, 10^{-9}$	$1{,}20 \,.\, 10^{-3}$	$0{,}93 \,.\, 10^{-1}$	$2{,}07 \,.\, 10^{-2}$
4	$3{,}93 \,.\, 10^{-12}$	$2{,}26 \,.\, 10^{-9}$	$1{,}15 \,.\, 10^{-3}$	$0{,}93 \,.\, 10^{-1}$	$2{,}07 \,.\, 10^{-2}$
5	$1{,}97 \,.\, 10^{-12}$	$1{,}45 \,.\, 10^{-9}$	$1{,}04 \,.\, 10^{-3}$	$0{,}96 \,.\, 10^{-1}$	$2{,}13 \,.\, 10^{-2}$

Auf Grund solcher Ergebnisse wurde festgestellt, dass für die Lösungen aus c_{Am}-Intervall 1,12 Mol/L bis 2,25 Mol/L die Gleichung (2,V) die Geschwindigkeit als Funktion vom c_H-Wert richtig ausdrückt, für die Lösungen dagegen von grösserem als 2,25 Mol/L c_{Am}-Wert die Gleichung (3,V).

Aus den Tabellen I–IV folgt ausserdem, dass der Zahlenwert der Koeffizienten k'' und k''' von der Ammoniakkonzentration abhängig ist und mit dieser Konzentration steigt.

Die Reaktionsgeschwindigkeit ist also—wie daraus ersichtlich ist—von der NH_3H_2O-Konzentration abhängig.

Diese Abhängigkeit wurde in Serien der Lösungen von verschiedenem c_{Am}-Wert und demselben pH-Wert so wie demselben c_{T}- und c_{Pb}-Wert durchgeführt.

Die Untersuchungsergebnisse einer solchen Serie sind in der Abb. 2 und der Tabelle V dargestellt.

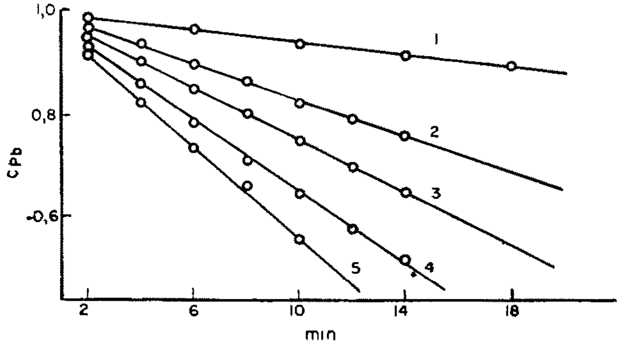

Abb. 2.—Reaktionsgeschwindigkeit der PbS-Fällung als Funktion der NH_3H_2O-Konzentration.
Temp. 25°: Pot. −1,0 v
$[Pb(NO_3)_2] = c_{\mathrm{Pb}} = 8{,}10 \cdot 10^{-4}$ Mol/L: $[CH_3CSNH_2] = c_{\mathrm{T}} = 5{,}82 \cdot 10^{-4}$ Mol/L:
$c_{\mathrm{H}} \cdot f_{\mathrm{H}} = a_{\mathrm{H}^+} = 3{,}92 \cdot 10^{-11}$
$[NH_3H_2O]$: 1 — 2,25 Mol/L: 2 — 3,37 Mol/L: 3 — 4,50 Mol/L:
4 — 6,75 Mol/L: 5 — 9,00 Mol/L

TABELLE V.—REAKTIONSGESCHWINDIGKEIT DER PbS-FÄLLUNG ALS FUNKTION DER NH_3H_2O-KONZENTRATION

Temp. = 25°
Pot. = −1,0 v
$\mu = 0{,}9$
$f_{\mathrm{H}^+} = 0{,}94$
$f_{\mathrm{Pb}^{2+}} = 0{,}15$

$[Pb(NO_3)_2] = c_{\mathrm{Pb}} = 8{,}10 \cdot 10^{-4}$ Mol/L
$[CH_3CSNH_2] = c_{\mathrm{T}} = 5{,}82 \cdot 10^{-4}$ Mol/L
$c_{\mathrm{H}} \cdot f_{\mathrm{H}} = a_{\mathrm{H}^+} = 3{,}92 \cdot 10^{-11}$

Nr	$[NH_3H_2O]$, *Mol/L*	k'''	k'''/c_{Am}
1	2,25	$4{,}00 \cdot 10^{-2}$	$1{,}83 \cdot 10^{-2}$
2	3,37	$6{,}10 \cdot 10^{-2}$	$1{,}85 \cdot 10^{-2}$
3	4,50	$9{,}00 \cdot 10^{-2}$	$2{,}03 \cdot 10^{-2}$
4	6,75	$1{,}30 \cdot 10^{-1}$	$1{,}95 \cdot 10^{-2}$
5	9,00	$1{,}67 \cdot 10^{-1}$	$1{,}96 \cdot 10^{-2}$

Die Abb. 2 illustriert, dass die Reaktionsgeschwindigkeit eine aufsteigende Funktion der NH_3H_2O-Konzentration ist.

Aus der Tabelle V folgt, dass der Ausdruck k'''/c_{Am} annähernd konstanten Wert für Lösungen der Serie aus dieser Tabelle hat. Denselben annähernd Wert hat dieser Ausdruck für Lösungen jeder übrigen untersuchten Serie, für welche der c_{Am} Wert nicht kleiner als 2,25 Mol/L ist, also auch für die Serien aus der Tabelle III und IV (was aus der letzten Kolonne dieser Tabellen ersichtlich ist).

Es ist also: $k'''/c_{\mathrm{Am}} = \text{constans} = k_2 \ldots\ldots (4,\mathrm{V})$. Aus den Tabellen I und II (letzte Kolonne) folgt, dass für Serien von c_{Am}-Wert 1,12 Mol/L und 2,25 Mol/L der Ausdruck k''/c_{Am} auch konstanten Wert hat. Dasselbe gilt auch für Lösungen jeder untersuchten Serie aus dem NH_3H_2O-Konzentrationsintervall vom 1,12 Mol/L bis 2,25 Mol/L. Für diesen Konzentrationsintervall ist also:

$$k''/c_{\mathrm{Am}} = \text{constans} = k_1 \qquad (5,\mathrm{V})$$

Aus Gleichungen (4,V) u. (5,V) folgt die proportionale Abhängigkeit der Reaktionsgeschwindigkeit von der NH_3H_2O-Konzentration.

Nach Einsetzen in die Gleichung (2,V) den Wert für k'' aus der Gleichung (5,V) und in die Gleichung (3,V) den Wert für k''' aus der Gleichung (4,V), bekommen die Gleichungen (2,V) und (3,V) folgende Form:

$$-\frac{dc_{\mathrm{Pb}}}{dt} = k_1 \frac{c_{\mathrm{Pb}} \cdot c_{\mathrm{T}} \cdot c_{\mathrm{Am}}}{c_{\mathrm{H}}^{1/2}} \cdot \frac{f_{\mathrm{Pb}}}{f_{\mathrm{H}}^{1/2}} \qquad (2',\mathrm{V})$$

$$-\frac{dc_{\mathrm{Pb}}}{dt} = k_2 \frac{c_{\mathrm{Pb}} \cdot c_{\mathrm{T}} \cdot c_{\mathrm{Am}}}{c_{\mathrm{H}}^{1/3}} \cdot \frac{f_{\mathrm{Pb}}}{f_{\mathrm{H}}^{1/3}} \qquad (3',\mathrm{V})$$

Der Zahlenwert der Geschwindigkeitskonstante k_1 und k_2 aus diesen Gleichungen wurde aus den experimentalen Ergebnissen—unter anderem auch aus den Daten der Serien aus der Tabellen I–IV—erhalten.

Für Temperatur 25° beträgt der Mittelwert von k_1: $3{,}67 \,.\, 10^{-4} \pm 0{,}65 \,.\, 10^{-4}$ $\mathrm{Mol}^{-3/2} \,.\, \mathrm{L}^{3/2} \,.\, \mathrm{Min}^{-1}$. Für dieselbe Temperatur beträgt der Mittelwert von k_2: $2{,}00 \,.\, 10^{-2} \pm 0{,}30 \,.\, 10^{-2}$ $\mathrm{Mol}^{-5/3} \,.\, \mathrm{L}^{5/3} \,.\, \mathrm{Min}^{-1}$. Die Geltung beider Gleichungen wurde überprüft. Die Reaktionsgeschwindigkeit wurde nämlich unter Anwendung entsprechend der Gleichung (2',V) oder (3',V) in jedem konkreten Fall berechnet (indem für k_1 und k_2 die eben angegebene Werte eingesetzt wurden) und der so erhaltene Geschwindigkeitswert wurde mit experimental gefundenem Wert verglichen.

Die Ergebnisse der Überprüfung sind in der Tabelle VI zusammengestellt. Die Übereinstimmung der berechneten Geschwindigkeitswerte mit den experimental gefundenen ist ziemlich gut wie aus der Tabelle VI ersichtlich ist.

Aus dieser Tabelle folgt zugleich, dass die Geltung der Gleichung (2',V) für c_{Am}-Gebiet vom 1,12 Mol/L bis 2,25 Mol/L im c_{H}-Intervall vom $2{,}09 \,.\, 10^{-12}$ bis $4{,}17 \,.\, 10^{-11}$ überprüft wurde und die Geltung der Gleichung (3',V) für c_{Am}-Gebiet vom 2,25 Mol/L bis 4,50 Mol/L in c_{H}-Intervall vom $1{,}26 \cdot 10^{-12}$ bis $8{,}31 \cdot 10^{-11}$. Die Lösungen der Serie vom c_{Am}-Wert 2,25 Mol/L haben vorübergehenden Charakter. Die Reaktionsgeschwindigkeit der Lösungen dieser Serie ist nämlich nicht nur durch die Gleichung (2',V) bestimmt sondern annähernd auch durch die Gleichung (3',V). Die auf Grund der Gleichung (3',V) berechneten Geschwindigkeitswerte sind für Lösungen dieser Serie von kleinem pH-Wert in ziemlich guter Übereinstimmung mit den experimental bestimmten. Mit Steigen des pH-Wertes aber steigt auch die Abweichung von den experimental bestimmten Werten, was aus der Tabelle VI ersichtlich ist.

Die Proben der Überprüfung der Gleichung (3',V) für die Lösungen von grösserer NH_3H_2O-Konzentration zeigten, dass diese Gleichung ihre Geltung auch im Gebiet

TABELLE VI.—ÜBERPRÜFUNG DER REAKTIONSGESCHWINDIGKEITSGLEICHUNG (2′,V) U. (3′,V)

Nr	$a_{Pb}(= c_{Pb} \cdot f_{Pb}$	a_T	$a_H(= c_H \cdot f_H$	c_{Am}, Mol/L	$-\frac{dc_{Pb}}{dt} \cdot 10^5$ Mol/L. Min.		
					Experim. bestimmt	Berechnet aus	
						Gleichung (2′,V)	Gleichung (3′,V)
1	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$1{,}95 \cdot 10^{-12}$	1,12	2,25	2,20	—
2	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$3{,}92 \cdot 10^{-12}$	1,12	1,80	1,56	—
3	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$1{,}95 \cdot 10^{-11}$	1,12	0,80	0,70	—
4	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$1{,}95 \cdot 10^{-12}$	2,25	3,75	4,41	2,65
5	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$5{,}92 \cdot 10^{-12}$	2,25	2,27	2,53	1,83
6	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$9{,}75 \cdot 10^{-12}$	2,25	1,77	1,97	1,56
7	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$1{,}95 \cdot 10^{-11}$	2,25	1,24	1,39	1,24
8	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$3{,}92 \cdot 10^{-11}$	2,25	0,90	0,98	0,98
9	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$1{,}38 \cdot 10^{-12}$	3,37	4,25	—	4,60
10	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$6{,}50 \cdot 10^{-12}$	3,37	2,66	—	2,80
11	$1{,}2 \cdot 10^{-4}$	$6{,}00 \cdot 10^{-4}$	$2{,}60 \cdot 10^{-11}$	3,37	1,79	—	1,69
12	$1{,}2 \cdot 10^{-4}$	$5{,}82 \cdot 10^{-4}$	$3{,}93 \cdot 10^{-12}$	4,50	4,23	—	4,07
13	$1{,}2 \cdot 10^{-4}$	$5{,}82 \cdot 10^{-4}$	$4{,}94 \cdot 10^{-12}$	4,50	3,93	—	3,80
14	$1{,}2 \cdot 10^{-4}$	$5{,}82 \cdot 10^{-4}$	$1{,}97 \cdot 10^{-11}$	4,50	2,65	—	2,40
15	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$1{,}56 \cdot 10^{-11}$	5,62	3,14	—	3,40
16	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$7{,}82 \cdot 10^{-12}$	5,62	4,00	—	4,30
17	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$1{,}56 \cdot 10^{-12}$	5,62	7,80	—	7,50
18	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$6{,}48 \cdot 10^{-12}$	6,75	4,87	—	5,50
19	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$3{,}93 \cdot 10^{-11}$	6,75	3,36	—	3,04
20	$1{,}2 \cdot 10^{-4}$	$6{,}25 \cdot 10^{-4}$	$5{,}90 \cdot 10^{-11}$	6,75	2,73	—	2,55

der c_{Am}-Werte vom 4,50 Mol/L bis 6,75 Mol/L, mit Beschränkung auf nicht hohe pH-Werte behält.

Doch für die Lösungen vom c_{Am}-Wert $> 4{,}50$ Mol/L ist der Verlauf der Reaktion nicht immer gut reproduzierbar.

Aus den hier dargestellten Untersuchungen folgt—unter anderem—dass die Geschwindigkeit der Reaktion zwischen TAA und Pb^{2+}-Ionen in NH_3H_2O-Lösungen im Gebiet der für amperometrische Bestimmungen entsprechender Werte enthalten sein kann.

Proben der Anwendung dieser Reaktion zu der amperometrischen Bestimmung dieser Ionen sind im Gange.

Die Ergebnisse dieser Untersuchungen sind aber nicht nur für amperometrische Zwecke anwendbar. Sie liefern auch neues experimentales Material, welches für das Problem des Mechanismus der Reaktionen der Metallionen mit TAA nützlich sein kann. Nicht ohne Bedeutung für dieses Problem ist z.B. die Feststellung, dass den untersuchten Reaktionen der Pb^{2+}-Ionen mit TAA zwei Geschwindigkeitsgleichungen (2′,V) und (3′,V) entsprechen.

Die untersuchten Reaktionen gehören zu den nicht durch Hydrolyse des TAA kontrollierten Reaktionen (die auch als direkte Reaktionen bezeichnet werden,[3] was sowohl aus ihrer ziemlich grossen Geschwindigkeit wie auch aus der Art der Abhängigkeit dieser Geschwindikgeit von dem c_H-Wert folgt.

Es gibt also—wie aus diesen Untersuchungen folgt—direkte Reaktionen von nicht ganz identischem Mechanismus, was auch früher im Fall der Cadmiumionen[1] gezeigt worden ist.

Summary—On the basis of polarographic investigations of the rate of precipitation of lead sulphide by thioacetamide (TAA), the following equations for the rate of reaction of Pb^{2+} with TAA have been derived:

$$-\frac{d[Pb^{II}]}{dt} = k_1 \cdot \frac{[Pb^{II}] \,.\, [TAA] \,.\, [NH_3.H_2O]}{[H^+]^{\frac{1}{2}}} \cdot \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{2}}} \quad \ldots (1)$$

$$-\frac{d[Pb^{II}]}{dt} = k_2 \,.\, \frac{[Pb^{II}] \,.\, [TAA] \,.\, [NH_3 \cdot H_2O]}{[H^+]^{\frac{1}{3}}} \cdot \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{3}}} \quad \ldots (2)$$

The value, at 25°, of the rate constant k_1 is $3{\cdot}67 \times 10^{-4} \pm 0{\cdot}65 \times 10^{-4}$ $mol^{-\frac{3}{2}} \,.\, litre^{\frac{3}{2}} \,.\, min^{-1}$, and of the rate constant k_2 is $2{\cdot}00 \times 10^{-2} \pm 0{\cdot}30 \times 10^{-2}$ $mol^{-5/3} \,.\, litre^{5/3} \,.\, min^{-1}$. The validity of equation (1) has been proved for $NH_3 \cdot H_2O$ concentrations from 1·12 mol/litre to 2·25 mol/litre in the c_H range $2{\cdot}09 \times 10^{-12} \leqslant c_H \leqslant 4{\cdot}17 \times 10^{-11}$, and of equation (2) for $NH_3 \cdot H_2O$ concentrations from 2·25 mol/litre to 4·5 mol/litre in the c_H range $1{\cdot}26 \times 10^{-12} \leqslant c_H \leqslant 8{\cdot}31 \times 10^{-11}$.

Résumé—En se basant sur les études polarographiques du taux de précipitation du sulfure de plomb par la thiocétamide (TAA), les équations suivantes relatives au taux de réaction de l'ion Pb^{2+} avec le TAA ont pu être établies:

$$-\frac{d[Pb^{II}]}{dt} = k_1 \,.\, \frac{[Pb^{II}]\, [TAA]\, [NH_3 \cdot H_2O]}{[H^+]^{1/2}} \times \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{2}}} \qquad (1)$$

$$-\frac{d[Pb^{II}]}{dt} = k_2 \,.\, \frac{[Pb^{II}]\, [TAA]\, [NH_3 \cdot H_2O]}{[H^+]^{\frac{1}{3}}} \times \frac{f_{Pb^{2+}}}{f_{H^+}{}^{\frac{1}{3}}} \qquad (2)$$

à 25° la valeur de la constante de réaction k_1 est

$3{,}67 \times 10^{-4} \pm 0{,}65 \times 10^{-4}\ mol^{-3/2}.litre^{3/2}.min^{-1}$

celle de la constante k_2 est

$2{,}00 \times 10^{-2} \pm 0{,}30 \times 10^{-2}\ mol^{-5/3}.litre^{5/3}.min^{-1}$

La validité de l'équation (1) a été mise en évidence pour des concentrations $NH_3 \,.\, H_2O$ variant de 1,12 à 2,25 mole/litre dans un domaine de c_H de l'ordre de:

$2{,}09 \times 10^{-12} \leqslant c_H \leqslant 4{,}17 \times 10^{-11}$

ainsi que l'équation (2) pour des concentrations $NH_3.H_2O$ variant de 2,25 à 4,5 mole/litre dans un domaine de $c_H = 1{,}26 \times 10^{-12} \leqslant c_H \leqslant 8{,}31 \times 10^{-11}$.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF IMPURITIES IN PURE AND ANALYTICAL REAGENTS—I

PROPOSED METHODS AND ALGEBRAIC FORMULAE*

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Summary—Algebraic formulae are proposed for the spectrophotometric determination of impurity ions in chemically pure or analytical reagents which do not themselves absorb in the spectral region to be used. These formulae require absorption measurements on the solution at two specified wavelengths, and a knowledge of the absorption coefficients of the ion to be determined. No information about either the nature or the concentration of the interfering ions, or about the background absorption of the solution is necessary.

INTRODUCTION

THE molar absorptivity of many simple inorganic ions and complexes in the ultraviolet range of the spectrum is of the order of 10^3–10^4. These high values suggest the application of absorption measurements to the determination of trace amounts of such ions.[1,2] In some published analytical papers, the use of sulphuric[3–5] or perchloric acid[6] solutions have been proposed. Many authors have employed concentrated hydrochloric acid[7–9] or alkali halide solutions, proving the general usefulness of the method very convincingly. The practical applications have not necessarily been to trace amounts of the constituents determined. However, too often tests only on artificial solutions have actually been described.

For the determination of two or more components, absorption measurements were taken at their characteristic wavelengths, and simultaneous linear equations, with determinants containing the specific absorbance of each of the components at every wavelength, were solved.[8,9] This straightforward though cumbersome method is useless if unknown absorbing species are present.

Our objective was to apply ultraviolet spectrophotometry to the determination of impurities in pure or analytical reagents. The absorption spectra of solutions of pure chemicals show, as a rule, characteristic absorption bands of trace elements present, but their concentration cannot be determined because of background absorbance, composed of various unaccountable factors. This difficulty can be overcome by the addition of specific reagents to the solution.[1] Such reagents are not always readily available, and may cause technical complications. Hence, a mathematical device is preferable, and in the present paper algebraic formulae developed for this purpose are described.

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* This and the following two papers with the same main title were taken from a Ph.D. thesis submitted by P. A. to the Senate of the Hebrew University of Jerusalem.

THEORETICAL CONSIDERATIONS AND FORMULAE

Method I

The spectrum of a concentrated salt solution (see Fig. 1) may often show a characteristic absorption band riding on a general background absorption of the solution arising from unknown contaminations. Measuring the absorbance at the peak wavelength would not yield any information about the concentration of the required constituent, *M*; but if it is assumed that the background absorption of all contaminants in the proximity of the absorption peak does not vary, or varies only slightly with the wavelength, concentration can be estimated from the slope of the absorption band. For this purpose, measurements at two wavelengths are required: at λ_1 near the absorption peak; and at λ_2, somewhat below the half-width of the band (both on the long-wave side of the peak, see Fig. 2). The difference between these two absorbances, $\Delta A^s_{\lambda_1-\lambda_2}$, is then divided by the difference of the known specific absorbances of the constituent, *M*, at the same wavelengths, $\Delta q^M_{\lambda_1-\lambda_2}$, to give the concentration in any units:

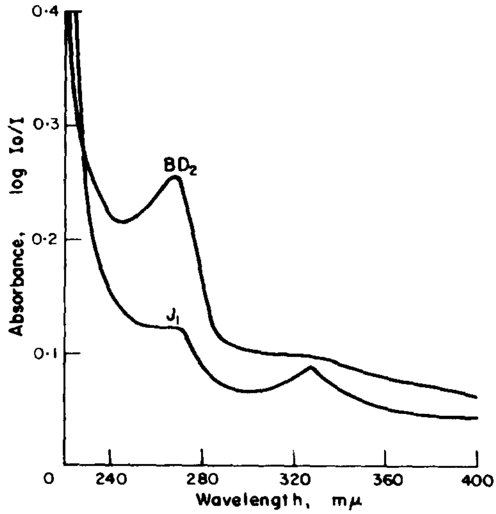

Fig. 1.—Absorption spectra of 4*M* KCl solutions with reference to water J_1 = J.T. Baker Analyzed Reagent; BD_2 = B.D.H. Laboratory Reagent.

$$Q^M = (\Delta A^s_{\lambda_1-\lambda_2})/(\Delta q^M_{\lambda_1-\lambda_2})$$

Q is expressed in ppm throughout this work.

The term $\Delta q^M_{\lambda_1-\lambda_2}$ can be evaluated by measuring the absorbance of a salt solution to which a known amount of the constituent has been added, with reference to another portion of the same salt solution which has not been treated.

There is a loss of precision involved in this method as compared to the spectrophotometric methods in common use: (*a*) the sensitivity is halved; (*b*) one measurement, at λ_2, is taken on the slope of the absorption curve. On the other hand, errors arising from the inequality of the cells containing the measured and the reference solutions are compensated for. The advantages of the simplicity of the method. and the elimination of the use of any specific reagents, are quite obvious.

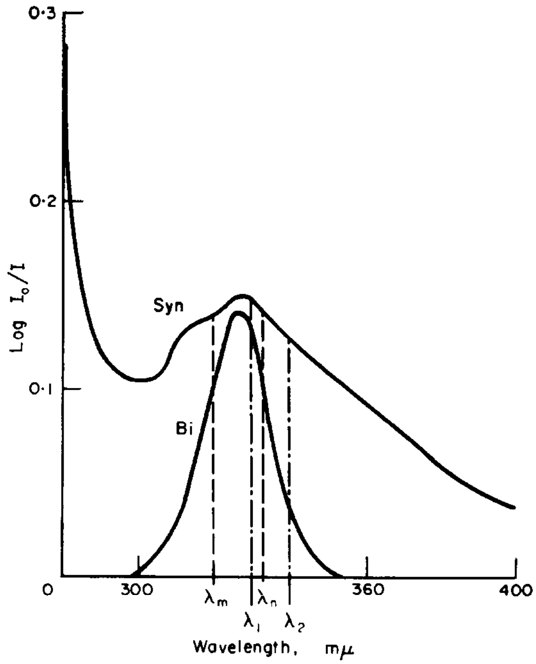

Fig. 2.—Absorption curves of 4*M* KCl solutions
Bi: contained 2 ppm of Bi^{3+} and 0·01*M* HCl
(measured against 4*M* KCl solution)
Syn; contained 0·4 ppm of Bi^{3+}, 0·01*M* HCl, 3·4 ppm of Fe^{3+}, 10·5 ppm of Pb^{2+},
and various other cations and anions
(measured against distilled water)

Method II

The background absorbance of the solution often varies nearly linearly with the wavelength, since the absorption band of the sought constituent, *M*, rides on the tail of another absorption band. This interference can be dealt with by making two additional measurements at wavelengths λ_m and λ_n, and introducing an appropriate modification in formula I. The wavelengths λ_m and λ_n are two wavelengths situated on either side of the band peak of constituent *M*, at which the absorbances of *M* are equal, *i.e.*, $A^M_{\lambda_m} = A^M_{\lambda_n}$, as illustrated in Fig. 2. These wavelengths are found experimentally by measuring the absorption spectrum of a solution to which a known amount of the constituent *M* has been added. The modified formula, then, assumes the form:

$$Q^M = \frac{\Delta A^s_{\lambda_1-\lambda_2} - K\Delta A^s_{\lambda_m-\lambda_n}}{\Delta q^M_{\lambda_1-\lambda_2}} \qquad \text{II}$$

where

$$K = \frac{\lambda_1 - \lambda_2}{\lambda_m - \lambda_n}.$$

It is desirable that all four wavelengths chosen for measurement should be in a narrow region of the spectrum, otherwise this approximation is not valid. A similar formula has previously been proposed by Kress for the determination of lead in rubber products.[10]

Method III

The background absorbance of the solution can also be compensated for by introducing a correction factor, K_R, into formula I. This device is adopted whenever Method II is inadequate, either because the peak absorbance of the constituent is too far out in the short ultraviolet, or because the absorbance of the contamination varies abruptly on passing from the region $\lambda_1 - \lambda_2$ to the region $\lambda_m - \lambda_n$ of the spectrum.

The correction factor proposed is $K_R = K^M_R/K^S_R$,

where $$K^M_R = A^M_{\lambda_1}/\Delta A^M_{\lambda_1-\lambda_2} = q^M_{\lambda_1}/\Delta q^M_{\lambda_1-\lambda_2},$$

the "slope ratio" of the constituent,

and $$K^S_H = A^S_{\lambda_1}/\Delta A^S_{\lambda_1-\lambda_2},$$

the "slope ratio" of the solution at the two chosen wavelengths. The parameter K^M_R is characteristic of the constituent, and can be evaluated experimentally. Hence, the final formula has the form:

$$Q^M = \frac{\Delta A^S_{\lambda_1-\lambda_2}}{\Delta q^M_{\lambda_1-\lambda_2}} K_R = \frac{(\Delta A^S_{\lambda_1-\lambda_2})^2 \times K^M_R}{A^S_{\lambda_1} \times \Delta q^M_{\lambda_1-\lambda_2}} \qquad \text{III}$$

necessitating measurements at only two wavelengths. This correction is an approximation, valid only under certain conditions, *i.e.*, when the absorption gradient of the contaminants between λ_1 and λ_2 is (*a*) positive, and (*b*) less steep than that of the desired constituent.

Inspection of the curves given in Fig. 1 shows that both conditions are valid, for example, in the case of the absorption band of lead with a peak at $\lambda = 268{\cdot}5$ mμ.

Under these conditions $K^M_R < K^S_R$ always, and therefore $K_R < 1$, as it should be. Also, the correction factor K_R varies in the right direction with variations of the background absorbance of the contaminants at λ_1 ($= L_1$), and of the relative absorbance of the desired constituent ($A^M_{\lambda_1}$), as may be seen in the following:

$$K_R = \frac{A^M_{\lambda_1} \times \Delta A^S_{\lambda_1-\lambda_2}}{A^S_{\lambda_1} \times \Delta A^M_{\lambda_1-\lambda_2}} = \frac{A^M_{\lambda_1} \times (\Delta A^M_{\lambda_1-\lambda_2} + l)}{(A^M_{\lambda_1} + L_1)\Delta A^M_{\lambda_1-\lambda_2}} = \frac{1 + l/\Delta A^M_{\lambda_1-\lambda_2}}{1 + L_1/A^M_{\lambda_1}},$$

where $l = L_1 - L_2$.

Formula III has been applied by us to the determination of the nitrate ion with satisfactory results; the absorbance of 4*M* potassium chloride solutions was measured at the wavelengths 220 and 230 mμ (see Part II of this series[11]). The number of interfering contaminants increases at the shorter wavelengths, and in some cases it was found advantageous, when using Formula III, to deduct from the measured absorbances the absorbance of certain ions whose concentrations had previously been measured at longer wavelengths.

In conclusion, it is suggested that the concentration of certain impurity ions having characteristic absorption bands in the ultraviolet may be determined by taking measurements at two wavelengths. A choice of three different algebraic formulae is proposed. The simplest formula (I) is for use when the absorption band of the desired constituent stands out clearly, and retains its symmetrical form. Formula II or III should be applied when the absorption band is distorted. A test of the proposed method, applied to concentrated KCl solutions prepared in the laboratory, is described in a subsequent paper.[11]

Zusammenfassung—Für die spektralphotometrische Bestimmung von verunreinigenden Ionen in chemische reinen oder analytischen Reagentien, die im fraglichen Spektralbereich selbst nicht absorbieren, werden algebraische Formeln vorgeschlagen. Diese Formeln erfordern Absorptionsmessungen an der Lösung bei zwei festgelegten Wellenlängen und Kenntnis der Extinktionskoeffizienten des zu bestimmenden Ions. Keine Information über Natur oder Konzentration der störenden Ionen oder Untergrundabsorption der Lösung ist notwendig.

Résumé—On propose de formules algébriques pour la détermination spectrophotométrique des impuretés ioniques dans les réactifs chimiquement purs ou pour analyse et n'absorbant pas eux-mêmes dans la région spectrale utilisée. Ces formules nécessitent la mesure de l'absorption de la solution à deux longeurs d'ondes spécifiques, et la connaissance des coefficients d'absorption de l'ion. Aucun autre renseignement, soit sur la nature de la concentration des ions génants, ou l'absorption de base de la solution n'est nécessaire.

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A SPECTROPHOTOMETRIC STUDY OF THE COMPLEX FORMED BETWEEN THE ACID CHLORANILATE AND MOLYBDATE IONS IN AQUEOUS SOLUTIONS

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Summary—Using the method of continuous variations of Job, a 1:1 complex between molybdate and acid chloranilate ions has been found in aqueous solutions at various values of pH and temperature. The pH has to be controlled to within 0·05 for obedience to Beer's law of the chloranilic acid. The dissociation constants of the complex at constant temperature decrease linearly with increasing pH up to pH 4, then increase linearly with pH. The changeover from the complex of one polymolybdate ion to another is suggested as the cause of this minimum in the K_d versus pH curve. This assumption is supported by the absorbance versus pH curve of the complex. This curve shows a rather sharp downward trend from the expected value beginning at pH 4. Thermodynamic data for the dissociation of the complex are presented.

CHLORANILIC acid (2,5-dichloro-3,6-dihydroxyquinone) has been investigated by several workers,[1,2] and it has been noted for its capacity to form complexes with various ions, such as calcium and zirconium. Because a chloranilic acid solution undergoes a colour change in the presence of the molybdate ion, it was decided to investigate the system to determine the empirical formula of the complex or complexes formed and to determine the thermodynamical properties.

Chloranilic acid, which forms a deep purple aqueous solution, turns light violet in the presence of molybdate ion. For this reason it was decided to employ a spectrophotometric approach. Several spectrophotometric methods have been applied to the investigation of the empirical formulae of coloured complexes in solution.[3–6] In this work, the continuous variations method of Job[4] was used.

The stability constants of a complex can be determined from the data used in the determination of the empirical formula of the complex. In this work, the method of Foley and Anderson[7] was used to determine the constants. The enthalpy of formation of the complexes would normally be determined by calculating the stability constant at different temperatures and plotting the logarithm of the stability constant versus the reciprocal of the absolute temperature. In this study, the concentrations of the complexes formed were found to be independent of temperature. This indicates that the enthalpy of formation is zero.

EXPERIMENTAL

Apparatus

Wavelengths that give maximum absorption at various pH values were measured on a Beckman DK-1 recording spectrophotometer using a tungsten lamp and silica cells of 10·00 ± 0·01-mm light path. Absorption values in the continuous variation runs were measured on a Beckman DU quartz spectrophotometer using a tungsten lamp and cells of 10·00 ± 0·01-mm light path. Measurements on the Beckman DK-1 were made from 400 to 700 mμ. The peaks at the different pH values ranged from 532 to 578 mμ. All measurements were made at the maximum sensitivity of the instruments. A Beckman Model G pH Meter was used to measure the pH of all solutions.

Reagents

Chloranilic acid. Reagent-grade material obtained from the Fisher Chemical Company, U.S.A., was used without further purification. A sample was also prepared by the purification method of Thamer and Voigt.[1] The purified sample melted at 283·8° and the unpurified sample melted at 283·65°. A maximum difference of $0·5 \times 10^{-3}$ was noted in the absorption values. This was not sufficient to cause any measureable differences.

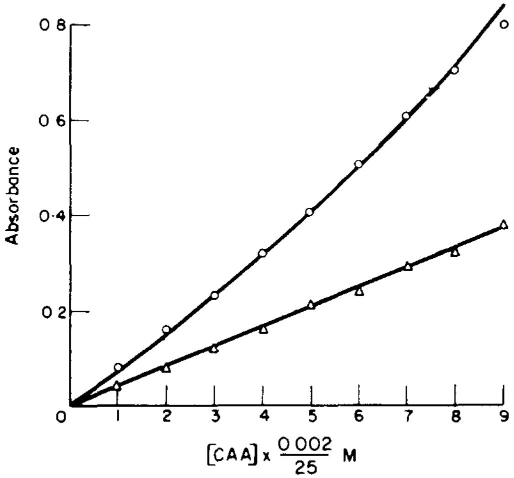

FIG. 1.—Obedience to Beer's Law:
O-pH controlled within 0·1,
Δ-pH controlled within 0·05.

Sodium molybdate. Reagent-grade material obtained from the Fisher Chemical Company, U.S.A., was used without purification.

Solutions of the above compounds were made with conductivity water at 25°. The buffer solutions were standard Clark and Lubb's[8] buffers. The chloranilic acid and sodium molybdate were prepared 0·002016 *M* by weight. All other solutions were prepared by weight.

Procedure

In the method of continuous variations, a series of solutions was prepared* in which the proportions of the molybdate and acid chloranilate ions were varied but the total concentration was constant. Before each run at any given pH the obedience of the choranilic acid to Beer's Law was determined. It was found that the pH had to be controlled within 0·05 in order to obtain obedience to Beer's Law. In Fig. 1 the absorbance is plotted against the concentration of chloranilic acid. The expected straight line through the origin is obtained only when the pH is controlled as described above.

The ionic strength in all runs was maintained constant at 0·37 by adding the necessary amount of purified sodium perchlorate. Except for added sodium perchlorate, the ionic strength in each run was derived mainly from the buffer solution. For this reason no ionic strength effect was observed on the absorption and therefore upon the formula of the complex or the values of the dissociation constants.

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* The order of preparation of solutions for absorption measurement was first to measure into a volumetric flask the requisite amount of acid chloranilate. To this was added the amount of buffer which by trial and error was found to give the desired pH in the final solution. Water was then added to the solution in an amount just short of the volume to give a correct final volume after molybdate was added to give the desired ratio of molybdate to acid chloranilate. The final volume was adjusted to the mark on the flask with a few drops of distilled water. Consistent results were obtained using this procedure.

This was proved by finding the same values for the absorption in the same concentrations of chloranilic acid, sodium molybdate and buffer, when the ionic strength was not controlled as when the ionic strength was controlled.

In the method used for calculating the equilibrium constants, calculations are based on comparisons between two solutions of equal optical density.

For the 1:1 complex found, solutions containing molybdate and acid chloranilate ions in a 1:1 ratio were prepared. The original solution for the 1:1 complex was diluted successively and hence each succeeding solution contained a smaller total concentration of the ions but each was maintained at the same pH by the addition of the appropriate buffer solutions. By this method solutions were obtained that had the same optical density as those of other ratios. Pairs of solutions with the same optical density have the same concentration of complex. These pairs have, however, different total concentrations of the reactants. Because the equilibrium constant would be the same for the two solutions, the constant may be calculated from the expression:

$$K = \frac{(a_1 - X)(b_1 - X)}{X} = \frac{(a_2 - X)(b_2 - X)}{X}$$

where a and b denote the original concentrations of the acid chloranilate and molybdate ions in the two solutions and X is the concentration of the complex.

The free energy of formation, ΔF°, of the complexes may be calculated from the relationship:

$$\Delta F^\circ = -2{\cdot}303\ RT \log K_s$$

where K_s is the stability constant of the complex, equal to the reciprocal of the equilibrium constant as calculated above.

The change in entropy, ΔS°, of the complex may be determined from the relationship:

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ = -T\Delta S^\circ.$$

It was determined that ΔH° was too small to be measured by the methods used in this work. Runs were made at temperatures of 25, 35, and 45°. No difference in the absorption was noted at the different temperatures.

For all spectrophotometric measurements, the blank for each sample contained the same amount of chloranilic acid as the sample with appropriate buffer to maintain the pH.

The pK_a of both chloranilic acid and the 1:1 complex was found. The ionisation constant of the chloranilic acid was also determined from pH measurements. A study of the dissociation constant of the complex versus the pH was also made.

RESULTS AND DISCUSSION

The results of the spectrophotometric investigations are presented in this section in both tabular and graphical form.

In graphical presentation, the optical density from the complex formation was plotted against the ratio of chloranilic acid to the total concentration. At every pH value employed (0.8–5.9), a 1:1 complex was found (see Fig. 3).

The ionisation equilibrium constants for chloranilic acid were determined in order to ascertain the charge on the complex. K_1 was found to be infinite and K_2 was found to be $5{\cdot}98 \times 10^{-4}$. The work of Thamer and Voigt[1] was repeated in order to check the technique. Because unbuffered chloranilic acid solutions do not obey Beer's law and a spectrophotometer with a 50-mm light path was not available, it was not possible to reproduce this data spectrophotometrically. By pH measurements it was possible to repeat the critical range of the data within an error of 10·5%. It was not possible to repeat the data in very concentrated perchloric acid-lithium perchlorate solutions with any degree of accuracy.

The dissociation constants of the complex were plotted against the pH. Instead of the expected smooth curve slowly approaching the ordinate, a sharply descending straight line was found from pH values of 0·8–4·0. This line intersected with another similar straight line that was found from pH values of 4·0–5·9 (see Fig. 3).

In an effort to explain this phenomenon, the pK_a values of both chloranilic acid and the 1:1 complex were determined. The pK_a of the chloranilic acid was found to be 2·75 while the pK_a of the 1:1 complex was found to be 2·30 (see Fig. 4).

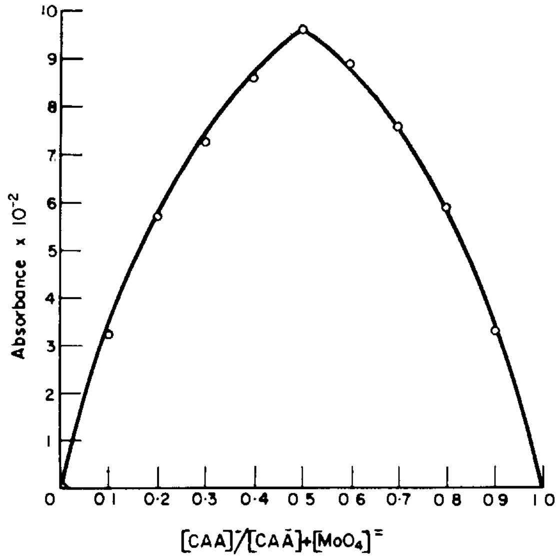

FIG. 2.—Typical plot by Job's method of continuous variations (25°; μ = 0·1818; pH 4·91–4·96).

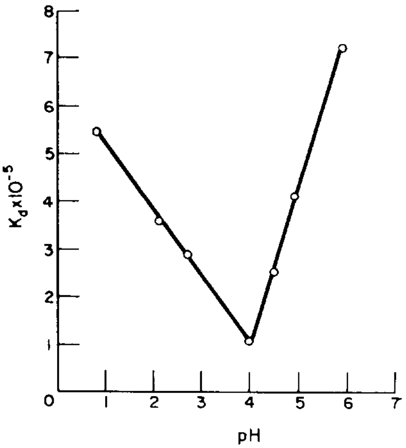

FIG. 3.—Plot of dissociation constants of complex against pH.

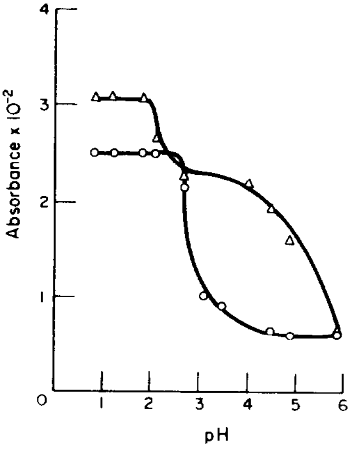

FIG. 4.—Determination of pK_A (25°; 556 mμ): O-chloranilic acid, Δ-1:1 complex.

All of the data concerning the complex is summarised in Table I.

TABLE I.—SUMMARY OF THERMODYNAMICAL DATA

pH	λ, *mμ*	Complex ratio	$K_d \times 10^{-5}$	$-\Delta F°$, *cal/mole*	$\Delta S°$, *cal/mole*	$\Delta H°$, *cal/mole*
0·8	532	1:1	5·44	5794	19·44	0
2·1	535	1:1	3·60	6036	20·25	0
2·7	556	1:1	2·91	6150	20·30	0
4·0	576	1:1	1·13	6722	22·58	0
4·5	578	1:1	2·51	6251	20·97	0
4·9	567	1:1	4·23	5943	19·94	0
5·9	542	1:1	7·20	5628	18·89	0

Observing Fig. 4 it is seen that the absorption versus pH curve* for the 1:1 complex has a normal shape out to pH 4, *i.e.*, there is a horizontal portion in the lower pH-range, followed by a rather vertical portion, which in turn is followed by an approximately horizontal portion extending to about pH 4. Beginning at pH 4 the curve turns down sharply. In Fig. 3 it will be observed that the minimum in the K_d-versus pH curve also occurs at pH 4. Now it is known that the normal molybdates, *e.g.*, Na_2MoO_4, form polymolybdates, the complexity of which depends on the hydrogen ion concentration.[9] The complex polyions and the corresponding pH-values include: $(Mo_{24}O_{78})^{12-}$, pH 1·0; $(Mo_{12}O_{41})^{10-}$, pH 1·25; $(Mo_6O_{21})^{6-}$, pH 1·5–4·5; $(Mo_3O_{11})^{4-}$, pH 4·5–6·3; MoO_4^{2-}, pH 6·5–14. One might interpret the data from Figs. 3 and 4 as arising from complexes of acid chloranilate ion with different polymolybdate ions, but in all cases the complexes had the ratio of constituents of 1:1 based on calculations using the normal molybdate. Evidently, over most of the range from pH 1·0 to 4·5, the complexing of the acid chloranilate ion was principally with the $(Mo_6O_{21})^{6-}$ polyion, though, at pH less than 1·5 the more complex polyions may be involved. However, not much of the data was taken at this lower pH range.

Whatever complexing of these higher polyions took place was evidently in harmony as to dissociation and absorbance with the complex of the $(Mo_6O_{21})^{6-}$ polyion.

The complexing of the acid chloranilate ion in the pH range 4·5–6·5 was principally with the $(Mo_3O_{11})^{4-}$ polyion. The critical region is where the $(Mo_6O_{21})^{6-}$ is converting to $(Mo_3O_{11})^{4-}$, as shown by the minimum at pH 4 in Fig. 3 and the beginning of the rapid decrease in absorbance at aboutp H 4 in Fig. 4. The ratio of the components based on the normal molybdate is always one, but the degree of dissociation and consequently the absorbance depends on which polyion is predominant in the formation of the complex. The decreased dissociation with increasing pH of the complex involving the $(Mo_6O_{21})^{6-}$ polyion is eventually balanced and eventually dominated by the increased dissociation of the complex with the $(Mo_3O_{11})^{4-}$ polyion. The changeover from the complex of one polyion to the other is rather sharp as is evidenced by the straight line segments meeting in the sharp minimum as given in Fig. 3 and by the rather abrupt decrease in absorbance above pH 4 as shown in Fig. 4. This rather abrupt change is to be expected because of the rather sharply delineated pH regions in which the two polyions exist. Because the ratio of the two constituents

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* The shapes of absorbance versus pH curves in the wavelength range 532–578 mμ were practically identical to that shown in Fig. 4 for 556 mμ, which is about the mid-point in wavelengths studied. The curves were merely raised or lowered along the absorbance axis, depending on wavelength.

was always 1 : 1 based on the normal molybdate one might speculate that the empirical formulae of the complexes in the pH ranges 1·0–4·5 and 4·5–6·5 were, respectively, $[(Mo_6O_{21})(HCh)_6]^{12-}$ and $[(Mo_3O_{11})(HCh)_3]^{7-}$, though the twice ionised acid chloranilate and even water may have entered into the formation of the complex. In the formulae, HCh^- represents the once ionised chloranilic acid.

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Zusammenfassung—Mit der Methode der kontinuierlichen Variationen von Job wurde zwischen Molybdat und saurem Chloranilat in wäßriger Lösung bei verschiedenen p_H-Werten und Temperaturen ein 1:1-Komplex gefunden. Damit die Chloranilsäure dem Beerschen Gesetz gehorchte, mußte der p_H auf 0,05 Einheiten konstant gehalten werden. Die Dissoziationskonstante des Komplexes fiel bei konstanter Temperatur linear mit steigendem p_H bis 4 und wuchs dann linear mit dem p_H. Als Grund dieses Minimums in der $K_\alpha p_H$-Kurve wurde der Übergang des Komplexes von einem Polymolybdation zu einem andern vermutet. Diese Annahme wurde durch die Extinktions-p_H-Kurve des Komplexes gestützt. Diese Kurve zeigte von p_H 4 an einen ziemlich scharfen Abfall unter den erwarteten Wert. Thermodynamische Daten für die Dissoziation des Komplexes werden angegeben.

Résumé—Par l'emploi de la méthode des variations continues de Job, on a trouvé un complexe 1:1 entre les ions molybdate et chloranilate acide en solutions aqueuses à diverses valeurs du pH et de la température. Le pH doit être respecté à 0,05 unité près pour que l'acide chloranilique obéisse à la loi de Beer. Les constantes de dissociation du complexe à température constante décroissent linéairement lorsque le pH croît jusqu'à pH 4, puis croissent linéairement avec le pH. On suggère le passage du complexe d'un ion polymolybdate à un autre comme cause de ce minimum dans la courbe du K_d en fonction du pH. Cette supposition est appuyée par la courbe d'absorption en fonction du pH du complexe. Cette courbe montre une tendance assez accentuée à décroître par rapport aux valeurs attendues à partir de pH 4. On présente des données thermodynamiques relatives à la dissociation du complexe.

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ISOTOPIC-DILUTION ANALYSIS BY ION EXCHANGE—II*

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF INDIUM

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Summary—A highly selective, substoichiometric method for determination of traces of indium has been developed. The procedure consists of the addition of a substoichiometric amount of EDTA to the test solution labelled with a known amount of radio-indium, followed by the separation of the complex formed from the excess of unreacted indium on a Dowex-50 column. Using a preliminary cupferron extraction, the procedure becomes highly selective. The average precision of the determination of indium for amounts of 1·1 μg/10 ml is 1·6% in the presence of an excess of many metals. The maximum sensitivity of the method is about 5 × 10^{-5} μg/10 ml.

INTRODUCTION

IN a previous paper[1] the essential conditions were given for the determination of traces of metals using isotopic-dilution analysis by ion exchange. This method can be used if the following conditions are fulfilled:

1. A radiotracer of suitable half-life and high specific activity is available.
2. It is possible to isolate very small and equal amounts of the metal under investigation from solutions containing it in different amounts.

The second condition can be fulfilled by adding equal amounts of a complexing agent to a standard solution containing only the radioisotope used and to the test solution to which a known amount of standard solution has been added. The amount of complexing agent added has to be smaller than stoichiometrically corresponds to the amount of the metal to be determined. This substoichiometric amount of the reagent must react quantitatively with the metal to be determined and the complex formed must be easily separated from the excess of unreacted metal ions. Obviously, EDTA is a very suitable reagent because it forms stable neutral or negatively charged complexes which are easily separable from the excess of unreacted metal ions on a cation-exchange column.

With EDTA indium forms a very stable negatively charged complex (log K_1 = 25·0: see Table I). Also, two radioisotopes of indium (^{114m}In and ^{115m}In) are available, and therefore isotopic-dilution analysis by ion exchange can be used for the determination of traces of this metal. Uni-, bi-, quinque- and hexavalent metals will not interfere in the determination because the stability constants of their complexes with EDTA are much lower than those of indium (see Table I). However, interference from some ter- and quadrivalent metal ions can be expected. Using a preliminary cupferron extraction followed by back-extraction of indium into dilute hydrochloric acid, indium

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* Part I: see reference 1.

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TABLE I.—STABILITY CONSTANTS (K_1) OF METAL COMPLEXES WITH EDTA AND EXTRACTION DATA OF METAL CUPFERRATES (K = EXTRACTION CONSTANT; $pH_{1/2}$ = pH AT WHICH 50% OF METAL IS EXTRACTED INTO 0·005*M* CUPFERRON SOLUTION IN CHLOROFORM).[2]

Metal ion	log K_1	log K	$pH_{1/2}$
Ag^+	7·1		P
Al^{3+}	16·1	−3·5	5·51
Ba^{2+}	7·8		N
Be^{2+}	9·3	−1·54	3·07
Bi^{3+}	26	5·08	0·6
Ca^{2+}	10·7		N
Cd^{2+}	16·9		P
Co^{2+}	16·6	−3·56	4·08
Cu^{2+}	18·9	2·66	1·03
Fe^{3+}	25·1	9·8	<0
Ga^{3+}	20·3	4·92	0·7
Hf^{4+}			<0
Hg^{2+}	21·8	0·91	1·85
In^{3+}	25·0	2·42	1·5
La^{3+}	15·3	−6·22	4·4
Mg^{2+}	8·7		N
Mn^{2+}	12·9		P
Mo^{VI}			<0
Nb^{V}			<0
Ni^{2+}	18·4		P
Pb^{2+}	18·3	−1·53	3·06
Pd^{2+}	18·5		<0
Sb^{3+}			<0
Sc^{3+}	23·0	3·34	1·2
Sr^{2+}	8·6		N
TiO^{2+}	17·5		<0
Tl^+	6·6		
Tl^{3+}	23·2	3	1·5
Th^{4+}	23·2	4·44	1·2
UO_2^{2+}			N
VO_2^+			<0
W^{VI}			P
Y^{3+}	18·0	−4·74	3·9
Zn^{2+}	16·3		8
Zr^{4+}	28		<0

N—metal ion is not extracted.
P—only partial extraction of metal ion occurs.

can be separated from most interfering metals. However, as with all other methods based on the isotope-dilution principle, this preliminary separation need not be quantitative.

EXPERIMENTAL

Apparatus

Scintillation counter: Well-type NaI(Tl) crystal.

Geiger-Müller end-window counter

pH-meter: Radiometer TTT 1 (Copenhagen, Denmark).

Glass test-tubes: With ground stopper.

Ion-exchange columns: A set of 12 columns, each 0·4 cm diameter and 10 cm high.

Reagents

Triple-distilled water: Used for dissolving all reagents and for all other operations.

Cupferron (ammonium salt of N-nitrosophenylhydroxylamine) solution: Prepared by extraction of a

0·005M solution of AnalaR cupferron in 0·001M hydrochloric acid with an equal volume of chloroform. This solution was prepared freshly before each series of experiments.

Hydrochloric acid: AnalaR grade purified by repeated distillation.

Ascorbic acid solution: 10% solution in water of the AnalaR reagent.

Ethylenediaminetetra-acetic acid (EDTA): AnalaR disodium salt.

Acetate buffer solution (pH 3·0): Purified by cupferron extraction.

Cation exchanger: Dowex 50 Wx in the Na-form, 50/100 mesh.

Indium chloride (carrier) solution: Prepared by dissolving 99·999% pure metallic indium in hydrochloric acid and diluting with water to the appropriate concentration.

Radioisotopes

^{114m}In ($t_{1/2}$ = 50 *day*, β, γ): Prepared by irradiation of metallic indium in a nuclear reactor.
^{115m}In ($t_{1/2}$ = 4·5 *hr*, β, γ): Carrier-free ^{115m}In was prepared by the nuclear reaction

$$^{115}\mathrm{Cd} \xrightarrow{43\ \mathrm{day}} {}^{115}\mathrm{In}$$
$$^{115}\mathrm{Cd} \xrightarrow{53\ \mathrm{hr}} {}^{115}\mathrm{In}$$
$$^{114}\mathrm{Cd}(n\gamma)^{115m}\mathrm{Cd} + {}^{115}\mathrm{Cd}.$$

The cadmium (as $CdCl_2$) was purified, before irradiation, from traces of indium originally present by acetylacetone solvent extraction. After irradiation, the sample was dissolved in slightly acidified water, the pH adjusted to *ca.* 5 and carrier-free indium extracted with 0·1M acetylacetone in chloroform.[3] The indium was stripped into 0·1M hydrochloric acid, evaporated to dryness and the residue dissolved in an acidified indium carrier solution of appropriate concentration.

Preparation of cation-exchange columns

The columns were filled with cation-exchanger Dowex 50 and washed 3-5 times with EDTA solution, then 3-5 times with water. This purification was repeated before each series of experiments.

Procedure

To 10 ml of a solution containing in addition to the indium to be determined an excess of other metal ions, a precisely known amount of radio-indium* (y) was added. The pH of the solution was

TABLE II.—INFLUENCE OF VARIOUS METAL IONS
(1·10 µg of In/10 ml; 1 ml of 5 × $10^{-6}M$ EDTA added)

Indium taken (x), µg	Active indium added (y), µg	Activity of eluate		Indium found, µg	Deviation from mean (Δ), µg	Other metals present, µg	
		A$_1$	A$_2$				
1·10	1·85	7499	4677	1·12	+0·02		0
		7499	4611	1·16	+0·06	100	Cu^{2+}, Hg^{2+}, Zn^{2+}, Ag^{+}
		7499	4870	1·00	−0·10	1000	Cd^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}
		7499	4681	1·12	+0·02	1000	Tl^{+}, Mn^{2+}, Fe^{3+}, K^{+}, Na^{+}, Ca^{2+}
		7499	4866	1·00	−0·10	1000	V^{V}, Mo^{VI}, W^{VI}, UO_2^{2+}, Cr^{3+} La^{3+}, Sr^{2+}.
		7499	4806	1·04	−0·06	10	Ga^{3+}
		7499	4816	1·04	−0·06	10	Zr^{4+}
		7139	4457	1·11	+0·01		0
		7139	4506	1·08	−0·02	1000	Ge^{4+}
		7139	4386	1·16	+0·06	1000	As^{3+}
		7139	4430	1·13	+0·03	1000	Sn^{4+}
		6441	3991	1·13	+0·03		0
		6441	4151	1·02	−0·08	10	Ti^{4+}
		6441	3893	1·21	+0·11	10	Th^{4+}
		6441	3880	1·21	+0·11	10	Bi^{3+}

$$\sigma = \frac{\sum_{x=1}^{x=n} x}{n} = 1{\cdot}10; \quad \delta = \pm\sqrt{\frac{\Sigma\Delta^2}{n/n - 1/}} = \pm 1{\cdot}6\%; \qquad \sigma - x = 0 = 0\%.$$

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* The procedure was checked with both ^{114m}In and ^{115m}In. In practice, the choice of isotope which will give the required sensitivity depends on its specific activity.

TABLE III.—DETERMINATION OF TRACES OF INDIUM
($2{\cdot}20 \times 10^{-1} - 5{\cdot}5 \times 10^{-5}$ μg of In/10 ml).

Indium taken (x), μg	Active indium added (y), μg	Activity of eluate[b]		Indium found, μg	Deviation from mean (Δ), μg	Deviations[a]	Remarks
		A_1	A_2				
0·220	0·220	57747	28405	0·227	+0·009	$\sigma = 0{\cdot}218$ μg of In	1·00 ml of $2 \times 10^{-6}M$
		57747	28300	0·229	+0·011		EDTA added.
		57747	28524	0·225	+0·007	$\delta = \pm 0{\cdot}006$ μg $= \pm 2{\cdot}7\%$	
		65675	34376	0·201	−0·017	$\sigma - x = -0{\cdot}002 = -0.9\%$	
		65675	34402	0·200	−0·018		
		65675	34182	0·203	−0·015		
0·0220	0·0220	4745	2238	0·0245	+0·0017		
		4745	2395	0·0216	−0·0012		
		4745	2212	0·0250	+0·0022	$\sigma = 0{\cdot}0228$ μg of In	1·30 ml of $2 \times 10^{-7}M$
		2896	1376	0·0242	+0·0014	$\delta = \pm 0{\cdot}0008$ μg $= \pm 3{\cdot}7\%$	EDTA added.
		2896	1452	0·0219	−0·0009	$\sigma - x = +0{\cdot}0008 = +3{\cdot}7\%$	
		2896	1519	0·0200	−0·0028		
0·00220	0·00220	79094	43585	0·00180	−0·00019		
		79094	39737	0·00218	+0·00019		
		79094	40842	0·00214	+0·00015	$\sigma = 0{\cdot}00199$ μg of In	1·00 ml of $2 \times 10^{-8}M$
		65869	33519	0·00206	+0·00007	$\delta = \pm 0{\cdot}00008$ μg $= \pm 3{\cdot}7\%$	EDTA added.
		65869	36273	0·00180	−0·00019	$\sigma - x = -0{\cdot}00031 = -14\%$	
0·000220	0·000220	14056	7030	0·000216	+0·000010	$\sigma = 0{\cdot}000206$ μg of In	0·100 ml of $2 \times 10^{-8}M$
		14056	6863	0·000229	+0·000013		EDTA added.
		14056	7845	0·000174	−0·000032	$\sigma - x = -0{\cdot}000014 = -6{\cdot}5\%$	
0·000055	0·000055	32774	15432	0·0000617	−0·0000190	$\sigma = 0{\cdot}0000807$ μg of In	0·05 ml of $1 \times 10^{-8}M$
		32774	12479	0·0000894	+0·0000087		EDTA added.
		32774	12304	0·0000910	+0·0000103	$\sigma - x = +0{\cdot}0000257 = +45\%$	

[a] For symbols see Table II.

[b] In general, 3 samples (A_2) were examined for 1 standard (A_1).

adjusted to 2-3 by adding hydrochloric acid or acetate buffer solution. This prepared solution was successively extracted with two 5-ml portions of cupferron solution in chloroform. The combined extracts were shaken with 2-3 ml of $0{\cdot}1M$ hydrochloric acid, then transferred into polyethylene bottles. The amount of indium recovered can be controlled by measuring the activity of the hydrochloric acid with a Geiger-Müller counter. However, this separation need not be quantitative. To the treated solutions some drops of ascorbic acid solution were added to reduce the last traces of iron^{III} present. After adding a substoichiometric amount of EDTA, the pH was adjusted to 2-3 with acetate buffer and the solution passed through a cation-exchange column at the rate of 0·3 ml/min. After washing the column with water, the activity (A_2) of the eluate was measured with a scintillation or Geiger-Müller counter. A standard solution containing only radio-indium was treated in exactly the same way. The amount of radio-indium present in this solution need not be known precisely, but it must be higher than stoichiometrically corresponds to the EDTA present. Furthermore, the amount of EDTA must be precisely the same as in the test solution. After measuring the activity of the eluate (A_1), the amount of indium (x) present in the test solution was calculated from the relation

$$x = y\left(\frac{A_1}{A_2} - 1\right).$$

Some results of the determination of indium in the range 1·1 μg/10 ml to about 5×10^{-5} μg/10 ml are summarised in Tables II and III.

DISCUSSION

From the results given in Table II it follows that the determination of traces of indium is very selective. Using the preliminary cupferron separation many metals are extracted simultaneously with indium (*i.e.*, metals for which $pH_{1/2} < 3{\cdot}5\text{–}4{\cdot}0$: see Table I). By shaking the extract with dilute hydrochloric acid, indium passes into the aqueous phase, whereas iron^{III}, zirconium, hafnium, *etc.*, remain in the organic phase (see Table I). Using a substoichiometric amount of EDTA, only indium and bismuth react, forming negatively charged complexes (see Table I). This fact was verified experimentally. It was found that a one hundred- to one thousand-fold excess of alkali metals, alkaline earths, copper, mercury^{II}, zinc, silver, cadmium, lead, nickel, cobalt^{II}, thallium^{I}, vanadium^{V}, molybdenum^{VI}, tungsten^{VI}, uranium^{VI}, chromium^{III}, iron^{III}, lanthanum, germanium, arsenic^{III} and tin^{IV}, and a ten-fold excess of titanium, zirconium, thorium and gallium, did not interfere. Bismuth interferes when present in excess, but its interference was eliminated by a preliminary extraction with $10^{-3}M$ dithizone in chloroform at pH 2–3.

The maximum sensitivity of the method (about 5×10^{-5} μg of In/10 ml) was reached using carrier-free indium. Correction was made for the ^{117m}In and ^{117}In present in the carrier-free indium as a result of

$$^{116}\text{Cd}\,(n\gamma)\,^{117m}\text{Cd}$$

$$^{117m}\text{Cd} \longrightarrow {}^{117m}\text{In} + {}^{117}\text{In}.$$

CONCLUSION

It has been shown that the use of EDTA for the substoichiometric determination of indium is advantageous not only for the high selectivity of the method, but also for the high stability of the EDTA solution against oxidation even at the lowest concentration. Thus, better reproducibility of the determination of a minute amount of the metal can be reached in comparison with isotopic-dilution analysis by solvent extraction.

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Zusamménfassung—Eine hochselektive unterstöchiometrische Methode zur Bestimmung von Indiumspuren wurde entwickelt. Man gibt eine unterstöchiometrische Menge EDTA zu der mit einer bekannten Menge Radio-Indium markierten Probelösung. Dann wird der Komplex vom überschüssigen, nicht gebundenen Indium auf einer Dowex 50-Säule abgetrennt. Nach vorhergehender Kupferronextraktion wird das Verfahren hochselektiv. Die mittlere Genauigkeit der Indiumbestimmung bei Mengen von 1,1 μg/10 ml ist 1,6% in Gegenwart eines Überschusses vieler Fremdmetalle. Die maximale Empfindlichkeit der Methode liegt bei etwa $5 . 10^{-5}$ μg/10 ml.

Résumé—On a élaboré une méthode substoechiométrique, hautement sélective, de dosage de traces d'indium. La technique consiste en l'addition d'une quantité substoechiométrique d'EDTA à la solution étudiée, marquée d'une quantité connue de radio-indium, suivie de la séparation du complexe formé de l'excès d'indium qui n'a pas réagi, sur une colonne remplie de Dowex 50. En procédant à une extraction préliminaire au cupferron, la technique devient hautement sélective. La précision moyenne du dosage de l'indium pour des quantités de 1,1 μg/10 ml est de 1,6% en présence d'un excès de nombreux métaux. La sensibilité maximale de la méthode est d'environ 5×10^{-5} μg/10 ml.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF METALS

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Summary—The possibilities of substoichiometric determination of traces of metals by activation analysis and isotope-dilution analysis are critically discussed and optimum conditions given for the determination of 24 metals.

INTRODUCTION

DURING the last few years procedures for the substoichiometric determination of traces of zinc, mercury, copper, iron, silver, molybdenum, indium, arsenic, antimony, cobalt and gallium in highly pure materials (*e.g.*, germanium dioxide, silicon, lead, *etc.*) have been developed in our laboratory.[1–15,22] Because of the high selectivity and simplicity the possibilities of this method are now being studied in other laboratories, but not in all cases are the best conditions (especially as regards suitability of reagent and pH for determination) selected. To stimulate the development of this method optimum conditions for the determination of 24 metals are given in the present paper.

Substoichiometry can be used in activation analysis and isotope-dilution analysis because in both methods the element to be determined need not be isolated quantitatively from the test sample, the amount being calculated from the activity of its radioisotope. It has previously been shown that for the substoichiometric determination of any element two basic conditions need to be fulfilled:[1,7,16,18]

1. A suitable radioisotope of the element to be determined is available.
2. It is possible to isolate *equal* amounts of the element to be determined from the standard and test solutions containing it in different amounts.

Radioisotopes suitable for the determination of traces of metals by activation analysis and isotope-dilution analysis are summarised in Table I.[19]

The second condition can be accomplished by adding a substoichiometric amount of a complexing agent. This reagent must be consumed quantitatively, forming a complex easily separable from the excess of unreacted metal ions. In our experience the most suitable reagents are organic reagents forming complexes extractable into organic solvents and complexones forming neutral or negatively charged complexes readily adsorbed on cation-exchange columns.

In activation analysis the amount of element handled is relatively high because 1 to 10-mg amounts of isotopic carrier are usually added. For this reason 10^{-2}–$10^{-3}M$ solutions of the organic reagents can generally be used and their stability towards oxidising agents and decomposition by light need not be so high as in the case of isotope-dilution analysis. For well known reasons any non-active trace contaminants carried into the treated sample after irradiation (originating from reagents, walls of

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vessels, *etc.*) cannot influence the result of the analysis. The disadvantages of activation analysis are:

1. The total activity handled is often high.
2. The nuclear interferences and shielding effects must be considered.
3. The proposed separation procedure has to be highly selective.

In isotope-dilution analysis an isotopic carrier cannot be added; therefore the amount of the element handled is often very low (10^{-6}–10^{-10} g) and the solutions of organic reagents used for substoichiometric determination are very dilute (10^{-5}–10^{-9} *M*). For this reason complexones are more advantageous than the organic reagents used in solvent extraction because their stability towards oxidising agents is much higher. In the later case it seems to be promising to use instead of organic reagents their metal complexes (*e.g.*, copper dithizonate can be used for the substoichiometric determination of mercury). The second disadvantage of isotope-dilution analysis, as in other destructive analytical methods (*e.g.*, spectrophotometry, polarography, *etc.*), lies in the fact that contamination of the treated sample by the element to be determined influences the result of the analysis. Therefore, in this type of determination, the reagents, vessels and distilled water must be especially purified. The advantages of isotope dilution are as follows:

1. The activity handled is negligible.
2. It is not necessary to irradiate the sample in a nuclear reactor.
3. In some cases (if a carrier-free isotope or one of high specific activity is available), a higher sensitivity can be reached than by activation analysis.

From the above it follows that activation analysis is more suitable than isotope-dilution analysis for determining traces of elements in such materials as metals, ores and minerals, the decomposition of which requires a large amount of reagents (*e.g.*, acids, hydroxides, *etc.*). Isotope-dilution analysis is advantageous for determination of traces of metals in easily decomposed or water-soluble materials. This method, when the neutron-activation cross section is low and/or when the half-life of the radioisotope formed is very short, is more sensitive than activation analysis.

SELECTED SEPARATION PROCEDURES FOR SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF METALS

Selective procedures for the substoichiometric determination of traces of 24 metals by activation analysis (AA) or by isotope-dilution analysis (IDA) are now summarised. The conditions for the determination of 11 of these metals have been verified experimentally. Optimum conditions for the determination of the other metals are predicted on the basis of the theory of substoichiometry. However, this method can also be used for the determination of many other elements, but, because of the lack of stability constants or extraction constants, conditions for their substoichiometric determination cannot be predicted. Ion-association complex extraction systems and precipitation reactions (especially precipitation from homogeneous solution) have not been considered, although these methods might be useful in activation analysis.

Antimony and arsenic can be determined by AA using diethylammonium diethyldithiocarbamate or lead diethyldithiocarbamate solution in chloroform as an organic reagent.[15] In the case of antimony cupferron can also be used.[22] Interfering metals are removed by preliminary extraction with the same reagents before the reduction of antimony^{V} and arsenic^{V} to the tervalent state. These reagents are not suitable for IDA because of their low stability in very dilute solutions. The determination of antimony^V by IDA was worked out by extraction with a substoichiometric amount of methyl violet into toluene from 1:1 hydrochloric acid.[20]

Bismuth can be determined using a substoichiometric amount of EDTA at pH 1–2. Using a preliminary dithizone extraction in the presence of potassium cyanide,[19] the method becomes very selective. This procedure can be used both in AA or IDA. For nuclear reasons (see Table I), a higher selectivity can be reached by means of IDA.

Cadmium can be determined at pH 4–5 using a substoichiometric amount of EDTA. However, this procedure in not very selective and a preliminary dithizone extraction from basic solution must be carried out to increase its selectivity.[17] The proposed procedure is suitable for AA as well as for IDA.

Chromium will probably be best determined by formation of the very stable chromium^{III}-EDTA complex. Interfering metals can be removed by preliminary extraction with dithizone and oxine.[17]

Cobalt, in trace quantities, has been determined by AA in iron^{II} sulphate. After a preliminary cupferron extraction using fluoride as masking agent, cobalt was determined by extraction with 1-nitroso-2-naphthol.[12] The substoichiometric determination of cobalt by IDA using EDTA was shown to be unsuitable, because many elements interfered.[12]

Copper has been determined by AA[8] and by IDA[5] using dithizone extraction into carbon tetrachloride. Using potassium iodide as masking agent and the technique of successive extraction with several substoichiometric amounts of reagent, the method becomes highly selective.

Gallium has been determined by AA using a preliminary α-benzoinoxime extraction for removing molybdenum, vanadium and tungsten, followed by extraction of gallium with a substoichiometric amount of oxine in chloroform at pH 3.6.[13] Thiosulphate and ascorbic acid were used as masking agents for copper and iron. A substoichiometric determination of gallium based on the formation of the gallium^{III}-EDTA complex at pH 2–2·5 seems to be advantageous for IDA.

Gold, in trace amounts, can be determined both by AA and IDA using extraction with a substoichiometric amount of dithizone in chloroform. Interference from palladium can be removed by a preliminary dimethylglyoxime extraction; bromides or iodides can be used for masking mercury and silver.

Indium, in trace quantities, in germanium dioxide, has been determined by AA using a substoichiometric amount of EDTA at pH 2–3.[11] This procedure becomes very selective if a preliminary dithizone or cupferron extraction is followed by back-extraction of indium into dilute mineral acid. The same procedure has been applied to the substoichiometric determination of indium by IDA. Using carrier-free indium, down to about 5×10^{-11} g of indium/10 ml was determined.[14]

Iron^{III} down to 2×10^{-9} g/5 ml has been determined using IDA. Separation procedures using a substoichiometric amount of EDTA[4] or substoichiometric extraction with cupferron[6] are both very selective. The separation procedure will also be valuable for AA.

Lead cannot be determined by AA for nuclear reasons. On the other hand, it can be determined by IDA because a carrier-free isotope of lead (see Table I) is available. The proposed procedure consists of adding a substoichiometric amount of EDTA at pH 4–5 and separation of the resulting complex on a cation-exchange

TABLE I.—SUITABLE RADIOISOTOPES FOR SUBSTOICHIOMETRIC DETERMINATIONS[a]

Element	Activation analysis (AA)				Isotopic-dilution analysis (IDA)	
	Radio-nuclide	Half-life	Activation cross section, *barns*	Natural abundance, %	Suitable radio-isotope	Half-life
Antimony	^{122}Sb	2·8 day	6·8	57·25	^{122}Sb	2·8 day
Arsenic	^{76}As	26·5 hr	5·4	100	^{76}As	26·5 hr
					^{74}As	17·5 day
	^{124}Sb	60 day	2·5	42·75	^{124}Sb	60 day
Bismuth	^{210m}Bi	5·0 day	0·019	100	^{210m}Bi	5·0 day
Cadmium	^{115}Cd	2·3 day	1·1	28·86	^{115}Cd	2·3 day
	^{115m}Cd	43 day	0·14	28·86	^{115m}Cd	43 day
	^{117}Cd	2·9 hr	1·5	7·58		
Chromium	^{51}Cr	27·8 day	15·9	4·31	^{51}Cr	27·8 day
	^{55}Cr	3·6 min	0·38	2·38		
Cobalt	^{60m}Co	10·5 min	16	100	^{58}Co	71 day
	^{60}Co	5·27 yr	20	100	^{60}Co	5·27 yr
Copper	^{64}Cu	12·8 hr	4·51	69·09	^{64}Cu	12·8 hr
	^{66}Cu	5·1 min	1·8	30·91		
Gallium	^{70}Ga	21·1 min	1·4	60·4	^{67}Ga	78 hr
	^{72}Ga	14·1 hr	5·0	39·6	^{72}Ga	14·1 hr
Gold	^{198}Au	2·7 day	96	100	^{198}Au	2·7 day
Indium	^{114m}In	50 day	56	4·28	^{114m}In	50 day
	^{116m}In	54 min	155	95·72		
Iron	^{55}Fe	2·6 yr	2·8	5·82	^{55}Fe	2·6 yr
	^{59}Fe	45 day	1·01	0·33	^{59}Fe	45 day
Lead					^{210}Pb (Ra D)	19·4 yr
Mercury	^{197m}Hg	24 hr	420	0·146		
	^{197}Hg	65 hr	880	0·146		
	^{203}Hg	47 day	3·8	29·8	^{203}Hg	47 day
Molybdenum	^{99}Mo	67 hr	0·51	23·78	^{99}Mo	67 hr
	^{101}Mo	15 min	0·20	9·63		
Nickel	^{65}Ni	2·56 hr	1·52	1·08	^{56}Ni	2·56 hr
Palladium	^{103}Pd	17 day	4·8	0·96	^{103}Pd	17 day
	^{109}Pd	13·6 hr	10·4	26·71	^{109}Pd	13·6 hr
Platinum	^{193m}Pt	4·4 day	90	0·78	^{193m}Pt	4·4 day
	^{197}Pt	18 hr	0·87	25·3	^{197}Pt	18 hr
Scandium	^{46}Sc	84 day	12	100	^{46}Sc	84 day
Silver	^{108}Ag	2·3 min	45	51·35		
	^{110m}Ag	253 day	3·2	48·65	^{110m}Ag	253 day
Thallium	^{204}Tl	3·9 yr	8	29·5	^{204}Tl	3·0 yr
	^{206}Tl	4·3 min	0·10	70·5		
Thorium	^{233}Th	22·4 min	7·33	100	^{234}Th (UX_1)	24·1 day
Vanadium	^{52}V	3·8 min	4·5	99·76	^{48}V	16·2 day
Zinc	^{65}Zn	245 day	0·47	48·89	^{65}Zn	245 day
	^{69m}Zn	13·9 hr	0·097	18·57		
	^{69}Zn	55 min	1·0	18·57		
Zirconium	^{95}Zr	65 day	0·076	17·40	^{95}Zr	65 day
	^{97}Zr	17 hr	0·053	2·80		

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[a] Data corrected to July 1961 from Chart of the Nuclides, Second Edition, prepared at Institute of Radiochemistry, Nuclear Research Centre Karlruhe, West Germany.

column. A preliminary dithizone extraction in the presence of potassium cyanide followed by back-extraction of lead into dilute acid increases the selectivity of the determination.[17]

Mercury has been determined by means of extraction with a substoichiometric amount of dithizone in carbon tetrachloride. This procedure is very selective and no preliminary separation steps need be carried out. It has been used successfully both in AA[16] and in IDA.[3]

Molybdenum has been determined by AA using extraction with a substoichiometric amount of oxine.[9] The method is very selective because only palladium interferes. To propose a substoichiometric separation for the determination of traces of molybdenum by IDA is very difficult because the extraction constants of molybdenum chelates are not known. However, the application of cupferron extraction for this purpose would be very interesting.

Nickel, using a substoichiometric amount of EDTA, can probably be determined by AA. However, a preliminary dimethylglyoxime extraction will be necessary for removing interfering elements.[17]

Palladium, because the extraction constant of palladium-dithizonate is very high, will be determined very selectively using a substoichiometric dithizone extraction. Thio-oxine also seems to be very promising for this purpose.

Platinum can be determined using a substoichiometric amount of dithizone in the presence of tin^{II} chloride. All interfering metals can be removed by a preliminary dithizone extraction when platinum is present in the solution in the tervalent state.[17]

Scandium can probably be determined by AA or by IDA with a preliminary oxine extraction[17] followed by substoichiometric EDTA separation at pH 2·5–3.

Silver. IDA by the extraction of silver with a substoichiometric amount of dithizone has been employed for the determination of traces of this element in biological materials.[21] EDTA was a suitable masking agent for many metals. The above procedure has also been applied to the determination of traces of silver by AA. In this case a high selectivity was obtained by the technique of successive extraction with a substoichiometric amount of dithizone.[10]

Thallium. The best separation procedure for its substoichiometric determination is based on the formation of the very stable thallium^{III}-EDTA complex at pH 2. The selectivity can be increased by a preliminary dithizone extraction.

Thorium, using a preliminary thenoyltrifluoracetone extraction,[17] can be separated from most metal ions which would interfere in a subsequent separation of the thorium-EDTA complex at pH 2–3, using a substoichiometric amount of EDTA. This method will probably be more advantageous for IDA than for AA.

Vanadium can be determined by AA using a substoichiometric extraction with oxine.

Zinc, in trace quantities, can be extracted very selectively with a substoichiometric amount of dithizone in carbon tetrachloride in the presence of diethanoldithiocarbamate at pH 7–9. This method has been used successfully for the determination of zinc both by AA[8] and IDA.[2]

Zirconium forms with EDTA one of the most stable complexes.[17] For this reason the determination of this element using a substoichiometric amount of EDTA at pH 1 will be very selective.

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Zusammenfassung—Unterstöchiometrische Bestimmung von Metallspuren. Die Möglichkeiten zur unterstöchiometrischen Bestimmung von Metallspuren durch Aktivierungsanalyse und Isotopenverdünnung werden kritisch diskutiert und optimale Bedingungen für die Bestimmung von 24 Metallen angegeben.

Résumé—On discute de façon critique des possibilités de dosage substoechiométrique de traces de métaux par analyse par activation et par dilution isotopique, et l'on donne les conditions optimales de dosage de 24 métaux.

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

TITRIMETRIC DETERMINATION OF VANADIUM^{IV}

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Summary—Results are presented of investigations leading to the development of a procedure for the titrimetric determination of vanadium^{IV} with potassium dichromate in a strong phosphoric acid medium ($> 12M$) at room temperature, using a potentiometric end-point. Cerium^{IV}, iron^{III}, chromium^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI}, cobalt^{II} and nickel^{II} do not cause any interference. Methods have also been developed for the differential potentiometric titration of iron^{II} plus vanadium^{IV}, manganese^{II} plus vanadium^{IV}, and iron^{II} plus manganese^{II} plus vanadium^{IV} in the same solution. The new reagent thus possesses several advantages over potassium permanganate and cerium^{IV} sulphate. Application of the new reagent to the analysis of a ferro alloy and an alloy steel is considered.

Müller and Just[1] observed that a temperature of 70–80° is necessary for the potentiometric titration of vanadium^{IV} with potassium permanganate, even though the difference in potential of the two redox couples involved is about 0·45 V. Willard and Young[2] investigated the visual titration of vanadium^{IV} with potassium permanganate in a solution buffered with sodium acetate using ferroïn as indicator. Because the reaction is observed to be slow at room temperature, they recommended the titration to be carried out at 50°, adding the oxidising agent slowly. Recently, Gopala Rao and Dikshitulu[3] improved the method by using phosphoric acid (2·5 ml of syrupy phosphoric acid/50 ml of mixture) as catalyst, which enables the titration of vanadium^{IV} with potassium permanganate to be made at room temperature at the usual speed using ferroïn as indicator in 0·1–0·15M sulphuric acid. Issa and Daes[4] proposed adding a known excess of potassium permanganate to the vanadium^{IV} solution in the presence of a barium salt, then making the solution alkaline and titrating the excess permanganate with a standard solution of formic acid or thallium^{I} salt solution. The barium salt precipitates both the products of reaction, manganate and vanadate, the first being formed by the reduction of permanganate and the second by the oxidation of vanadium^{IV}. If telluric acid is used in place of a barium salt, the permanganate is reduced to manganese^{IV}, which forms a manganese^{IV} tellurate complex.

Willard and Young[5] reported that the potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate is quantitative in sulphuric, hydrochloric or perchloric acid solution at 70–75°. The break in potential at the end-point decreases as the acidity is increased. Furman[6] independently found that the potentiometric titration of vanadium^{IV} with cerium^{IV} sulphate gives accurate results when carried out at 50–60°.

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* Part I: see reference 13.

Gopala Rao and Dikshitulu[7,8] found that the reaction between vanadium^{IV} and cerium^{IV} sulphate is catalysed by phosphoric acid, so that the titration of vanadium^{IV} can be made with cerium^{IV} sulphate at room temperature in 0·75–1·25*M* sulphuric acid with a potentiometric end-point or using Rhodamine-6G as a fluorescent indicator.

Smith and Getz[9] found that vanadium^{IV} perchlorate can be titrated at room temperature in 8*M* perchloric acid with a solution of ammonium hexanitratocerate(IV) in perchloric acid with a potentiometric end-point. Obviously the method has little practical significance, because it is tedious to obtain vanadium^{IV} as a perchlorate in a perchloric acid medium.

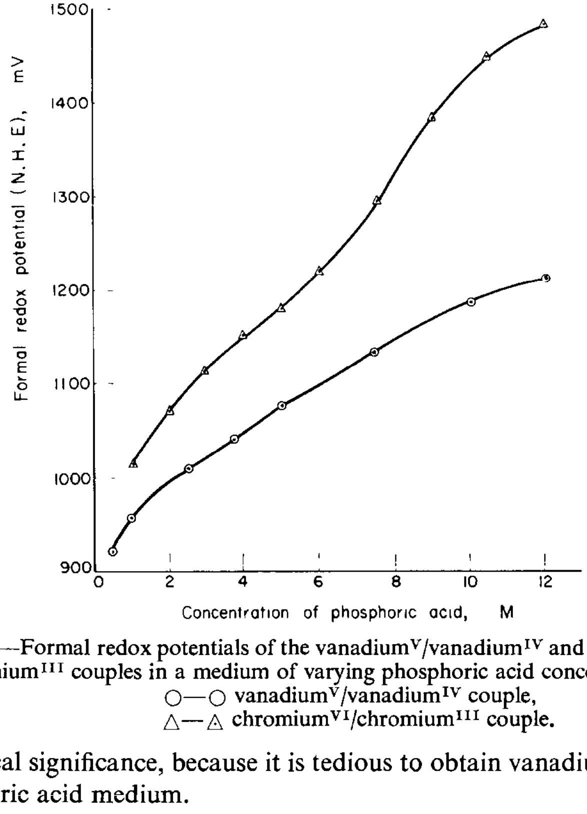

FIG. 1.—Formal redox potentials of the vanadium^{V}/vanadium^{IV} and chromium^{VI}/chromium^{III} couples in a medium of varying phosphoric acid concentration:[13,14]
○—○ vanadium^{V}/vanadium^{IV} couple,
△—△ chromium^{VI}/chromium^{III} couple.

Riolo and Soldi[10] proposed boiling a vanadium^{IV} solution to eliminate all dissolved oxygen and treating the same with a known excess of alkaline sodium chlorite. The vanadium^{IV} is instantaneously oxidised to vanadium^{V} by the chlorite. The vanadium^{V} is precipitated as barium vanadate and the excess sodium chlorite determined iodometrically. It is obvious that the method is indirect and tedious. Willard and Manalo[11] recommended the use of 2-carboxy-2′-methoxydiphenylamine and similar diphenylamine derivatives in the titration of alkaline hexacyanoferrate(III) with vanadium^{IV} at room temperature.

Willard and Merritt[12] found that vanadium^{IV} is rapidly and completely oxidised by ozone in a dilute sulphuric acid medium at room temperature. The addition of phosphoric acid to give an over-all concentration of 0·75*M* is recommended. The resulting vanadium^{V} is titrated with a standard solution of Mohr's salt, after the excess of ozone is eliminated. The method has the disadvantage that it is indirect and is subject to interference by manganese^{II}, which is partially oxidised to permanganate.

From the foregoing review of the literature, it is seen that potassium dichromate has not been tried as an oxidant for vanadium^{IV} in an acid medium. Therefore we have now undertaken such a study. We[13] have previously reported the formal redox potential of the chromium^{VI}/chromium^{III} couple in a medium of varying phosphoric acid concentration. These values and those of the formal redox potential of vanadium^{V}/vanadium^{IV} couple as determined by Gopala Rao and Dikshitulu[14] in a medium of varying phosphoric acid concentration are graphically represented in Fig. 1. From the curves it will be observed that in a 12*M* phosphoric acid medium, the difference in the formal potential of the two couples is 0·273 V at 28°, which is sufficient for a rapid oxidation of vanadium^{IV} by chromium^{VI} to proceed. Using this value the equilibrium constant of the reaction can be calculated from the cell reaction

$$6VO^{2+} + Cr_2O_7^{2-} + 5H_2O \rightarrow 6VO_3^{-} + 2Cr^{3+} + 10H^{+}$$

to be $K = 2{\cdot}692 \times 10^{27}$ ($\log_e K = nF \times E_{cell}/RT$). Several electrometric titrations have shown that the time required for the attainment of steady potentials in the vicinity of the equivalence point is about 6 min when the concentration of phosphoric acid is 9*M*, about 3 min when the concentration of phosphoric acid is 10·5*M* and only 1 min when the concentration of phosphoric acid is about 12*M*.

EXPERIMENTAL

Reagents

0·1M Vanadium^{IV} sulphate solution. Prepared by reducing an aliquot volume of about 0·2*M* sodium vanadate solution in a sulphuric acid medium with sulphur dioxide at boiling temperature, driving off the excess of sulphur dioxide by passing a rapid stream of carbon dioxide, then making up the solution to the desired volume. The solution is standardised potentiometrically with a standard solution of cerium^{IV} sulphate according to the procedure of Dikshitulu and Gopala Rao.[7]

0·033M Potassium dichromate solution. Prepared from "Pro Analysi" grade potassium dichromate supplied by E. Merck (Germany).

Phosphoric acid. Syrupy phosphoric acid of AnalaR grade supplied by British Drug Houses Limited (England) and syrupy phosphoric acid of "Pro Analysi" grade of E. Merck (Germany) have both been used successfully in this investigation. The potential break at the equivalence point with the B.D.H. phosphoric acid is about 35 mV and with the Merck phosphoric acid about 40 mV in the titration of 2–10 ml of about 0·1*M* vanadium^{IV} sulphate solution (diluted to 50 ml)/0·04 ml of 0·033*M* potassium dichromate solution.

Apparatus

The potentiometric assembly consists of a Cambridge potentiometer and a suspension galvanometer. A bright platinum rod electrode is used as indicator electrode and a saturated calomel electrode as reference electrode. The salt bridge consists of an inverted U-tube with porous end plates. The indicator electrode and reference electrode are connected through two salt bridges, one filled with saturated sodium perchlorate and the other filled with saturated sodium nitrate. The mixture is stirred during the titration by means of an electromagnetic stirrer.

Experiments have shown vanadium^{IV} to be quite stable in a strong phosphoric acid medium so that the titration of vanadium^{IV} with potassium dichromate can be made safely in air. It may be of interest to note in this connection that Del Fresno and Mairlot[15] carried out the titration of chromate in 6·0*M* sodium hydroxide solution at 70° with vanadium^{IV} sulphate solution, an inert atmosphere being maintained because of the sensitivity of quadrivalent vanadium in an alkaline medium.

Potentiometric Titration of Vanadium^{IV}

From 2 to 10 ml of 0·1*M* solution of vanadium^{IV} are taken in a 150-ml Pyrex beaker and treated with 40–50 ml of syrupy phosphoric acid (90%). The mixture is connected to the saturated calomel electrode through a saturated sodium perchlorate bridge and a saturated sodium nitrate bridge, then titrated with a standard solution of 0·033*M* potassium dichromate while it is stirred by means of an electromagnetic stirrer. Potentials are measured 1 min after the addition of each portion of the titrant using the potentiometric assembly already described. A typical potentiometric titration curve

(E *vs.* V) is given in Fig. 2. Because the potential break at the equivalence point is not very high, the equivalence point of the titration is better read from the curve obtained by plotting ΔE/ΔV against V. A representative curve of this type is shown in Fig. 3. A large number of titrations of vanadium^{IV} have been carried out in this manner and some typical results are given in Table I. The method enables vanadium^{IV} to be determined with an error not exceeding ±0·3%.

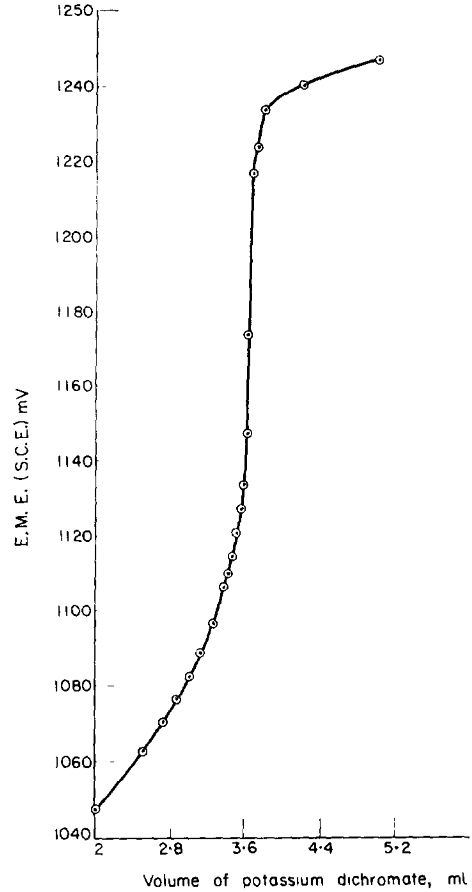

FIG. 2.—Potentiometric titration of vanadium^{IV} (37·32 mg) with 0·033*M* potassium dichromate in a 12*M* phosphoric acid medium.

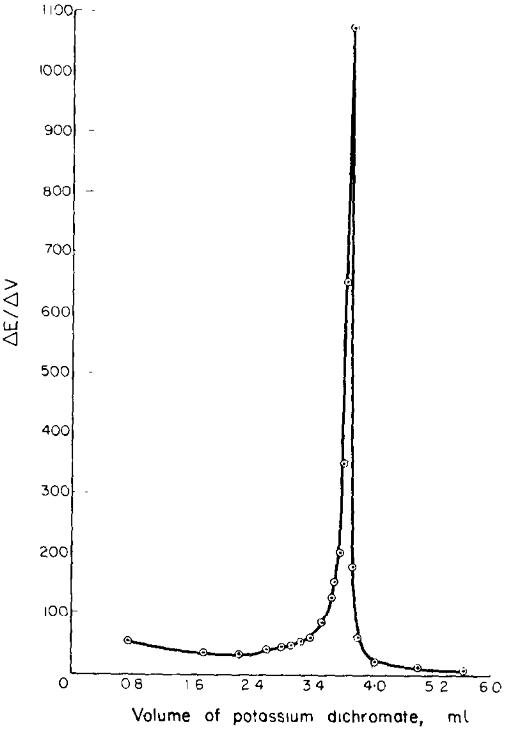

FIG. 3.—Potentiometric titration of vanadium^{IV} (37·32 mg) with 0·033*M* potassium dichromate in a 12*M* phosphoric acid medium.

If a higher break in potential is desired, the alternative procedure prescribed later in this paper may be followed.

Interferences

In the presence of chloride no potential break is found at the equivalence point. Nitrate interferes by slowly reacting with vanadium^{IV}. When the over-all concentration of nitrate is 0·5*M* and 1·0*M* the results are low by 1·7% and 2·5%, respectively. Iron^{II}, uranium^{IV}, molybdenum^{V}, tungsten^{V}, cerium^{III}, arsenic^{III}, antimony^{III} and manganese^{II} are also oxidised by potassium dichromate under the conditions proposed for the titration of vanadium^{IV}. Cobalt^{II}, cerium^{IV}, nickel^{II}, iron^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI} and chromium^{III} do not interfere as can be seen from Table II. Calcium, aluminium, and magnesium also do not interfere. Sulphuric and perchloric acids do not interfere even up to an over-all 1*N* concentration.

TABLE I.—POTENTIOMETRIC TITRATION OF VANADIUM^{IV} WITH POTASSIUM DICHROMATE IN A 12*M* PHOSPHORIC ACID MEDIUM

Vanadium^{IV} taken, *mg*	Vanadium^{IV} found, *mg*
12·53	12·51
19·23	19·23
22·75	22·80
28·39	28·46
33·43	33·53
38·46	38·46
45·10	45·17
49·33	49·39

Differential Potentiometric Titration of a Mixture of Iron^{II} and Vanadium^{IV}

Willard and Young[5] achieved the differential potentiometric assay of iron^{II} and vanadium^{IV} with cerium^{IV} sulphate by titrating the mixture first at 5–10°, then at 70–75°. The first break in potential corresponds to iron^{II} and the second break to vanadium^{IV}. Furman[6] published a somewhat similar procedure almost simultaneously. The first part of the titration with cerium^{IV} sulphate is recommended to be carried out at room temperature and the second part at 50–60°. However, the method has the disadvantage that the first break in potential is very low. Gopala Rao and Dikshitulu[7] reported the simultaneous differential titration of iron^{II} and vanadium^{IV} in a 0·5–1.0*M* sulphuric acid medium with cerium^{IV} sulphate at room temperature using a small quantity of orthophosphoric acid as a catalyst for the oxidation of vanadium^{IV} by cerium^{IV} sulphate. They found that the potential breaks are about 60–70 mV and 55–65 mV/0·05 ml of 0·05*M* cerium^{IV} sulphate for the oxidation of iron^{II} and vanadium^{IV}, respectively.

TABLE II

Addenda	Amount added, *mg*	Vanadium^{IV} found,[a] *mg*
Cobalt^{II}	33	37·20
Cobalt^{II}	66	37·20
Nickel^{II}	19	37·20
Nickel^{II}	38	37·20
Iron^{III}	27	37·20
Iron^{III}	56	37·20
Molybdenum^{VI}	48	37·20
Molybdenum^{VI}	96	37·26
Tungsten^{VI}	55	37·20
Tungsten^{VI}	110	37·28
Uranium^{VI}	58	37·20
Uranium^{VI}	116	37·11
Chromium^{III}	20	37·20
Tungsten^{VI} Iron^{III}	55 27	37·29
Cobalt^{II} Nickel^{II}	33 19	37·20
Cerium^{IV}	70	37·20

[a] 37·20 mg of vanadium^{IV} taken.

When one attempts the titration of a mixture of iron^{II} and vanadium^{IV} with potassium dichromate in a strong phosphoric acid medium, two different cases arise, firstly when the iron^{II} is in excess of vanadium^{IV} (Case I) and secondly when the amount of iron^{II} is less than that of the vanadium^{IV} (Case II). Vanadium^{IV} is reduced to vanadium^{III} by iron^{II} as soon as phosphoric acid is added, as already reported by Gopala Rao and Dikshitulu,[16] so that in Case I there will be a mixture of vanadium^{III}, iron^{II} and iron^{III} and in Case II there will be a mixture of vanadium^{III}, vanadium^{IV}

and iron^{III}. Because iron^{II} is unstable to atmospheric oxygen in a strong phosphoric acid medium, strict precautions should be taken to see that in all experiments corresponding to Case I, the phosphoric acid is added only after all atmospheric oxygen is driven off by a strong current of carbon dioxide, which is also maintained during the subsequent titration. The titrations should also be made with a solution of potassium dichromate which is free from dissolved oxygen. In titrations of Case I, three potential breaks have been observed, the first corresponding to the oxidation of iron^{II} to iron^{III}, the second corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the third corresponding to the further oxidation of vanadium^{IV} to vanadium^{V}. When the amount of iron^{II} (Case II) is less than that of vanadium^{IV}, an amount of vanadium^{III} equivalent to that of iron^{II} is formed. Only two breaks are observed, the first corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the second corresponding to the oxidation of vanadium^{IV} to vanadium^{V}. An advantage with these systems is that it is not necessary to maintain an inert atmosphere, because the vanadium^{III} formed is resistant to atmospheric oxidation for the duration of a titration. The results presented in Table III show that the error is $\pm 0{\cdot}4\%$ for the iron^{II} determination and $\pm 0{\cdot}3\%$ for the vanadium^{IV} determination. Figs. 4 and 5 give potentiometric titration curves typical of Cases I and II, respectively. The potential at the first equivalence point attains a steady value only after 8 min, in titrations corresponding to Case I. After the first break is obtained the potentials are noted 2 min after each addition of potassium dichromate solution. After the second break the potentials are noted 1 min after each addition of potassium dichromate solution. The first break in potential amounts to about 120 mV, the second to about 200 mV, and the third to about 40 mV/0·04 ml of 0·033*M* potassium dichromate solution, when the total volume of titration mixture is about 50 ml. Because the potential break for vanadium^{IV} oxidation is not very high, a plot of $\Delta E/\Delta V$ *vs.* V is also given for the vanadium^{IV} part of the titration in Figs. 4 and 5.

TABLE III.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND VANADIUM^{IV} WITH POTASSIUM DICHROMATE IN A 12*M* PHOSPHORIC ACID MEDIUM

Iron^{II}, *mg*		Vanadium^{IV}, *mg*			
			Found		
Taken	Found	Taken	From second break	From third break	Remarks
8·527	8·56	24·36	24·30	—	Iron^{II} content less than that of vanadium^{IV}; hence titrations carried out in presence of air.
14·70	14·70	41·12	41·06	—	
14·92	14·98	30·20	30·13	—	
18·09	18·14	18·62	18·67	—	
22·44	22·39	40·27	40·17	—	
22·68	22·68	30·21	30·21	—	
34·85	34·79	22·47	22·52	22·52	Iron^{II} content greater than that of vanadium^{IV}; hence titrations carried out in carbon dioxide atmosphere.
37·92	37·81	26·04	26·04	26·04	
50·49	50·27	33·62	33·52	33·42	
56·10	55·88	37·25	37·25	37·25	

Alternative Procedure for Potentiometric Titration of Vanadium^{IV}

In the procedure described above, it has been noted that during the potentiometric titration of vanadium^{IV} in a 12*M* phosphoric acid medium, the potential jump at the inflection point is about 40 mV/0·04 ml of 0·033*M* potassium dichromate solution. If a more satisfactory jump is desired, one can resort to the expediency of adding an amount of iron^{II} sulphate in excess of that required for reducing vanadium^{IV} to vanadium^{III}. Gopala Rao and Dikshitulu[16] have already reported that vanadium^{IV} is quantitatively reduced by iron^{II} in a strong phosphoric acid medium. Thus, when an excess of iron^{II} is added to vanadium^{IV} in a strong phosphoric acid medium, the mixture will contain unreacted iron^{II}, vanadium^{III} and iron^{III}. If this mixture is titrated with potassium dichromate solution, three inflections will be observed in the titration curve, the first corresponding to the oxidation of iron^{II} to iron^{III}, the second corresponding to the oxidation of vanadium^{III} to vanadium^{IV} and the third corresponding to the oxidation of vanadium^{IV} to vanadium^{V}. Because one is interested only in the determination of vanadium^{IV}, the exact amount of iron^{II} added does not matter, provided it is somewhat in excess of vanadium^{IV} and the titration can also be carried out under ordinary atmospheric conditions. The advantage of this procedure for vanadium^{IV} is twofold. Firstly, the inflection corresponding to the oxidation of vanadium^{III} to vanadium^{IV} is about

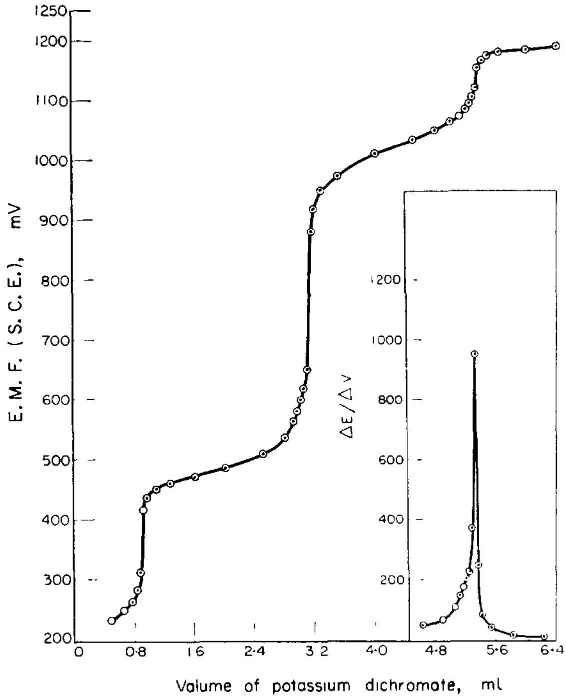

FIG. 4.—Differential potentiometric titration of a mixture of iron^{II} (34·85 mg) and vanadium^{IV} (22·47 mg) with 0·033*M* potassium dichromate in a 12*M* phosphoric acid medium (Case I).

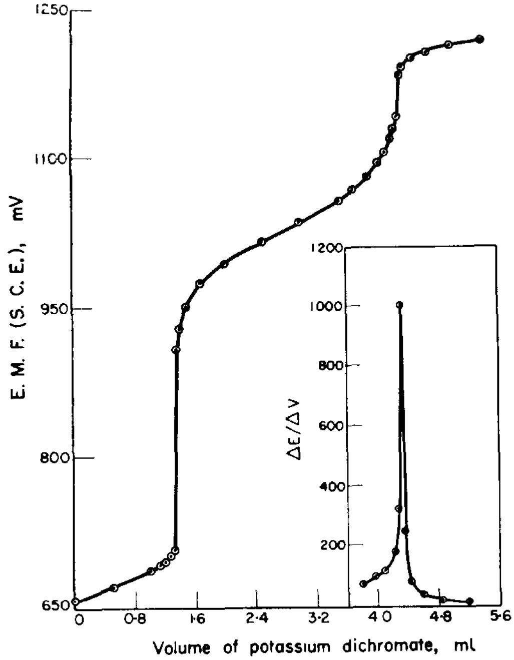

FIG. 5.—Differential potentiometric titration of a mixture of iron^{II} (14·92 mg) and vanadium^{IV} (30·20 mg) with 0·033*M* potassium dichromate in a 12*M* phosphoric acid medium (Case II).

200 mV/0·04 ml of 0·033*M* potassium dichromate solution; secondly, the last part of the titration (corresponding to the oxidation of vanadium^{IV} to vanadium^{V}) gives a check on the determination of vanadium. A large number of assays of vanadium^{IV} according to the above alternative procedure indicates that the error for vanadium^{IV} is not greater than ±0·3%.

Differential Potentiometric Titration of a Mixture of Vanadium^{IV} and Manganese^{II}

When a mixture of vanadium^{IV} and manganese^{II} is titrated with potassium dichromate in a 12*M* phosphoric acid medium only one potential break is observed, vanadium^{IV} and manganese^{II} reacting simultaneously with the oxidant. However, this difficulty can be overcome by the expediency of adding an excess of iron^{II} sulphate solution. When an amount of iron^{II} greater than required to reduce vanadium^{IV} to vanadium^{III} is added to a mixture of vanadium^{IV} and manganese^{II} in 12*M* phosphoric acid and the mixture titrated in air with potassium dichromate, three different breaks are obtained. The first inflection corresponds to the oxidation of unreacted iron^{II} to iron^{III}, the second inflection corresponds to the oxidation of vanadium^{III} to vanadium^{IV} and the third inflection corresponds to the simultaneous oxidation of vanadium^{IV} and manganese^{II} to vanadium^{V} and manganese^{III}, respectively. In titrations conducted with 0·033*M* potassium dichromate solution, the jump at the first inflection point is found to be about 120 mV/0·04 ml of the titrant, the jump at the second inflection point is found to be about 200 mV/0·04 ml of the titrant and the jump at the third inflection point is found to be about 25 mV/0·04 ml of the titrant. In view of the small break, the third inflection point is better obtained from the $\Delta E/\Delta V$ *vs.* V curve. The amount of dichromate added between the first and second inflections corresponds to the amount of vanadium^{III} (or vanadium^{IV}). The amount of dichromate between the third and second inflections corresponds to vanadium^{IV} plus manganese^{II}. Hence the amount of manganese^{II} can also be calculated. Some typical results are given in Table IV. They show that vanadium^{IV} and manganese^{II} can be determined with an error not exceeding ±0·3% and ±0·4%, respectively.

TABLE IV.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF VANADIUM^{IV} AND MANGANESE^{II}

Vanadium^{IV}, *mg*		Manganese^{II}, *mg*	
Taken	Found	Taken	Found
15·20	15·18	21·74	21·75
13·21	13·24	19·97	20·04
22·75	22·81	36·25	36·39
24·70	24·77	26·14	26·14
31·32	31·26	29·19	29·30
24·10	24·17	17·69	17·69

Differential Potentiometric Titration of a Mixture of Iron^{II}, Manganese^{II} and Vanadium^{IV}

When it is desired to assay a mixture for iron^{II}, vanadium^{IV} and manganese^{II}, it is desirable to carry out the potentiometric titration under the conditions described for the assay of a mixture of iron^{II} and vanadium^{IV}, having the iron^{II} in excess. If in the experimental mixture, the amount of iron^{II} is actually less than that required for the reduction of vanadium^{IV}, it is necessary to add a known amount of iron^{II} to the mixture and allow for the same in the calculations. Table V gives some typical results, showing that iron^{II}, vanadium^{IV} and manganese^{II} can be determined in the same solution with an error not exceeding ±0·45%, ±0·3% and ±0·4%, respectively.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II}, VANADIUM^{IV} AND MANGANESE^{II}.

Iron^{II}, *mg*		Vanadium,^{IV} *mg*		Manganese^{II}, *mg*	
Taken	Found	Taken	Found	Taken	Found
32·72	32·60	15·20	15·18	21·74	21·75
48·23	48·07	13·21	13·24	19·97	20·04
38·75	38·58	22·75	22·81	36·25	36·39
50·20	49·98	24·70	24·77	26·14	26·14
50·13	49·91	31·32	31·26	29·19	29·30
63·53	63·31	24·10	24·17	17·69	17·69

Analytical Applications

Determination of vanadium in ferrovanadium

About 3 g of the alloy (dried at 110°) are decomposed in a platinum dish with a mixture of 60 ml of sulphuric acid (1:3) and 25 ml of nitric acid (1:1) and any silica is expelled by heating with hydrofluoric acid to dryness. The residue is treated with a mixture of sulphuric and nitric acids and evaporated until copious fumes of sulphuric acid are evolved. After cooling, the solution is made up to 250 ml in a volumetric flask. To 10 ml of this solution 50 ml of syrupy phosphoric acid (90%) are added and treated with a slight excess of iron^{II} sulphate, which reduces the vanadium^{V} to vanadium^{III}. The mixture is then titrated potentiometrically with $0{\cdot}033M$ potassium dichromate solution. The first break in potential may be neglected. The volume of titrant between the first and second breaks corresponds to that required for the oxidation of vanadium^{III} to vanadium^{IV} and that between the second and third breaks to the oxidation of vanadium^{IV} to vanadium^{V}.

Determination of vanadium in chrome-vanadium-tungsten steel

About 2 g of the steel are taken in a 250-ml Pyrex beaker, treated with 15 ml of water, 10 ml of syrupy phosphoric acid (90%) and 6 ml of concentrated sulphuric acid, and gently heated to decompose the steel completely; then 3 ml of concentrated nitric acid are added and the solution evaporated to fumes of sulphuric acid. The solution is cooled and made up to 100 ml in a volumetric flask. A 15-ml portion of this solution is taken in a beaker, treated with enough phosphoric acid so that the over-all concentration is $12M$, then with enough iron^{II} solution to reduce the vanadium^{V} to vanadium^{III}. The mixture is finally titrated potentiometrically with $0{\cdot}033M$ potassium dichromate. Results of some typical analyses are presented in Table VI.

TABLE VI.—ANALYSIS OF VANADIUM IN ALLOYS

Sample	Vanadium found by present method, %	Vanadium found[7] using cerium^{IV}, %
Ferrovanadium	31·20, 31·09, 31·18	31·19, 31·12, 31·08
	Av. 31·16	Av. 31·13
Chrome-vanadium-tungsten steel	2·88, 2·89	2·89, 2·88
	Av. 2·885	Av. 2·885

Acknowledgement—One of us (P. K. R.) desires to thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Die Ergebnisse von Untersuchungen werden vorgelegt, die zur Entwicklung eines Verfahrens zur titrimetrischen Bestimmung von Vanadin^{IV} mit Kaliumdichromat führten, und zwar in starker Phosphorsäure ($>12M$) bei Zimmertemperatur mit potentiometrischer Endpunktsanzeige. Cer^{IV}, Eisen^{III}, Chrom^{III}, Wolfram^{VI}, Molybdän^{VI}, Uran^{VI}, Kobalt^{II} und Nickel^{II} stören nicht. Es wurden auch Methoden entwickelt zur gleichzeitigen potentiometrischen Titration von Eisen^{II} und Vanadin^{IV}, Mangan^{II} und Vanadin^{IV}, sowie Eisen^{II}, Mangan^{II} und Vanadin^{IV} in derselben Lösung. Das neue Reagens hat daher verschiedene Vorteile vor Kaliumpermanganat und Cer^{IV}-Sulfat. Die Anwendung des neuen Reagens zur Analyse einer Ferrolegierung und eines legierten Stahls wird ebenfalls erörtert.

Résumé—On présente les résultats d'études conduisant au développement d'une méthode de dosage volumétrique du vanadium (IV) au moyen de bichromate de potassium en milieu acide phosphorique concentré ($>12M$) à température ambiante, avec détermination potentiométrique du point de virage. Les cérium (IV), fer (III), chrome (III), tungstène (VI), molybdène (VI), uranium (VI), cobalt (II) et nickel (II) n'interfèrent pas. On a également développé des méthodes de dosage potentiométrique différentiel pour fer (II) avec vanadium (IV), manganèse (II) avec vanadium (IV), et fer (II) avec manganèse (II) et vanadium (IV) dans la même solution. Le nouveau réactif possède

ainsi plusieurs avantages sur le permanganate de potassium et le sulfate de cérium (IV). On considère aussi l'application du nouveau réactif à l'analyse d'un alliage de fer et d'un alliage d'acier.

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PRELIMINARY COMMUNICATION

Silver^{II} in aqueous perchlorate solutions

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BECAUSE of its potential usefulness as a powerful homogeneous oxidising agent, silver^{II} is of considerable interest to analytical chemists. A few analytical applications of silver^{II} as an oxidising agent have already been reported,[1-3] but relatively little is known concerning the characteristics and behaviour of silver^{II} as a solution species. Apart from a comprehensive review by McMillan[4] on the higher oxidation states of silver, a recent optical and kinetic study of silver^{II} in aqueous solution, reported by Kirwin *et al.*,[5] is particularly noteworthy.

The present investigation was undertaken to examine the absorption spectra of silver^{II} from the analytical standpoint and, if possible, to gain some information on the nature of silver^{II} species in aqueous perchlorate media.

EXPERIMENTAL

Silver^{II} oxide of 98·5% minimum purity was obtained from Handy and Harman Company, New York, U.S.A.; perchloric acid, silver^{I} perchlorate, and sodium perchlorate (all reagent-grade) from G. F. Smith Chemical Company, Columbus, Ohio, U.S.A. Spectra were recorded using a Beckman Model DB ultraviolet-visible spectrophotometer equipped with matched quartz cells held at 10·00 ± 0·15°. Solid silver^{II} oxide was dissolved in pre-cooled solvent and pipetted directly into the thermostatted spectrophotometer cell. Decomposition rates were determined from slopes of absorbance-time curves recorded at 475 mμ, and rate constants were calculated using standard kinetic techniques.

RESULTS AND DISCUSSION

Ultraviolet and visible spectra of silver^{II} in perchloric acid solutions revealed a previously unknown maximum at 265 mμ, as well as the 475-mμ peak reported by Kirwin *et al.*[5] The effect of perchloric acid concentration on the 265-mμ and 475-mμ peaks was investigated in the 6–11·5*M* range, and showed a steady (roughly three-fold) increase in the ratio of absorbance at 265 mμ to that at 475 mμ over the range studied. No isosbestic point was found, however, suggesting that silver^{II} is appreciably complexed by perchlorate and that at least three different solution species of silver^{II} are involved.

Kinetic experiments for the decomposition of silver^{II} at constant acidity and ionic strength yielded an empirical rate law second order in silver^{II} and inverse first order in silver^{I} concentration, with an over-all activation energy of 11·6 Kcal/mole. These findings are in complete agreement with the results of Kirwin *et al.*,[5] who suggest a rate-determining step of the type

$$2\,Ag^{II} \rightleftarrows Ag^{I} + Ag^{III}.$$

If this disproportioning step is, in fact, rate-determining, the equilibrium must be strongly shifted to the left, and absorbance studies at zero time should show that silver^{II} obeys Beer's law. Plots of reciprocal absorbance *versus* time were, therefore, constructed from decomposition rate experiments carried out with no silver^{I} initially present. The resulting straight lines were extrapolated to zero time, and the corresponding absorbance values were plotted against initial silver^{II} concentrations. These plots showed that silver^{II} does obey Beer's law, and indicate that the steady-state concentration of silver^{III} must indeed be small compared with the concentration of silver^{II}.

Efforts are in progress to determine the stoichiometry and formation constants of the silver^{II} perchlorate complexes observed, and to elucidate the role of higher oxidation states of silver in several reactions of analytical interest.

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Summary—Spectrophotometric and kinetic studies show that silver^{II} is complexed by perchlorate in aqueous solutions and that such silver^{II} species obey Beer's law when decomposition kinetics are taken into account.

Zusammenfassung—Silber(II) in wäßrigen Perchloratlösungen. Spektralphotometrische und kinetische Untersuchungen zeigen Komplexbildung zwischen Silber(II) und Perchlorat in wäßrigen Lösungen. Wenn man die Kinetik der Zersetzung in Rechnung stellt, gehorcht dieses komplex gebundene Silber(II) dem Beerschen Gesetz.

Résumé—Des études spectrophotométriques et cinétiques montrent que l'argent (II) est complexé par le perchlorate, en solution aqueuse, et que de tels composés de l'argent (II) obéissent à la loi de Beer lorsqu'on prend en considération les cinétiques de décomposition.

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SHORT COMMUNICATIONS

Absorptiometric determination of indium with Thorin

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IT has already been shown that microgram quantities of indium interfere seriously in the absorptiometric determination of bismuth with Thorin [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzenearsonic acid] or its disodium salt in 0·02*M* perchloric acid.[1] Consequently, it was decided to examine the use of Thorin as an absorptiometric reagent for indium.

EXPERIMENTAL

Apparatus

Spectrophotometer: Beckman Model B, with 1-cm Pyrex cells.

pH meter: Beckman Model 76, with Type E-2 glass electrode.

Reagents

Thorin: Supplied as its disodium salt by J. T. Baker Chemical Co., U.S.A. (Analysed Reagent). It was used without further purification as a 0·1% aqueous solution.

Standard indium solution: Indium metal ("Spec-pure", Johnson Matthey & Co., England) was dissolved in the smallest possible amount of analytical-reagent grade acid (perchloric, hydrochloric or sulphuric) and made up to the appropriate final volume with distilled water. All other solutions were prepared from analytical-reagent grade materials.

Effect of variables on colour development

Preliminary tests showed that indium and Thorin form a red-orange compound in moderately acidic solution or a red precipitate when indium is in a great excess. The reagent blank solution is yellow under such conditions. The absorption spectra of the indium–Thorin complex obtained at different hydrogen ion concentrations, using the corresponding reagent blank as reference, indicated an absorption maximum at about 520–525 mμ with an inflection around 490 mμ. The wavelength of the absorption peak remains constant with pH but the sensitivity is markedly pH dependent. The value of the absorbance at the wavelength of the absorption peak remains practically constant between pH 3·0 and 5·0, but decreases considerably at higher or lower pH. No difference in absorption from the blank was observed at a pH lower than 1·5 or higher than 6·0.

The colour is formed rapidly and is stable up to 150 μg of indium/25 ml. The absorbance decreases about 0·5% after standing for 48 hr at room temperature (solutions exposed to daylight and/or fluorescent light). Indium concentrations higher than 150 μg/25 ml gave non-reproducible results with absorbance falling off with time. This behaviour is considerably pronounced above 200 μg of indium/25 ml.

The colour may be developed either in perchloric, sulphuric or hydrochloric acid. The absorption spectra obtained are similar. Nitric acid must be free from nitrogen oxides if used to provide the acid medium. The sensitivity in hydrochloric acid is somewhat lower than in perchloric acid or sulphuric acid. Sensitivity values expressed as proposed by Sandell[2] are 0·022 μg of indium/cm^2 for log Io/I = 0·001 in perchloric acid or sulphuric acid (plus sodium hydroxide to obtain a pH of *ca.* 3·5). It was observed that the reproducibility is increased if Thorin is added in an acidic medium (pH *ca.* 2), the solution made basic (pH $\geqslant$ 9), then the pH adjusted to the desired value with dilute acid.

The spectra of solutions with different ratios of reagent to metal were measured against reagent blanks and at varying pH. No isobestic point was observed. The absorption spectrum of the indium-Thorin complex at pH *ca.* 3·5 is shown in Fig. 1. Higher concentrations of Thorin than the recommended $1{\cdot}4 \times 10^{-4}M$ do not increase the sensitivity appreciably; this concentration was chosen to limit the blank.

The effect of Thorin concentration on the absorbance of the indium-Thorin complex at 520 mμ showed that a concentration near $1{\cdot}4 \times 10^{-4}M$ seems to be the most suitable for photometric measurements.

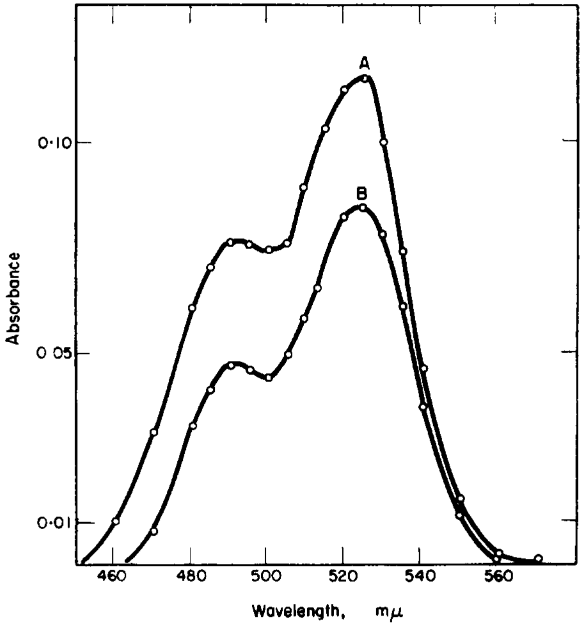

FIG. 1.—Absorption spectrum of indium-Thorin complex (pH *ca.* 3·5, with pH adjustment according to *Procedure*; perchloric acid-sodium perchlorate medium; 1-cm cell; 0·07–0·12 mm slit width; reagent blank as reference)
(A) 1·4 × $10^{-4}M$ Thorin and 0·24 × $10^{-4}M$ indium,
(B) 0·35 × $10^{-4}M$ Thorin and 0·24 × $10^{-4}M$ indium.

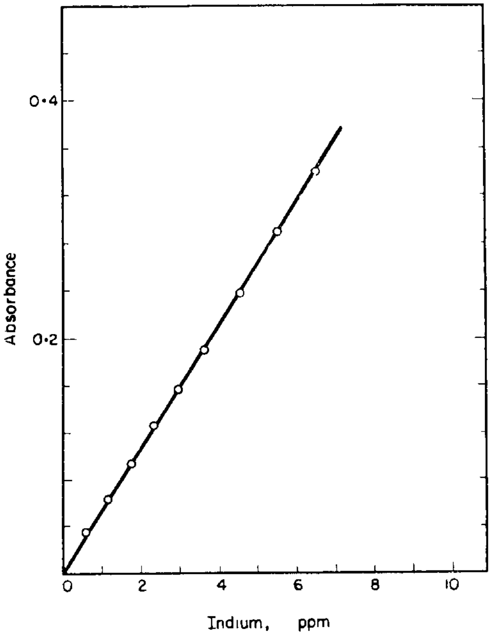

FIG. 2.—Calibration curve for determination of indium with Thorin (1·4 × $10^{-4}M$ Thorin pH *ca.* 3·5; perchloric acid-sodium perchlorate medium; 520 mμ; 0·1 mm slit width; reagent blank as reference)

Under the experimental conditions reported here the absorbance is proportional to the indium concentration from approximately 15 to 150 μg of indium/25 ml (0·6 to 6 ppm). The average of 10 determinations in pure solution run according to the directions given in the *Procedure* was 100·1 (standard deviation 1·3) for 100 μg of indium/25 ml, and 15·5 (standard deviation 1·5) for 15 μg of indium/25 ml.

A Ringbom plot[3] of the data in Fig. 2 shows that the concentration range for the highest accuracy lies between 2·5 and 6 ppm. From least square calculation, the molar absorptivity (based on indium) is 6,100 at 520 mμ.

The great variation in absorbance with time and the poor reproducibility of results when the indium concentration is higher than 150 μg/25 ml do not allow the determination of the molar ratio indium: Thorin by known methods.[4,5] Consequently, the use of the reaction in photometric titrations gives poor results.

The foreign species which interfere in the determination of bismuth with Thorin[1] are expected to interfere in this determination of indium. It may be noted that gallium under similar conditions and at 520 mμ shows a sensitivity value of 0·015 μg of gallium/cm[2] for log Io/I = 0·001. Lead interferes above 25 μg/25 ml. Bismuth does not interfere up to 0·25 mg/25 ml. As much as 10 mg of thallium[1] failed to show interference.

Procedure

Transfer the acidic solution, containing 15–140 μg of indium, to a 100-ml beaker. The volume of the solution must be less than 18 ml. Add 2 ml of 0·1% Thorin solution, then 10% sodium hydroxide solution dropwise until the colour changes to red. Adjust the pH to *ca.* 3·5 (pH meter) by adding drops of a dilute solution of acid. Transfer to a 25-ml volumetric flask, make up to volume with distilled water and measure the absorbance at 520–525 mμ against a reagent blank solution as reference. Prepare a standard curve from known amounts of indium following the same procedure.

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Summary—2-(2-Hydroxy-3,6-disulpho-1-naphthylazo)-benzene-arsonic acid (Thorin) is proposed as a chromogenic agent for indium. Optimum conditions for the colour development have been established and a simple, sensitive and precise absorptiometric method for 15–140 μg of indium is described.

Zusammenfassung—Das organische Reagens 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo-) benzolarsonsäure (Thorin) ist ein nützliches Farbreagens auf Indium. Die optimalen Bedingungen für die Farbreaktion wurden ermittelt und eine einfache, empfindliche und genaue absorptiometrische Bestimmungsmethode für 15 bis 140 μg Indium wird beschrieben.

Résumé—Le réactif organique: acide 2-(2-hydroxy-3,6-disulfo-1-naphtylazo) benzènearsonique (Thorin) est un agent chromogène utile pour l'indium. On a établi les conditions optimales de développement de la couleur, et on décrit une méthode absorptiométrique simple, sensible et précise pour 15 à 140 μg d'indium.

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Spot tests for chlorate, bromate and iodate in admixture

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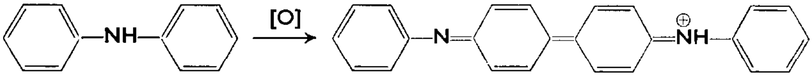
THE three halates, chlorate, bromate and iodate, are well known primary standard reagents in analytical chemistry. Selective identification methods for them are usually based on the difference between the three oxidation potentials. Clear-cut differentiation is, however, difficult, and we propose new selective reactions utilising the potential difference of the three halates in oxidising three different organic compounds. The colour reactions described here are selective for each of the halates in the presence of the remaining two.

Detection of Chlorate

It has recently been found[1] that diphenylamine in suitable media (ethyl acetate and trichloracetic acid) shows selective properties towards oxidising material. Thus, it is oxidised by elementary chlorine, but not by bromine or iodine, to the meriquinoidal diphenylbenzidine blue:



It was expected that chlorine dioxide might behave in the same manner. Indeed, when concentrated sulphuric acid acts on chlorate (solid or in solution), the evolved gas (chlorine dioxide) oxidises diphenylamine. Bromate and iodate were tested for the same reaction, but gave negative results. Because neither gives a dioxide by the action of concentrated acid and the bromine slightly liberated from the bromate does not oxidise diphenylamine, the reaction between chlorine dioxide liberated from the chlorate and diphenylamine is specific for the latter in the group of the halates.

Horovka and Holzbecher[2] proposed a method also involving the liberation of chlorine dioxide for detecting chlorate. The reagent used by them, benzidine acetate, is, however, oxidised not only by the chlorine dioxide but also by the bromine liberated by the action of concentrated acid on the bromate, which prevents the detection of chlorate in the presence of bromate by this method.

Procedure

One drop of the test solution is mixed with 1 drop of concentrated sulphuric acid in a micro test tube and immersed in a boiling water bath. A disk of filter paper is moistened with freshly prepared diphenylamine reagent solution and placed over the tube. The appearance of a green fleck within a few min is indicative of the presence of chlorate. Even large quantities of the other halates and perhalates do not interfere.

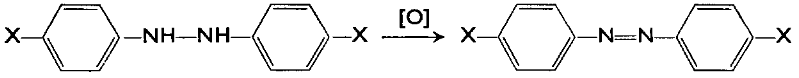
Diphenylamine reagent solution. To 10 ml of a saturated solution of diphenylamine in ethyl acetate, *ca.* 0·5 g of solid trichloracetic acid is added.

Limit of identification: 3 μg of chlorate.

Detection of Bromate

It is well known that the oxidation potential of bromate is higher than either that of chlorate or iodate. Bearing this fact in mind, a reagent was sought which would be oxidised by the compound with the higher potential, *i.e.*, by bromate alone.

It was found that aromatic amines, which contain an acidic group in the *p*-position, are oxidised selectively by bromate in nitric acid to a violet-blue compound which is subsequently transformed to a yellowish-brown colour. The oxidation probably proceeds via a hydrazo intermediate to the azo compound:



Chlorate and iodate in the same conditions give negative results. This reaction can be carried out by sulphanilic acid, arsanilic acid and *p*-amino-benzoic acid.[3]

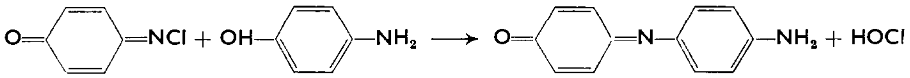
Procedure

To 1 drop of the test solution, 2 drops of 6*M* nitric acid are added and mixed in a micro test tube with 1 drop of a saturated aqueous solution of sulphanilic acid. The appearance of a violet colour within a few min is a positive response for the presence of bromate. This violet colour slowly changes to brown. None of the other halates and perhalates interferes.

Limit of identification: 0·5 μg of bromate.

Detection of Iodate

A mixture of quinonechlorimide and *p*-aminophenol gives a blue-violet indamine dye:



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The hypochlorite liberated by this condensation can easily be detected as chlorine in the gas phase. *p*-Aminophenol can be oxidised to quinonimine which subsequently condenses with any remaining unchanged *p*-aminophenol. Thus, mild oxidants will give the coloured indamine dye similar to I with *p*-aminophenol, while strong oxidants convert it wholly to the colourless quinone via the quinonimine intermediate. This is the reason for the absence of a colour reaction in the case of bromate and chlorate, while the weaker oxidising agent iodate[4] yields the indamine dye on the partial oxidation of *p*-aminophenol. Minute quantities of periodate interfere, because they give the same reaction.

Procedure

To 1 drop of the test solution 1 drop of *p*-aminophenol reagent is added in a micro test tube. A violet colour appearing within a few min is a positive response for iodate. The other halates do not interfere, but periodate must be absent.

p-Aminophenol reagent solution. A 5% *p*-aminophenol chloride aqueous solution is used, and it should be nearly colourless.

Limit of identification: 0·5 μg of iodate.

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Summary—Detection by selective spot tests for each of the halates, chlorate, bromate and iodate, is detailed.

Résumé—Des réactions à gouttes sont données pour la détection de chacun des halates (chlorate, bromate et iodate).

Zusammenfassung—Selektive Tüpfelreaktionen für die Nachweise von den verschiedenen Halate(Chlorat, Bromat und Jodat) sind beschrieben.

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ION EXCHANGE IN NON-AQUEOUS SOLVENTS

ADSORPTION BEHAVIOUR OF URANIUM AND OTHER ELEMENTS ON STRONG-BASE ANION-EXCHANGE RESIN FROM ORGANIC ACID-ORGANIC SOLVENT MEDIA

METHODS FOR THE SEPARATION OF URANIUM

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Summary—In the present paper the anion-exchange behaviour of hexavalent uranium and of a number of other elements in organic solvents containing organic acids is described. The solvents employed include aliphatic alcohols, acetone and dioxan. As organic acids the monocarboxylic acids, *i.e.*, formic, acetic and propionic acid, and also chloro-derivatives of acetic acid, have been investigated. Through the determination of the distribution coefficients and separation factors in the various media, separation methods for uranium from other elements have been developed.

INTRODUCTION

Investigations of the isolation of uranium, and its separation from other elements by employing anion-exchange resins in combination with monocarboxylic acids acting as complexing agents for uranium, have been carried out in the past.[1–9] For this purpose, buffered aqueous solutions of acetic acid[1–5] were successfully employed. Similar experiments performed in buffered solutions of monochloro- and trichloro acetic acid did not, however, give promising results.[1] But ascorbic acid proved to be a valuable complexing agent for uranium and a series of other elements.[6–9]

In continuation of work on the ion-exchange behaviour of uranium and thorium in mixed and non-aqueous solvents,[10–13] the use of some organic acids in combination with various organic solvents, has now been investigated for the separation of uranium from other elements. Previous results using mineral acid-organic solvent mixtures showed that a great increase of adsorption could be observed by employing organic solvents in place of water. The next logical step was to investigate the adsorption behaviour of uranium and other elements in the presence of both organic acid and solvent. In the conditions selected, similar results were obtained to those when using mineral acids, *e.g.*, hydrochloric, nitric or sulphuric acids.

The experimental conditions selected and the results obtained in organic acid-organic solvent mixtures, using the strongly basic anion-exchanger Dowex 1, are here reported.

EXPERIMENTAL

Reagents

Ion-exchange resin: That used was the strongly basic anion-exchanger Dowex 1, ×8 (100–200 mesh, chloride form). For the equilibrium and separation experiments in organic acid-organic

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solvent solutions, the resin was transformed into the corresponding organic acid forms, *i.e.*, the formate, acetate, monochloroacetate, dichloroacetate, trichloroacetate (this form of the resin slowly decomposed into the carbonate form and chloroform; see also page 740) and propionate forms. This was done by treating the chloride form of the resin with an aqueous solution of the acid in question, in the presence of an excess of its ammonium salt. This treatment, which should preferably be carried out on an ion-exchange column, was continued until no more chloride ions could be detected in the effluent. Thereafter, the resin was thoroughly washed with distilled water in order to remove the excess of the organic acid and its salt. (For the column separations the resin was then treated with the corresponding solution used for pretreatment; see also *Column operations*). Then the resin was washed with methanol and dried in air.

Standard solutions of uranium and other elements: Hydrochloric- or nitric acid solutions of the chlorides or nitrates, of exactly known element content, were employed. For each individual experiment an aliquot portion corresponding to the desired amount of the element to be tested was evaporated to dryness on a water-bath, and the residue was dissolved in the organic acid.

Organic acids: The following reagent-grade acids were employed: formic acid, acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid and propionic acid.

Organic solvents: The following reagent-grade solvents were employed: methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, acetone and dioxan.

Apparatus

Ion-exchange columns: The column operations were carried out in columns of the same type and dimensions as described earlier.[5]

Spectrophotometer: For the spectrophotometric determination of all elements investigated with the exception of uranium, which was determined fluorometrically, the Beckman Model B spectrophotometer was employed.

Fluorimeter: The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

Quantitative determinations

Determination of uranium: The quantitative determination of uranium in the eluates or filtrates (after removal of the resin by filtration) was usually performed fluorimetrically by means of a procedure described by Schönfeld, El Garhy, Friedmann and Veselsky.[14] Polarographic[2] or spectrophotometric methods, as described previously,[15,16] were also employed.

Determination of other elements: The most suitable and accurate photometric procedures described by Sandell[17] and Snell and Snell[18] were used. For the determination of lanthanum and gadolinium, representing the rare earths, a spectrophotometric method employing the azo dye Solochromate Fast Red was used.[12]

Determination of distribution coefficients

The distribution coefficients given by the equation

$$\text{Distribution coefficient} = \mathrm{K_d} = \frac{\mu\text{g element/g of resin}}{\mu\text{g element/ml of solution}}$$

were determined employing the batch equilibrium method (batch method).[10–13,19–28] Each $\mathrm{K_d}$-value for uranium, shown in Figs. 2, 5, 6, 8, 9 and 11, was obtained by equilibrating 1 g of the resin with 10 ml of solvent + 0–4 ml of acid (or 0–4 g of acid if solid) containing 10 mg of uranium. In the case of the results recorded in Figs. 1, 4, 7 and 10, varying ratios of solvent to liquid acid, with a constant volume of 10 ml of mixture, were used. The distribution coefficients for the other elements (see results shown in Tables I–VI) were obtained by employing mixtures consisting of 9 ml of solvent (10 ml in the case of the pure acids) + 1 ml of acid (if solid 1 g of acid) + 5 mg of the element + 1 g of resin. The relative experimental error in the determination of the $\mathrm{K_d}$-values was usually ±10% for low and ±20% for high $\mathrm{K_d}$-values. Not much reliance can, however, be placed on the $\mathrm{K_d}$-values measured at zero concentration of acid, because in those media hydrolysis or insolubility of the uranium salt is to be expected.

From the distribution coefficients thus obtained, the separation factors shown in Tables I–VI were calculated using the simple relationship:

$$\text{Separation factor} = \frac{\mathrm{K_d}\ \text{element}}{\mathrm{K_d}\ \text{uranium}}.$$

Because uranium is the key element in these investigations, all values for the separation factors have therefore been expressed relative to uranium.

Column operations

The column operations for the individual separation methods were performed in a standard manner. The resin (2 g of the corresponding form) was transferred to the ion-exchange column, and the resin bed was pretreated with a solution of the same composition as that employed as a sorption solution. After passage of the sorption solution the resin was usually treated with a "wash solution," also of the same composition. Thereafter the adsorbed elements (mostly uranium) were eluted by means of 1*M* hydrochloric acid.

RESULTS AND DISCUSSION

(1) *Adsorption of uranium from organic solvents containing formic acid*

In this section, and in sections (2), (4) and (6), the effect of the concentration of the organic acid on the K_d of uranium will be displayed twice in the case of each of the liquid acids, in order to show the influence of very low acid concentrations more clearly, and to demonstrate the effect of many organic solvents.

Fig. 1 shows that the adsorption of uranium is decreasing by orders of magnitude when the concentration of formic acid is increased from 0% to 100%. In pure formic acid, as well as in all mixtures of this acid with water, the adsorption is too low to be of any practical analytical importance.

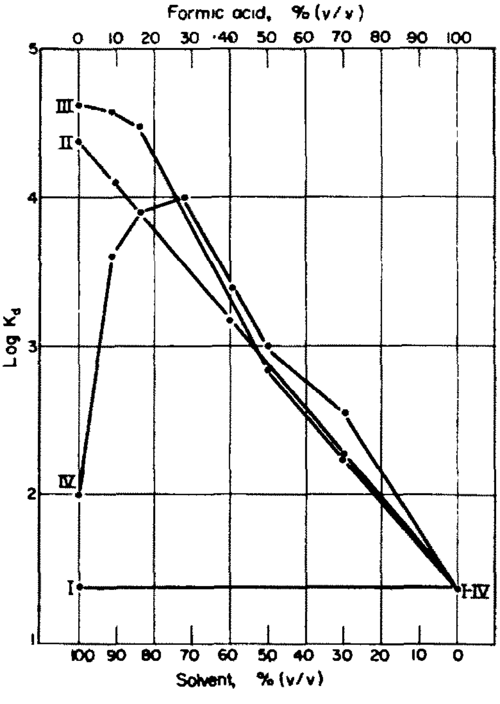


FIG. 1.—Influence of formic acid concentration:

I—Water	III—Acetone
II—Methanol	IV—Dioxan

In the range of concentration from 10% to 80% formic acid and from 90% to 20% organic solvent, the distribution coefficients of uranium have convenient values. In this region uranium is strongly adsorbed; *i.e.*, it is forming a relatively stable negatively charged formate complex.

In Fig. 2 the effect of the formic acid concentration on the distribution coefficients of uranium in aliphatic alcohols, acetone and dioxan is shown.

As can be seen from the curves shown in Fig. 2, the K_d of uranium has in all formic acid-organic solvent mixtures high values, which decrease, in the case of the aliphatic alcohols and acetone, regularly with an increase in the formic acid concentration. In dioxan-formic acid solution the K_d reaches a minimum and a maximum; and finally a relatively low value is obtained at zero formic acid concentration, suggesting hydrolysis of the uranyl ions in this medium. In the presence of 1 ml of formic acid the distribution coefficients of uranium show, in all media, log K_d-values ranging from 4·25 to 5·0, which means that in all these cases identical or very similar conditions of adsorption seem to exist. For this reason, all further experiments (for instance those relating to the effect of the uranium concentration or of the salt concentration on the distribution coefficient of uranium, and the determination of the distribution coefficients of other elements) were always performed in mixtures in

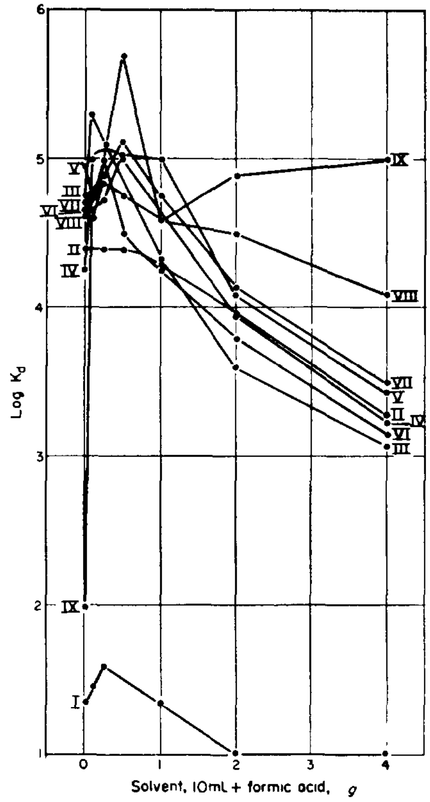


FIG. 2.—Influence of formic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

which the ratio of formic acid to organic solvent was 1:9 (usually 1 ml of formic acid + 9 ml of solvent).

Investigations of the influence of concentration of uranium on its K_d have shown that the K_d of uranium regularly decreases with increasing uranium concentration in the solutions containing formic acid and in all the solvents shown in Fig. 2. At a uranium concentration of 200 mg/10 ml of mixture, a log K_d value of 1·8–2·3 is reached; this does not decrease appreciably when higher uranium concentrations are employed. In the concentration range 0–100 mg of uranium/10 ml of mixture, the K_d of uranium remains constant, *i.e.*, the coefficient is independent of the uranium concentration in the solution. This means that a quantitative enrichment of mg- amounts of uranium from such mixtures is feasible, and is suitable for analytical purposes.

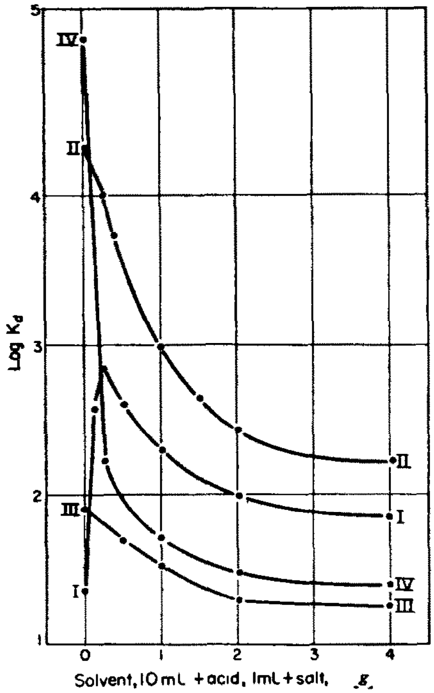


FIG. 3.—Influence of salt concentration on the adsorption of uranium:
I—Water-formic acid-ammonium formate
II—Methanol-formic acid-ammonium formate
III—Water-acetic acid-ammonium acetate
IV—Methanol-acetic acid-ammonium acetate

In Fig. 3 the influence of ammonium formate and ammonium acetate on the distribution coefficients of uranium is shown. Because the influence of the salt concentration on the K_d of uranium was investigated only in formic and acetic acid solutions, the results obtained in acetic acid medium have also been recorded in this diagram.

From Fig. 3 it is seen that the K_d of uranium in aqueous formic acid-formate solution first increases with increasing concentration of ammonium formate, but decreases at higher formate concentration. In methanol solution the decrease of adsorption with an increase of the formate concentration is regular, without formation of a maximum. In acetic acid-acetate-methanol solution the K_d of uranium in all cases decreases rapidly with increasing ammonium acetate content of the solutions. This means that for the analytical separation of mg-amounts of uranium, only acetic or formic acid solutions which contain very small amounts of acetate or formate salts can be employed. Previous experiments[2] showed that the breakthrough capacity for uranium in aqueous acetic acid solution buffered with acetate was only around 50 μg of uranium under the conditions employed. The results shown in Fig. 3 serve as examples of the effect of salts containing the same anion as that which complexes the uranium. This salt effect was not further investigated in other organic acid-organic solvent mixtures because it is assumed that in all cases a decrease will occur with increasing salt concentration. A similar effect has earlier[9] been observed in hydrochloric acid-ethanol solution where an increase of the sodium or ammonium chloride concentration is followed by a decrease of the K_d of uranium. In nitric acid-organic solvent mixtures, however, no change of the K_d of uranium by the addition of alkali or ammonium nitrate could be found. In pure aqueous nitric acid solutions, on the other hand, the K_d of uranium and the distribution coefficients of other elements frequently increase with increasing nitrate ion concentration.

Investigations on the adsorption behaviour of other elements in formic acid-organic solvent mixtures furnished the results recorded in Table I, in which the distribution coefficients of these elements, and the separation factors (in brackets), are shown. In this and in Tables II–VI water has been included amongst the solvents for the purpose of comparison.

The results in Table I show that the distribution coefficient and the separation factor of uranium usually differ by orders of magnitude from those of the other elements, so that the following three separation methods, which were developed in formic acid solutions, always gave quantitative results irrespective of whether μg- or mg-amounts of the elements uranium, copper, lead and gadolinium were employed for the separation experiments.

(*a*) *Separation of uranium from copper*

Ten ml of formic acid containing uranium and copper were diluted with 90 ml of methanol, and the solution was passed through the ion-exchange column (the resin having been pretreated appropriately; see *Experimental*) at a flow rate of 0·5 ml/min. During this sorption operation uranium $K_d = 2 \times 10^4$) was strongly adsorbed, whereas copper ($K_d = 11{\cdot}7$) passed into the effluent. Thereafter the resin was washed with 100 ml of a wash solution (see *Experimental*) in order to remove the last traces of copper from the column. Afterwards the uranium was eluted by means of 100 ml of 1*M* hydrochloric acid, and was determined quantitatively as described earlier (see *Experimental*).

(*b*) *Separation of uranium from lead*

The same experimental conditions were used here as described above under (*a*).

(*c*) *Separation of uranium from gadolinium*

Ten ml of formic acid containing uranium and gadolinium were mixed with 90 ml of isobutanol, and the solution was passed through an appropriately pretreated (see *Experimental*) resin bed at a flow rate of 0.5 ml/min. During this operation uranium ($K_d = 57 \times 10^3$) and gadolinium ($K_d = 2 \times 10^3$) were adsorbed simultaneously. Afterwards, a mixture consisting of 90 ml of methanol and 10 ml of acetic acid was percolated through the column; the gadolinium ($K_d = 47{\cdot}0$) was eluted, whereas uranium ($K_d = 64 \times 10^3$) was still strongly retained by the resin (compare with the results shown in Table II). The elution and quantitative determination of uranium in the eluate was performed as has been described above under (*a*).

From the results shown in Table I it can be seen that a great number of other separation possibilities exist, *e.g.*, separation of uranium from copper, nickel or lead

TABLE I—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN FORMIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	25 (1·0)	1·1 (4×10^{-2})	61·6 (3·0)	123 (5·0)	0·1 (4×10^{-3})	7·0 (0·33)	10·0 (0·4)
Methanol	2×10^{4} (1·0)	11·7 (1×10^{-3})	29·0 (1×10^{-3})	2·6 (13×10^{-5})	20·0 (1×10^{-3})	X	X
Ethanol	21×10^{3} (1·0)	39·0 (2×10^{-3})	15·0 $(7{\cdot}1 \times 10^{-4})$	0·1 (5×10^{-6})	39·6 (2×10^{-3})	X	890 (42×10^{-3})
n-Propanol	45×10^{3} (1·0)	71·0 $(1{\cdot}5 \times 10^{-3})$	202 $(4{\cdot}5 \times 10^{-3})$	410 (91×10^{-4})	1×10^{3} (22×10^{-3})	X	813 (18×10^{-3})
Isopropanol	1×10^{5} (1·0)	X	X	X	X	X	812 (8×10^{-3})
n-Butanol	18×10^{3} (1·0)	X	146 (7×10^{-3})	410 (22×10^{-3})	754 (42×10^{-3})	X	16×10^{2} (9×10^{-2})
Isobutanol	57×10^{3} (1·0)	X	X	X	X	X	2×10^{3} (35×10^{-3})
Acetone	38×10^{3} (1·0)	X	X	X	X	X	9×10^{2} (24×10^{-3})
Dioxan	4×10^{4} (1·0)	XX 8·0 $(4{\cdot}4 \times 10^{-4})$	X	X	X	X	830 (27×10^{-3})

X—In these media either insoluble or hydrolysed.
XX—In this medium Cu^{2+} ions show an intense blue colour.

in formic acid-ethanol solution; separation of uranium from copper in formic acid-dioxan mixture; simultaneous adsorption of uranium and gadolinium from all formic acid-solvent mixtures except aqueous and methanol mixtures; separation of cobalt from uranium, nickel, lead, lanthanum and gadolinium in aqueous formic acid solution, *etc.*

Many of these separations can, of course, also be performed successfully by other anion-exchange methods, *e.g.*, in pure aqueous hydrochloric acid solutions of various molarities. However, the separation of various elements can be effected by changing the solvent only, without any change in the other experimental conditions. The results in Table I show that the simultaneous adsorption of uranium and cobalt from a formic acid-n-propanol mixture is possible. For the separation of the two coadsorbed elements the resin needs only to be washed with a formic acid-ethanol solution in order to remove the cobalt from the resin, thus effecting the separation of these two elements from one another. A simultaneous adsorption of uranium and cobalt from a pure aqueous hydrochloric acid solution (around $10M$ in HCl) is also possible. To separate the adsorbed elements the resin is washed with $6M$ hydrochloric acid, whereby cobalt is eluted whereas uranium is still retained by the resin. Comparison of these two separation possibilities shows that the exchange of solvent in the first method has the same effect as the change of the concentration of the complexing agent (hydrochloric acid) in the second case. This is one of the fundamental differences between ion exchange in pure aqueous solutions and in organic acid mixtures.

Determinations of distribution coefficients of a number of other elements in pure formic acid showed that these elements, in common with uranium, were only little or not at all adsorbed by the resin.

(2) *Adsorption of uranium from organic solvents containing acetic acid*

In Fig. 4 the influence of acetic acid concentration on the distribution coefficients of uranium in acetic acid-water, -methanol -acetone and -dioxan solutions is shown.

By comparing Fig. 4 with Fig. 1 it can be seen that the adsorption of uranium in acetic acid mixtures is high in the whole concentration range; and even in pure acetic acid the coefficient of uranium is high enough to guarantee the quantitative retention of even mg-amounts of this element by the resin. This also means that uranium forms a negatively charged acetate complex of high stability.

In Fig. 5 the effect of acetic acid concentration on the distribution coefficient of uranium in the acid concentration range 0–4 ml of acid + 10 ml of solvent is shown.

Fig. 5 shows that the distribution coefficients of uranium, in all solvents except water and n-propanol, have log K_d-values between 4·4 and 5·2 in the range 0·5–4 ml of acetic acid. Because here also, as in the case of formic acid mixtures (see Fig. 2), the difference of the log K_d values is smallest in the presence of 0·5–2·0 ml of acetic acid, all further experiments were performed in mixtures each of which contained 1 ml of acetic acid and 9 ml of the solvent, or a ratio of acetic acid to solvent of 1:9. As can further be seen from Fig. 5, uranium is adsorbed very strongly by the resin from all acetic acid-solvent mixtures, which means that all of these media are suitable for analytical purposes (see Table II). The adsorption from aqueous acetic acid is, however, lower by two orders of magnitude, although still high enough to effect the quantitative retention of even mg-amounts of uranium by the resin. In dioxan-acetic acid solution of low acidity the uranyl ions also hydrolyse, as was the case in the formic acid solutions of the same acidity (*cf.* Fig. 2) so that the K_d of uranium reaches a very low value. Up to a concentration of 50 mg of uranium/10 ml of solvent (in all solvents) no change of the K_d could be observed. At higher uranium concentrations the K_d decreases rapidly with increasing concentration, and then reaches in some solvents (*e.g.*, water and the aliphatic alcohols) a value at 150 mg of uranium/10 ml of solvent, which does not decrease appreciably with a further increase of the uranium concentration in the solutions.

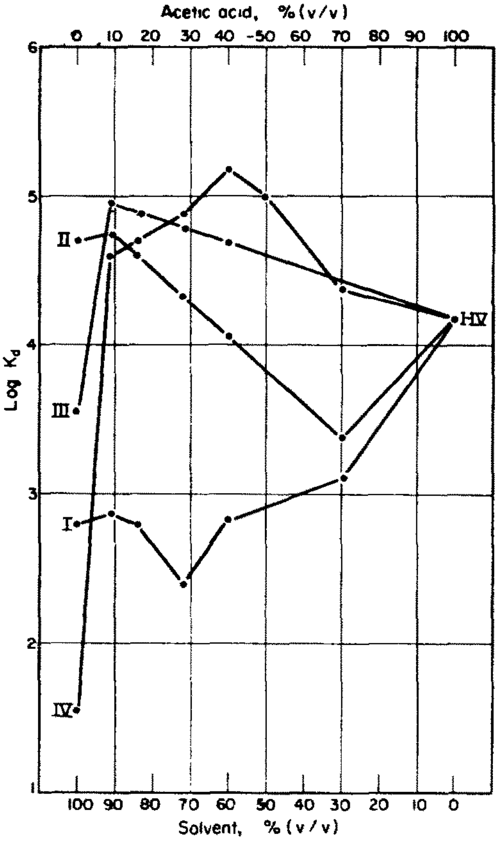


FIG. 4.—Influence of acetic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

In Table II the distribution coefficients and separation factors (in brackets) of several elements in acetic acid-organic solvent mixtures are shown. Each mixture consisted of 1 ml of acetic acid and 9 ml of solvent. Pure acetic acid has also been incorporated into Table II, which means that those results were obtained in solutions which consisted of 10 ml of acetic acid only. Besides the elements recorded in Table II, the adsorption behaviour of a series of other elements in pure acetic acid was investigated. Practically only uranium is adsorbed, whereas other elements, as for instance Fe^{III}, the rare earths, alkaline earth metals, Mn^{II}, Zn^{II}, Cd^{II}, Mg, Be, In, *etc.*, are not retained by the resin; therefore the analytical separation of these elements from uranium should readily be achieved. In this medium the elements Al, Th and Bi hydrolyse; Pb, Sr and Ba are practically insoluble.

Based on the results shown in Table II a further series of ion-exchange separations

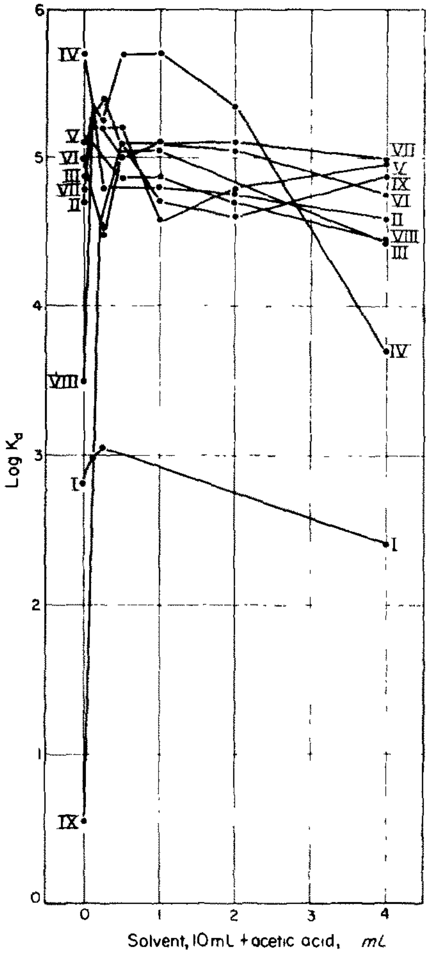


FIG. 5.—Influence of acetic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

can be carried out. All these methods have in common that uranium is always strongly adsorbed, but the other elements are not adsorbed on the resin. As examples the following separation methods can be mentioned: separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in aqueous acetic acid solution; separation of uranium from copper, cobalt, lanthanum and gadolinium in acetic acid-methanol mixture; separation of uranium from copper, nickel and cobalt in

TABLE II.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN ACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	8×10^{2} (1·0)	0·6 (85×10^{-5})	3·1 (62×10^{-4})	5·9 (66×10^{-4})	X	7·0 (87×10^{-4})	25 (32×10^{-3})
Methanol	$6{\cdot}4 \times 10^{4}$ (1·0)	0·72 (12×10^{-6})	X	1·2 (2×10^{-5})	X	7·0 (11×10^{-5})	47·0 (73×10^{-5})
Ethanol	$11{\cdot}3 \times 10^{4}$ (1·0)	2·6 (23×10^{-6})	5·3 (44×10^{-6})	0·48 (4×10^{-6})	X	94·3 (83×10^{-5})	80·0 (7×10^{-4})
n-Propanol	5×10^{5} (1·0)	2·6 (5×10^{-6})	X	1·9 (4×10^{-6})	X	X	140 (3×0^{-4})
Isopropanol	$3{\cdot}8 \times 10^{4}$ (1·0)	9·4 (22×10^{-4})	4·5 (12×10^{-5})	32·4 (8×10^{-4})	X	X	670 (17×10^{-3})
n-Butanol	$12{\cdot}6 \times 10^{4}$ (1·0)	2·6 (2×10^{-5})	X	4·3 (34×10^{-6})	X	X	112 (8×10^{-4})
Isobutanol	$12{\cdot}6 \times 10^{4}$ (1·0)	2·7 (2×10^{-5})	5·0 (4×10^{-5})	3·9 (32×10^{-6})	X	X	132 (12×10^{-4})
Acetone	7×10^{4} (1·0)	8·0 (11×10^{-5})	X	7×10^{2} (1×10^{-2})	X	X	721 (1×10^{-2})
Dioxan	5×10^{4} (1·0)	0·3 (6×10^{-6})	X	20·2 (4×10^{-4})	X	288 (57×10^{-4})	670 (13×10^{-3})
Acetic acid	$1{\cdot}5 \times 10^{4}$ (1·0)	0·15 (1×10^{-5})	0·45 (3×10^{-5})	3·0 (2×10^{-4})	X	0·1 $(6{\cdot}6 \times 10^{-6})$	0·1 $(6{\cdot}6 \times 10^{-6})$

X—In these media either insoluble or hydrolysed.

acetic acid-isobutanol mixture; separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in pure acetic acid.

Because in some solvents uranium and other elements are strongly adsorbed by the resin, the simultaneous adsorption of two or more elements becomes possible. By a change in the solvent the separation of the coadsorbed elements on the resin column can be effected. Examples for such solvent exchange separations are: simultaneous adsorption of uranium and cobalt from acetic acid-acetone solution followed by elution of cobalt by means of acetic acid-ethanol mixture (see below); simultaneous adsorption of uranium and gadolinium from acetic acid-isopropanol mixture and elution of gadolinium with acetic acid-methanol mixture; simultaneous adsorption of uranium, lanthanum and gadolinium from acetic acid-dioxan solution and elution of the rare earths by means of pure acetic acid, *etc.*

Closer investigation of the first example enabled the following separation method to be developed.

Separation of uranium from cobalt

Ten ml of acetic acid, which contained uranium and cobalt, were diluted with 90 ml of acetone, and the solution was passed through an appropriately pretreated resin column at a flow rate of 0·5 ml/min. During this process uranium ($K_d = 7 \times 10^4$) and cobalt ($K_d = 7 \times 10^2$) were adsorbed simultaneously. The separation of cobalt from uranium was effected by washing the resin with 100 ml of a solution consisting of 90% ethanol and 10% acetic acid. The cobalt ($K_d = 0{\cdot}48$) was eluted, but uranium ($K_d = 11{\cdot}3 \times 10^4$) still remained adsorbed. For the removal of uranium the resin was treated with 100 ml of 1*M* hydrochloric acid.

A series of separation experiments performed in this manner showed that μg- and mg-amounts of uranium and cobalt can quantitatively be adsorbed and separated by the method described.

(3) *Adsorption of uranium from organic solvents containing monochloroacetic acid*

Because monochloroacetic acid at room temperature is a solid acid, the effect of its concentration on the distribution coefficient of uranium could not be determined over the complete concentration range 0–100% acid; this can be investigated only for the liquid acids (see Figs. 1, 4, 7 and 10).

In Fig. 6 the influence of the concentration of monochloroacetic acid on the K_d of uranium is shown.

From Fig. 6 it is seen that the difference between the K_d-values of uranium under similar experimental conditions is smallest in the presence of 1 g of acid. The difference in this case is 0·84 log K_d units. Except with isopropanol, isobutanol and dioxan, the log K_d of uranium increases linearly with decreasing concentration of monochloroacetic acid. In dioxan solution the K_d shows first a small regular, and later a steeper, decline. This sharp decrease of the K_d of uranium at low monochloroacetic acid concentration is very probably caused by hydrolysis of the uranyl ions. As in formic acid-water mixtures (*cf.* Fig. 2) the adsorption from aqueous monochloroacetic acid solutions is also relatively low, so that only at low concentrations of monochloroacetic acid were somewhat higher values obtained.

The K_d for uranium in the solvents, except methanol and ethanol, starts to decrease steeply in the region of 10–25 mg of uranium/10 ml of mixture, in spite of the fact that the distribution coefficients of uranium in these media are fairly high. In methanol and ethanol solutions the K_d of uranium remains constant up to a concentration of uranium of 60 mg/10 ml of solution; the decrease in the case of ethanol is more pronounced than in methanol medium. For the analytical separation of mg-amounts of uranium these two solvent systems are therefore the most suitable.

In Table III the distribution coefficients and separation factors (in brackets) of all the elements recorded in the previous two Tables are shown. These results were obtained by using solutions consisting of 10 ml of solvent + 1 g of monochloroacetic acid.

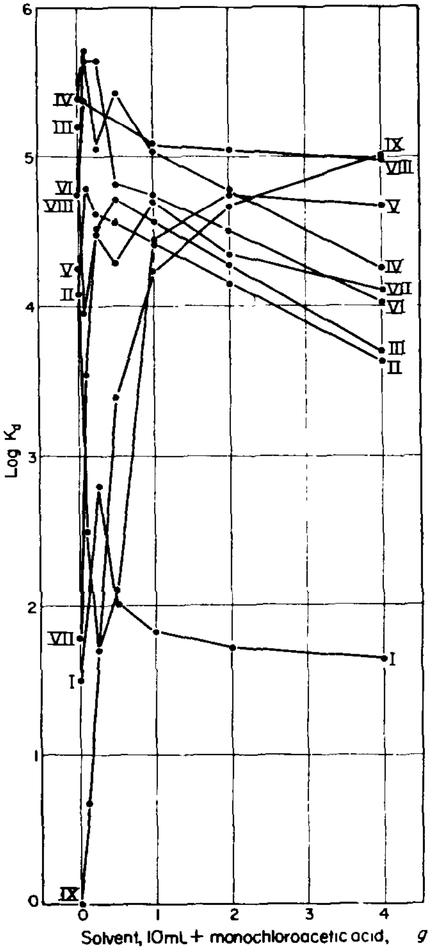


FIG. 6.—Influence of monochloroacetic acid concentration:

I—Water II—Methanol
III—Ethanol IV—n-Propanol
V—Isopropanol VI—n-Butanol
VII—Isobutanol VIII—Acetone
IX—Dioxan

Based on the results recorded in Table III the following method for the separation of uranium from nickel was developed.

Separation of uranium from nickel

The chlorides or nitrates of uranium and nickel were dissolved in 100 ml of ethanol containing 10 g of monochloroacetic acid, and the solution was passed through a pretreated (see *Experimental*)

TABLE III.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN MONOCHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	*Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	66·0 (1·0)	71·0 (1·0)	0·3 (45×10^{-4})	0·31 (4×10^{-3})	3·4 (5×10^{-2})	7·0 (0·1)	91·1 (1·3)
Methanol	25×10^3 (1·0)	134 (53×10^{-4})	10·0 (4×10^{-4})	7·4 (3×10^{-4})	$1·6 \times 10^3$ ($6·3 \times 10^{-2}$)	8·8 (35×10^{-5})	88·7 (35×10^{-4})
Ethanol	37×10^3 (1·0)	906 (23×10^{-3})	0·4 (1×10^{-5})	44·3 (11×10^{-4})	$3·5 \times 10^3$ (9×10^{-2})	28·0 (75×10^{-5})	$1·3 \times 10^2$ (35×10^{-4})
n-Propanol	108×10^3 (1·0)	20×10^3 (0·2)	0·3 (3×10^{-6})	$2·7 \times 10^2$ (25×10^{-4})	X	43·0 (4×10^{-4})	5×10^2 (46×10^{-4})
Isopropanol	$28·5 \times 10^3$ (1·0)	X	10·0 (35×10^{-3})	85·0 (3×10^{-3})	X	94·3 (33×10^{-4})	$8·9 \times 10^2$ (31×10^{-3})
n-Butanol	57×10^3 (1·0)	$6·2 \times 10^3$ (0·11)	2·1 (36×10^{-6})	95·0 (17×10^{-4})	X	24·0 (42×10^{-5})	$3·8 \times 10^2$ (66×10^{-4})
Isobutanol	50×10^3 (1·0)	$7·7 \times 10^3$ (0·16)	X	34·0 (68×10^{-5})	X	21·2 (42×10^{-4})	5×10^2 (1×10^{-2})
Acetone	120×10^3 (1·0)	$16·6 \times 10^3$ (0·13)	X	$8·6 \times 10^3$ (71×10^{-3})	X	113·3 (1×10^{-3})	$1·6 \times 10^3$ (13×10^{-3})
Dioxan	17×10^3 (1·0)	$12·5 \times 10^3$ (0·74)	X	X	X	113·3 (66×10^{-4})	$1·3 \times 10^3$ (8×10^{-3})

* The adsorbed copper ions are of intensive yellow colour.
X—In these media either insoluble or hydrolysed.

resin bed at a flow rate of 0·5 ml/min. During this operation uranium ($K_d = 37 \times 10^3$) was adsorbed whereas nickel ($K_d = 0 \cdot 4$) passed into the effluent. Afterwards, 100 ml of a washing solution (of appropriate composition) was percolated through the column in order to remove the last traces of nickel. Finally, the uranium was eluted by means of 100 ml of 1*M* hydrochloric acid.

The results of several experiments performed in this manner have shown that this method is suitable for the quantitative separation of μg- and mg-amounts of uranium and nickel.

Other simple separation procedures are: separation of uranium from cobalt in monochloroacetic acid-methanol solution; separation of uranium from lanthanum in the same medium; separation of cobalt from nickel in monochloroacetic acid-n-propanol solution; separation of copper from nickel in the same medium; separation of lathanum from gadolinium in monochloroacetic acid-isobutanol solution.

It is also possible to adsorb two or more elements simultaneously, and to separate these subsequently on the resin by a change in the solvent. As an example, the simultaneous adsorption of copper and cobalt from monochloroacetic acid-n-propanol solution may be mentioned. After the adsorption of these two elements their separation can be effected by means of monochloroacetic acid-isobutanol solution, whereby the cobalt is eluted and the copper remains adsorbed.

(4) *Adsorption of uranium from organic solvents containing dichloroacetic acid*

In Fig. 7 the influence of the concentration of dichloroacetic acid on the distribution coefficient of uranium is shown.

The K_d of uranium in the non-aqueous solvents first increases with increasing concentration of the acid, and then reaches a maximum, subsequently decreasing to its value in pure dichloroacetic acid. In pure aqueous acid mixtures (curve I) a minimum is obtained, from which a strictly linear increase of the K_d in both directions (*i.e.*, to 0 and 100% dichloroacetic acid) takes place.

The dependence of the distribution coefficient of uranium on the concentration of dichloroacetic acid in all solvents previously used (see Figs. 2, 5 and 6) is shown in Fig. 8.

In water, methanol and ethanol only, the curves show a similarity with those shown in Figs. 2 and 5. In all other solvents containing dichloroacetic acid the K_d of uranium increases with increasing dichloroacetic acid content of the solutions after passing through a minimum. This is a phenomenon which was not observed in other solvents containing organic acids (*cf.* Figs. 2, 5 and 6) and is only weakly recognisable in trichloroacetic acid solutions (see Fig. 9). The extremely steep increase of the K_d in n-propanol solutions low in dichloroacetic acid could be explained by the assumption that in such media a decarboxylation of dichloroacetic acid, $CHCl_2COOH$, into carbon dioxide and methylene dichloride (CH_2Cl_2) takes place under the catalytic action of the resin. It cannot, however, be explained why this reaction should occur only in n-propanol solution and not in the other solvents. In trichloroacetic acid solution, however, a similar reaction can actually take place [see Section (5)].

Under the experimental conditions employed (1 ml of dichloroacetic acid + 9 ml of solvent + uranium), the K_d of uranium is independent of the concentration, in the region from 0 to about 30 mg of uranium/10 of mixture if methanol, ethanol or acetone is used as solvent. In the other solvents the K_d of uranium starts to decrease rapidly when the uranium concentration in the solution exceeds 10 mg/10 ml. For the adsorption of mg-amounts of uranium, therefore, only the three solvents in which uranium has its highest K_d values can be employed successfully.

Although media containing dichloroacetic acid were not used for separation purposes, the adsorption behaviour of other elements in such mixtures was investigated. The results of these experiments, performed in mixtures each containing 1 ml of dichloroacetic acid and 9 ml of solvent, are recorded in Table IV in which the distribution coefficients of several elements, together with the separation factors (in brackets) expressed relative to uranium, are recorded.

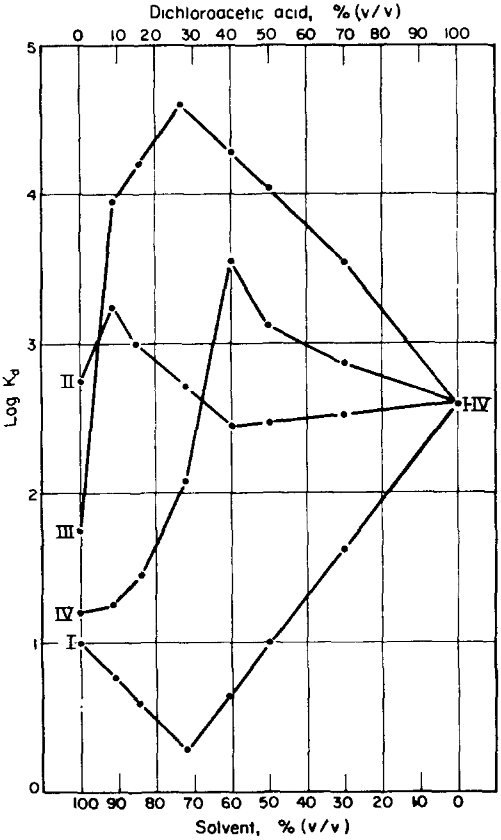


Fig. 7.—Influence of dichloroacetic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

These results show that it would be easily possible to separate uranium in dichloroacetic acid-methanol solution from all elements investigated except lead. On the other hand, lead could be separated from uranium by elution of uranium with aqueous dichloroacetic acid solution, when lead is still retained by the resin.

Other combinations will not be discussed here, because they can easily be deduced from the results presented in Table IV.

(5) *Adsorption of uranium from organic solvents containing trichloroacetic acid*

In Fig. 9 the adsorption behaviour of uranium in solutions containing 0–4 g of trichloroacetic acid/10 ml of solvent is shown.

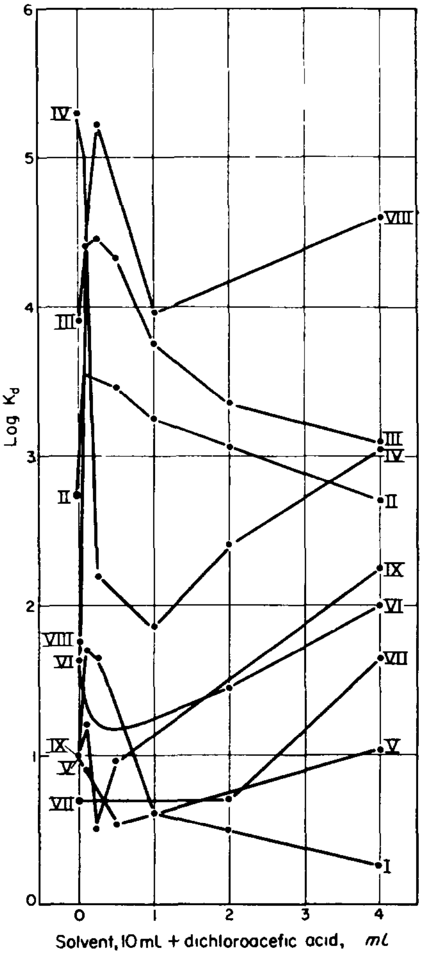


FIG. 8.—Influence of dichloroacetic acid concentration:

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone
IX—Dioxan	

TABLE IV.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN DICHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	4·0 (1·0)	13·3 (5·0)	0·2 (5 × 10^{-2})	0·2 (5 × 10^{-2})	117 (29·2)	2·5 (0·62)	9·2 (2·3)
Methanol	1·8 × 10^3 (1·0)	30·0 (11 × 10^{-3})	0·15 (83 × 10^{-6})	0·15 (83 × 10^{-6})	169 (9 × 10^{-2})	3·2 (17 × 10^{-4})	16·4 (9 × 10^{-3})
Ethanol	5·7 × 10^3 (1·0)	13·3 (35 × 10^{-4})	40·0 (7 × 10^{-3})	0·17 (3 × 10^{-5})	X	60·0 (1 × 10^{-2})	52·0 (9 × 10^{-3})
n-Propanol	71 (1·0)	30·0 (0·3)	0·2 (3 × 10^{-3})	0·2 (3 × 10^{-3})	X	80·0 (1·1)	73·0 (1·03)
Isopropanol	2·2 (1·0)	X	X	2·5 (0·6)	X	26·0 (12·0)	137 (62·0)
n-Butanol	18·0 (1·0)	30·0 (1·6)	X	0·15 (8 × 10^{-3})	X	80·0 (4·4)	56·0 (3·1)
Isobutanol	5·0 (1·0)	13·3 (4·0)	X	0·2 (4 × 10^{-2})	X	73·0 (17·6)	73·0 (14·6)
Acetone	9 × 10^3 (1·0)	47·0 (22 × 10^{-4})	X	75·5 (84 × 10^{-4})	X	480 (53 × 10^{-3})	X
Dioxan	14·0 (1·0)	20·0 (1·4)	X	X	X	140 (10·0)	X

X—In these media either insoluble or hydrolysed.

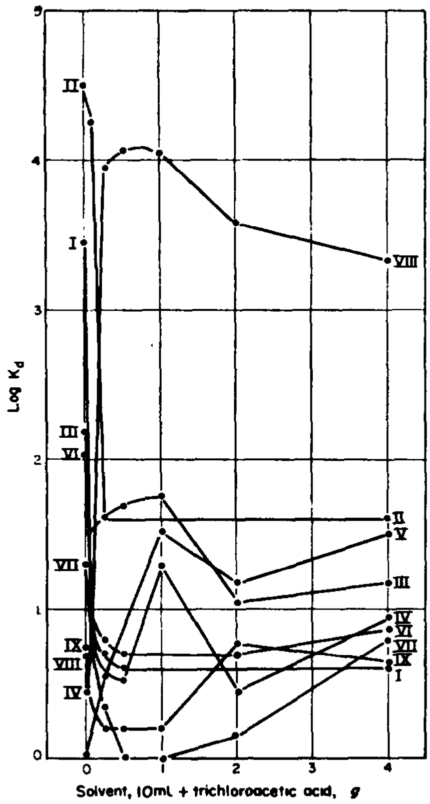
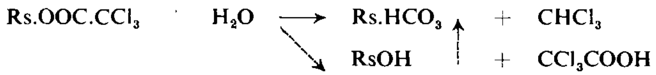


FIG. 9.—Influence of trichloroacetic acid concentration.

I—Water	II—Methanol
III—Ethanol	IV—n-Propanol
V—Isopropanol	VI—n-Butanol
VII—Isobutanol	VIII—Acetone

IX—Dioxan

Uranium is only appreciably adsorbed by the resin from solutions consisting of trichloroacetic acid and acetone, *i.e.*, only from such solutions is the quantitative adsorption of uranium on the resin possible. In the presence of less than 0·25 g of trichloroacetic acid/10 ml of acetone, however, the K_d of uranium decreases rapidly because of the hydrolysis of uranyl ion. The steep increase in the K_d value of uranium in water and methanol solutions in the presence of 0–0·1 g of trichloroacetic acid/10 ml of solvent can be explained by the occurrence of the following reaction preventing the adsorption of the uranium as a negatively charged trichloroacetate complex (which has high stability only in acetone solutions) but as a uranyl carbonate complex:



(Rs = resin phase; ⇢ possible side reaction)

As was stated earlier (see *Experimental*), the above reaction already occurs in the dry resin (trichloroacetate form) because of the humidity of the air. In aqueous solution, therefore, this reaction will be speeded up, and will not only be restricted to the counter ion (trichloroacetate ion on the resin) but will also extend to the acid molecules in solution, which will thus be decomposed either directly in the solution, or on the resin, forming carbon dioxide and chloroform, as long as free molecules of this acid are present in solution. After the free acid has been completely decomposed only chloroform will be formed until all counter ions of the resin are transformed into bicarbonate ions. The reason why this reaction also takes place in methanol solution, to an even greater extent, is probably because the chloroform formed during this reaction is much more readily soluble in methanol than in water, so that the chloroform cannot block the exchange sites of the resin (as they can in an aqueous solution) and thus slow down the rate of decomposition. This seems to be the reason why the K_d of uranium in methanol solution, in which the formation of bicarbonate can proceed unobstructed, is markedly higher than in aqueous solution.

The K_d did not change with increasing uranium concentration in the solution except when acetone is employed as a solvent. The K_d values of uranium are, however, very low, which means that uranium, if at all, only forms a very weak nagatively charged trichloroacetate complex. In acetone solution, however, the effect of uranium concentration on the K_d shows the usual results, *i.e.*, it remains constant first, in this case up to 30 mg of uranium/10 ml of mixture, and then decreases in order to reach, at 100 mg of uranium/10 ml of mixture, a value which does not further change appreciably with an increase of uranium concentration in the solution. Therefore acetone can be regarded as the most suitable solvent from which to adsorb uranium quantitatively in the presence of trichloroacetic acid.

In Table V the adsorption behaviour of other elements is shown (as determined in the presence of 1 g of trichloroacetic acid + 10 ml of solvent).

Not only is uranium strongly adsorbed from trichloroacetic acid-acetone solution, but so also are copper and gadolinium; these can, however, not be separated on the resin by a change of solvent. From the other solvents uranium and practically all other elements investigated can only be adsorbed weakly, so that the analytical application of trichloroacetic acid solutions is rather limited. An exception may be made for lead, which can be adsorbed fairly strongly from three solvents, and can thus be

TABLE V.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN TRICHLOROACETIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	4·0 (1·0)	5·0 (0·8)	11·5 (2·8)	0·12 (3 × 10^{-2})	123 (31·0)	7·0 (1·7)	36·1 (9·0)
Methanol	40·0 (1·0)	23·5 (1·7)	10·8 (0·27)	0·12 (3 × 10^{-3})	145 (3·6)	10·3 (0·26)	40·2 (1·0)
Ethanol	57·0 (1·0)	51·4 (1·0)	14·1 (0·24)	0·15 (26 × 10^{-4})	594 (10·4)	28·0 (0·5)	52·0 (0·9)
n-Propanol	20·0 (1·0)	71·0 (0·3)	X	0·29 (14 × 10^{-3})	X	0·5 (25 × 10^{-3})	44·1 (2·0)
Isopropanol	36·0 (1·0)	32·7 (1·1)	X	2·9 (83 × 10^{-3})	X	10·2 (0·3)	33·2 (0·9)
n-Butanol	5·0 (1·0)	32·7 (0·15)	80·0 (16·0)	0·12 (24 × 10^{-3})	X	7·0 (1·4)	47·0 (9·4)
Isobutanol	1·0 (1·0)	20·0 (0·05)	X	0·12 (12 × 10^{-2})	X	7·0 (7·0)	33·2 (33·0))
Acetone	11·3 × 10^{3} (1·0)	2·48 × 10^{3} (4·5)	X	21·0 (19 × 10^{-4})	X	94·3 (83 × 10^{-4})	302·6 (96 × 10^{-3})
Dioxan	1·6 (1·0)	5·0 (1·0)	X	0·15 (1 × 10^{-1})	X	5·3 (0·3)	33·2 (20·7)

X—In these media either insoluble of hydrolysed.

separated from all the other elements investigated. By comparing Table V with Tables I–IV, it may be seen that solutions containing trichloroacetic acid are the least suitable for analytical purposes.

(6) *Adsorption of uranium from organic solvents containing propionic acid*

From experiments performed in nitric acid-propionic acid mixtures, it was found that the adsorption of uranium from such solutions was higher than from corresponding mixtures containing acetic acid. It was expected, therefore, that in pure propionic acid, or in solutions containing a high percentage of propionic acid, the K_d of uranium would also be higher than in acetic acid mixtures of comparable composition (*cf.* Fig. 10 with Fig. 4).

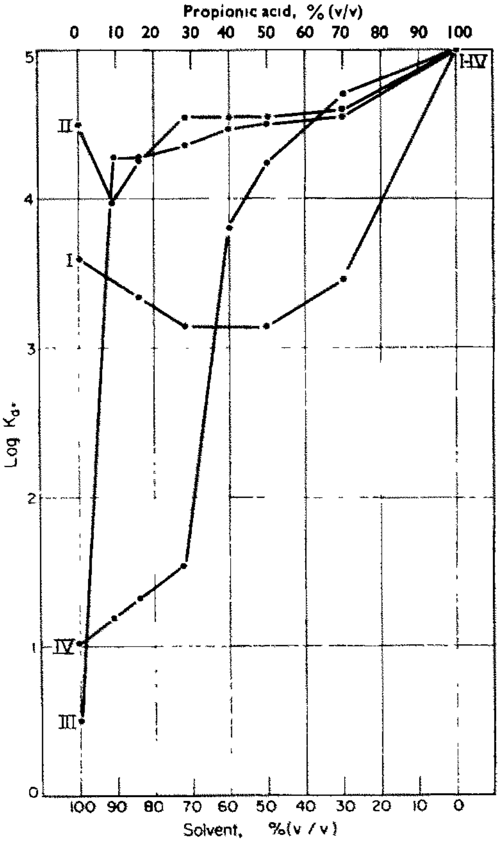


Fig. 10.—Influence of propionic acid concentration:
I—Water II—Methanol
III—Acetone IV—Dioxan

In Fig. 10 the influence of the percentage of propionic acid on the K_d of uranium is shown.

The K_d of uranium, apart from a few breaks, increases with an increase of the concentration of propionic acid, and reaches a maximum in 100% propionic acid. This means that pure propionic acid, compared with pure formic, acetic and dichloroacetic acids (*cf.* Fig. 10 with Figs. 1, 4 and 7), is a solvent which is more suitable for the adsorption of uranium, because in it the K_d of uranium has a much higher value than in the other liquid acids.

Investigation of the adsorption behaviour of uranium in mixtures consisting of 10 ml of solvent containing 0–4 ml of propionic acid gave the results shown in Fig. 11.

Contrary to the results obtained in formic and acetic acids, the influence of propionic acid on the K_d of uranium is rather irregular. Especially remarkable is the steep decline of the K_d with decreasing concentration of propionic acid in the case of the butanols (curves VI and VII of Fig. 11) and acetone (curve VIII); this is attributable to the hydrolysis of the uranyl ions in these media of low acid concentration. By employing 1 g of acid/10 ml of solvent, all solvents except the butanols

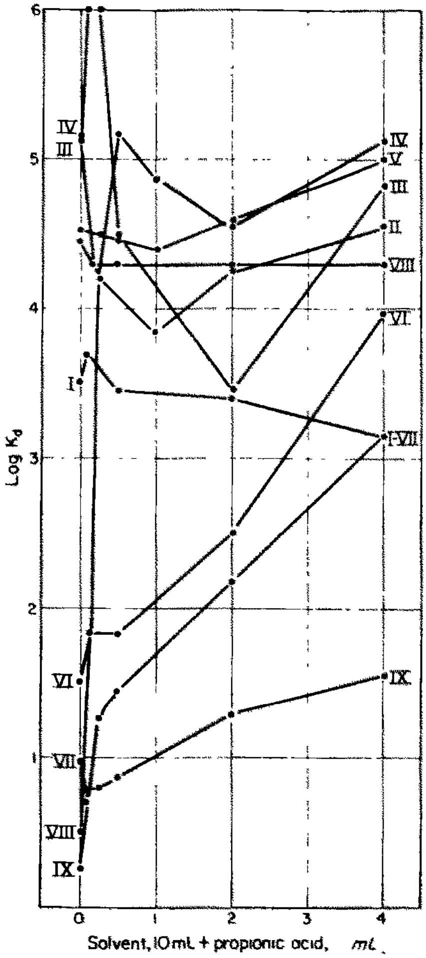


FIG. 11.—Influence of propionic acid concentration:

I—Water II—Methanol
III—Ethanol IV—n-Propanol
V—Isopropanol VI—n-Butanol
VII—Isobutanol VIII—Acetone
IX—Dioxan

TABLE VI.—DISTRIBUTION COEFFICIENTS AND SEPARATION FACTORS OF URANIUM AND OTHER ELEMENTS IN PROPIONIC ACID-ORGANIC SOLVENTS

Solvent	Element						
	UO_2^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Pb^{2+}	La^{3+}	Gd^{3+}
Water	$2{\cdot}8 \times 10^{3}$ (1·0)	0·4 (2×10^{-4})	50·0 (18×10^{-3})	25·7 (9×10^{-3})	0·7 (25×10^{-4})	7·0 (25×10^{-4})	102 (36×10^{-3})
Methanol	$6{\cdot}8 \times 10^{3}$ (1·0)	0·2 (7×10^{-5})	45·5 (66×10^{-5})	3·6 (53×10^{-5})	2·9 (42×10^{-4})	7·0 (1×10^{-3})	102 (15×10^{-3})
Ethanol	$14{\cdot}2 \times 10^{3}$ (1·0)	0·7 (25×10^{-6})	45·5 (33×10^{-4})	3·6 (25×10^{-5})	X	8·0 (56×10^{-5})	155 (11×10^{-3})
n-Propanol	75×10^{3} (1·0)	0·5 (6×10^{-6})	51·0 (6×10^{-4})	17·0 (26×10^{-5})	X	30·0 (4×10^{-4})	83 (11×10^{-4})
Isopropanol	$25{\cdot}2 \times 10^{3}$ (1·0)	0·9 (2×10^{-5})	X	66·0 (26×10^{-4})	X	288 (11×10^{-3})	6×10^{2} (24×10^{-3})
n-Butanol	118 (1·0)	0·4 (42×10^{-4})	X	22·1 (0·18)	X	1·5 (11×10^{-3})	64·1 (0·54)
Isobutanol	50 (1·0)	0·5 (1×10^{-2})	X	5·0 (0·1)	X	25·0 (0·5)	73·4 (1·46)
Acetone	20×10^{3} (1·0)	0·4 (25×10^{-6})	X	X	X	480 (24×10^{-3})	$1{\cdot}1 \times 10^{3}$ (55×10^{-3})
Dioxan	10 (1·0)	0·7 (5×10^{-2})	X	X	X	288 (28·8)	1×10^{3} (98·0)
Propionic acid	1×10^{5} (1·0)	0·12 (12×10^{-7})	0·2 (2×10^{-6})	5·0 (5×10^{-6})	X	7·0 (7×10^{-5})	0·1 (1×10^{-6})

X—In these media either insoluble or hydrolysed.

and dioxan will be suitable for analytical purposes, because the distribution coefficients of uranium in these solvents will be sufficiently high to guarantee the quantitative adsorption of uranium on the resin. Also, the K_d of uranium reaches a value of 10^6 in ethanol solution containing 0·1–0·25 ml of propionic acid. Such a high adsorption of uranium has previously been reported to occur only in sulphuric acid-organic solvent mixtures.[10]

Studies of the influence of the uranium concentration on the K_d of uranium showed that the K_d first remained constant from 0 to 50 mg of uranium/10 ml of solvent (in all solvents except the butanols and dioxan) and then decreased with increasing uranium concentration in the solution.

The adsorption behaviour of a series of other elements has also been measured. The distribution coefficients and separation factors are recorded in Table VI.

Based on the results shown in Table VI the following method for the separation of uranium from lanthanum in propionic acid-acetone and -water mixtures was developed.

Separation of uranium from lanthanum

The nitrates of uranium and lanthanum were dissolved in 100 ml of a mixture consisting of 90 ml of acetone and 10 ml of propionic acid, and the solution was passed through a pretreated resin bed (see *Experimental*) at a flow rate of 0·5 ml/min. During this operation a simultaneous adsorption of uranium ($K_d = 2 \times 10^4$) and lanthanum ($K_d = 480$) took place. Thereafter the resin was washed with 100 ml of a solution consisting of 90 ml of water and 10 ml of propionic acid; the lanthanum ($K_d = 7{\cdot}0$) was eluted, but uranium ($K_d = 2{\cdot}8 \times 10^3$) was still retained on the resin. Afterwards the uranium was eluted by means of 100 ml of $1M$ hydrochloric acid, and the quantitative determination was carried out as described earlier.

The results of a series of column operations carried out in this manner showed that μg- and mg-amounts of uranium and lanthanum can be separated quantitatively from one another by means of this procedure.

Table VI suggests many other separation possibilities, *e.g.*, separation of uranium from copper, nickel, cobalt, lanthanum and gadolinium in pure propionic acid; separation of uranium and nickel from lanthanum and gadolinium in propionic acid-dioxan solution. In these conditions only lanthanum and gadolinium are adsorbed, whereas uranium and nickel pass into the effluent. In order to separate lanthanum from gadolinium on the resin column, the resin is washed with propionic acid-ethanol solution; lanthanum is eluted, whereas gadolinium remains still adsorbed.

The fact that lanthanum and gadolinium have high distribution coefficients in propionic acid-dioxan solution, whereas uranium shows only little adsorption from such a medium, could be of importance for the separation of uranium from the rare earth fraction of its fission products. The use of such a mixture would thus make it possible to separate high amounts of uranium (from the spent reactor fuel uranium) from the rare earths which are formed in lesser amounts and could thus be adsorbed on relatively small amounts of resin.

CONCLUSION

From the experimental results presented it can be seen that anion-exchange in non-aqueous media containing organic acids can be employed to solve many separation problems encountered in analytical chemistry. In particular, the examples cited show that these organic media can successfully be used to separate uranium from other elements, a fact which is of special importance in reactor chemistry.

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Zusammenfassung—In der vorliegenden Arbeit wird das Anionenaustauschverhalten von Uran(VI) und einer Anzahl anderer Elemente in organischen Säuren-organischen Lösungsmittelgemischen beschrieben. Als organische Lösungsmittel wurden einige aliphatische Alkohole, Aceton und Dioxan verwendet. Als organischen Säuren widen untersucht Ameisen-, Essig- und Propionsäure sowie einige Chlorderivate der Essigsäure. Auf Grund von Bestimmungen der Verteilungskoeffizienten und Trennungsfaktoren in den verschiedensten Medien konnten Trennungsmethoden des Urans von anderen Elementen entwickelt werden.

Résumé—Dans le présent mémoire, on décrit le comportement, au point de vue échange anionique, de l'uranium hexavalent et d'un certain nombre d'autres éléments, en solvants organiques contenant des acides organiques. On a utilisé comme solvants quelques alcools aliphatiques, l'acétone et le dioxane. Comme acides organiques, on a étudié les acides monocarboxyliques suivants: formique, acétique, propionique. ainsi que les dérivés chlorés de l'acide acétique. Par l'intermédiaire de la détermination des coefficients de distribution et des facteurs de séparation dans les différents milieux. on a développé des méthodes de séparation de l'uranium d'autres éléments.

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EXTRACTION OF THE ZIRCONIUM–ALIZARIN S COMPLEX WITH BUTANOL

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Summary—Optimum conditions are established for the formation of the zirconium–alizarin S lake. Trichloracetic acid exerts a stabilisation action over the lake in hydrochloric acid solutions, enabling extraction of the lake with butanol over a large range of pH. The butanol lake solutions are stable almost indefinitely. The distribution constant has been determined, and the 1:1 composition of the complex in butanol proved by the continuous variations, the slope ratio and the molar ratio methods. Lambert-Beer's law is obeyed up to at least 11 μg of zirconium. The influence of elements commonly associated with zirconium in its natural compounds is less in butanol than in the case of determinations in an aqueous medium.

THE sodium salt of alizarin sulphonic acid (alizarin S), was proposed as a reagent for the identification of zirconium by de Boer.[1] About 20 years later, Yoe and Overholser[2] studied the possible use of this reagent in quantitative analysis. Green[3] was the first to present a method for the colorimetric determination of zirconium with alizarin S. Subsequently, Dorta-Schaeppi and his coworkers[4] showed that formation of the coloured zirconium–alizarin S lake takes place with an equimolar ratio of the constituents.

The reproducibility of the analytical results by colorimetry was contested by Mayer and Bradshaw[5] who attributed low values of the optical densities obtained to an irreversible hydrolysis of the zirconium ions. The formation of zirconium isopolyoxocations also often produces complications in the colorimetric determination of zirconium with alizarin S.[6] This polymerisation had already been observed by Nazarenco.[7] It can be avoided by working with freshly prepared solutions.[8] More systematic research in this direction was undertaken by Gübeli and Jacob,[9] who demonstrated the reversibility of the polymerisation process caused by hot concentrated acids. Kuznetsov and coworkers[10] accorded great attention to this behaviour.

Though many new reagents have recently been proposed for the colorimetric determination of zirconium, the zirconium–alizarin S lake still remains of great interest.[10,11] In the present paper we have studied conditions for the liquid–liquid extraction of this lake from aqueous solution with butanol* in order to establish its composition and stability as well as the possibility of a colorimetric determination of zirconium in this medium.

EXPERIMENTAL

Apparatus

The colorimetric determinations were carried out with a Pulfrich photometer (C. Zeiss, Jena, DDR) and the pH determinations with an Orion KTS type 2518/S potentiometer (Hungary).

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* Butanol was chosen as the extractant because among several solvents investigated it gave the best results; it was also readily accessible.

Reagents

0·001*M Zirconyl chloride solution.* Obtained by dissolving reagent grade $ZrOCl_2.8H_2O$ in 0·01*M* hydrochloric acid. The zirconium content was determined gravimetrically as ZrO_2.

0·001*M Alizarin S solution.* The sodium salt of alizarin sulphonic acid (Riedel de Haen A.G. indicator) was purified by extraction with ether and recrystallisation from ethanol,[5] then dissolved in 0·01*M* hydrochloric acid.

25% *aqueous trichloracetic acid* (TCA) *solution.* Prepared from reagent-grade material.

n-Butyl alcohol. C.p. reagent.

0·01*M Hydrochloric acid*

Procedure

The basic working procedure was as follows. To a mixture of equal volumes (1–3 ml) of 0·001*M* zirconyl chloride and alizarin S solutions, 25% TCA solution was added, and the whole diluted to the mark with 0·01*M* hydrochloric acid in a 100-ml flask. The dark cherry-red coloured zirconium–alizarin S lake was subsequently extracted with butanol.

RESULTS AND DISCUSSION

Optimum conditions for formation of the zirconium–alizarin S lake

In Fig. 1 are shown the absorption spectra of the zirconium–alizarin S lake in butanol measured against alizarin S in butanol and against pure butanol, as well as the absorption spectrum of alizarin S in butanol measured against the pure solvent. At 531 mμ the absorption of the reagent is small compared with that of the complex, and all subsequent optical density measurements were carried out with the "S 53" filter of our photometer corresponding to this wavelength, using the pure solvent as reference solution.

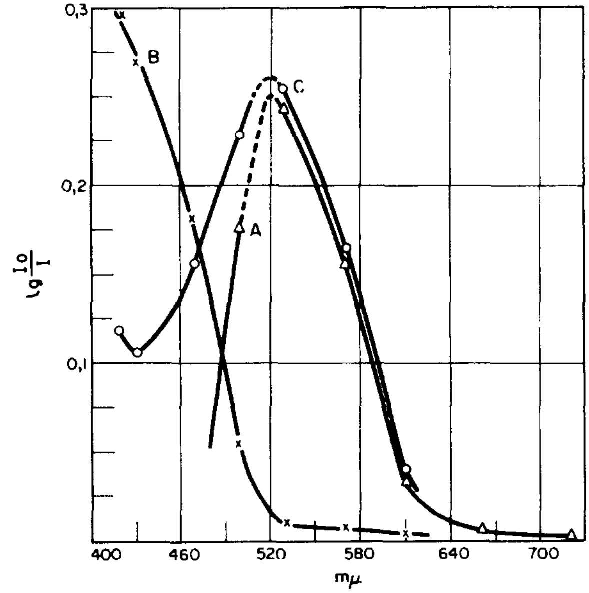

Fig. 1—Absorption spectra:
A—zirconium-alizarin S lake in butanol against alizarin S in butanol,
B—alizarin S in butanol against pure butanol,
C—zirconium-alizarin S lake in butanol against pure butanol.

Fig. 2 shows that the optimum pH conditions for formation of the zirconium–alizarin S lake are limited to a very narrow range (optimum at pH 1·15).

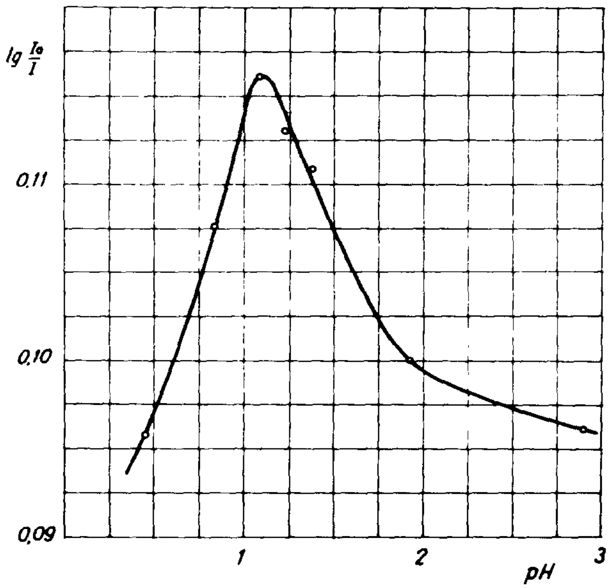

Fig. 2—Influence of pH on absorption of zirconium-alizarin S lake (3 ml of 0·001*M* zirconyl chloride and 3 ml of 0·001*M* alizarin S diluted to 100 ml with various quantities of hydrochloric acid).

It is known[3] that the reaction which leads to the formation of the lake takes some time to be completed. Fig. 3 shows that after 60 min the reaction is almost complete and continues to develop sufficiently slowly (2% during the next 50 min) to allow reproducible measurements to be made.

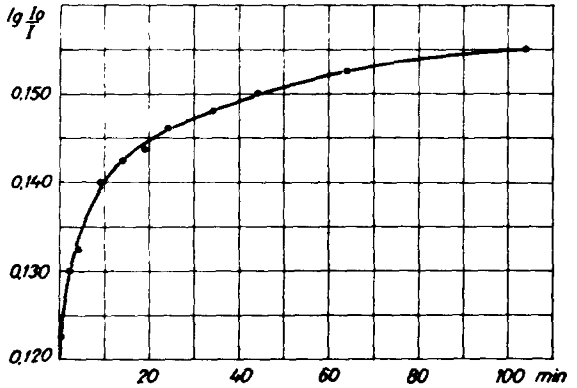

Fig. 3—Influence of time on formation of the zirconium-alizarin S lake (equimolar quantities of zirconyl chloride and alizarin S plus 5 ml of 25% TCA, diluted to 100 ml with 0·01*M* hydrochloric acid; pH 1·15)

With regard to the excess of reagent used, Fig. 4 shows that it has no influence on the optical density of the lake once the amount of alizarin S present exceeds that required for formation of the lake.

Conditions for extraction of the lake

For high concentrations of acid, extraction of the lake with butanol from aqueous hydrochloric acid is complete. The butanol phase becomes dark cherry-red and the

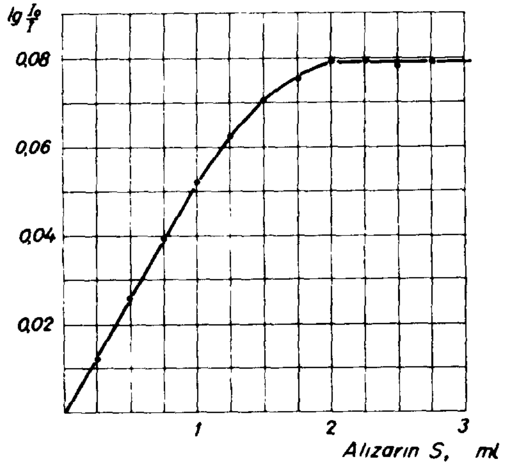

FIG. 4—Influence of amount of alizarin S on formation of the zirconium–alizarin S lake (483 μg of zirconyl chloride and variable amounts of alizarin S plus 5 ml of 25% TCA, diluted to 100 ml with 0·01*M* hydrochloric acid; pH 1·15)

aqueous phase colourless. With less acid solutions (pH 0·8–3), but otherwise the same conditions, the lake is no longer extracted and it settles out as a film at the interphase. Extraction becomes possible for the whole pH range studied (pH 0·8–3) if trichloracetic acid (TCA) is added.

Large amounts of TCA acid have little influence on the pH of the solution and thus do not alter the acidity required for a favourable extraction. The optimum extraction conditions (pH 1·15) are obtained when the lake formation takes place in 0·01M hydrochloric acid solutions containing 1·25% of TCA.

The extractions were carried out 60 min after mixing of the reagents (because the lake has then become sufficiently stable) first with a volume of butanol approximately 30%, then 20% of that of the aqueous solution. The combined organic extracts were centrifuged to separate traces of water, and the colour measured photometrically.

TCA exerts a definite stabilising action on the aqueous lake solutions. Under the given working conditions the lake solutions are stable for 168 hr, whereas in the absence of TCA 25% decomposition occurs within 68 hr. Butanol solutions of the lake are stable almost indefinitely compared with the aqueous solutions.

Under the above conditions, the distribution constant of the zirconium–alizarin S complex between water and butanol is K = 0·054, and the percentage extraction[12] is E = 85·6%.

Stability of zirconyl chloride solutions

Because polymerisation of the zirconyl ion to form polyoxocations of zirconium is well known,[7,8] the same behaviour is to be expected for the zirconium–alizarin S lake formation under our conditions. To illustrate this, we present in Fig. 5 absorption spectra of the zirconium–alizarin S lake prepared from zirconyl chloride solutions of varying age (0–14 days). The spectra show that as the age of the zirconyl solution increases there is a gradual lowering of the absorption maximum (Fig. 6). This supports the existence of an equilibrium between a monomer and polycation of zirconium.

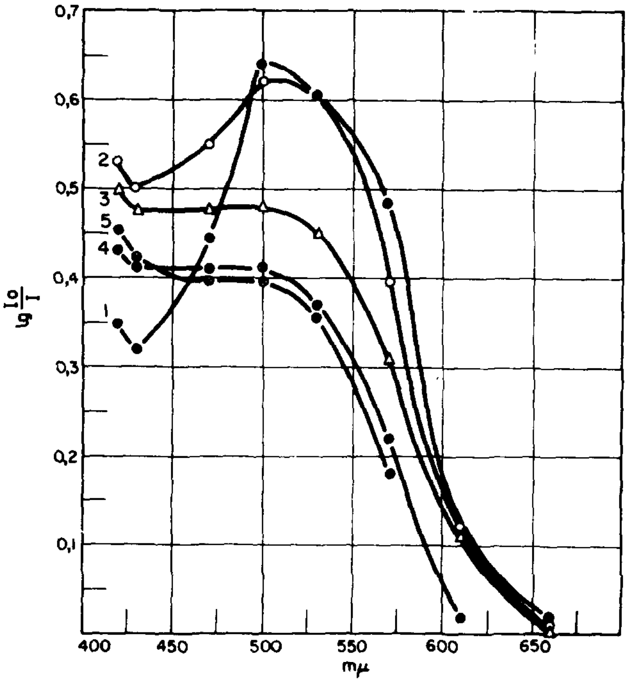

FIG. 5—Absorption spectra of zirconium-alizarin S lake prepared from zirconyl chloride solutions of varying age:

1—fresh solution, 3—7-day old solution,
2—2-day old solution, 4—12-day old solution,
5—14-day old solution.

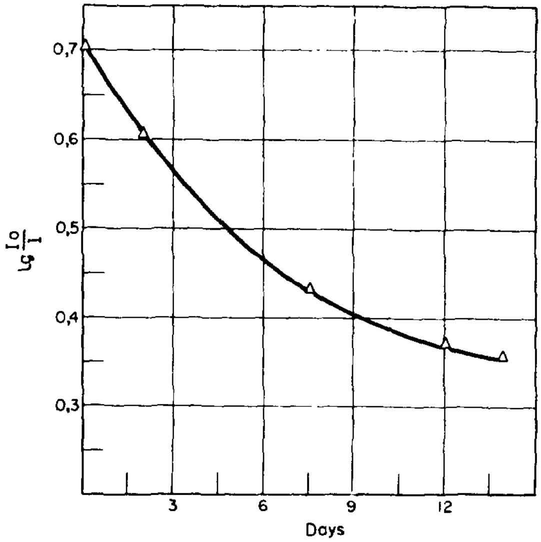

FIG. 6—Influence of age of zirconyl chloride solution on absorption maximum of the zirconium-alizarin S lake.

The absorption spectrum of the lake derived from the 14-day old zirconyl solution (curve 5 of Fig. 5) is very similar to that of the lake obtained under the same condition from a freshly prepared zirconyl solution of half the strength. This leads us to assume that in the 14-day old solution, 50% of the original zirconium is present in a polymerised form.

Validity of Lambert-Beer's law and colorimetric determination of zirconium

From Fig. 7 it follows that for both aqueous and butanol media the Lambert-Beer law is obeyed up to at least 11 µg of zirconium.

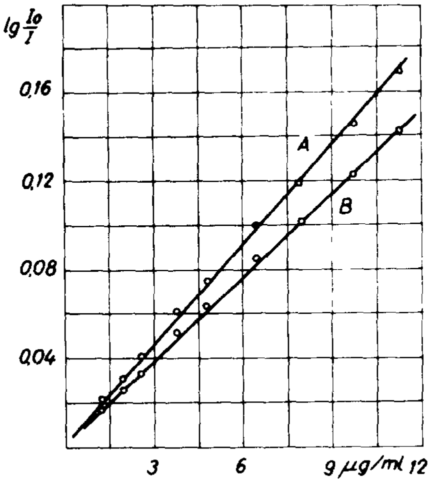

FIG. 7—Absorption of the zirconium–alizarin S lake:
A—aqueous solution,
B—butanol extract.

For the colorimetric determination of zirconium, the optical density of the lake developed from the test solution is measured and compared with a calibration curve obtained with a freshly prepared solution of zirconyl chloride. The error does not exceed 3%.

Effect of foreign ions

Al^{3+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, In^{3+}, Ga^{3+}, La^{3+}, Mn^{2+}, Pb^{2+}, Zn^{2+} and Fe^{2+} do not interfere unless present in a quantity 100 times as large as that of zirconium. Thorium up to a concentration 150 times and chromium 25 times that of the zirconium are also without effect. Anions with which zirconium forms complexes influence its determination.

Composition of the zirconium–alizarin S complex

The optical densities of the complex are plotted against wavelength in Fig. 8 for various molar ratios. Because the curves have the same characteristics, with their maxima at the same wavelength, the formation of a single complex is indicated. We have confirmed this as well as its 1:1 composition. The methods used were those of continuous variations (Fig. 9),[13] the slope ratio method (Fig. 10)[14] and the molar ratio method (Fig. 11).[15]

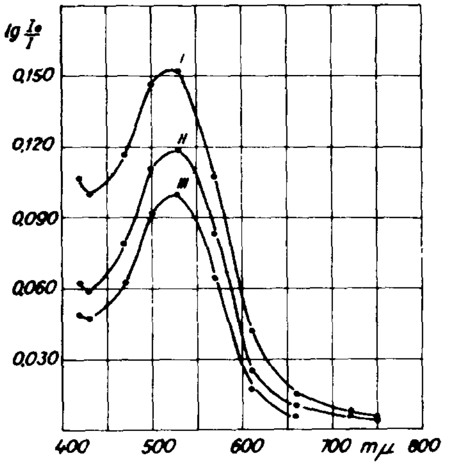

FIG. 8—Absorption spectra of zirconium-alizarin S lake for various molar ratios of zirconium: alizarin S:—I—1:1, II—1:2, III—1:2·5.

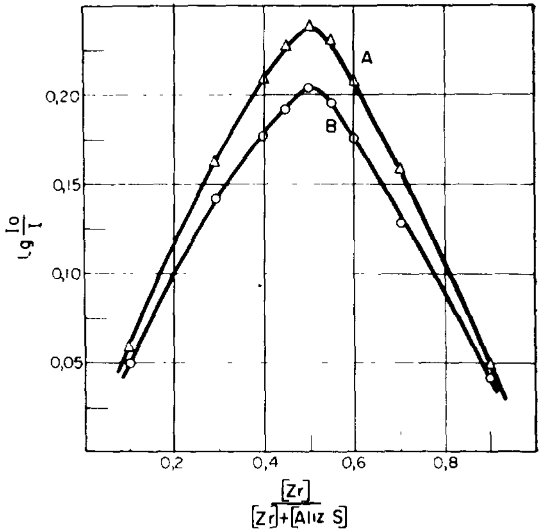

FIG. 9—Continuous variations curves for zirconium-alizarin S lake (each reactant in ml of 0·001M solution):
A—aqueous solution, B—butanol extract.

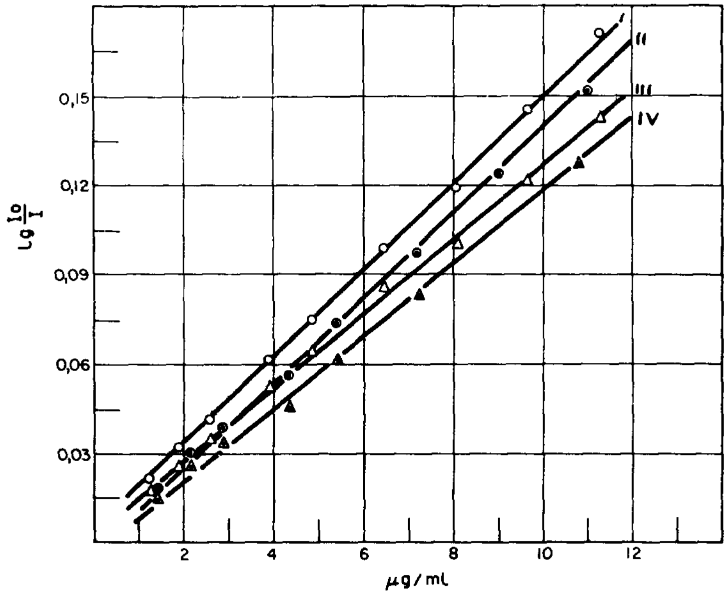

FIG. 10—Slope ratio curves for zirconium-alizarin S lake (0·001M reactants, with 5 ml of the constant component per 100 ml of solution):

I, II—aqueous solution, ○, △—zirconium variable,
III, IV—butanol extract, ○, △—alizarin S variable.

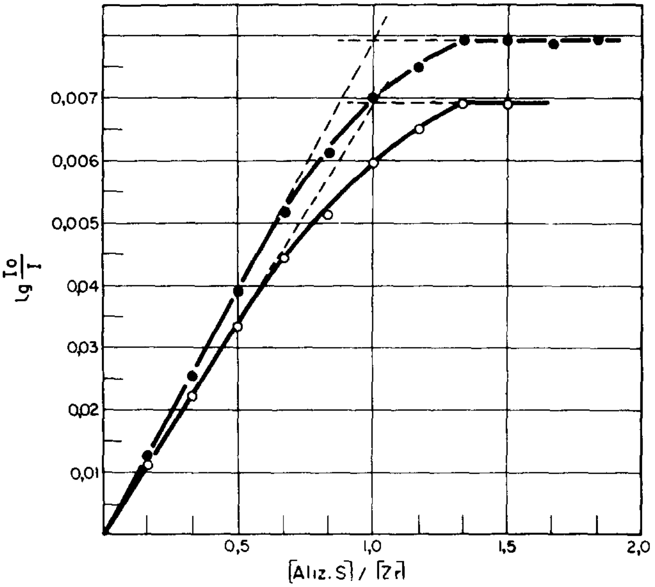

FIG. 11—Molar ratio curves for zirconium–alizarin S lake (483 μg of zirconium and variable amounts of 0·001*M* alizarin S, diluted to 100 ml of solution): ●—aqueous solution, ○—butanol extract.

Degree of dissociation and equilibrium constant

The curves in Fig. 11 demonstrate the existence of an appreciable dissociation in the system as studied by us, which makes possible the calculation of the degree of dissociation, α, from the relationship[15]

$$\alpha = (E_m - E_s)/E_m$$

where E_m is the maximum optical density for the horizontal portion of the curve, corresponding to complete reaction of the zirconium, and E_s is the optical density for the stoichiometric molar ratio of alizarin S to zirconium. From the molar ratio curves (Fig. 11), we have obtained for E_m and E_s, respectively, the values 0·0792 and 0·0700, which lead to $\alpha = 0{\cdot}1314$.

The instability constant of the zirconium–alizarin S complex

$$K = \frac{\alpha^2 \cdot c}{1 - \alpha}$$

where c, the total concentration of the complex, equal to the zirconium concentration is $1{\cdot}5 \times 10^{-5}$ mole/l., was found to be $2{\cdot}98 \times 10^{-7}$ mole/l.

Zusammenfassung—Die optimalen Bedingungen für die Bildung des Zirkonium-Alizarin S-Farblacks werden festgelegt. Trichloressigsäure stabilisiert den Farblack in salzsauren Lösungen und ermöglicht seine Extraktion mit Butanol in einem großen p_H-Bereich. Die Lösungen des Farblacks in Butanol sind fast unbegrenzt stabil. Die Verteilungskonstante wurde bestimmt und die Zusammensetzung des Komplexes in Butanol mit den Methoden der kontinuierlichen Variationen, des Neigungsverhaltnisses und der molaren Verhältnisse bewiesen. Das Lambert-Beersche Gesetz gilt bis 11 μg Zirkonium. In Butanol ist die Störung durch Elemente, die gemeinhin mit Zirkonium zusammen in dessen natürlichen Verbindungen auftreten, geringer als bei Bestimmungen in wäßrigem Medium.

Résumé—On a établi les conditions optimales de formation de la laque zirconium-alizarine S. L'acide trichloracétique exerce une action stabilisatrice sur la laque en solutions chlorhydriques, rendant possible son extraction au butanol dans un grand domaine de pH. Les solutions butanoliques de laque sont stables presqu'indéfiniment. On a déterminé la constante de distribution, et établi la composition du complexe en butanol par les méthodes des variations continues, du rapport de pente et du rapport molaire. La loi de LAMBERT-BEER est respectée jusqu'à 11 μg de zirconium. L'influence des éléments communément associés au zirconium dans ses composés naturels est plus faible dans le butanol que dans le cas des dosages en milieu aqueux.

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PRECIPITATION FROM MIXED SOLVENTS—VI

NICKEL DIMETHYLGLYOXIMATE

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Summary—The addition of dimethylglyoxime to an acetone–water solution of nickel results in the production of nickel dimethylglyoximate crystals much larger than those obtained from aqueous solution. Immediate filtration yields reproducible results about 3 parts per 1000 low. Filtration following an evaporation period allows quantitative recovery. In either case the precipitate is more easily filtered and more free from diverse ions than that normally obtained.

EARLIER reports have described the advantages to be obtained by precipitating the 8-hydroxyquinolates of aluminium,[1] nickel,[2] magnesium,[3] copper[4] and uranium[5] from acetone–water mixtures. In these cases, with the exception of magnesium, the initial solution composition was such as to keep all materials in solution. Gradual volatilisation of the acetone resulted in decreased solubility and eventual precipitation of the metal 8-hydroxyquinolate. The present investigation was undertaken to explore the behaviour of other metal chelate precipitates when formed under these conditions.

This report describes the investigation of nickel dimethylglyoximate. Although the precipitate forms very rapidly, without the heating period required for most 8-hydroxyquinolates, a great increase in particle size is still achieved, and a marked reduction in diverse ion coprecipitation is effected. The method may readily be adopted to routine analysis, or to the rapid separation of nickel from solutions.

EXPERIMENTAL

Reagents

Nickel: Nickel solutions were prepared from reagent-grade $NiSO_4 \cdot 6H_2O$ (Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.) and standardised by precipitation with dimethylglyoxime.[6] Such solutions contained approximately 3 mg of nickel per ml of solution.

Copper: Reagent-grade copper shot (Fisher Scientific Company, Fair Lawn, New Jersey, U.S.A.), 99·98% assay, was used to prepare a solution of copper^{II} ion as previously described.[4]

Cobalt: Reagent-grade $Co(NO_3)_2 \cdot 6H_2O$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey, U.S.A.) was used to prepare a solution which contained 3 mg of cobalt per ml.

Iron: Reagent-grade $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used to prepare a solution which contained 10 mg of iron per ml. Dilute nitric acid was added to prevent hydrolysis.

Dimethylglyoxime: Reagent-grade powder (Mallinckrodt Chemical Works, St. Louis, Missouri, U.S.A.) was used without further purification. The reagent was used as a 1% solution in 95% ethanol.

Acetone: Reagent-grade acetone was distilled through a 30-cm Vigreaux column.

All other chemicals were reagent-grade and used without further purification.

Procedure

Nickel precipitation: To a 250-ml beaker were added, in the order given, about 10 ml of a solution containing 5–30 mg of nickel, 50 ml of distilled water, 75 ml of acetone, and 10 ml of a tartaric acid solution which contained 250 g of solute per litre. Concentrated ammonia was added dropwise until the solution developed a pale blue color and the odour of ammonia was noticeable. The mixture was then heated to 65°, and 18 ml of 1% dimethylglyoxime solution were added. When less than 10 mg of nickel was in the sample the amount of reagent solution was reduced to 10 ml to prevent precipitation of excess reagent. The samples were heated for up to 2 hr at 65° on the water-bath, cooled, filtered, washed with water, dried for 1 hr at 150° and weighed as Ni $(C_4H_7N_2O_2)_2$. The gravimetric factor is 0·20319. All filtrates were found to have a pH in the range 8·1–8·4.

Coprecipitation: The effect of copper, cobalt and iron, as diverse ions, was studied by introducing various amounts of these materials into the initial solution. The above procedure was then followed except in the presence of cobalt, in which case the amount of reagent was increased so as to be 10% in excess above that required to form the bis-complex of both cobalt and nickel.

RESULTS AND DISCUSSION

The most striking result of these experiments was the increased size of the individual particles that are produced. This effect is demonstrated in Figs. 1 and 2 which show, with the same degree of magnification, precipitates obtained by the conventional direct addition method and those obtained by the above procedure. For comparison, Fig. 3 shows a sample of nickel dimethylglyoximate obtained by the method of Gordon and Salesin,[7] in which biacetyl and hydroxylamine hydrochloride react to effect the *in situ* generation of dimethylglyoxime. In all observed respects of color, particle size, crystal habit, filterability, *etc*., the precipitates obtained by the *in situ* generation of the reagent are identical to those produced when the reagent is directly introduced into a solution with a high acetone content. It is, therefore, surprising to learn that the precipitation from the acetone-water medium is nearly complete within 2 min after the addition of the reagent. While some crystal growth, probably mainly Ostwald ripening, does occur during the 2-hr heating period, this change is small when compared with the difference in particle size obtained if precipitations are compared between aqueous and acetone–aqueous media. It is also interesting to note that the very similar crystals produced by the *in situ* reagent generation are formed slowly over a 3-hr period.

TABLE I.—EFFECT OF EVAPORATION TIME UPON RECOVERY OF NICKEL DIMETHYLGLYOXIMATE

Number of samples	Evaporation time, *hr*	Nickel added, *mg*	Nickel found, *mg*	Error, *mg*
8	0	29·88	29·78	−0·10
6	1	29·88	29·85	−0·03
7	2	29·88	29·89	0·01
3	3	29·88	29·88	0·00

Table I shows the effect of the length of evaporation time on the amount of nickel recovered. The eight samples which were not heated were filtered approximately 2 min after the addition of the reagent. In all cases the precipitates were easily and rapidly filtered and washed. It is seen from these results that the direct filtration of the water–acetone mixture yields results which are low by 3 parts per 1000. Assuming this loss to be caused by the increased solubility of the chelate in this medium (an assumption supported by the observation that heating the filtrate at 65° for 2 hr results in the formation of a red film on the solution) and approximating the solution volumes employed, one calculates on approximate value for the solubility of 60×10^{-8} g of nickel per ml of solution. The aqueous solubility is reported as 8×10^{-8} g per ml.[8]

The analysis of six 10-ml aliquots of one nickel solution by the above procedure

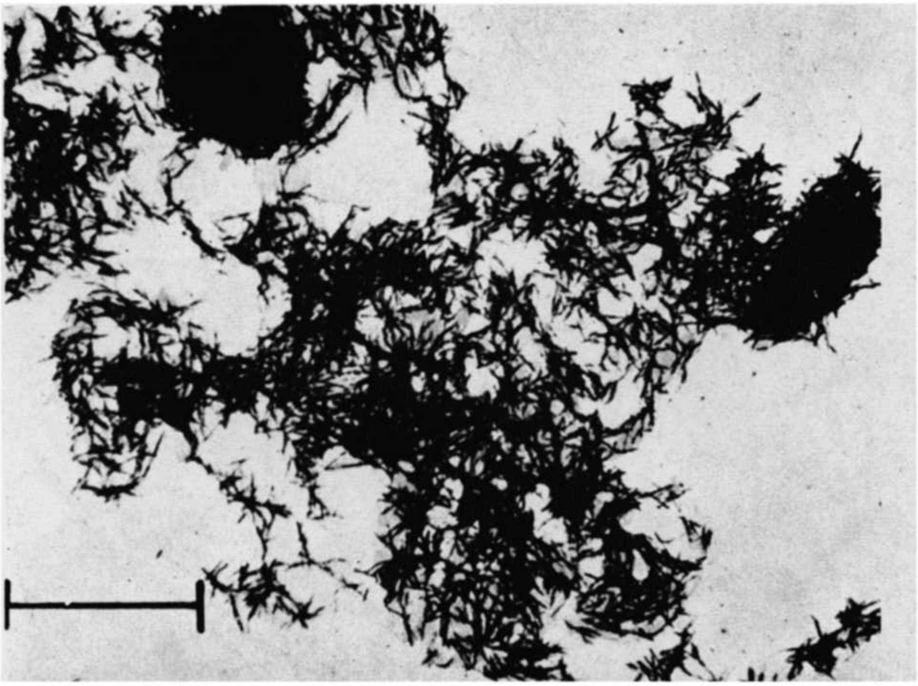

FIG. 1.—Nickel dimethylglyoxímate precipitated from aqueous solution.

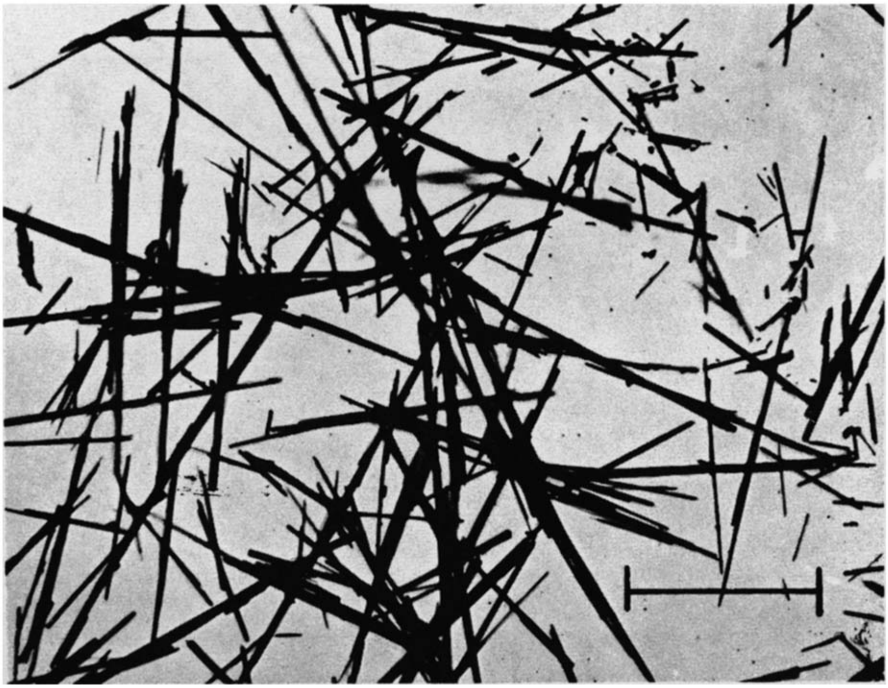

FIG. 2.—Nickel dimethylglyoximate precipitated from acetone–water solution.

FIG. 3.—Nickel dimethylglyoxìmate precipitated by *in situ* generation of reagent
(Distance shown is 0·1 mm in all Figures)

TABLE II.—PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM WATER-ACETONE

Nickel added, *mg*	Nickel found, *mg*	Error, *mg*
1·49	1·48[a]	−0·01
2·99	2·96[b]	−0·03
5·98	5·99[a]	+0·01
8·96	8·96	0
14·94	14·95	+0·01
20·92	20·92	0
26·89	26·87	−0·02
35·86[c]	35·81	−0·05
41·83[c]	41·83	0
59·76[c]	59·70	−0·06

[a] Average of 2 determinations

[b] Average of 3 determinations

[c] Twice the amount of DMG was added for the larger samples.

TABLE III.—COPRECIPITATION OF DIVERSE IONS WITH NICKEL DIMETHYLGLYOXIMATE PRECIPITATED FROM A WATER-ACETONE MIXTURE

Nickel added, *mg*	Diverse ion	Diverse ion added, *mg*	Nickel found, *mg*	Error, *mg*
29·88	Cu	9	29·82	−0·06
29·88	Cu	15	29·86	−0·02
29·88	Cu	30	29·88	0·00
29·88	Cu	45	29·90	0·02
29·88	Cu	60	29·86	−0·02
14·94	Cu	45	14·88	−0·06
14·94	Cu	60	14·90	−0·04
14·94	Cu	75	14·91	−0·03
29·88	Co	9	29·78	−0·10
29·88	Co	15	29·84	−0·04
29·88	Co	30	29·92	0·04
29·88	Co	45	29·96	0·08
29·88	Co	60	29·98	0·10
14·94	Co	45	14·96	0·02
14·94	Co	60	14·94	0·00
14·94	Co	75	15·05	0·11
29·88	Fe	30	29·86	−0·02
29·88	Fe	40	29·90	0·02
29·88	Fe Co	10 9	29·88	0·00

yielded an average value of 29·88 mg of nickel with a standard deviation of 0·03 mg. This result is in exact agreement with that obtained when the dimethylglyoximate was precipitated in the normal manner.[6] Table II reports the results of the analysis of varying nickel concentrations. In addition to the values reported in this Table, analysis of samples containing up to 60 mg of nickel were successfully performed by increasing the amount of reagent added.

Table III reports the results obtained when nickel was precipitated in the presence of copper, cobalt or iron. These results indicate that the separation of nickel from equal amounts of copper or cobalt may easily be achieved, and that analysis of solutions containing an excess of these diversions is attainable. It was observed in initial experiments that the presence of cobalt led to a brown filtrate, and when the larger amounts of cobalt were present low results were obtained. This is believed to be the result of the formation of a soluble cobalt-dimethylglyoxime complex. The low results were replaced by those of the Table when the amount of reagent was increased as described above.

Separations from equal amounts of iron were also effective, but when iron and cobalt were present simultaneously in amounts greater than 10 mg of iron or 9 mg of cobalt, consistently high results were obtained, and a suspension of a dark brown material appeared in the filtrates.

CONCLUSIONS

The precipitation of nickel dimethylglyoximate from a water–acetone solution is an effective and efficient means of generating this precipitate. The material thus obtained is of much larger particle size and much more easily filtered than that produced from strictly aqueous media. Quantitative recovery of the nickel is possible after heating at 65° for 2 hr.

Acknowledgement—The authors would like to recognize the support given this work by the U.S. Atomic Energy Commission under contract AT(40-1)-2954.

Zusammenfassung—Zugabe von Dimethylglyoxim zu einer Aceton–Wasser-Lösung von Ni liefert viel größere Dimethylglyoximnickelkristalle als in wäßriger Lösung. Sofortige Filtration gibt reproduzierbarum 0,3% zu niedrige Resultate; schaltet man eine Verdunstungszeit ein, dann ist die Ausbeute quantitativ. In jedem Fall läßt sich der Niederschlag leichter filtrieren und enthält weniger Fremdionen als bei der normalen Fällung.

Résumé—L'addition de diméthylglyoxime a une solution de nickel dans l'acétone et l'eau fournit des cristaux de diméthylglyoximate de nickel plus gros que ceux obtenus à partir des solutions aqueuses. La filtration immédiate fournit des résultats reproductibles à environ 3 pour 1000 au minimum. La filtration après évaporation permet la récupération complète. Dans chacun de ces cas le précipité est plus facilement filtré et plus pur que celui obtenu par voie normale.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF IMPURITIES IN PURE AND ANALYTICAL REAGENTS—II*

SOME ABSORPTION SPECTRA IN CONCENTRATED CHLORIDES AND THEIR APPLICATIONS

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Summary—The ultra-violet spectra of Bi^{3+}, Cu^{2+}, Cu^{+}, Fe^{3+}, Pb^{2+} and NO_3^- in 4*M* KCl and in other concentrated chloride solutions have been recorded, and their absorptivities, at wavelengths useful for analytical purposes, have been evaluated. Similar values for the cyano-complexes, $[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$, in 4*M* KCl solutions, have also been obtained. These values have then been used for the independent determination of six ions in "synthetic" KCl solutions by the methods already proposed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 677). Some of the results are given in detail.

INTRODUCTION

A COMPARATIVELY large amount of information on the ultraviolet absorption spectra of cations in concentrated halide solutions has accumulated since the first publications of Fromherz *et al.*[1] Much of this material is qualitative. Also, in most cases the wavelengths of the absorption peaks as well as the absorbances vary with the concentration of the halide and with the medium in general.[2] For these reasons, it was found necessary to repeat the measurement of some of the spectra already recorded in the literature, and to evaluate the absorption coefficients at various wavelengths, the adherence to Beer's law, *etc.*, under well-defined experimental conditions.

Results thus obtained were then introduced into the formulae developed in Part I, and the usefulness of these formulae was tested with 4*M* KCl solutions to which trace amounts of various salts were added in different combinations. The additions were chosen to simulate impurities indicated on the labels of chemically pure or analytical reagents. The impurities determined were bismuth, iron, lead, copper, nickel and the nitrate ion. Typical results obtained from the seventy solutions tested are given in tabular form.

EXPERIMENTAL

Materials

For the preparation of concentrated salt solutions, KCl, KBr, KI, NaCl, NaBr, $MgCl_2·6H_2O$, $CaCl_2·2H_2O$, $AlCl_3·6H_2O$ and $ZnCl_2·2H_2O$, J. T. Baker Analyzed reagents, were used. Other reagents employed were also of analytical grade, mostly J. T. Baker. CuCl was prepared in the laboratory.

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* Part I: *Talanta*, 1964, **11**, 679.

Only specially purified water was used. The laboratory distilled water was passed over ion exchangers and was then double-distilled in an all-Pyrex apparatus with alkaline permanganate and phosphoric acid in series. The water thus purified was sometimes stored in polyethylene bottles for a few days, but solutions were mostly prepared from freshly distilled water.

Preparation of solutions

Stock solutions containing 1 mg/ml of the desired cation were prepared by dissolving 150–450 mg of the chloride, accurately weighed, in 100-ml volumetric flasks. To salts liable to hydrolyse, HCl was added to give a final concentration of 0·01*M*; or other variations were adopted as necessary.

These solutions were then further diluted to 40 ppm in concentrated alkali halides or other concentrated salt media as required.

Solutions containing any number of ppm (from 1 to 20) of a cation were prepared by mixing the 40-ppm standard with an equi-normal pure concentrated salt solution in the proper proportion in 50-ml volumetric flasks. Mixtures containing several "impurities" of a known concentration were prepared in a similar manner. Calibrated full pipettes or burettes were used for all volumetric measurements, and all solutions were prepared close to the time of taking their spectra, and were kept in stoppered polyethylene bottles.

Apparatus

For the spectrophotometric measurements an Optica CF4 Grating Spectrophotometer, Single Beam, Manual Model, was employed with four matched 1-cm (or 4-cm) quartz cells. Small corrections for the self-absorption of the cells had to be made, varying with the wavelength in the 200–400 mμ range. and were evaluated by comparison of the cells when filled with distilled water.

Keeping the slit width fixed at 0·05 mm, deviations of repeated measurements in absorbance units (log I_0/I) were less than ±0·003. By very careful manipulations, the deviations were reducible to ±0·002 – 0·001 unit.

All measurements were made at room temperature, 25° ± 3°, with no corrections for temperature variations.

For the evaluation of the spectrum and absorption coefficients of each individual ion a reference solution of an identical medium was employed. The absorption spectrum of the synthetic 4*M* KCl solutions, when determining the amount of impurities present, was taken with reference to distilled water.

RESULTS AND DISCUSSION

Absorption spectra in the ultraviolet

Some representative absorption spectra of various ions are given in Figs. 1–4. In Table I, the positions of the measured absorption peaks, their molecular extinctions

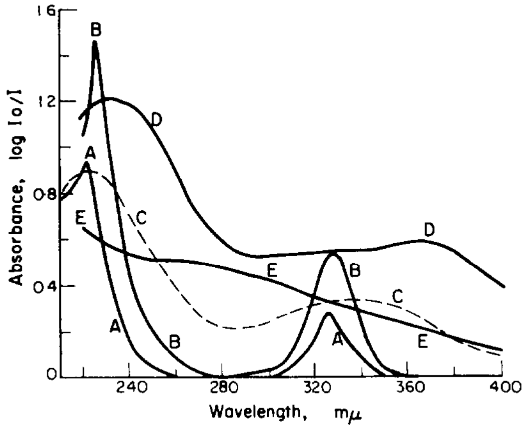


FIG. 1.—Spectra of Bi^{3+} and Fe^{3+} in concentrated chloride solutions:
A: 4 ppm of Bi in 4*M* KCl; B: 8 ppm of Bi in 2*M* $MgCl_2$;
C: 8 ppm of Fe in 4*M* KCl; D: 10 ppm of Fe in 4*M* $MgCl_2$;
E: 10 ppm of Fe in 6*M* $ZnCl_2$.

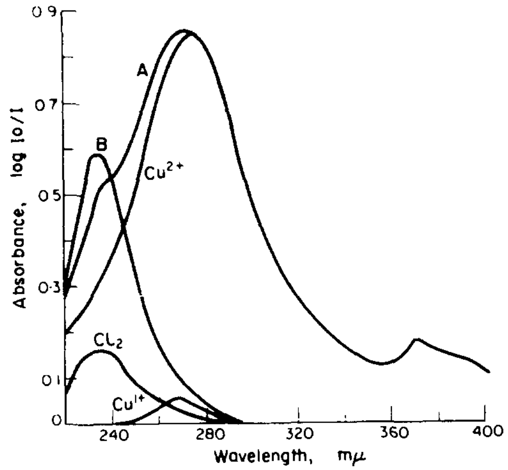


FIG. 2.—Spectrum of 12 ppm of Cu^{2+} in 5*M* CaCl$_2$ (A), and its resolution to Cu^{2+}, Cu^{+} and Cl$_2$ spectra. (B). Spectrum of Cl$_2$.

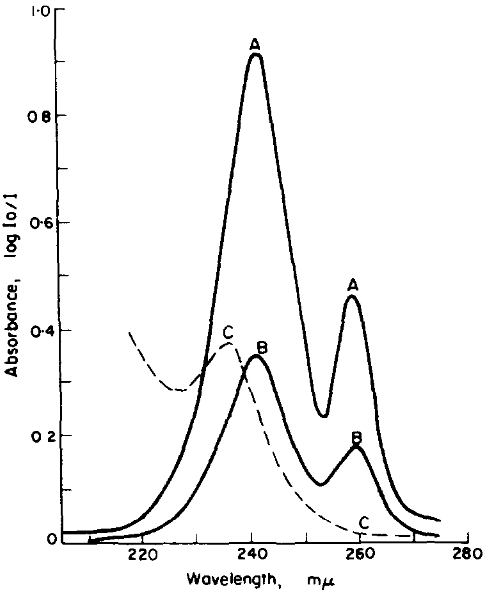


FIG. 3.—[Cu(CN)$_4$]$^{3-}$ and [Ni(CN)$_4$]$^{2-}$ spectra in 4*M* KCl:

A: 5 ppm of Ni; C: 2 ppm of Cu.
B: 2 ppm of Ni;
The wavelength scale is for [Cu(CN)$_4$]$^{3-}$; for the Ni-complex add 25 mμ units.

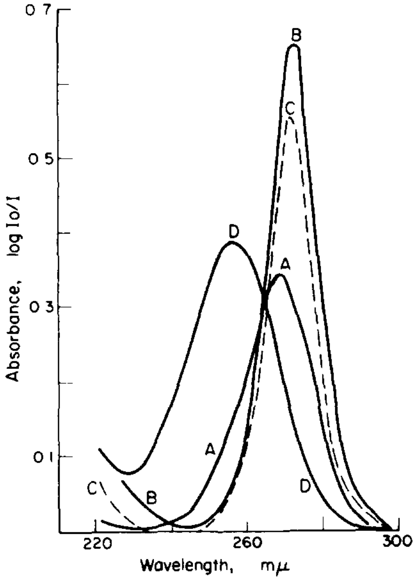


FIG. 4.—Spectra of Pb^{2+} in concentrated chloride solutions:

A: 8 ppm of Pb in 2*M* MgCl$_2$;
B: 9 ppm of Pb in 4*M* MgCl$_2$;
C: 8 ppm of Pb in 5*M* CaCl$_2$;
D: 10 ppm of Pb in 6*M* ZnCl$_2$.

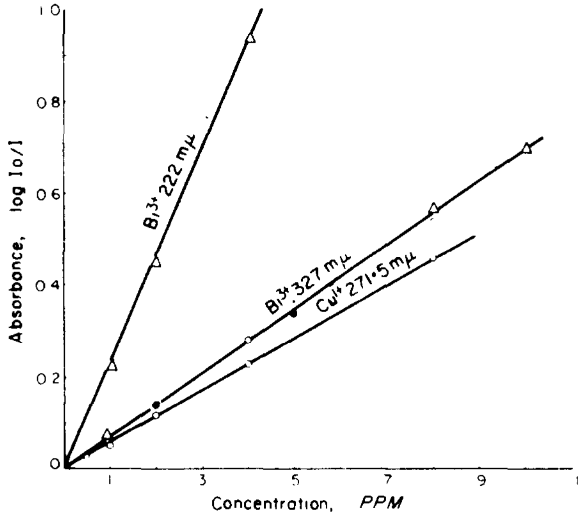


Fig. 5.—Variation of absorbance of Bi^{3+} (in 4*M* KCl at 222 mμ, and in 4*M* KCl, 2*M* $MgCl_2$ or 4*M* $MgCl_2$ at 327 mμ) and of Cu^+ (in 4*M* KCl at 271 mμ) with concentration.

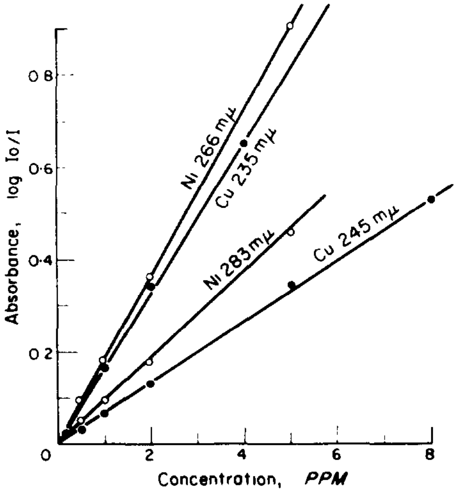


Fig. 6.—Variation of absorbance of $[Cu(CN)_4]^{3-}$ (at 235 and 245 mμ), and of $[Ni(CN)_4]^{2-}$ (at 266 and 283 mμ), with concentration, in 4*M* KCl solutions.

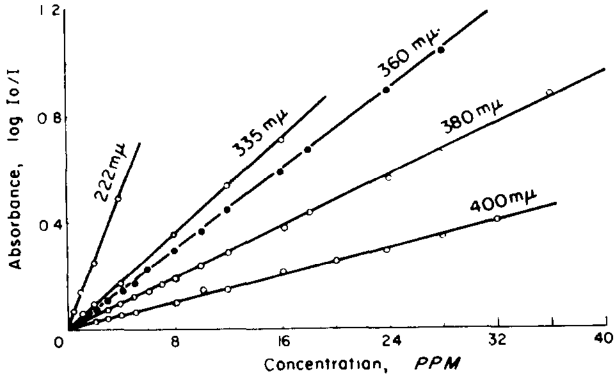


Fig. 7.—Variation of absorbance of Fe^{3+} with concentration in 4*M* KCl solutions, at the wavelengths indicated.

and other relevant values are summarised. Figs. 5–7 show the linearity of the absorbances at selected wavelengths; concentrations are expressed in ppm, *i.e.*, μg per ml of solution.

Bismuth: The absorption spectrum of bismuth was measured in 4*M* KCl and in 2*M* and 4*M* $MgCl_2$ solutions (see Fig. 1). There are two absorption bands peaking at 327 and 222 mμ (the latter is slightly shifted to longer wavelengths in the $MgCl_2$ solutions). Newman and Hume[3] attribute the 327-mμ band to the species $[BiCl_5]^{2-}$, and assign to it a molecular extinction of 16·1 × 10^3. This value is slightly higher than that obtained by other authors[2,4,5] in 6*M* HCl (0·0694–0·0720 for 1 ppm). Our results agree with the lower values (see Table I). Beer's law is observed (see Fig. 5), and there is no change in absorbance on passing from 6*M* to 10*M* HCl[2] or from 2*M* to 4*M* $MgCl_2$ solutions.

Incidentally, the short wavelength band at 222 mμ coincides with an absorption peak attributed by Newman and Hume[3] to Bi^{3+} ion, but the chloro- complex has a four-fold intensity in absorbance. In spite of this high molar extinction, the use of the

TABLE I.—A SUMMARY OF SPECTRAL DATA

Ion	Medium	Absorption peak, mμ	Specific absorptivity, *ppm*	Molar absorptivity	Miscellaneous
Bi^{3+}	KCl	222	0·230	48,070	
		327	0·070	14,630	$\Delta q^{Bi}_{(330-340)} = 0{\cdot}046$
	2*M* or 4*M*	225	0·200	41,800	
	$MgCl_2$	327·5	0·069	14,360	
Cu^{2+}	KCl	257·5	0·037	2350	Shifting spectra and partial decomposition to $2Cu^+ + Cl_2$.
	2*M* $MgCl_2$	257·5	0·037	2350	
	4*M* $MgCl_2$	271	0·064	4066	
	2·6*M* $AlCl_3$	271	0·062	3940	
	5*M* $CaCl_2$	270	0·070	4430	
	6*M* $ZnCl_2$	252	0·023	1460	
Cu^+	KCl	270	0·057	3620	Reduced by SO_3^{2-}
	4*M* $MgCl_2$	270	0·061	3870	Reduced by $[HONH_3]Cl$
	2·6*M* $AlCl_3$	269	0·069	4385	
	5*M* $CaCl_2$	268	0·068	4320	
	6*M* $ZnCl_2$	267	0·041	2610	
$[Cu(CN)_4]^{3-}$	KCl	235	0·176	11 180	$\Delta q^{Cu}_{235-245} = 0{\cdot}098$
Fe^{3+}	KCl	222·5	0·125	6980	
		335	0·0455	2540	$\Delta q^{Fe}_{360-380} = 0{\cdot}0143$
	4*M* $MgCl_2$	226·5	0·125	6980	
		363·5	0·060	3350	
	2·6*M* $AlCl_3$	227	0·135		
		362	0·063		
$[Ni(CN)_4]^{2-}$	KCl	266	0·185	10,860	$\Delta q^{Ni}_{265-275} = 0{\cdot}115$
		284	0·095	5,580	$\Delta q^{Ni}_{284-293} = 0{\cdot}083$
Pb^{2+}	KCl	268	0·0455	9,430	$\Delta q^{Pb}_{270-280} = 0{\cdot}0270$
	2*M* $MgCl_2$	268	0·0425	8,800	
	4*M* $MgCl_2$	271	0·0700	14,500	
	2·6*M* $AlCl_3$	270	0·0667	13,810	
	5*M* $CaCl_2$	271	0·0700	14,500	
	6*M* $ZnCl_2$	257	0·0388	8,040	

long wavelength band is more convenient for analytical purposes. Tervalent iron, which has in concentrated chloride solutions a nearly level absorption in the 327-mμ region (see Fig. 1), is the element most liable to interfere. The absorbance of Fe^{III} was found to be identical at the two wavelengths 330 and 340 mμ; hence it is proposed to determine the concentration of bismuth by taking measurements at these two wavelengths; the difference in the specific absorptivities is $\Delta q^{Bi}_{330\;\;340} = 0{\cdot}0460 \pm 0{\cdot}0004$ per ppm of bismuth.

Copper^{II}: The absorption spectrum of the cupric ion in concentrated chloride (or bromide) solutions is anomalous. In a previous publication[6] it has been suggested that this anomaly results from a partial decomposition to cuprous halide and halogen molecules. The evidence with respect to the identity of the absorbing species is inconclusive.[7,8] It may be observed (Table I) that as the activity in the chloride solutions increases there is a shift of the peak absorbance to longer wavelengths with a parallel increase in molar absorptivity. As a rule, such behaviour indicates the gradual formation of a more highly co-ordinated chloride complex, probably $[CuCl_4]^{2}$. In Fig. 2 the absorption spectrum of copper^{II} in 5*M* $CaCl_2$ is shown with three distinct peaks at 370, 273 and 235 mμ. The spectra of cupric chloride in 4*M* $MgCl_2$ and in 6·7*M* HCl[4] appear very much alike, in contrast to the single-peaked spectra in 4*M* KCl[6] and in 6*M* HCl.[2] On passing chlorine through a pure $CaCl_2$ solution, a band with a peak at 235 mμ is also obtained. The shape of the chlorine band together with a knowledge of the absorption spectrum of the cuprous chloride (see below) allows the complete resolution of the original irregular cupric chloride spectrum to its constituents, as shown by the thin lines in Fig. 2. Accordingly, the highly co-ordinated chloro complex of copper^{II} has a maximum absorbance at 276 mμ and a secondary band at ~370 mμ.[9]

Copper^{I}: Cupric salts may be reduced to the cuprous state by hydroxylamine more conveniently than by other reducing agents, in slightly acid or neutral solutions but not in concentrated acid solutions.[2] As a rule, heating the solution (to which a few grains of the solid reagent, $NH_2OH.HCl$, were added) below boiling for 1–2 sec was found to be necessary in order to complete the reduction, which was also successfully accomplished by sulphite or hydrogen peroxide. In these last cases, the solutions had to be boiled to destroy the excess of the reagents which absorb in the ultraviolet.[6] Beer's law is observed (see Fig. 5), but because of the closeness of the absorption band of the cuprous complex to that of Pb^{2+}, the use of this band for the determination of copper cannot be recommended wherever lead is present in larger amounts. A trial determination of copper in pure zinc metal, after dissolution in hydrochloric acid and reduction, proved promising.

Cupric chloride is readily converted to the cuprous cyanide complex,[10–12] $[Cu(CN)_4]^{3-}$, even in concentrated KCl solutions, on adding a small excess of KCN. The cyano complex has two narrow absorption bands with peaks at 215 and 235 mμ (see Fig. 3), which serve for the safe identification of copper. The excess of cyanide does not interfere with the determination of copper in the region of the long wavelength band. The absorbance of the neutral or slightly alkaline 4*M* KCl solution at 235 and 245 mμ is to be measured with reference to a portion of the same solution to which no cyanide has been added. Beer's law is observed; the difference in absorptivities is $\Delta q^{Cu}_{235-245} = 0{\cdot}098 \pm 0{\cdot}008$ per ppm of copper, in good agreement with results recorded by the authors cited above (see Fig. 6 and Table I).

Iron^{III}: Solutions of tervalent iron in 4*M* KCl absorb strongly in the whole range of the ultraviolet. There are two distinct bands with peaks at 222·5 and 335 mμ, the latter being less intense and very broad. The absorption spectrum is attributed[13] to the four co-ordinated species $[FeCl_4]^-$.

In neutral solutions the absorption is less intense throughout, and the iron is hydrolysed and precipitates with time. All solutions were therefore made up to contain 0·01*M* HCl, and were found to be stable and to give reproducible results. Typical absorption spectra in KCl (and other concentrated chlorides) are shown in Fig. 1, the relevant values being recorded in Table I. Beer's law is observed at all wavelengths (Fig. 7). Methods for the determination of iron in concentrated HCl have been previously proposed.[5,14]

For the determination of iron in KCl solutions, the use of method I (see Part I) is advised, taking measurements at the wavelengths 360 and 380 mμ. The difference in absorptivities $\Delta q^{Fe}_{360-380} = 0{\cdot}0143 \pm 0{\cdot}0005$ per ppm of iron. Most common cations (including Bi^{3+}) and anions do not interfere with the determination of iron at these wavelengths. The most serious deviations were observed in the presence of Sn^{2+} (because of reduction), BrO_3^-, IO_4^- and $S_2O_8^{2-}$ ions.

As a rule, a part of the iron in KCl products is present in the reduced bivalent state. Hence the solutions should be oxidised by adding 1 drop of an $S_2O_8^{-2}$ or ClO_3^- solution, containing 5 mg/ml of the reagent, and boiled.

In 4*M* $MgCl_2$ solutions the absorption peaks of Fe^{III} shift to longer wavelengths, being identical in position and intensity with those recorded in 6·7*M* HCl solutions.[4] The deformation of the spectrum is even more pronounced in 5*M* $CaCl_2$ solutions, whilst in 6*M* $ZnCl_2$ solutions there is a gradual rise in absorbance towards shorter wavelengths, but no well-defined absorption bands may be distinguished (see Fig. 1).

Hydroxylamine hydrochloride reduces iron^{III} to iron^{II} on boiling the solutions. The absorbance of the latter is comparatively small, and the reaction may be used for the determination of iron by a differential method,[15] or for elimination of the interference of iron in the determination of other ions.

Nickel: The absorptivity of the chloro complex of Ni^{2+} is too small for its determination in the ppm range. On the other hand, nickel yields an extremely stable cyano complex, $[Ni(CN)_4]^{2-}$, on the addition of the slightest excess of cyanide.[16] The absorption spectrum of this complex in 4*M* KCl solutions has two narrow and intense bands with peaks at 266 and 284 mμ (Fig. 3 and Table I), in excellent agreement with results obtained in aqueous solutions by previous investigators.[10,17,11] The cyano-nickel complex has already been used for the spectrophotometric determination of nickel in the 0·2–2·5 ppm range.[18] Beer's law is observed at both wavelengths, and the nickel may be determined by using Method I and either, or both, absorption bands. Acid solutions should be neutralised by ammonia before adding 20–40 ppm of KCN (according to the concentration of the nickel present) to the test solution. A blank to which no cyanide has been added serves as reference solution. $\Delta q^{Ni}_{265-275} = 0{\cdot}115 \pm 0{\cdot}005$ and $\Delta q^{Ni}_{284-293} = 0{\cdot}083 \pm 0{\cdot}005$ per ppm of nickel. The determination of 1 ppm of Ni in KCl solutions containing up to 150 ppm of various cations resulted in a deviation of 0·01–0·02 ppm. The interference of Fe^{3+} and of Pb^{2+} was more serious than that of other cations, and results obtained were too low by 0·08 ppm. This interference may be eliminated by making the solutions slightly alkaline with ammonia, before adding the cyanide.

Lead: The spectrum of the chloro complexes of Pb^{2+} was investigated by Fromherz,[1] and more recently by other authors,[2,4,5] with analytical purposes in mind, using concentrated HCl solutions. Two effects were noted[2] with increases in concentration of HCl: (*a*) a shift of the absorption peak towards longer wavelengths (maximum 271 mμ), and (*b*) a simultaneous increase in absorptivity. The absorption band at 271 mμ is attributed to the species $[PbCl_4]^{2-}$, whilst those at shorter wavelengths result from chloro complexes with less than four chlorine ions.

Parallel changes in the spectra of Pb^{2+} with increase in the concentration of $MgCl_2$ solutions were observed in the present work (Table 1) and Fig. 4. It is notable that in 6*M* $ZnCl_2$ solutions the Pb^{2+} band has a peak at 257 mμ, and is much broader and less intense that the absorption spectra in the other concentrated chloride solutions, in accord with the low activity coefficients of concentrated $ZnCl_2$ solutions[19] and the binding of the Cl^- ions in the complex $[ZnCl_4]^{2-}$. The intensity of absorbance of Pb^{2+} in concentrated chloride solutions may thus be considered to be a measure of the relative activity of the chloride ion in these solutions. Another aspect which characterises the formation of the tetrachloro-complex, $[PbCl_4]^{2-}$, is the half-width of the absorption band; in 2*M* $MgCl_2$ and in 4*M* KCl the half-width is 22 mμ, whilst in 4*M* $MgCl_2$, 2·6*M* $AlCl_3$ and 5*M* $CaCl_2$ it is only 14 mμ.

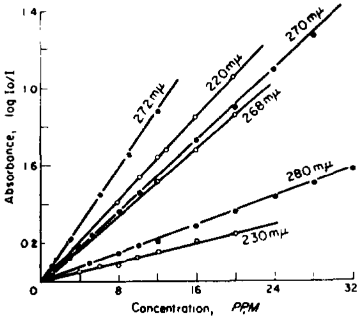


FIG. 8.—Variation of absorbance of Pb^{2+} with concentration in 4*M* KCl (at 270 and 280 mμ) and in 2*M* and 4*M* $MgCl_2$ (at 268 and at 272 mμ) solutions. NO_3^- in 4*M* KCl at 220 and 230 mμ.

In KCl, as well as in the other chloride solutions, Beer's law is observed if the concentration of the "mother salt" is kept constant (Fig. 8). $\Delta q^{Pb}_{270-280}$ (in KCl solutions) = 0·0270 ± 0·0006 ppm of lead.

In actual determinations of lead present in solid KCl, Cu^{2+} and Fe^{3+} interfere to a great extent. Therefore Method I is not valid. Kress[20] proposed a method formally resembling Method II of the present authors. It has been found that Method III yields much more satisfactory results, and this has been used by us in the synthetic test solutions, as well as for the determination of lead present in pure and analytical grade KCl. The characteristic correction ratio necessary for this method, $K^{Pb}_{R} = A^{Pb}_{270}/\Delta A^{Pb}_{270-280} = 1{\cdot}62 \pm 0{\cdot}02$.

Nitrate: The absorption spectrum of the nitrate ion in aqueous and in electrolyte solutions has recently been investigated by a number of authors.[21,22] It is characterised by two absorption bands with peaks at 300 mμ and in the region of 200 mμ. The first band is too weak to serve for the determination of the nitrate ion in small concentrations. The intense band is too far out in the ultraviolet, hence only Method

III can be expected to be of analytical use, taking measurements on the long-wave tail of this band.

In 4*M* KCl solutions, Beer's law is observed at wavelengths 220 and 230 mμ (see Fig. 8), the specific absorptivity at these wavelengths being 0·051 and 0·011 per ppm of NO_3^- in solution, *i.e.*, $\Delta q_{220-230}^{NO_3^-} = 0{\cdot}0398 \pm 0{\cdot}0018$, and the correction ratio $K_R^{NO_3^-} = A_{220}^{NO_3^-}/\Delta A_{220-230}^{NO_3^-} = 1{\cdot}27 \pm 0{\cdot}03$.

Cations and anions which do not absorb in this range of the spectrum do not disturb the determination of the nitrate ion, even if present in a concentration of 100–1000 ppm. Relatively high concentrations of SO_4^{2-}, PO_4^{3-}, ClO_3^- and Br^- ions also do not interfere seriously. On the other hand, many cations, such as Bi^{3+}, Fe^{3+}, Cu^{2+} and Pb^{2+}, if present in concentrations higher than a few ppm, distort the results. When the concentration of these ions is known from previous determinations, appropriate corrections may be introduced in Formula III (see Part I of this series. For example:

$$\Delta q_{220-230}^{Bi} = 0{\cdot}095\ ; \qquad q_{220}^{Bi} = 0{\cdot}220$$

$$\Delta q_{220-230}^{Pb} = 0{\cdot}018\ ; \qquad q_{220}^{Pb} = 0{\cdot}020.$$

It has also been found that the interference of many of these cations can be eliminated simply by making the solution slightly alkaline with ammonia; the slight precipitates remain in suspension and do not disturb the determination of the nitrate ion.

TABLE II.—EQUATIONS AND EXPERIMENTAL RESULTS ON THE QUANTITATIVE DETERMINATION OF IONS IN 4*M* KCl SOLUTIONS

Ion detd.	[a]Equation used	Sensitivity of method, *ppm*	Mean deviation, *ppm*	No. of detns.
Bi^{3+}	$\frac{\Delta A^s_{330-340}}{0{\cdot}0460}$	±0·06	±0·2	9
[c]Cu^{2+}	$\frac{\Delta A^s_{235-245}}{0{\cdot}0980}$	±0·03	±0·08	29
Fe^{3+}	$\frac{\Delta A^s_{360-380}}{0{\cdot}0143}$	±0·2	±0·4	62
[b]Ni^{2+}	$\frac{\Delta A^s_{265-275}}{0{\cdot}1150}$	±0·03	±0·05	37
Pb^{2+}	$\frac{(\Delta A^s_{270-280})^2 \times 60}{A^s_{270}}$	±0·06	±0·2	64
NO_3^-	$\frac{(\Delta A^s_{220-230})^2 \times 31{\cdot}9}{A^s_{220}}$	±0·08	±0·7	55

[a] On substituting the measured absorption values in the equation the concentration of the ion is obtained in ppm.

[b] Equation $Q_{ppm}^{Ni} = \frac{A^s_{284-293}}{0{\cdot}083}$ may also be used; results recorded are the mean of both determinations.

[c] Determination in the form of the cyanide complex $[Cu(CN)_4]^{3-}$.

TABLE III.—IONS DETERMINED (*F*) AND COMPOSITION (*P*) OF 18 SYNTHETIC 4*M* KCl SOLUTIONS, PPM

		Fe^{3+}	Pb^{2+}	Ni^{2+}	Cu^{2+}	Bi^{3+}	NO_3^-	Other ions	
								Total	Principal
1.	*P*	3·0	5·6	0·90	0·30	—	20·0	270	75 Br^-
	F	2·2	5·5	—	—		22·0		
2.	*P*	3·8	2·2	1·20	0·70	—	60·0	247	80 SO_4^{2-}
	F	3·6	1·8	1·18	—	—	—*		
3.	*P*	0·9	0·3	0·80	0·20	—	3·0	35	12 I
	F	0·9	0·3	0·76	0·22	—	3·1		14 Br
4.	*P*	0·7	0·5	0·40	1·00	—	4·0	21	12 Br
	F	0·4	0·5	0·40	1·00	—	4·5		
5.	*P*	4·8	2·8	0·25	0·10	—	24·0	645	250 Na
	F	4·8	2·2	—	—	—	25·0		360 SO_4^{2-}
6.	*P*	3·2	1·7	0·55	1·70	—	32·0	104	30 SO_4^{2-}
	F	3·6	1·8	0·35	1·20	—	31·0		20 Br^-
7.	*P*	0·3	0·9	0·50	1·10	—	10·0	36	15 Zn^{2+}
	F	0·2	0·9	—	—	—	10·1		
8	*P*	4·0	3·0	0·40	0·30	—	6·0	—	—
	F	4·1	3·3	—	—	—	5·0		
9.	*P*	0·6	0·1	0·10	0·10	—	12·8	21	10 SO_4^{2-}
	F	0·7	0·2	0·15	0·14	—	12·1		
10.	*P*	0·9	3·0	0·35	—	—	8·0	33	27 ClO_3^-
	F	0·9	3·0	0·37	—	—	8·6		
11.	*P*	2·8	3·5	0·60	1·5	—	3·3		
	F	—	3·1	0·61	—	—	3·7	—	4 SO_4^{2-}
12.	*P*	2·1	2·6	0·38	0·26	—	1·3	127	100 Br^-
	F	1·4	2·4	0·42	0·21	—	1·4		
13.	*P*	2·3	2·1	0·90	0·59	—	4·5	67	20 ClO_3^-
	F	1·3	2·1	0·94	0·59	—	4·2		
14.	*P*	—	3·9	0·64	1·04	—	3·9	92	36 SO_4^{2-}
	F	0·2	4·0	0·65	1·06	—	4·4		
15.	*P*	3·2	10·3	0·90	0·21	0·3	1·5	277	60 SO_4^{2-}
	F	2·8	10·4	0·86	0·08	0·4	1·0		48 Br^-
16.	*P*	7·7	3·7	—	—	4·0	9·0*	—	—
	F	7·5	3·3	—	—	4·1	—		
17.	*P*	10·8	—	4·50	5·31	2·8	—	363	180 SO_4^{2-}
	F	10·0	—	—	—	3·1	—		150 Br^-
18.	*P*	9·6	—	3·60	0·75	0·5	4·5	107	74 Br^-
	F	9·2	0·9	3·46	—	0·7	3·4		

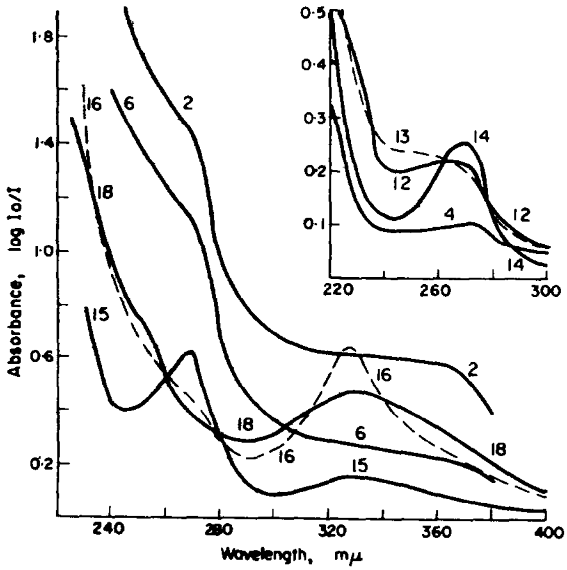
* Absorbance at 220 mμ was too high, and therefore NO_3^- could not be determined.

Determination of Bi^{3+}, Cu^{++}, Fe^{3+}, Ni^{2+} *and* NO_3^- *in synthetic solutions of* 4*M* KCl

Seventy "synthetic" solutions of 4*M* KCl (0·01*M* in HCl) were prepared in order to test the proposed method for the determination of the above "impurities". The KCl solutions were prepared from a J. T. Baker Analyzed stock (lot No. 27162), to which the sought cations were added up to 10 ppm, and many other ions (Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+, NH_4^+, Zn^{2+}, Br^-, I^-, NO_3^-, ClO_3^-, SO_4^{2-} and PO_4^{3-}) in widely varying concentrations.

Determinations were made by the use of the equations tabulated in Table II. The sensitivity of the method was calculated by assuming that the precision of the absorbance readings was ±0·003.

Table III records the concentrations (*P*) of 18 (of the 70) "synthetic" solutions and the concentrations of each ion found (*F*). Only the total concentrations, and that of the main constituent of the ions not determined, is given in the Table. In the case of the first 4 solutions, the "pure" 4*M* KCl solution served for reference, whilst the rest were compared to distilled water. The absorbance of the cyanide complexes of copper and nickel was measured in all cases by reference to the same KCl solutions without cyanide. A few of the measured spectra are shown in full in Figs. 9–11, the numeration and order being those of the solutions in Table III. The mean deviations, and the number of determinations of each ion, are also given in Table II.



FIGS. 9–10.—Spectra of synthetic 4*M* KCl solutions (with reference to water, except for Nos. 2 and 4). The composition of the solutions is given in Table III.

The following remarks are thought to be of some interest.

The presence of Fe^{III} in a concentration of more than 1 ppm is clearly indicated by the slope of the spectra in the region of the wavelengths 360–380 mμ.

Four ppm of bismuth are distinctly revealed by an absorption band with a peak at 327 mμ (spectrum No. 16), but even less than 1 ppm may be apprehended by the presence of a hump in this region of the spectrum (Nos. 15 and 18).

The absorption band of Pb^{2+} (peak at 268 mμ) stands out clearly if comparatively small amounts of Fe^{III} and Cu^{II} are present (spectra Nos. 4, 12, 14); otherwise the presence of lead is indicated only by the inflections on the spectral curve (Nos. 2, 6, 16).

The cyanide determinations of nickel were very satisfactory, but the results for copper were too low in some cases. Apparently this discrepancy results from insufficient additions of the cyanide reagent (25 ppm), especially when large amounts of iron were present (compare, for example, solutions No. 14 and 15). For the development of the $[Cu(CN)_4]^{3-}$ spectrum itself, at least 20 equiv of CN^- are required.

All spectra of the KCl solutions show a steep rise in absorbance below 240 mμ. This strong absorbance in the short wavelength region of the ultraviolet may result from a large number of other cationic and anionic impurities in addition to the nitrate ion. In some cases (Nos. 2 and 16), the absorbance was too high and the concentration of the nitrate ion could not be determined.

Whenever distilled water was used as the reference solution, 1·3 ppm were deducted from the determined values of the nitrate ion, this being the amount of the nitrate ion found in "Baker Analyzed" KCl (see Part III of this series of articles*). No corresponding corrections were made in the case of the cations determined here. The absorbance of lead (if more than 5 ppm were present) and the absorbance of bismuth (if more than 2 ppm were present) were deducted from the measured absorbances at 220 and 230 mμ before estimating the nitrate ion by Method III (Nos. 1, 15 and 18).

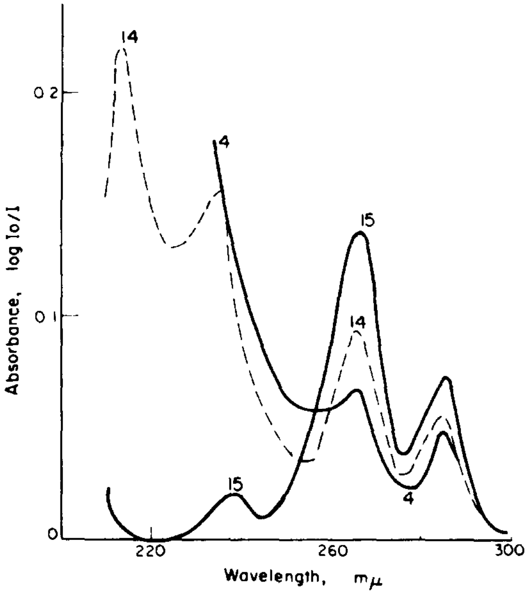


FIG. 11.—Cyanide spectra of synthetic 4*M* KCl solutions (with reference to KCl solution of the same composition).

In conclusion, the test carried out on the synthetic solutions proves that each of the six ions dealt with can be determined by the methods proposed, with an accuracy of less than 1 ppm. Best results were obtained with nickel: mean deviation ±0·05 ppm (see Table II).

In Part III of this series of articles, the method is applied to the determination of "impurities" present in chemically pure and analytical grades of KCl.

Preliminary work provides evidence that the same methods can be applied to the determination of "impurities" in other halides, such as KBr, $MgCl_2$, $CaCl_2$, $AlCl_3$ and $ZnCl_2$, or to the metals and alloys, oxides, carbonates, *etc.*, of the above salts after dissolution in HCl.

The methods proposed may improve the results and help in the spectrophotometric determination of constituents present in multicomponent solutions in general.

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* Part III, Talanta, 1964, **11**, 775.

Résumé—Les spectres d'absorption ultraviolets du Bi^{3+}, Cu^{2+}, Cu^+, Fe^{3+}, Pb^{2+} et NO_3^- dans KCl 4M et dans d'autres solutions concentrées de chlorure ont été enregistrés et leur absorptivité aux longueurs d'ondes important pour l'analyse a été évaluée. Des valeurs analogues pour les complexes cyanés tels $[Cu(CN)_4]^{3-}$ et $[Ni(CN)_4]^{2-}$ en solution KCl 4M ont été aussi obtenues. Ces valeurs sont ensuite utilisées pour le dosage de 6 ions en solution KCl "synthétiques" (méthode déjà proposée par A. GLASNER et P. AVINUR, *Talanta*, 1964, **11**, 679). Certains de ces résultats sont donnés en détail.

Zusammenfassung—Die ultravioletten Absorptionsspektren von Bi^{3+}, Cu^{2+}, Cu^+, Fe^{3+}, Pb^{2+} und NO_3^- in 4m KCl und anderen konzentrierten Chloridlösungen wurden aufgenommen und ihre Extinktionskoeffizienten bei analytisch geeigneten Wellenlängen berechnet. Diese Werte wurden auch für die Cyanokomplexe $[Cu(CN)_4]^{3-}$ und $[Ni(CN)_4]^{2-}$ in 4m KCl ermittelt. Diese Werte wurden für die unabhängige Bestimmung von sechs Ionen "synthetische" KCl-Lösungen nach den vorher (A. GLASNER, P. AVINUR, *Talanta*, 1964, **11**, 679) entwickelten Methoden verwendet. Einige Ergebnisse werden im Detail angegeben.

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SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF IMPURITIES IN PURE AND ANALYTICAL REAGENTS—III*

THE DETERMINATION OF SIX IONS IN KCl

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Summary—The absorption spectra of $4M$ KCl solutions of 15 different products have been measured, and the concentrations of the impurities, bismuth, copper, iron, lead, nickel and nitrate, present in these salts, have been determined by the methods already developed (A. GLASNER and P. AVINUR, *Talanta*, 1964, **11**, 679, 761). Pairs of products, of two different grades of purity, originating from the same firm, have been compared. The results are critically discussed.

INTRODUCTION

THE methods developed in Parts I and II have been applied to the determination of 5 metallic ions and the nitrate ion, present as impurities in KCl products from different sources. The products were from 9 different firms, and in most cases 2 grades from the same firm were taken for examination. The results are relevant only with respect to the ions actually determined, and contain no information on impurities which do not absorb in the ultraviolet.

EXPERIMENTAL

Samples of 14·912 g of KCl, dried at 120°, were weighed out of the freshly-opened containers and dissolved in triply-distilled water and 5 ml of $0{\cdot}1M$ HCl, in 50-ml volumetric flasks. The solutions of two products (from the Dead Sea Works and from J. T. Baker USP) were turbid, supposedly because of the presence of organic matter, and were filtered through fritted-glass crucibles. The spectra were measured by comparing with distilled water in an "Optica" CF4 spectrophotometer (single beam, manual model) using matched quartz cells of 1- and 4-cm width. The measurements of each spectrum were repeated 2 or more times, and at least 2 samples of each product were prepared.

Iron was determined in the freshly prepared solution, and again after oxidising the solution, as explained in Part II. In this way, information on both iron^{III} and iron^{II} has been obtained.

For the determination of copper and nickel, 1 drop of concentrated NH_4OH (B.D.H. AnalaR) was added to the solution to make it slightly alkaline (pH = 7–8). A portion of this neutralised solution was poured into the reference cell, while to another portion (10 ml) 1 more drop of a KCN solution containing 5 mg of CN^- per ml was added.

Absorption measurements over the whole range of the ultraviolet were taken, although absorbance values at only two wavelengths, for each ion determined, are required. The equations employed for calculating the amount of impurity present in the solid KCl, in ppm (or $10^{-4}\%$), have been tabulated in Part II (Table II). When measurements were made in 4-cm quartz cells, final results were obtained after division by a factor of 1·2.

RESULTS AND DISCUSSION

Table I lists the firms and qualifying specifications of the KCl products examined by us.

The determined amounts of the ions Fe^{3+}, Bi^{3+}, Pb^{2+}, Ni^{2+}, Cu^{2+} and NO_3^-

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* Parts I and II see *Talanta*, 1964, **11**, 679, 761.

TABLE I.—LIST OF KCl PRODUCTS

Firm	Product	Our designation
Agan, Tel-Aviv, Israel.	1. A.R.	A_1
	2. C.P.	A_2
J. T. Baker Chemical Co., Philipsburg, N.J., U.S.A.	1. Analyzed Reagent, 3040, 99·9% KCl, Lot. No. 27162	J_1
	2. U.S.P. powder, Lot. No. 73047	J_2
The British Drug Houses Ltd., Poole, England.	1. AnalaR 99·8% KCl	BD_1
	2. Laboratory reagent 99.5% KCl	BD_2
May and Baker Ltd., Dagenham, England.	1. BP.	MB_1
	2. Laboratory chemicals, 99·5% KCl	MB_2
E. Merck AG., Darmstadt, Germany.	1. *pro analysi*, 4933, max. 0·005% Br^-, Lot. No. 6013799	M_1
	2. *pro analysi* 4936, Lot. No. 121152	M_2
Dead Sea Works, Israel.	1. Twice recrystallised in this laboratory	D_1
	2. No. 2868, 97·69% KCl, 1·87% NaCl	D_2
Mallinckrodt Chemical Works, St. Louis. Mo., U.S.A.	U.S.P. granular, 6838	MK
Riedel-de Haën AG, Seelze, Hannover, Germany.	für Analyse, 31248, Lot. No. 503121	R
Baker and Adamson, New York, U.S.A.	A.C.S. reagent, Code 2150	BA

present in 15 different products of KCl are listed in Table II. 0·0 or 0·00 indicate results within the limits of the sensitivity of our methods. In the case of iron, the amount determined after oxidation is shown, whilst that found in the freshly prepared solutions is given in brackets. The difference is supposedly Fe^{2+}. The determined amount of the "impurities" is invariably less than that declared on the labels of the analysed reagents. Considering that the latter are "maxima", determined as a rule by the sensitivity of the test applied, this favourable result was to be expected.

TABLE II.—IMPURITIES IN VARIOUS KCl PRODUCTS, *ppm*, OR 10^{-4}%

Source of KCl		Fe		Heavy metals					NO_3^-	
		Found	Declared	Bi	Pb	Ni	Cu	Declared	Found	Declared
Agan	A_1	1·4 (1·1)	5	0·1	0·3	0·70	0·00	10	12	20
Agan	A_2	4·7 (4·2)	—	0·4	0·4	0·55	0·00	—	10	—
J. T. Baker	J_1	0·6 (0·5)	1	0·3	0·5	0·08	0·08	1	4·0	<30
J. T. Baker	J_2	18·7(17·2)	—	0·9	1·5	0·53	0·90	—	3·2	—
B.D.H.	BD_1	1·4 (0·9)	5	0·1	0·3	0·05	0·00	10	3·0	20
B.D.H.	BD_2	0·7 (0·6)	20	0·1	1·6	0·10	0·35	—	5·0	—
May and Baker	MB_2	4·2 (4·0)	40	0·1	1·3	0·50	0·00	—	23	—
May and Baker	MB_1	4·5 (3·7)	—	0·1	1·0	0·20	0·00	—	23	—
Merck	M_1	1·1 (1·0)	3	0·0	0·3	0·15	0·00	9	0·3	10*
Merck	M_2	1·4 (1·2)	3	0·0	0·4	0·20	0·00	9	12·0	10*
Dead Sea Works	D_2	10·5 (9·2)	—	0·2	1·4	0·00	0·00	—	45	—
Recrystallised	D_1	0·5 (0·2)	—	0·0	0·7	0·05	0·17	—	5·7	—
Mallinckrodt	MK	0·5 (0·2)	—	0·0	0·3	0·50	0·00	—	4·4	—
Riedel de Haen	R	0·5 (0·4)	3	0·1	0·3	0·10	0·00	10	21	10*
Baker and Adamson	BA	0·8 (0·5)	3	0·05	1·3	0·00	0·00	5	0·9	10*

* Nitrogen compounds, as N

Figs. 1–3 show the absorption spectra of the solutions, marked by the initials of the firms, and numbered according to the grade of the product, for easy reference. These spectra are similar to those of the "synthetic" solutions given in Part II, and their general forms and singularities, with respect to the "impurities" determined, are discussed there.

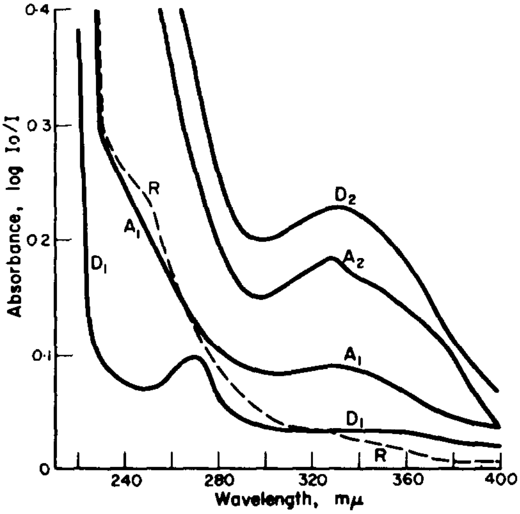

FIG. 1.—The absorption spectra of 4*M* KCl solutions of Dead Sea Works (D_1 and D_2), Agan (A_1 and A_2) and Riedel de Haën (R) products.

The total absorbance of the "chemically pure" (or similar lower-grade products) is always higher than that of the analysed reagent of the same firm. Evidently this results from the presence of further impurities, apart from those determined here, including finely divided solids and organic material. The absorption curves of such pairs of products exhibit a parallel run, indicating that the purer product was obtained from the lesser reagent, by recrystallisation or another process. The same applies to the two Merck products, both marked "*pro analysi*" (see Fig. 2). A study of such pairs should therefore be instructive with respect to the utility of the purification process employed. An exception are the two May and Baker products, which seem to differ only in packaging. (see Fig. 3).

In the case of the Dead Sea product (D_1), recrystallised in this laboratory, iron and bismuth were effectively removed, but lead appears to be more tenaciously retained (the least amount of lead in any of the analysed products was 0·3 ppm). On the other hand, the recrystallised product was contaminated by spurs of nickel and copper (see Table II). Two sources are suspect as sources of this contamination: (*a*) the filter paper used (with a Buchner funnel) for filtration, and (*b*) small particles of the floating agent present in the original product. The floating agent seems to be able to remove these (and other) metals from the mother liquor, but releases them on dissolving the salt in hot water.

The large amount of nitrate originally present in D_2 has been only partly removed; even so, the total absorbance of this recrystallised salt is quite low (Fig. 1, D_1). The absorbance of the small amount of lead present (0·7 ppm) is brought into clear relief (the absorption band being somewhat distorted on the short wavelength side

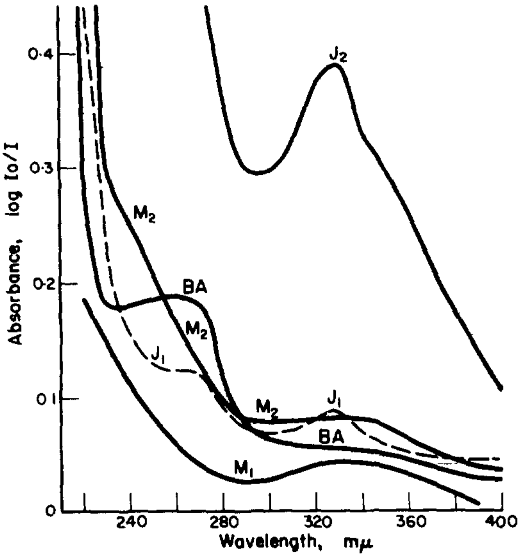

FIG. 2.—The absorption spectra of 4*M* KCl solutions of J. T. Baker (J_1 and J_2), Merck (M_1 and M_2) and Baker and Adamson (BA) products.

by the copper) and the greater part of the absorbance at 230 mμ is caused by the NO_3^- ion. Hence, the steep continuous rise in absorbance, starting at 250–240 mμ towards the shorter wavelengths, that may be observed on the absorbance spectra of some of the analytical reagents (J_1, MK), cannot be attributed to the NO_3^- ion. This absorbance is indicative of the presence of a number of impurity cations (*e.g.*, Tl^+) and anions (*e.g.*, MoO_4^{2-}) not studied in this work.

It should be further observed, in this connection, that the absorption spectra of products which contain a large amount of iron start to rise at about 290 mμ (A_1 and A_2, J_2, MB, D_2, *etc.*) The spectra of the two Merck products also exhibit this

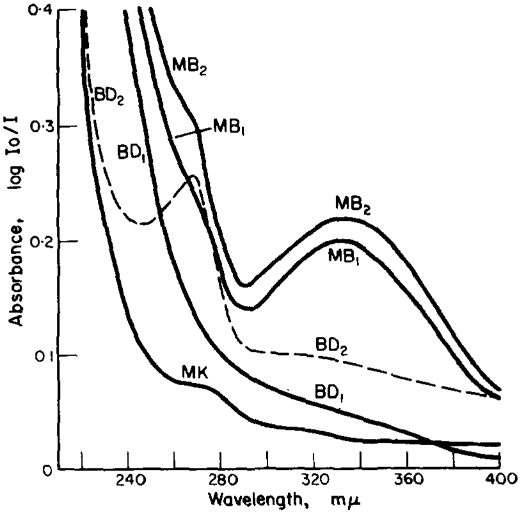

FIG. 3.—The absorption spectra of 4*M* KCl solutions of B.D.H. (BD_1 and BD_2), May and Baker (MB_1 and MB_2) and Mallinckrodt (MK) products.

feature, because of the presence of a relatively large amount of iron. Apparently these products were processed in Ni-steel vessels. The same may be said of B.D.H. "AnalaR", which contains more iron than the "Lab. Reagent" (Fig. 3); and of J. T. Baker U.S.P. (J_2, Fig. 2), which contains more iron than any of the other products examined.

The J. T. Baker products also contain more bismuth than the other products. The presence of bismuth is clearly observed on both absorption spectra. Similar amounts of bismuth (0·3 ppm) were detected in other bottles of the "Analyzed" reagent in our stock room, with the exception of one (Lot No. 25119).

Mallinckrodt's U.S.P. can be favourably compared to "Analyzed" reagents either in respect of the "impurities" determined, or the total absorbance of the solution of the product (Fig. 3).

The concentration of NO_3^- was calculated in each case by Equation III (Part I):

$$Q^{NO_3^-} = \frac{(\Delta A^s_{220-230})^2\, 31{\cdot}9}{A^s_{220}},$$

taking measurements at 220 and 230 mμ. In a few cases of comparatively low total absorbance, the more simple Equation, I: $Q^{NO_3^-} = \Delta A^s_{220-230}/0{\cdot}0398$, can also be used in two ways: (*a*) by assuming that the total difference of the absorbance of the solution at the above wavelengths is caused by the nitrate ion (I) and (*b*) by correcting the absorbance readings for the absorbance of the cations which were previously determined (I*). In the latter case, there is still a possibility of obtaining too high values owing to unknown impurities. The results obtained by the two methods are compared in Table III for 3 KCl products, backing up the reliability of Method III.

TABLE III.—A COMPARISON OF METHODS I AND III FOR THE DETERMINATION OF NO_3^- ION

Source of KCl	NO_3^- determined by method, *ppm*		
	I	I*	III
D_1	6·0	5·7	5·7
M_1	1·0	0·7	0·3
BA	2·1	1·2	0·9

I* After correction of absorbance readings for the cations Fe^{3+}, Pb^{2+} and Bi^{3+} present.

The authors wish to apologise for any misapprehensions, or unfounded conclusions; they will be grateful for comments and corrections from those concerned.

Acknowledgement—A. G. wishes to express his deep gratitude to the Department of Chemistry, Princeton University, Princeton, N.J., U.S.A., for the Visiting Lectureship granted to him in 1961–2. The many-sided discussions at Princeton and elsewhere in the U.S.A. contributed much to this and other publications by him.

Zusammenfassung—Die Absorptionsspektren von Lösungen 15 verschiedener Substanzen in 4m KCl wurden gemessen und die Konzentration der Verunreinigungen Wismut, Kupfer, Eisen, Blei, Nickel und Nitrat in diesen Salzen wurde nach den vorher (A. GLASNER und P. AVINUR, *Talanta*, 1964, **11**, 761) angegebenen Methoden bestimmt. Paare von Substanzen verschiedenen Reinheitsgrads derselben Herstellerfirma werden verglichen und die Ergebnisse kritisch diskutiert.

Résumé—Les spectres d'absorption de 15 produits différents en solution KCl 4M ont été mesurés. La concentration des impuretés, bismuth, cuivre, fer, plomb, nickel et nitrate présents dans ces sels, a été déterminée par la méthode déjà proposée par (A. GLASNER et P. AVINUR, *Talanta*, 1964, **11**, 761). Un ensemble de 2 produits de deux degrés de pureté différents venant du même endroit a été comparé. Discussion critique des résultats.

Talanta, 1964, Vol. 11, pp. 781 to 788. Pergamon Press Ltd.

THE DETERMINATION OF MERCURY IN ROCKS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A radioactivation method for the determination of the small concentrations of mercury which occur in rocks is described. The procedure involves assay of the radioactivity of ^{197}Hg by use of a thin NaI(Tl) crystal scintillator. The applicability of such a detector in neutron-activation analysis is discussed.

THE determination of mercury in rocks poses major problems. An analytical method of high sensitivity is required, because the abundance of the element in an average igneous rock has been estimated[1] to be 0·06 ppm. In addition, contamination of specimens for analysis is by no means unusual, for mercury has an appreciable vapour pressure at room temperature, and most chemical laboratories contain the metal. Moreover, a number of compounds of mercury are readily volatilised, and losses may occur during chemical processing.

Neutron-activation analysis provides outstanding advantages for obviating these difficulties. The method gives adequate sensitivity, and the possibility of errors from contamination by traces of mercury after irradiation is eliminated. Furthermore, after exchange between activated mercury and inactive carrier has been achieved, any chemical purification need not be quantitative. There is the possibility of contamination of rock samples before activation, but a feature of the radioactivation method is that samples require little pretreatment before irradiation.

NEUTRON ACTIVATION OF MERCURY

When mercury of natural isotopic composition is irradiated with neutrons of thermal energies, radiative capture reactions occur which give rise to radioisotopes of the element. Relevant nuclear data are presented in Table I. These nuclear reactions can be used for activation analysis of mercury.[2–13] In the present work 65 h ^{197}Hg was counted. For an irradiation period of 1 week the use of ^{197}Hg can be shown to give a sensitivity 50 times better than that attainable with ^{203}Hg. In the present study chemical and counting operations were performed at a distance from the neutron source, and therefore the short-lived nuclides ^{199m}Hg and ^{205}Hg could not be used.

The decay scheme of ^{197m}Hg and ^{197}Hg is shown in Fig. 1. The electromagnetic radiations emitted by ^{197}Hg are 77 keV gamma rays (IC 80%), X-rays of 68 keV (average energy of two α satellites) and 10 keV following electron capture, and gamma rays of energy 191 keV. Detailed discussion of the decay of ^{197}Hg and its application to activation analysis of mercury has been given by Westermark and Sjöstrand.[6]

EXPERIMENTAL

Irradiation

About 0·8-g samples of rock were accurately weighed and sealed in cylindrical aluminium capsules of 6-mm diameter. Standards were prepared by weighing out 0·1-ml aliquots of a dilute standard

Table I.—Nuclear data for thermal neutron activation of mercury

Target nuclide	Abundance, %	Isotopic activation cross section, *barns*	Product radionuclide on thermal neutron irradiation	Radiation and energy, *MeV*	Half-life
^{196}Hg	0·146	420	^{197m}Hg	IT (96·5%) $e^- \gamma_1$ 0·134 (31%) γ_2 0·165 (0·28%) 0·071 – Hg X ray EC (3·5%) via 7·2 s ^{197m}Au $e^- \gamma_1$, 0·130 (7%) γ_2 0·279 (74%) γ_3 0·407 (0·3%)	24 h
		880	^{197}Hg	EC (100%) $e^- \gamma_1$ 0·0773 (23%) γ_2 0·191 (5%) 0·068 – Au X ray	65 h
^{198}Hg	10·02	0·018	^{199m}Hg	IT γe^- 0·368, 0·158	42 m
^{202}Hg	29·80	3·8	^{203}Hg	β^- 0·21 (100%) $\gamma_1 e^-$ 0·279	47 d
^{204}Hg	6·85	0·43	^{205}Hg	β^- 1·8; γ 0·203	5·5 m

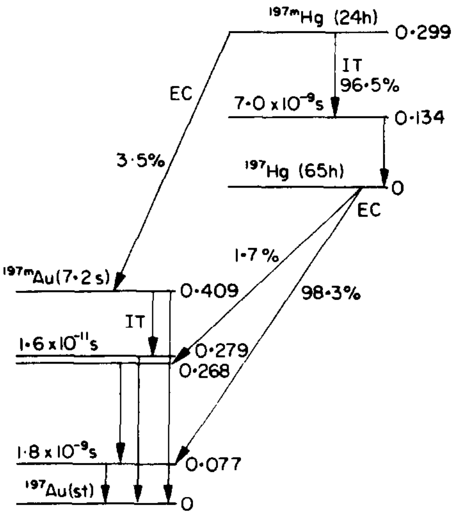

Fig. 1.—Decay scheme of ^{197m}Hg–^{197}Hg: energies in MeV. [After NAS-NRC Data Sheets (Aug. 1962) A = 197 (5-1-17)]

solution of mercury^{II} nitrate (50 mg of Hg/litre) into silica tubes of 4-mm internal diameter. The silica tubes were sealed with a burner, the lower parts being cooled to avoid any possibility of losses by evaporation. Containers of samples and standards were packed together with silica wool in a standard 1 inch diam. × 3 inch long screw-top aluminium can, and sent to Harwell for irradiation. Irradiations were for 6 days in a nuclear reactor flux of $1 \cdot 2 \times 10^{12}$ thermal neutrons. cm^{-2}. sec^{-1}.

Radiochemical separation

Because of the complex nature of rocks, non-destructive analysis using scintillation spectrometry was impossible. On the other hand, a simple radiochemical procedure for separating mercury from other contaminants was easily developed. Experimental details are as follows:

Step 1: Remove the irradiation capsules containing portions of rock from the can, open them, and transfer the samples to 60-ml platinum crucibles, each containing 1 ml of standard mercury carrier [10 mg of Hg/ml as mercury^{II} nitrate in 1*M* nitric acid; standardised gravimetrically through bis(ethylenediamine) copper^{II} tetra-iodomercurate(II)]. Wash out the capsules with a little warm 6*M* nitric acid and transfer the washings quantitatively to the crucibles (*Note* 1).

Step 2: To each sample add 10 ml of 40% hydrofluoric acid, cover the crucible loosely with the platinum lid, and digest on a steam-bath until the sample has completely dissolved. Add 3 ml of 9*M* perchloric acid and 2 ml of 16*M* nitric acid, and heat the mixture till white fumes of perchloric acid begin to be given off, taking care to avoid spattering. Replace the cover loosely, and continue to heat for about 5 min at a temperature at which the perchloric acid fumes moderately but does not rapidly evaporate. Heat for 5–10 min longer and finally evaporate carefully almost to dryness (*Note* 2).

Step 3: Transfer the residue with 10 ml of water to a 50-ml centrifuge tube. Add 5-6 drops of 20% tin^{II} chloride solution. Centrifuge and discard the supernate. Wash the precipitate of mercury^{I} chloride thoroughly with water and ethanol. Discard the supernates.

Step 4: Slurry the mercury^{I} chloride with acetone and transfer to the bottom of a long cold-finger condenser packet (17 × 2 cm) using a long-tipped dropping pipette for the purpose. Evaporate the acetone with gentle heating. Cover the solid mercury^{I} chloride with powdered iron, and insert the cold finger. Apply increasing heat from a microburner, and maintain the flame for a few min to drive all the mercury on to the tip of the cold finger (*Note* 3). Allow to cool completely before removing the jacket and replacing it with another containing 6 drops of 12*M* hydrochloric acid and 4 drops of 16*M* nitric acid. Gently distil the acid on to the finger (water flow now shut off) until the grey film of mercury is dissolved. Cool again and dismantle, rinsing the cold finger thoroughly as it is withdrawn.

Step 5: Transfer the acid solution from the outer jacket to a 50-ml centrifuge tube. Wash thoroughly with water and add the washings to the contents of the centrifuge tube. Make the resulting solution faintly ammoniacal and add 5 ml of 2% potassium iodide solution. Heat on a steam-bath and add, dropwise, a hot concentrated aqueous solution of bis(ethylenediamine) copper^{II} nitrate. Allow to cool to room temperature. Centrifuge, wash the precipitate several times with a solution containing 0·2 g of KI and 0·2 g of $[Cu\ en_2](NO_3)_2 \cdot 2H_2O$ in 200 ml of water, and then with ethanol. Slurry the precipitate with ethanol on to a weighed aluminium counting tray and dry under an infrared lamp. Cool and weigh to determine the chemical yield (usually $\sim 80\%$).

Treatment of irradiated mercury standards: At a suitable time open the silica irradiation tubes containing the mercury standards. Using a transfer pipette drawn out almost to a point, transfer the irradiated mercury solution quantitatively to a 50-ml volumetric flask. Make up to the mark with 3*M* nitric acid. Transfer a 10-ml aliquot to a 50-ml centrifuge tube containing 1 ml of standard mercury carrier. Precipitate $[Cu\ en_2][HgI_4]$, mount, dry and weigh it as described in Step 5 of the procedure for rock samples.

Notes

(1) Where pieces of rock, as opposed to powdered samples, are irradiated, remove surface contamination by cleaning with warm 6*M* nitric acid. After attack of the cleaning solution has proceeded for 1·5 min, remove the portion of rock and wash it thoroughly with water.

(2) When an irradiated standard was put through Steps 1 and 2 of the radiochemical procedure, it was found that no loss of radiomercury occurred before exchange with carrier had been achieved.

(3) The vapour pressure of mercury at 400° is 2·07 atm.

Activity determination

The electromagnetic radiations from ^{197}Hg in final precipitates from samples and standards were measured at constant geometry by scintillation spectrometry using counting techniques rather similar to those employed by Westermark and Sjöstrand.[6] In the present work a thin (3 inch diam. × 0·25 inch thick) NaI(Tl) crystal with a beryllium window was used as a detector to reduce the effect of any high-energy gamma radiation. The ^{197}Hg spectrum was generally studied after 3 days from the end of irradiation in the region 0–150 keV. This region is lower than the Compton distribution resulting from any higher-energy gamma rays, and the background is relatively low and flat. With the present technique the 68-keV X-rays and 77-keV gamma rays could not be resolved. Typical spectra obtained are shown in Fig. 2. and the activity of ^{197}Hg was determined from the area under the composite peak. Background correction was made by extrapolation as indicated in the figure. This method of subtraction proved practical and reproducible, although a more refined method could possibly be devised. A self-absorption correction curve, prepared in the conventional manner by precipitating different amounts of [Cu en_2][HgI_4] with fixed amounts of mercury, showed that with the range of weights of precipitates obtained from the radiochemical procedure count rates could be compared directly. A total photopeak area of 100 cpm was considered to be the practical limit of detection.

Decay curves indicated that only mercury activities were assayed (Fig. 3).

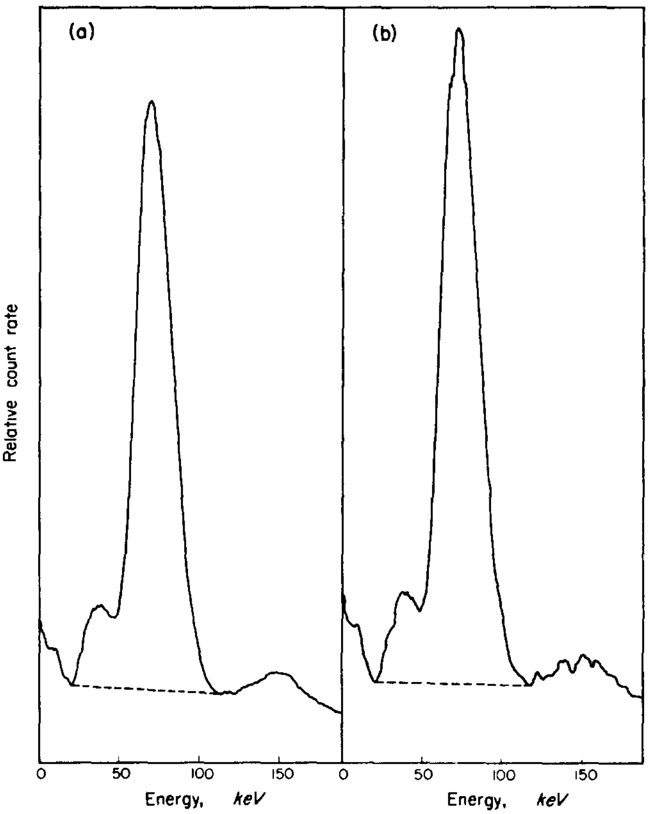

FIG. 2.—Spectra of final precipitates:
A from a mercury standard,
B from a rock sample,
as detected by a 3 × 0·25-inch NaI(Tl) crystal.
(The bump at the low energy side of the photopeak results from *K*-escape in the crystal. The dotted lines represent suggested background. Spectra measured using a single-channel pulse-height analyzer.)

DISCUSSION

Results obtained from activation analyses of international standard rocks are summarised in Table II, and give a general indication of the precision obtainable with this method. It is felt that these results must be accepted as maximum values for mercury in the standard rocks, because the samples were supplied in powder form by the U.S. Geological Survey and could possibly have become slightly contaminated before irradiation.[14]

Neutron self-shielding effects are unimportant in the application of the method to the analysis of an "average rock".[15–17] In the case of rocks or minerals enriched in elements which have high neutron absorption cross sections, *e.g.*, lepidolite, special steps may need to be taken to avoid serious self-shielding differences between samples and standards. In such circumstances it is probably most desirable to irradiate two similar quantities, *a* and *b*, of the sample, a very small known amount *c* of a suitable mercury compound having been mixed homogeneously with *b* to form the standard.[18]

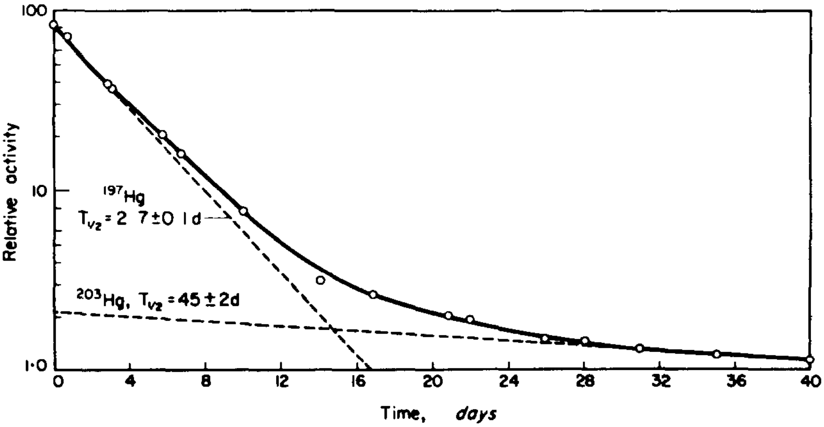

FIG. 3.—Part of the decay curve of a final precipitate indicating the small contribution of radiation from ^{203}Hg.
(Time 0 is ~100 hr from the end of neutron irradiation).

TABLE II.—MERCURY CONTENTS OF POWDERED SAMPLES OF THE STANDARD GRANITE *G* 1 AND THE STANDARD DIABASE *W* 1 DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

G 1 Hg, *ppm*	W 1 Hg, *ppm*
0·33	0·16
0·34	0·18
0·32	0·17
0·36	0·17
0·36	0·18
0·33	0·17
Average 0·34	Average 0·17

It seems appropriate to make some general observations on the utility in activation analysis of a NaI(Tl) crystal 3 inch diam. × 0·25 inch thick fitted with a beryllium window 0·008 inch thick. A thin crystal is of particular advantage when it is necessary to record low-energy quanta (15–100 keV) in the presence of high-energy quanta. An illustration of this is shown in Fig. 4, which refers to the *K* X-radiation of barium in the spectrum of ^{137}Cs. The spectra were obtained with crystals of 3-inch diameter under analogous conditions.

In the recording of spectra in the 33–150 keV range, for every photoelectric peak corresponding to energy E keV an additional "escape peak" appears corresponding to energy (E — 28·6) keV. This effect, caused by the escape of the characteristic K X-ray quanta of iodine from the surface layer of the front face of the crystal where the recording process mainly occurs, reduces the intensity of the main photopeak.[19,20] Generally, the main peak is reduced more the closer the recorded energy approaches the absorption edge of iodine (K_{ab} = 33·6 keV), but the reduction also depends to some extent on the divergence of the incident beam of rays and increases as the measurement geometry deteriorates.

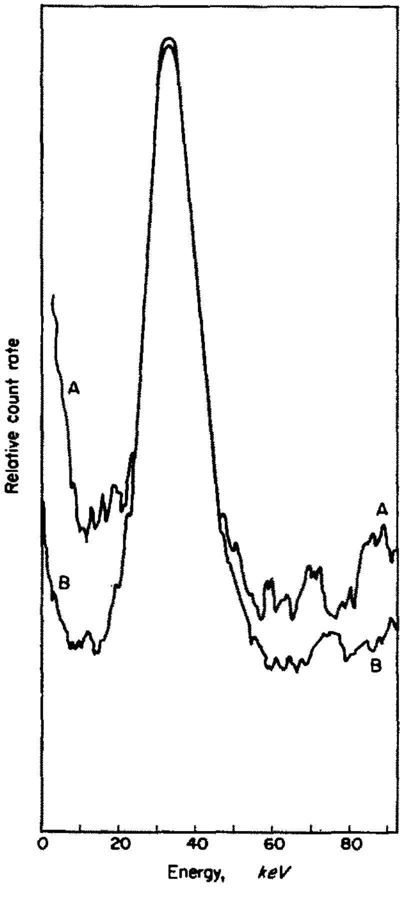

FIG. 4.—Photopeak from Ba K X-ray in the spectrum of ^{137}Cs measured with crystals of 3-inch diameter:
A. Spectrum obtained with NaI(Tl) crystal 3 inch thick.
B. Spectrum obtained with NaI(Tl) crystal 0·25 inch thick

Górski[21] has calculated the total photoelectric efficiency as well as the photoelectric efficiency recorded for the main photopeak without the escape peak for thin crystals.

Values for estimating neutron-activation sensitivities for certain elements have been determined in our laboratory (Table III). The neutron source was the reactor

TABLE III.—NEUTRON-ACTIVATION SENSITIVITIES USING A FLUX OF $1{\cdot}2 \times 10^{12}$ THERMAL NEUTRONS. CM^{-2}. SEC^{-1}

Element	Activated form	Half-life	Counts per min per μg of element		
			Geiger-Müller counting	Thin crystal gross counting	Thin crystal discriminated counting (with energy range, *keV*)
Gold	^{198}Au	2·70 d	$2{\cdot}1 \times 10^{6}$	$3{\cdot}7 \times 10^{6}$	$3{\cdot}28 \times 10^{6}$ (21–110)
Hafnium	^{175}Hf ^{180m}Hf ^{181}Hf	70 d 5·5 h 42·5 d	$1{\cdot}7 \times 10^{4}$	$1{\cdot}0 \times 10^{5}$	$5{\cdot}6 \times 10^{4}$ (21–110)
Indium	^{114m}In ^{116m}In	50 d 54 m	$4{\cdot}5 \times 10^{3}$	$8{\cdot}8 \times 10^{3}$	$2{\cdot}7 \times 10^{3}$ (12·5–39)
Iridium	^{192}Ir ^{194}Ir	74·4 d 19 h	$2{\cdot}2 \times 10^{6}$	$4{\cdot}7 \times 10^{6}$	$3{\cdot}1 \times 10^{6}$ (45–89)
Mercury	^{197m}Hg ^{197}Hg ^{203}Hg	24 h 65 h 47 d	$1{\cdot}9 \times 10^{4}$	$1{\cdot}5 \times 10^{5}$	$1{\cdot}3 \times 10^{5}$ (21–110)
Palladium	^{109}Pd–^{109m}Ag	13·6 h	$1{\cdot}0 \times 10^{4}$	$1{\cdot}3 \times 10^{4}$	$4{\cdot}5 \times 10^{3}$ (12·5–39)
Rhenium	^{186}Re ^{188}Re	3.7 d 16·7 h	$2{\cdot}0 \times 10^{6}$	$4{\cdot}4 \times 10^{3}$	$9{\cdot}1 \times 10^{5}$ (37–82)
Ruthenium	^{97}Ru ^{103}Ru–^{103m}Rh ^{105}Ru–^{105m}Rh	2·9 d 40 d 4·4 h	$7{\cdot}2 \times 10^{3}$	$1{\cdot}5 \times 10^{4}$	$9{\cdot}5 \times 10^{3}$ (7–37)
Tantalum	^{182}Ta	115 d	$7{\cdot}0 \times 10^{4}$	$2{\cdot}0 \times 10^{5}$	$9{\cdot}5 \times 10^{4}$ (45–89)
Tungsten	^{185}W ^{187}W	73 d 24·0 h	$1{\cdot}4 \times 10^{5}$	$3{\cdot}5 \times 10^{5}$	$3{\cdot}0 \times 10^{5}$ (21–110)

BEPO at the Atomic Energy Research Establishment, Harwell, and samples were irradiated for 1 week or to saturation, whichever was shorter. Activities were measured with the irradiated samples mounted on aluminium trays (3 cm diam. and 3 mm deep) and placed on standard shelf 1 of counting assemblages. A Geiger-Müller counter of the EHM 2/S type (window thickness 1·7 mg/cm^{2}) and a NaI(Tl) crystal 3 inch diam. × 0·25 inch thick with a 0·008 inch thick beryllium window were used for measurement. The latter detector was mounted on a 9531B E.M.I. photomultiplier tube. Discriminated scintillation count rates were determined using a single-channel pulse-height analyser. All count rates were normalised to 6 hr after the end of irradiation and 1 μg of target element.

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Zusammenfassung—Eine Radioaktivierungsmethode zur Bestimmung der kleinen in Gesteinen vorkommenden Quecksilberkonzentrationen wird beschrieben. Dabei wird die Radioaktivität von ^{197}Hg mit Hilfe eines dünnen NaJ(Tl)-Kristallszintillators gemessen. Die Anwendbarkeit eines solchen Detektors bei der Neutronenaktivierungsanalyse wird diskutiert.

Résumé—On décrit une méthode de dosage par radioactivation des petites concentrations de mercure que l'on trouve dans les roches. Le procédé comprend l'essai de la radioactivité de ^{197}Hg par emploi d'un scintillateur à cristal mince de NaI(Tl). On discute de l'applicabilité d'un tel détecteur à l'analyse par activation aux neutrons.

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COULOMETRIC TITRATION OF WEAK ACIDS IN NON-AQUEOUS SOLVENTS

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Summary—The coulometric generation of base will proceed with 100% current efficiency in isopropanol and in some solvent mixtures containing isopropanol. The conditions for non-aqueous titration of weak acids have been investigated. The best results were obtained when the anode was separated from the test solution by sintered-glass discs; 50–100 μmole of acid were titrated with a standard deviation of less than 0·5 μmole.

DEVELOPMENTS in coulometric analysis and coulometric titration have been reviewed.[1,2] The coulometric generation of base in non-aqueous solvents offers many advantages. The instability of many standard solutions, especially of dilute solutions, makes frequent standardisation necessary. Preparation, storage and handling are less convenient than for aqueous solutions.

Carson and Ko[3] described a method for base generation in isopropanol–water solutions, but were unable to carry out successful coulometric titrations in nonaqueous solutions. The main advantage of the coulometric generation of the base was that interference from carbon dioxide was reduced.

Methods for the coulometric titration of bases have been the subject of more investigations than methods for the titration of acids. Streuli[4] titrated amines in acetonitrile + 0·3% water. Mather and Anson[5,6] generated hydrogen ion in acetic acid-acetic anhydride by oxidation of a mercury electrode. The method developed by Mather and Anson is a completely non-aqueous titration. They have also studied the electrode reactions at platinum electrodes[7] in acetic acid-acetic anhydride solutions.

In this paper an investigation has been made of the conditions necessary for coulometric base generation, especially for the titration of small amounts of acid.

EXPERIMENTAL

Supporting electrolyte

It has been shown[8] that lithium methoxide behaves as a weak base in non-aqueous titrations. If it were not for this the good solubility of lithium salts in organic solvents would make it a natural choice as a supporting electrolyte. The best inorganic electrolyte is, in fact, sodium perchlorate. Tetra-n-butylammonium iodide has also been used in some titrations. Other quaternary ammonium salts have not been tried. Differences in the behaviour of these electrolytes in acetonitrile have been reported,[9] but in the media used in this investigation no differences have been observed.

Solvents

The ideal solvent for non-aqueous coulometric titration should dissolve sufficient quantities of supporting electrolyte. The conductivity of the solution should be high, so that large currents can be passed through the solution.

The substance formed in the cathodic reduction must be a suitable titrant for weak acids. Sodium alkoxides have been used extensively as titrants. These bases can easily be formed by reduction of the corresponding alcohol. Thus, the solvent must contain an alcohol.

The possibility of the existence of extremely strong bases in non-aqueous acetonitrile[9] would make this solvent suitable. There might be difficulties, however, because of the more severe reduction of the substance to be titrated.

Solutions of supporting electrolyte containing methanol have higher conductivity than those containing isopropanol. The acidic properties of methanol may, however, limit its usefulness. For this reason isopropanol has been used as the most generally suitable solvent constituent.

Apparatus

Non-aqueous solvents have much lower conductivity than aqueous solutions. If constant-current coulometry is to be used, an electronically regulated constant-current source must be used for accurate results.

An alternative method, which has been used by the present author, is to use an inexpensive current source and compute the time integral. The integrator employed a chopper-stabilised operational amplifier. It was similar to that described by Booman.[10] Different ranges were obtained by changing the input resistor. The voltage was read by a bridge circuit. The integral could be read to 1 part in 10,000; the accuracy is 3 parts in 10,000. The integrator was calibrated by connecting a known voltage to the input for a known time. No change in the calibration has been observed over a period of 6 months.

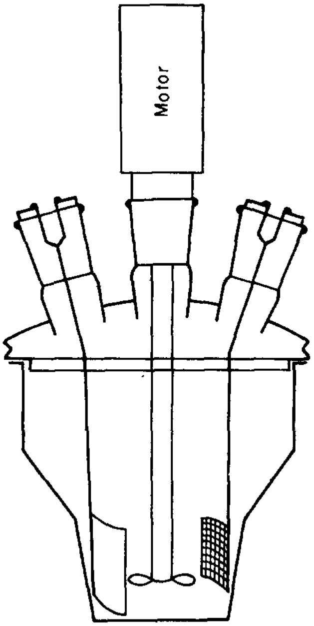

FIG. 1.—Cell for coulometric titration with cathode and anode in the same solution.

The electrolysis current could be adjusted by a variable resistor in series with the cell. The current was reduced near the end-point of a titration.

A Metrohm glass electrode, type EA 109U, and a Radiometer calomel electrode, type K 100, were used in the potentiometric measurements. The calomel electrode was connected to the non-aqueous solutions *via* a saturated solution of KCl in alcohol. The tube containing this solution was separated from the titration vessel by a fine-porosity glass filter.

Chronopotentiometric measurements were made with an arrangement similar to that described by Lingane.[1]

Cells

A titration cell for externally generated reagent, similar to that described by DeFord *et al.*[11] was tried. In this work it was found, however, that the electrode surfaces of the cell were too small for use in non-aqueous solvents. Bett *et al.*[12] have described a cell which seemed to be more suitable. When this cell was used in non-aqueous solvents it was found that the current efficiency was less than 100%. The highest efficiency, about 90%, was obtained for the fastest flow rates. Obviously, the mobility of the ions is so high that the generated base and acid move into the central compartment and neutralise each other.

The cell used when both electrodes were in the same solution consisted of a Metrohm titration vessel EA 615 (Fig. 1). All electrodes, nitrogen inlet, *etc.*, were inserted through the five ground joints on the top. The bottom of the vessel could be removed for easy changing of solutions. The solution was stirred by a Teflon propeller. The motor was fitted into the ground joint at the top of the vessel. Fifty ml of solvent were used throughout.

In most of the titrations a cell similar to that described by Smith and Taylor[13] was used. Two titration vessels, EA 615, were sealed together by a glass tube into which three sintered-glass discs were fused (Fig. 2). The solutions in the compartments between the glass discs could be transferred into the cathode compartment or could be titrated separately. In this cell 120 ml of solvent were required. The cathode compartment then contained about 50 ml of solvent.

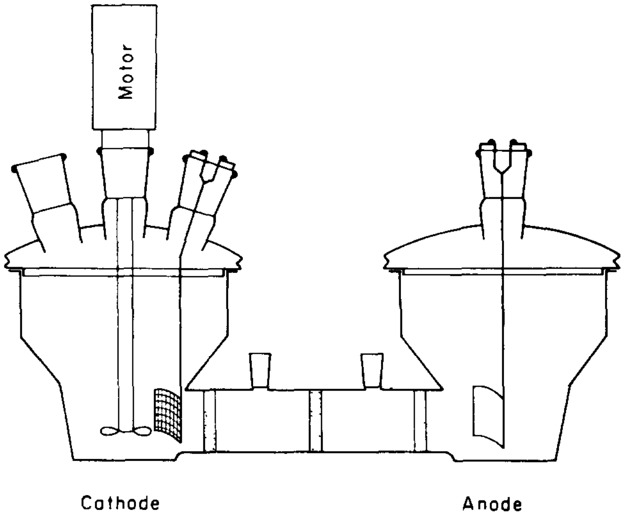

FIG. 2.—Cell for coulometric titration with cathode and anode separated by 3 sintered-glass discs.

The resistance between the electrodes was measured when the cells were filled with isopropanol-methyl ethyl ketone containing 4 g of $NaClO_4$ per litre. The resistance of the cell in Fig. 1 was 1000 ohms and the resistance of the cell in Fig. 2 was 5000 ohms.

Reagents

Pro analysi quality solvents were used throughout. The last traces of water were removed by the procedures recommended by Vogel.[14] Sodium perchlorate was dried at 115°. The water content was checked by a Karl Fischer titration. It was less than 0·1 %.

RESULTS

Current efficiency and electrode reactions

The weak acid HA can be titrated by either of the following cathode reactions.

$$2HA + 2e^- \rightarrow H_2 + 2A^- \qquad (1)$$

$$2i\text{-}PrOH + 2e^- \rightarrow 2i\text{-}PrO^- + H_2 \qquad (2a)$$

$$i\text{-}PrO^- + HA \rightleftharpoons i\text{-}PrOH + A^- \qquad (2b)$$

In either case, 1 mole of hydrogen ion is consumed per faraday, and this is all that matters stoichiometrically.

Coulometric titrations were performed to determine if base generation will proceed with 100 % current efficiency in the absence of the acid HA.

Non-aqueous solvents containing $NaClO_4$ were electrolysed in the cell shown in Fig. 2 using a silver anode and a platinum cathode. Sodium tetraphenylboron was added to the anode solution. Oxygen was removed from the cathode solution by a nitrogen stream. The base generated in the cathode compartment was continuously titrated with non-aqueous perchloric acid in isopropanol, so that the solution was almost neutral all the time. When 10 ml of perchloric acid had been added, the solution between the glass filters was transferred to the cathode compartment. Base was then generated in small increments so that the end-point could be determined potentiometrically. The results are shown in Table I.

TABLE I.—COULOMETRIC TITRATION OF PERCHLORIC ACID

Solvent	Acid, *µmole*	Generated base, *µmole*	No. of samples	Standard deviation, %	Dev. from calculated, %
Isopropanol, 50% Methyl ethyl ketone, 50%	165·1	164·9	5	0·4	−0·1
Isopropanol	260·2	258·7	3	0·8	−0·6

White[15] has found that the current efficiency was only 96%. The results presented in Table I show that the current efficiency is 100% within experimental error. (The titrations in Table IV also confirm this.)

The stoichiometric generation of base does not prove conclusively that the electrode reaction is that of Equation (2a). In the mixed solvents the other constituents might take part in the electrode reactions. It was found, however, that the form and size of a potentiometric titration curve was the same for a coulometric titration as for a titration using sodium isopropoxide in isopropanol. The electrolysed solutions were analysed by gas chromatography and by ultraviolet spectrophotometry. It was not possible to detect any impurity which could be an indication of side reactions.

End-point determination

It has been found[6] that the flow of current will interfere with the operation of the glass electrode. This has been verified in the present investigation. The interference was less if the glass electrode could be placed in a region where the voltage drop was very small. Ground loops may cause erroneous readings of the potential of the glass electrode. It was necessary to disconnect the coulometric apparatus completely when the potential measurements were made.

Because of the convenience of indicator titrations, Thymol Blue was used in most of the end-point determinations. The indicator end-point was checked by potentiometric titration. No interference from Thymol Blue on the coulometric reaction has been observed.

Shain and Svoboda[16] used constant-current potentiometry to indicate end-points in non-aqueous titrations. This technique was also tried in the present work, but it was found to be inferior to indicator titrations. In some cases no change at all could be observed. The reason for the failure of constant-current potentiometry may be, as Shain and Svoboda pointed out, that oxygen was removed from the solutions.

Both electrodes in the same solution

Lingane[1] pointed out that diaphragm cells are troublesome and that electrodes placed directly in the test solution are more convenient. A similar arrangement to that described by Lingane and Small[17] was set up. Titrations were performed in non-aqueous solution using a silver anode (20 cm^2) and a platinum cathode (8 cm^2). The cell shown in Fig. 1 was used. Various concentrations of LiCl, NaCl, NaBr, and NaI, together with an inert salt, such as Na_2SO_4 or Na_2ClO_4, were tried as electrolytes. The solubility product for AgX is much smaller in the non-aqueous solvents than in water. In spite of this it was found that large quantities of silver were deposited on the cathode. Unexpectedly, the results were low in a few cases. Some results are shown in Table II.

Table II.—COULOMETRIC TITRATION WITH PLATINUM CATHODE AND SILVER ANODE IN THE SAME SOLUTION

Substance	Solvent	Electrolyte	Taken, *μmole*	No. of samples	Found, *μmoles*	Standard deviation
Malonic acid	Isopropanol 50% Methyl ethyl ketone, 50%	KBr saturated	57·66	5	55·34	2·07
Malonic acid	Isopropanol	KBr saturated	19·22	3	19·18	0·92
Malonic acid	Isopropanol, 50% Acetone, 50%	KBr saturated	57·66	5	59·33	2·08
Malonic acid	Isopropanol, 50% Methyl ethyl ketone, 50%	NaBr saturated	57·66	6	58·34	4·98
Malonic acid	Isopropanol, 50% Methyl ethyl ketone, 50%	NaBr saturated	96·10	2	92·60	0·82
Salicylic acid			36·06	10	37·23	1·82

No silver was deposited on the cathode if sodium tetraphenylboron was used to precipitate the silver formed in the anode reaction. Typical results are shown in Table III. It was observed that a white-grey precipitate was formed at the anode.

TABLE III.—COULOMETRIC TITRATION WITH PLATINUM CATHODE AND SILVER ANODE IN THE SAME SOLUTION WITH SODIUM TETRAPHENYLBORATE PRESENT

(Electrolyte: sodium perchlorate, 4 g per litre)

Substance	Solvent	Taken, *μmole*	No. of samples	Found, *μmole*	Standard deviation
Salicylic acid	Isopropanol 50% Methyl ethyl ketone 50%	35·77	8	35·21	1·22
Salicylic acid	Isopropanol	35·77	3	33·14	1·91
Salicylic acid	Isopropanol, 99% Water, 1%	36·45	5	33·92	1·94
Salicylic acid	Methanol	36·24	2	32·41	0·59
Salicylic acid	Isopropanol, 50% Dioxan, 50%	36·45	5	35·25	0·72
Malonic acid	Isopropanol, 50% Methyl ethyl ketone, 50%	58·06	4	58·48	6·11
Malonic acid	Isopropanol, 50% Methyl ethyl ketone, 50%	246·78	1	229·37	—

Small deposits on the cathode were also observed. The results tend to be low, which indicates that side reactions probably occurred.

Geske[18] has studied the electro-oxidation of tetraphenylboron ion at a platinum anode. His work gives some idea of the side reactions to be expected. It is evident that the inconvenience of separated electrode vessels has to be accepted in order to obtain accurate results.

Separate anode and cathode compartments

Coulometric titrations were performed in the vessel shown in Fig. 2. It was necessary to titrate the solution in the small left-hand compartment between the discs. This titration was performed with an auxiliary platinum cathode, the current of which was also measured by the integrator. It was found that migration into this compartment corresponded to at least 0·5% of the weak acid added. Typical titration results are shown in Table IV.

TABLE IV.—COULOMETRIC TITRATION WITH A PLATINUM CATHODE AND A SEPARATE ANODE COMPARTMENT.
(Solvent: isopropanol, 50%, methylethylketone, 50%;
electrolyte: sodium perchlorate, 4 g per litre.)

Substance	Taken, *μmole*	No. of samples	Found, *μmole*	Standard deviation	Dev. from calculated, %
Salicylic acid	72·47	6	72·38	0·33	−0·12
5,5-Dimethyl-dihydroresorcinol	71·52	6	71·42	0·50	−0·14
Phenobarbital	86·26	4	86·11	0·28	+0·17
Phenobarbital	43·14	2	42·95	0·00	−0·45
Barbital	54·42	3	54·75	0·48	+0·61
Barbital	108·85	1	109·19	—	+0·31
m-Nitrobenzoic acid	100·41	2	100·34	0·35	−0·06

The uncertainty in the results is of the same order as the uncertainty in the end-point. The values are distributed evenly about the value calculated from electrical units.

In most of the titrations 4 g of $NaClO_4$ per litre were added; the current was then 10–25 mA. No influence from varying the amount of perchlorate has been observed. To prevent migration of hydrogen ions from the anode compartment, a silver anode was used, and sodium tetraphenylboron was added to the anode solution.

Chronopotentiometric reduction

If an acid undergoes reduction at the cathode, an error in the titration will follow. A reduction should cause high results because several faradays are generally required for the reduction of 1 mole of acid.

A chronopotentiometric investigation of the compounds used was made, a chronopotentiogram being taken under the same conditions as those of the titration. It was found that the acids yielded concentration-dependent single waves. These waves are caused by the discharge of the hydrogen ions.[19] The sodium salts of the acids gave no waves. There were no signs of reduction of the acids. The solvents exhibited no waves indicating side reactions.

Organic nitro compounds can be analysed by reduction with controlled potential.[20,21] However, the hydrogen overvoltage is less on platinum than on mercury. Substances which are reduced at a mercury cathode may be titrated at a platinum cathode. This is illustrated by *m*-nitrobenzoic acid, which gave two chronopotentiometric waves in water but only one in isopropanol. Table IV shows that *m*-nitrobenzoic acid can be titrated successfully, and that therefore the method may even be used with some reducible compounds.[19]

DISCUSSION

Coulometric titration in non-aqueous solvents is a very useful analytical tool, but it has several limitations. Reducible acids cannot be titrated with an internal generation technique (the reducibility can be tested by chronopotentiometry of the salts).

In the present investigation only relatively small amounts of acids have been titrated. Larger amounts of acid would permit a more accurate end-point determination. However, it has been observed that the accuracy decreases if the amount of acid is increased by an order of ten. If side reactions occur, their effect may be negligible at the concentrations employed in this investigation, but may cause an appreciable error at higher concentrations.

This effect is especially pronounced for salicylic acid. In the titration of large amounts of this acid a deposit is formed at the cathode. The infrared spectrum of this deposit shows significant differences from the spectrum of sodium salicylate and salicylaldehyde. The deposit is slightly soluble in organic solvents but soluble in water; it behaves as a very strong base; its equivalent weight is 180. This indicates that a sodium salt is formed with the hydroxide group of salicylic acid (calculated equivalent weight 182). This compound is slightly soluble and removes base from the titration reaction. Salicylic acid could be titrated quantitatively using tetra-n-butylammonium hydroxide as an electrolyte.

Most of the titrations have been performed in alcohol-ketone solvents. Some titrations have been made in pyridine, acetonitrile and dimethylformamide with 25% isopropanol added. The results indicate that these solvent combinations, too, may be used.

In this pilot investigation the solvents were purified and dried. In some experiments unpurified solvents were used, and water was added. No significant differences were observed for most solvents except that the sharpness of the end-point decreased when the water content increased. Some batches of undistilled methyl ethyl ketone contained an impurity which yielded a chronopotentiometric wave.

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Zusammenfassung—Die coulometrische Erzeugung von Basen verlauft in Isopropanol und einigen isopropanolhaltigen Lösungsmittelgemischen mit hundert-prozentiger Stromausbeute. Die Bedingungen für die Titration schwacher Säuren in nichtwäßrigem Medium wurden untersucht. Die besten Resultate wurden bei Trennung der Anode von der Probelösung durch Sinterglasscheiben erhalten. 50–100 μMol Säure wurden mit einer Standardabweichung von weniger als 0,5 μMol titriert.

Résumé—La formation coulométrique de base a lieu avec une efficacité de courant de 100% en isopropanol et dans quelques mélanges de solvants contenant de l'isopropanol. On a étudié les conditions de titrage des acides faibles en milieu non aqueux. Les meilleurs résultats sont obtenus lorsque l'anode est séparée de la solution à doser par des disques de verre fritté. On a dosé 50–100 μmole d'acide avec un écart type de moins de 0,5 μmole.

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AN INVESTIGATION OF THE ELECTROLYTIC DETERMINATION OF RHODIUM AND ITS SEPARATION FROM IRIDIUM

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Summary—A detailed study has been made of the electrolytic separation of rhodium and iridium published by MacNevin and Tuthill in 1949. By the use of carbon anodes the need to introduce hydroxylamine during the electrolysis is avoided. By the elimination of hydroxylamine a high residual current is avoided, and it is revealed that depositions of rhodium where the cathode potential is automatically controlled proceed with a periodically fluctuating current. The deposition of rhodium may be carried out in buffered solutions to avoid the onset of hydrogen evolution at the cathode; this takes precedence on occasion over rhodium plating and causes low recovery of rhodium. From buffered solutions with the pH raised to avoid hydrogen evolution the rhodium deposited appears to contain more oxide, and the separation of iridium is less effective than from solutions prepared by MacNevin's procedure. A compromise is required between working with a more acidic electrolyte from which, because of hydrogen evolution, the recovery of rhodium is incomplete, and working with a more alkaline buffered electrolyte from which the rhodium is deposited with a considerable oxide content (which can be reduced) and contaminated more by iridium. It is doubtful if the electrolytic method of separation is as reliable as other procedures.

INTRODUCTION

MACNEVIN and Tuthill[1] have published a procedure for the electrolytic determination of rhodium and the separation of rhodium from iridium. We have studied this procedure at some length to test its reliability, to try to simplify or improve it, and to try to understand the mechanisms involved.

The procedure of MacNevin and Tuthill is characterised by several unusual features:

(i) The electrolytically deposited rhodium is dark and contains oxide. Before determination of the metal the whole electrode must be heated in an atmosphere of hydrogen to reduce this oxide.

(ii) The current efficiency during the electrolysis is remarkably low. Considerable current flows throughout the duration of the electrolysis, and there is no indication by diminution of the current that the rhodium has all been removed from the solution.

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(iii) The potential of the cathode is maintained at a selected value relative to a saturated calomel electrode; during the 90 min prescribed for the analysis this potential is lowered from −0·25 V to −0·40 V in three stages. Iridium is not electrolytically deposited from solutions of its chloride even when the cathode potential is as low as −1·00 V. Nevertheless, when rhodium and iridium are present together in solution and the electrodeposition of rhodium is carried out, the plated metal generally contains iridium. MacNevin and Tuthill found that special treatment of solutions containing rhodium and iridium (chlorination, addition of ammonium chloride to a molarity of 3·5) enabled rhodium to be deposited free from iridium.

These observations have been confirmed repeatedly in our experiments, except that the separation of the two metals is not always assured by the prescribed pretreatment of their chloride solution. We have also recorded a number of other observations which may shed some light on the mechanism of the deposition of rhodium and the almost unavoidable codeposition of iridium.

The chemical reduction of rhodium salts in the presence of iridium salts has been achieved by titanium^{III},[2] vanadium^{II},[3] chromium^{II},[4] antimony[5] and copper.[6] For all but the last of these, rhodium and iridium are converted to sulphates or sulphate-complexes before the reducing agent is added. A thorough study of the selective reduction of chlororhodite by copper metal, and of the separation thereby of rhodium and iridium,[6] shows that an analytically acceptable separation of these two metals is possible, although small and partially compensating amounts of rhodium remain in solution, and of iridium are deposited with the rhodium.

The standard potentials for the reduction of the tervalent chloro-salts of these metals according to Latimer[7] are:

$$e + IrCl_6^{-2} \rightarrow IrCl_6^{-3} \qquad E^\circ = 1.017\ V$$

$$3e + IrCl_6^{-3} \rightarrow Ir + 6Cl^- \qquad E^\circ = 0{\cdot}77\ V$$

$$3e + RhCl_6^{-3} \rightarrow Rh + 6Cl^- \qquad E^\circ = 0.44\ V.$$

Obviously, such thermodynamically derived standard potentials must be cautiously interpreted in relation to the actual deposition of these metals. However, if the above values are correct (they actually are based on *estimates* of entropies of the complex ions), the deposition of rhodium unaccompanied by iridium from a solution of the chloro-salts requires that the reduction of chloro-iridite be accompanied by a considerable overpotential. Expressed in another way, the reduction of chlororhodite is kinetically favoured over that of chloro-iridite, in spite of the fact that reduction of the latter is thermodynamically more favourable. Obviously, one step in the reduction of these chloro-complex ions is the rupture of the M-Cl bonds. Evidence concerning the actual stability of these complexes is lacking, but one indication that chloride is more labile in chlororhodite than in chloro-iridite is the comparatively easy hydrolysis of the former and not of the latter, at room temperature. The conditions surrounding the electrodeposition of rhodium may catalyse that of iridium, because it is only when rhodium is present that any deposition of iridium occurs. In this connection it is noteworthy that induced reduction of iridium occurs during chemical precipitation of palladium metal.[8] Alternatively, the occurrence of iridium in the deposited rhodium may be associated with the mechanism of deposition of the latter which leads to an appreciable content of oxide in the metal (often exceeding 30 atomic per cent).

EXPERIMENTAL

The experiments described here were carried out at intervals over a period of years, as a consequence of which the equipment used, and the solutions of rhodium and iridium were not the same at all times.

Solutions of rhodium and iridium

These were prepared either from very pure chloro-salts, or from spectrographically pure metal sponge. The metal content of the solutions prepared from salts was determined by gravimetric analysis; rhodium by precipitation with thiobarbituric acid,[9] and iridium by precipitation as the hydrated dioxide.[10] For the other solutions, weighed portions of metallic sponge were dissolved by the sealed-tube chlorination technique of Wichers *et al.*,[11] and the resulting solutions made up to known volumes.

Electrolysis cell

Platinum gauze cathodes of cylindrical form, 1 inch × 1 inch, with No. 18 gauge wire stems were used throughout. Platinum anodes consisted of a 0·5 inch × 1 inch helix of No. 18 gauge wire. These were secured in position in brass bushings threaded into 1/8-inch Perspex sheet, the latter serving as cover-glass for the electrolytic beaker. Carbon anodes were prepared from graphite rod of the quality used to make spectrographic electrodes. The stationary anodes consisted of 3/16-inch rod machined to 1/8-inch at the upper end to fit into the brass bushing; the rotating anodes consisted of a ¼-inch rod, machined to fit the chuck of the Fisher Electroanalyzer at the top end, and drilled transversely near the bottom end to take a 1-inch length of 1/8-inch graphite rod. When stationary electrodes were used, the electrolyte was stirred by a magnetic rotor in the solution.

A probe electrode, consisting of a saturated calomel half-cell and a saturated potassium chloride-3% agar bridge, was mounted by the electrolysis cell in such a position as to allow the tip of the salt bridge in the electrolytic solution to rest against the outer surface of the cathode.

Regulated d.c. supply

Power to the electrolysis cell was delivered to operate with controlled cathode potential from one of three sources:

(a) a manually operated supply, consisting of two parallel Cenco wire-wound rheostats in series with a multi-range ammeter and the cell, connected to the 110-V laboratory d.c. supply. The rheostats permitted fine and coarse adjustment of plating current, which was adjusted throughout the electrolysis as necessary to maintain the cathode at a selected potential relative to the probe electrode.

(b) an all-electronic potentiostat of the design proposed by Greenough *et al.*[12] Indication of the cathode potential by means of the microammeter incorporated in this unit was unsatisfactory, and accordingly this meter was removed from the circuit. All settings of this controller were based on the observed cathode potential given by an auxiliary valve voltmeter.

(c) a Fisher Electroanalyzer used in later electrolyses.

Valve voltmeter

An a.c. line-operated meter of a bridge type, very similar in design to that incorporated in the potentiostat of Diehl *et al.*,[13] was used to observe the cathode-to-probe potential difference. The full-scale reading was set, and from time to time checked, against the output of a student potentiometer which in turn was calibrated against a Weston standard cell.

Reduction chamber

A glass vessel with surrounding heating jacket, patterned after the description of MacNevin and Tuthill, but smaller because of the smaller cathodes (1·5-inch tubing, 45/50 joint), was built to permit reduction of the deposit by hydrogen gas.

All electrolyses were carried out, unless otherwise noted, with the electrolyte solution at room temperature. The cathode was weighed on a semi-micro analytical balance before each deposition, and afterwards, following reduction in hydrogen. It was observed latterly that the reduction of oxide in the deposited metal was, doubtless because of the catalytic action of the rhodium, complete in less than 5 min in the warm chamber. By accelerating the heating and cooling of the electric heating jacket and taking advantage of this rapid reduction of the oxide, the time for reducing the electrode before its final weighing was shortened to about 40 min.

DISCUSSION OF RESULTS

*Hydrogen evolution**

During electrolysis of rhodium solutions, with or without iridium added, and following the directions of MacNevin and Tuthill, hydrogen was evolved at the cathode in many cases, especially after the greater part of the rhodium had been deposited. When this occurred, a small amount of rhodium was often, though not invariably, left in solution, even if the electrolysis was prolonged to 2 hr. It appeared that the evolution of hydrogen took precedence over the plating of rhodium.

The addition of more hydroxylammonium chloride usually checked this cathodic gassing. The presence of hydroxylamine in solution was found to be responsible for the high "residual" current often amounting to 1 or 2 A (see below). This was assumed to involve oxidation and reduction of the hydroxylamine as follows:

$$\begin{array}{rl} \text{CATHODE} & 2e + NH_3OH^+ + 2H^+ \rightarrow NH_4^+ + H_2O \\ \text{ANODE} & 2NH_3OH^+ \rightarrow N_2O + H_2O + 6H^+ + 4e \\ \text{OR} & NH_3OH^+ + 2H_2O \rightarrow NO_3^- + 8H^+ + 6e \\ \text{OR} & NH_3OH^+ + H_2O \rightarrow HNO_2 + 5H^+ + 4e. \end{array}$$

Because by any of the anodic processes more hydrogen ions are produced per coulomb, the effect of prolonged discharge of hydroxylamine is to increase the hydrogen ion concentration of the solution. This was confirmed in one experiment by a decrease in pH of the electrolyte following a period of this passage of current. The onset of hydrogen evolution in the later stages of electrolysis probably results from this increased hydrogen ion concentration.

The readiness with which hydrogen is evolved at a platinum electrode is regulated in part by the hydrogen overpotential; this is commonly known to depend on the state of the surface of the platinum. We have found that the longer our cathodes were in service, the more readily hydrogen came to be evolved at them during the deposition of rhodium. We have attributed this to a roughening of the surface of the platinum resulting from the repeated removal of rhodium deposits in molten potassium pyrosulphate. After each such treatment the surface of the electrode became less lustrous and although the dark-looking surfaces could be cleaned and rendered brighter by rubbing them through the fingers with a fine-grade household scouring powder, the electrodes steadily lost weight after each immersion in pyrosulphate. Some platinum is obviously removed by each cleaning of the electrodes, and we judge that this attack of the platinum has been facilitated by a certain amount of mutual dissolution of platinum and rhodium during the repeated heating and cooling of the electrode necessitated by the reduction of oxide in the deposited rhodium.

MacNevin and Tuthill do not state that hydrogen was evolved during the deposition of rhodium, but do attribute the presence of oxide in the deposit to the "rapid discharge of hydrogen ion at the cathode, which increases the pH of the adjacent solution and causes hydrolytic precipitation of the rhodium". The validity of this supposition is questionable for two reasons. In the first place, we have carried out electrodepositions of rhodium from buffered solutions (see below) with no hydrogen

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* Some electrolyses were tried from sulphate solutions, but complete recovery of rhodium was never obtained and in some cases there was no recovery because of cathodic evolution of hydrogen. Although Rudorff[19] plated from sulphate solutions and some commercial rhodium plating solutions are based on sulphates, the authors did not find this medium satisfactory for semi-micro work.

evolution whatever, and we have found in these cases that the proportion of oxide in the plate is as high or higher than in the case of depositions where hydrogen was evolved. Secondly, the supposed local increase in pH in the solution adjacent to the cathode would be very likely to cause hydrolytic precipitation of iridium along with rhodium. The pH at which precipitation of rhodium and iridium as hydrous oxides occurs from solutions of their chlorides is as follows:

Rhodium^{III}	6·4	(Gilchrist[14])
Iridium^{III}	4	(this investigation)
Iridium^{IV}	5–5·5	(Gilchrist; this investigation)

The values given above for iridium were determined from the point of inflection of the titration curve observed when iridium chloride solutions were titrated with sodium hydroxide. The pH was measured with a glass electrode, and the solution maintained at 95° by an immersed glass coil through which steam was passed. The value for iridium$^{(III)}$ was measured after addition of just enough hydroxylamine to decolourise the iridium$^{(IV)}$ chloride. The values were not appreciably altered by the presence of a high concentration (3*M*) of sodium chloride.

Variation in electrolytic procedure

Concerning the preliminary treatment of the solution advocated by MacNevin and Tuthill to inhibit the deposition of iridium during electrolysis, these authors state that "the temporary precipitation prior to electrolysis of much of the iridium as ammonium chloroiridate tends to minimise the co-deposition...... As the electrolysis proceeds, the ammonium chloroiridate slowly dissolves, evidently because of the electrolytic reduction of $IrCl_6^{2-}$ ion to $IrCl_6^{3-}$." Although our experiments do not conclusively prove what the function of the high concentration of ammonium chloride is, it is certain that precipitation of ammonium chloro-iridate plays no part in inhibiting the deposition of iridium. In all cases, when hydroxylammonium chloride was added as specified, the precipitate of ammonium chloro-iridate dissolved and the dark colour of the chloro-iridate ion was discharged because of reduction to chloro-iridite, and *this happened before electrolysis*. Moreover, as the results of Table I show, results of comparable validity were obtained when sodium chloride was present at the same molarity as ammonium chloride; from this solution no precipitation of iridium occurred.

These electrodepositions, the results of which are summarised in Table I, were performed in the manner described by MacNevin and Tuthill, with stepwise decrease in the cathode potential and the addition of more hydroxylammonium chloride part way through the electrolysis. The difference in our experiments was that, except as noted, the electrolyses were stopped when profuse gassing began at the cathode, and this generally resulted in shortening the duration of the electrolyses from the 90 min recommended by these authors. Among 37 electrolyses carried out in this manner, 21 gave recoveries of rhodium that were low by 2% or greater. However, when hydrogen gas was allowed to form copiously at the cathode some iridium deposited with the rhodium.

Table I.—Separation of rhodium and iridium: variations on procedure of MacNevin and Tuthill[1]

Composition of electrolyte	Rhodium taken, *mg*	Iridium taken, *mg*	Cathodic deposit, *mg*	Remarks
3·5*M* NH_4Cl chlorinated	10·20	5·0	10·16	75 min
	10·20	5·0	10·07	75 min
	10·20	5·0	10·98	Cathodic gassing 15 min
	5·03	nil	4·88	No gassing allowed
	5·03	20·0	4·75	No gassing allowed
	10·07	nil	10·05	No gassing allowed
	10·07	20·0	10·03	No gassing allowed
3·5*M* NH_4Cl not chlorinated	10·20	5·0	10·22	No gassing allowed
	10·20	5·0	10·42	Cathodic gassing 15 min
	5·03	nil	4·80	No gassing allowed
	5·03	10·0	5·34	No gassing allowed
	10·07	10·0	10·10	No gassing allowed
	15·10	20·0	15·06	No gassing allowed
	15·10	nil	14·73	No gassing allowed
3·5*M* NaCl	10·20	5·0	10·18	No gassing allowed
	10·20	5·0	10·13	No gassing allowed
	10·20	5·0	10·34	Cathodic gassing 15 min
	5·03	nil	4·50	No gassing allowed
	5·03	10·0	5·07	No gassing allowed
	5·03	10·0	4·93	No gassing allowed
	10·07	20·0	10·02	No gassing allowed
	15·10	nil	14·58	No gassing allowed
	15·10	20·0	14·46	No gassing allowed

Action of hydroxylamine

The relatively high extraneous current accompanying the deposition of rhodium was identified with a process involving hydroxylamine through observations such as the following. With a brand new platinum cathode in the electrolysis vessel and a solution containing hydroxylammonium chloride but no rhodium, no current flowed until the cathode potential was lowered below —0·5 V (S.C.E.), when some hydrogen evolution began at the cathode. Without stopping the electrolysis, several drops of a rhodium chloride solution (*ca.* 0·5 mg of rhodium) were added to the solution; and after a few min the current rose to 150 mA at a cathode potential of —0·3 V, and remained at this value for some time. A second solution containing a few drops of rhodium chloride solution was placed into the cell, equipped now with a used rhodium-plated platinum cathode, and again no appreciable current flowed until hydrogen evolution began at a cathode potential below —0·5 V. Several small crystals of hydroxylammonium chloride were then added, whereupon almost immediately a current of 1·5 A flowed at a potential of —0·3 V. It was concluded that some process involving hydroxylamine was occurring at one or both electrodes, and presumably both because little gassing was observed, and that this was catalysed by the presence of rhodium in the solution or on the cathode surface, or both.

The presence of too high a concentration of hydroxylamine at the beginning of an electrolysis caused incomplete recovery of rhodium. This is shown by the data of Table II, and confirms the necessity of adding the hydroxylamine in small portions as the electrolysis continues. These results suggest that a complex salt had formed, be stopped by the addition of a few drops of dilute aqueous ammonia to the solution in the cell; it was inferred that the onset of hydrogen evolution at the cathode was the consequence of a gradual increase in acidity of the solution resulting from discharge of oxygen at the anode. The results shown in Table III were obtained with a carbon anode in solutions 3·5*M* in ammonium chloride also containing 1 % w/v of ammonium sulphate. The last 4 experiments were carried out in such a way as to avoid hydrogen evolution at the cathode by the dropwise addition of dilute aqueous ammonia at the first sign of cathodic gassing.

Electrolyses from buffered solutions

The suppression of cathodic hydrogen evolution by the addition, as necessary, of aqueous ammonia to the solution in the cell, as described in the preceding paragraph, encouraged the hope that satisfactory depositions of rhodium might be accomplished if the solution were buffered against change in pH. Such electrolytic depositions were carried out by the procedure described in detail below. No gas was seen to be evolved at either electrode. The absence of any cathodic gassing did not diminish the proportion of oxide in the deposited rhodium. The absence of anodic gassing suggested that acetate from the buffer acted as a depolariser for the evolution of oxygen or chlorine.

Table IV.—Deposition of rhodium from buffered solutions

Rhodium taken, *mg*	Iridium added, *mg*	Cathodic deposit, *mg*	Duration of electrolysis, *min*
10·04	nil	10·02	90
9·95	nil	9·98	75
9·95	nil	9·95	90
10·02	nil	10·04	90
9·95[a]	nil	10·02	90
9·95[a]	nil	10·02	75
10·02[a]	nil	10·12	90
10·02[a]	nil	9·81	90
9·95	4·53	10·89	60
9·95	4·53	10·19	60
9·95	4·53	10·47	60
9·95	4·53	10·52	75
9·95	4·53	10·52	90

[a] In these 4 determinations the sample was heated for 15 min in NH_4Cl solutions, the molarities of which were, respectively, 3·5, 3·5, 5·0 and 1·0, to ensure conversion to the rose-coloured $RhCl_6^{3-}$ ion. The other samples were prepared from a brown, partially hydrolysed stock solution.

In the absence of extraneous processes occurring at the electrodes, the deposition of rhodium took place at a current efficiency of nearly 100 %. Moreover, apart from the periodicity of the plating current which is discussed in a later section, the course of the electrolysis followed more normally the behaviour described by Lingane[15] for "controlled cathode" depositions. Thus, the current in most cases began at 300 to 400 mA and declined more or less exponentially to 3 or 4 mA at the end of deposition of the metal.

The recoveries of rhodium were quantitative in many determinations, but when iridium was also present in the solution some of the latter metal was invariably included in the electrolytic deposit. Some representative results are given in Table IV.

completely or in part, from rhodium and hydroxylamine, and that from it rhodium could not be quantitatively deposited. Amounts of rhodium not accounted for in the cathode deposit were found in the plating solutions when these were tested colorimetrically after destruction of hydroxylamine. Electrodeposition of rhodium did not occur at all in an analogous experiment from the yellow-coloured solution of the complex formed in 0·5*M* thiocyanate solution; when the cathode potential was taken below −0·5 V, hydrogen was evolved but no metal was found on the cathode.

TABLE II.—EFFECT OF HYDROXYLAMINE ON DEPOSITION OF RHODIUM

Composition of electrolyte	Rhodium taken, *mg*	Rhodium recovered, *mg*
0·15*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	5·02
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	4·66
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	4·71
0·40*M* $HONH_2$, 3·5*M* NH_4Cl	5·03	3·66[a]
1·0*M* $HONH_2$	5·03	4·19

[a] The electrolyte, containing hydroxylammonium chloride, was allowed to stand overnight before deposition of rhodium. This solution, as well as the last, was yellow instead of the usual rose or brown.

Electrolyses with carbon anodes

When electrolyses were carried out with no hydroxylamine in the solution, the gain in weight of the cathode exceeded the weight of the rhodium taken; this was traced to a corresponding loss in weight of the anode. Platinum is appreciably corroded when operating as an anode in 3·5*M* chloride solution. By substituting a very pure carbon spectrographic electrode as anode we were able to carry out rhodium depositions in the absence of hydroxylamine. The carbon rods could be used again and again provided they were allowed to soak in distilled water for some time to leach out the iridium salt, which appeared to concentrate in the porous anode during the electrolysis of solutions containing this metal.

TABLE III.—DEPOSITION OF RHODIUM WITH ANODES OF CARBON ROD

Rhodium taken, *mg*	Iridium taken, *mg*	Cathodic deposit, *mg*	Duration of electrolysis, *min*
5·03	—	5·13, 5·20	60
10·20	—	10·16	60
10·07	—	9·96, 9·97	60
10·07	—	10·09	90
15·10	—	14·88, 14·90	60
15·10	—	15·08	120
5·03	10·0	5·30, 5·11	60
20·14	20·0	20·17	120
10·07	20·0	10·28	90
10·07	20·0	10·25	90
5·03	20·0	4·94	50

During the early stages of these electrolyses there was considerable gassing at the anode but no significant amount at the cathode. After about 1 hr profuse gassing began at the cathode. By continuing the electrolyses with this hydrogen evolution, all or most of the rhodium was recovered on the cathode. The cathodic gassing could

Although codeposition of iridium had been noticed especially in cases where profuse cathodic gassing occurred, and was accordingly thought to be the result of localised increases in pH in the vicinity of the cathode, its occurrence in these experiments where no gas was evolved proves that the suspected mechanism cannot alone account for the presence of this metal amidst the deposited rhodium.

Because the course of the electrolysis could be followed by observing the current flowing through the cell, and therefore a satisfactory indication of complete deposition of rhodium observed, we have adopted this way of carrying out quantitative depositions of this metal. The following directions apply to chlororhodite solutions in the absence of other metals.

Recommended analytical electrodeposition of rhodium

Before electrolysis the rhodium should be dissolved as chloride in 100 ml of 3·5*M* ammonium chloride solution to which are added 5 ml of a concentrated buffer solution (3*M* acetic acid, 1*M* sodium acetate) and 1 g of ammonium sulphate. Electrolyse with a previously reduced and weighed platinum gauze cathode and an anode fabricated from spectrographic carbon, and maintain the cathode potential at −0·40 V *vs.* S.C.E. Continue the electrolysis until the current falls to zero, or to a steady small residual current (3 or 4 mA); this usually requires from 1·5 to 2 hr. Remove the cathode without interrupting the current, wash well with distilled water, dry in an oven at 100°, reduce in a hydrogen atmosphere, cool and weigh.

The pH in the buffered electrolyte is about 4. To test for completeness of deposition, evaporate the residual solution on the steam bath with concentrated nitric acid to destroy the ammonium chloride, take up the residue with hydrochloric acid and test for rhodium with tin$^{\mathrm{II}}$ chloride.

Fluctuations in plating current

It quickly becomes apparent that, when the potential of the cathode was controlled by an instrument, the deposition of rhodium from buffered solutions, especially after the first 30 min, took place in such a way as to cause a periodically fluctuating current. This phenomenon was not observed when cathode potential was maintained manually.

The electronic controller produced rather violent fluctuations. In a typical case, the current passed in pulsating bursts, suddenly reaching a maximum of 1A and falling more gradually to zero. This "saw-tooth" current was investigated as follows. With a 3·5*M* solution of sodium chloride in the cell the cathode potential was set to control at −0·45 V (S.C.E.). The cathode had been freshly stripped of rhodium by repeated immersion in molten potassium pyrosulphate, and washing in warm water. Only a very small current flowed through the cell when the e.m.f. was applied. On the addition of a small amount of chlororhodite solution (*ca.* 1 mg of rhodium), the current increased but did not oscillate. When 1 ml of an acetate buffer was added, a "saw-tooth" current was observed immediately. After 20 min of this the electrodes were removed from the cell, washed thoroughly, placed into a fresh 3·5*M* sodium chloride solution, and connected to the power supply without changing the settings of the latter. Current again flowed in the same intermittent fashion. In another similar experiment the same observations were induced by the addition of a phosphate buffer of the same pH. If no buffer was added, the onset of oscillations was delayed until after current had flowed for some min, and was in some cases obscured by the relatively greater current from hydrogen evolution.

The mechanical controller also produced a "saw-tooth" current, but of a somewhat different character. The "saw-tooth" effect was usually delayed until about half-way through the duration of the electrolysis; the rise and fall of current was much slower than that observed with the electronic controller. This slower response to whatever caused the fluctuation was undoubtedly caused by the inertia of the mechanical control system as compared with the all-electronic circuit of the former instrument. In the cycle of rise and fall of current the ammeter on the instrument recorded a slow rise to about 60 mA, followed by a slow decrease to a very small current of polarity reversed to the plating current; the latter was maintained for several sec, then the cycle was repeated. When this instrument was manually operated to hold a steady cathode potential no such variations in current were observed.

The fluctuations in current observed during the deposition of rhodium must be connected in some way with the nature of the rhodium deposit. It was observed with two different buffers in the electrolyte, and even in the absence of buffer; the fact that it had not been recorded for depositions when hydroxylamine was present is undoubtedly caused by the high residual current observed when this substance is present. An hypothesis that seems consistent with our observations, but which we were unable to prove, is that the cathode becomes slightly polarised as the result of the deposition on it of a sparingly conducting layer of oxide. This polarisation causes the controlling device to reduce the applied voltage, and the current drops. Now, while a decrease in current density would have the effect of diminishing concentration polarisation, and so would ultimately lead to restoration of the applied voltage to nearly its original value, this compensation would not be expected to occur when the polarisation is the result of a film on the surface of the metal; so once the current starts to drop in this case it will fall to zero. When the current has stopped we presume the oxide slowly dissolves from the electrode by chemical action until the plating can resume. This dissolution does not necessarily remove all of the oxide, so that a pure deposit is not

TABLE V.—EFFECTS OF CONDITIONS ON OVERWEIGHT IN RHODIUM DEPOSITION
(rhodium taken: 20·00 mg)

Rhodium recovered, *mg*	Overweight, *mg*	Temperature, °*C*	Remarks
18·56	1·20	Room (22°)	Acetate buffer, no NH_4Cl
18·89	1·60	Room	Acetate buffer, no NH_4Cl
18·69	0·56	60°	Acetate buffer, no NH_4Cl
20·02	1·80	Room	Acetate buffer, 3·5*M* NH_4Cl
19·95	1·28	Room	Acetate buffer, 3·5*M* NH_4Cl
19·70	0·74	60°	Acetate buffer, 3·5*M* NH_4Cl
19·20	0·99	60°	Acetate buffer, 3·5*M* NH_4Cl
19·37	0·80	60°	Acetate buffer, 3·5*M* NH_4Cl, manual control
13·11	0·63	60°	Acetate buffer, 3·5*M* NH_4Cl, plating for 10 min
5·76	1·98	60°	Acetate buffer, 3·5*M* NH_4Cl, gelatin added
20·57	0·97	Room	KH_2PO_4, 3·5*M* NH_4Cl
20·18	0·95	60°	KH_2PO_4, 3·5*M* NH_4Cl
20·15	0·20	60°	No buffer, 3·5*M* NH_4Cl
20·06	0·28	60°	No buffer, 3·5*M* NH_4Cl
19·95	0·44	Room	Acetate buffer, 3·5*M* NH_4Cl, hydroxylamine
19·78	0·72	Room	Acetate buffer, 3·5*M* NH_4Cl, hydroxylamine
20·02	0·82	60°	Acetate buffer, 3·5*M* NH_4Cl, hydrazine
19·59	0·54	60°	Acetate buffer, 3·5*M* NH_4Cl, hydrazine

obtained. This hypothesis is consistent with the observation that, in general, the depositions carried out in buffered solutions exhibited the "saw-tooth" fluctuations in current earlier and more consistently than those in unbuffered solutions, while the oxide content of deposits formed from buffered solutions was on the average greater than that from unbuffered solutions (see the following section and the data of Table V).

Contamination of the deposit of oxide

Electrolyses were carried out with solutions containing a fixed weight of rhodium and other constituents varied as recorded in Table V. The electrode was cleaned, dried and weighed after each deposition; it was then reduced in hydrogen and reweighed. The difference in the two weights (which we call *overweight*) was taken to be oxide. In a few cases the electrode was also heated after the first weighing without introducing any hydrogen in the small furnace, then cooled and weighed, at most only a very small loss in weight was observed in these cases, so that the overweight is apparently only removed by reduction.

TABLE VI.—DEPOSITIONS OF RHODIUM WITH IRIDIUM PRESENT
(rhodium taken: 20·00 mg; iridium taken: 14 mg)

Rhodium recovered, *mg*	Overweight, *mg*	Temperature, °*C*	Remarks
20·15	0·62	Room	Acetate buffer
20·51	0·15	60°	No buffer
20·61	0·42	Room	Acetate buffer
21·39	0·40	60°	No buffer[a]
21·68	0·43	60°	Acetate buffer
19·92	0·36	Room	KH_2PO_4
21·70	0·41	60°	KH_2PO_4
19·89	0·34	Room	KH_2PO_4

[a] pH maintained *ca.* 3 by addition of aqueous ammonia.

The results are recorded in Table V, from which the effect of the variables investigated can be seen. In general, the overweight is lower in deposits from heated solutions than from solutions at room temperature. Deposits from buffered solutions show in nearly every case a greater overweight than those from unbuffered solutions.* In view of the greater tendency to hydrogen evolution observed with unbuffered solutions, it is unlikely that the presence of oxide in the deposit can be attributed to hydrolytic precipitation resulting from localised production of alkali in the vicinity of the cathode (*cf.* molybdenum[16]). From the data of Table VI it may be noted that the overweight increases with, but not in direct proportion to the weight of rhodium deposited; the average overweights for 10, 20 and 30 mg of rhodium were, respectively, 0·82, 1·18 and 1·57 mg. Two electrolyses were performed with hydroxylamine added, following the directions of MacNevin and Tuthill, and two others in the presence of 0·05*M* hydrazine. These all proceeded with a high residual current, and the former two with considerable cathodic gassing; the overweight in these cases was somewhat lower than the average for this weight of rhodium.

To test if there was a connection between the presence of oxide in the deposit and the fluctuating current during the later stages of the deposition, we stopped one electrolysis after a few min and determined the amount of overweight in the portion of

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* See also the data of MacNevin and Tuthill, reference 1, Table I, p. 1054.

the rhodium on the cathode. From the result it must be concluded that a substantial fraction of the overweight is laid down during the early stages of the deposition before the "saw-tooth" current becomes evident.

Further depositions of rhodium in the presence of iridium

Similar electrodepositions of rhodium were carried out with known amounts of iridium in the solutions. The results, which are summarised in Table VI, show that no connection can be traced between the amount of overweight and the codeposition of iridium. In most cases the increase in weight of the cathode was somewhat greater than the weight of rhodium taken, presumably because of the presence of iridium.

TABLE VII.—DEPOSITIONS OF RHODIUM IN WHICH PART OF THE IRIDIUM WAS REMOVED AS $(NH_4)_2IrCl_6$

Iridium taken, *mg*	Rhodium taken, *mg*	Weight of deposit, *mg*	Overweight, *mg*	Remarks or conditions
14·0	20·00	19·82	0·91	22°, KH_2PO_4 buffer
14·0	20·00	19·87	0·59	22°, KH_2PO_4 buffer
14·0	20·00	20·23	0·64	60°, KH_2PO_4 buffer
20·0	20·00	19·63	1·10	22°, acetate buffer
20·0	20·00	19·67	1·10	22°, acetate buffer
10·0	10·00	9·99	1·10	22°, acetate buffer
30·0	10·00	10·05	0·79	22°, acetate buffer
10·0	20·00	20·26	1·39	22°, acetate buffer
30·0	20·00	20·15	1·00	22°, acetate buffer
10·0	30·00	29·73	1·63	22°, acetate buffer
30·0	30·00	30·14	1·46	22°, acetate buffer
8·5	10·00	9·87	0·81	Ir recovery: 7·5 mg
8·5	10·00	10·00	0·86	7·5
8·5	10·00	9·87	0·75	8·8
8·5	10·00	9·93	0·73	8·5
25·5	10·00	9·93	0·75	25·5
25·5	10·00	10·26	0·78	25·5
17·0	20·00	20·14	0·87	16·6
17·0	20·00	20·34	1·33	16·4
25·5	20·00	20·17	1·35	28·0
25·5	20·00	19·65	1·17	24·3

In these solutions, containing a high concentration of ammonium chloride, a black precipitate of ammonium chloro-iridate is formed. A few experiments were carried out in which this precipitate was removed by filtration before electrodeposition of the rhodium from the filtrate. The precipitation of iridium is not complete under these conditions, but its concentration is lowered considerably. It was hoped that this reduction in concentration before commencement of electrolysis might diminish the codeposition of iridium. The results of these determinations are shown in Table VII. It is seen that in these cases the gain in weight of the cathode is, on the average, within 1 % of the weight of rhodium taken. This cannot, however, be taken as proof of the completeness of separation of the two metals.

Further information concerning the separation was sought as follows. To test for coprecipitation of rhodium with the ammonium chloro-iridate, the precipitate was dissolved in water and iridium reprecipitated from this solution. The second precipitate of ammonium chloro-iridate was removed by filtration, and the filtrate tested absorptiometrically for rhodium. No more than a few μg of rhodium were found among 11 samples investigated in this way. The electrolytic solution, following deposition of the rhodium, was evaporated to dryness; ammonium chloride was destroyed by nitric acid, and the residue converted to chlorides by repeated treatment with hydrochloric acid. Absorptiometric tests revealed no more than a few μg of rhodium present. Iridium was determined in 10 cases by combining the ammonium chloro-iridate, the electrolyte solution following deposition of the rhodium, and any iridium leached out of the carbon anodes. From this combined residue ammonium chloride had to be removed by heating with nitric acid; the nitric acid and its degradation products were then removed by repeated evaporations with hydrochloric acid almost to dryness. Iridium was determined absorptiometrically in an aliquot of this residue by a procedure that could tolerate moderate amounts of rhodium.[17] The results showed complete recovery of iridium in 5 cases and low recovery in 5 others. The low recovery of iridium may be interpreted as indicating that some of this metal may have been deposited on the cathode; it could just as easily be caused by mechanical loss of iridium during the rather ebullient removal of ammonium salts, or to loss by steam distillation of iridium^{IV} chloride.

The foregoing results suggest, but cannot be taken as conclusive proof, that an acceptable separation of the two platinum metals may be achieved by precipitation and separation of most of the iridium as ammonium chloro-iridate, followed by electrodeposition to separate the rhodium from the remainder of the iridium. However, it is doubtful whether these combined operations have any advantages to recommend them over other analytical separations for rhodium and iridium.

All of the experimental evidence in this paper supports, but does not prove, the hypothesis that rhodium deposited from chloride solutions is contaminated by oxides because of prior hydrolysis of the $RhCl_6^{3-}$ ion to species such as $RhCl_5OH^{3-}$, *etc.*[18] Increased hydrolysis in buffered solutions led to increased contamination by oxide. The hydrolysis is repressed in concentrated ammonium (or sodium) chloride solution. The hydrolysis can be suppressed at lower pH, but this also leads to the onset of hydrogen evolution at the cathode, and possible incomplete recovery of rhodium. It would be interesting to see if rhodium could be recovered free from oxide by deposition from more acidic solutions into a mercury cathode. It is the authors' view that the codeposition of iridium is related to the contamination of the rhodium deposits by oxide; the best separations were obtained in moderately acidic solutions following the procedure of MacNevin and Tuthill; but in a number of these the recovery of rhodium was incomplete because of premature hydrogen evolution. The best conditions for complete deposition of rhodium (from buffered solutions) led to appreciable contamination of the rhodium by iridium when the latter was present in solution. In the absence of a detailed mechanism of deposition of the metal from the complex ions in these solutions, it is impossible to offer an explanation for the way in which contamination by iridium occurs.

CONCLUSIONS

The results of the experiments described here must be judged inconclusive in their attempts to account for the mechanism of the deposition of rhodium contaminated by oxide and by a periodically fluctuating current, and for the rarely avoidable contamination of the deposit by iridium when this element is present in the electrolyte. It would be interesting to re-examine the nature of the "saw-tooth" current with a recording potentiometer. Also it would be revealing to carry out depositions of rhodium from solutions in which the pH was systematically varied in order to test further the possible correlation between extent of oxide contamination, extent of codeposition of iridium, and hydrogen-ion content of the electrolyte. Because of the changed circumstances of the authors it has proved impossible to do this additional work. The present communication makes available our results for anyone else who might wish to study the phenomena further.

Acknowledgement—This investigation was supported by a grant from the University of Toronto's Advisory Committee on Scientific Research, for which the authors record their thanks.

Zusammenfassung—Die von MacNevin und Tuthill 1949 publizierte elektrolytische Trennung von Rhodium und Iridium wurde in ihren Einzelheiten untersucht. Durch Verwendung von Kohleanoden wird die Zugabe von Hydroxylamin während der Elektrolyse unnötig. Dadurch wird ein hoher Reststrom vermieden, und es zeigt sich, daß die Abscheidung von Rhodium bei automatisch kontrolliertem Kathodenpotential mit periodisch sich änderendem Strom abläuft. Die Rhodiumabscheidung kann in gepufferten Lösungen vorgenommen werden, um Wasserstoffentwicklung zu vermeiden; diese überwiegt gelegentlich die Rhodiumabscheidung und bewirkt zu niedrige Rhodiumausbeute. Das aus gepufferten Lösungen, deren p_H zur Vermeidung der Wasserstoffentwicklung erhöht wurde, abgeschiedene Rhodium enthält offenbar mehr Oxyd und die Trennung von Iridium ist weniger vollständig als bei nach MacNevin bereiteten Lösungen. Man muß einen Kompromiß schließen zwischen saurerem Elektrolyten, der wegen der Wasserstoffentwicklung zu wenig Rhodium liefert, und stärker alkalischem gepuffertem Elektrolyten, aus dem Rhodium mit beträchtlichem Oxydgehalt (der reduziert werden kann) und Iridiumverunreinigung abgeschieden wird. Es ist zweifelhaft, ob die elektrolytische Trennungsmethode so zuverlässig ist wie andere Methoden.

Résumé—On a étudié en détail la méthode de séparation électrolytique du rhodium et de l'iridium publiée en 1949 par MacNevin et Tuthill. Par l'emploi d'anodes en carbone, l'introduction d'hydroxylamine au cours de l'électrolyse n'est plus nécessaire. Par l'élimination de l'hydroxylamine, on évite un courant résiduel élevé, et ceci est révélé par le fait que, lorsque le potentiel de cathode est automatiquement contrôlé, les dépôts de rhodium se développent avec un courant périodiquement variable. On peut effectuer le dépôt de rhodium en solutions tamponnées pour éviter l'apparition d'un dégagement d'hydrogène à la cathode, qui peut éventuellement prédominer sur le dépôt de rhodium et conduire à une faible récupération de celui-ci. A partir de solutions tamponnées dont le pH a été élevé de façon à éviter le dégagement d'hydrogène, le rhodium déposé se révèle contenir plus d'oxyde, et la séparation de l'iridium est moins efficace qu'à partir de solutions préparées selon la technique de MacNevin. Un compromis est nécessaire entre le travail avec un électrolyte plus acide à partir duquel, par suite du dégagement d'hydrogène, la récupération du rhodium est incomplète, et le travail avec un électrolyte tamponné plus alcalin, à partir duquel le rhodium qui se dépose a une teneur considérable en oxyde (qui peut être réduit) et est davantage contaminé par l'iridium. Il est douteux que la méthode électrolytique de séparation soit aussi sûre que d'autres techniques.

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF NITROGEN WITH ORGANIC SOLVENT EXTRACTION*

APPLICATION TO METALLURGICAL ANALYSIS

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Summary—Spectrophotometric determination of nitrogen, as ammonia, with organic solvent extraction has been studied. The blue coloured compound formed from ammonia, phenol and hypochlorite (chloramine-T) is completely extracted with isobutyl alcohol or isoamyl alcohol only by using a salting-out reagent, and the optimum conditions have been established. This procedure has been applied to the determination of nitrogen in iron, steel and aluminium.

VARIOUS methods have been reported for the determination of a micro quantity of nitrogen in metals, but that used in practice is the Nessler method.[1,2,3] Although the latter is simple and highly sensitive, the reaction product is colloidal in nature and the blank value is large because the reagent itself has a high absorption.

The blue coloration of ammonia with thymol and hypochlorite (chloramine-T)[4] or hypobromous acid[5] can be extracted with organic solvents, such as isoamyl alcohol,[6,9] and this has been applied to the determination of nitrogen in iron and steel.[6] Although the extraction can be effected easily, the sensitivity of this reaction is not satisfactory. The analogous blue coloration of ammonia with phenol and hypochlorite, originating with Berthelot last century, is more sensitive for nitrogen in metals[7,8] than that with thymol, but this colour is not easily extracted with an organic solvent. Consequently, only photometry using this coloration in aqueous solution has previously been reported.

An attempt was therefore made to extract the phenol reaction product, reported as indophenol,[9,10] and it was found to be easily extracted with isobutyl alcohol or isoamyl alcohol by first saturating the solution with a suitable salting-out agent. The molar absorptivity of the coloured substance extracted with isobutyl alcohol is slightly greater than that extracted with isoamyl alcohol and because this solvent is more convenient to use, optimum conditions for the determination of ammonia by the use of isobutyl alcohol were examined. Subsequently, the method was applied to the determination of nitrogen in iron, steel and aluminium, the accuracy of the results being about 2% (standard deviation).

EXPERIMENTAL

Reagents

Standard nitrogen solution. 1·9095 g of ammonium chloride, dried for about 1 hr at 110° and cooled in a desiccator, were dissolved in water to make 1 litre of solution containing 0·5 mg of

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nitrogen/ml. 10 ml of this solution were diluted exactly to 500 ml to make a solution containing 10 μg of nitrogen/ml.

Phenol solution. 25 g of phenol dissolved in 50 ml of 40% sodium hydroxide solution was diluted with water to 100 ml.

Chloramine-T solution. 5% and 10% aqueous solutions prepared from reagent supplied by Kanto Chemical Co. (Japan).

1M Sodium hydroxide solution.

All reagents used were analytical grade.

Apparatus

An Hitachi photoelectric spectrophotometer Model EPU-2A with 1-cm cell and an Hitachi glass electrode pH-meter Model FEM-2 were used for the various measurements.

Experimental procedure

Standard nitrogen solution, containing less than 60 μg of nitrogen, was placed in a 50-ml glass-stoppered conical flask, neutralised with sodium hydroxide solution (litmus paper), then 1 ml of phenol solution and 7 ml of 5% chloramine-T solution were added to bring the whole volume to about 25 ml and the pH adjusted to 12 (pH meter). The flask was immersed in a boiling water bath for about 22 min to allow full development of the colour. After cooling the solution in water, about 9 g of sodium chloride were added and the saturated solution shaken with 10 ml of isobutyl alcohol for about 1 min. The aqueous solution was drained off, the upper isobutyl alcohol layer placed in a dry test tube and the solution lightly shaken with about 2 g of anhydrous sodium sulphate for dehydration. Part of this solution was transferred to the photometer cell and its absorbance measured at 655 mμ, from which the quantity of nitrogen present was calculated.

Selection of organic extractant

The coloured substance is extracted by isobutyl alcohol and isoamyl alcohol but not by other solvents, such as methyl isobutyl ketone, chloroform, benzene, xylene, carbon tetrachloride, amyl acetate, butyl acetate or ethyl acetate. Therefore, extractions were carried out with isobutyl alcohol and isoamyl alcohol, using 30 μg of nitrogen. The two extracts differed slightly in colour and their absorbances were measured at the wavelength of maximum absorption in each solvent (Table I).

TABLE I.—SPECTROPHOTOMETRIC DATA FOR EXTRACTION OF 30 μg OF NITROGEN

Solvent	Wavelength for maximum absorption, *m*μ	Absorbance		Molar absorptivity at maximum absorption
		Blank	Corrected for blank	
Isobutyl alcohol	655	0·020	0·320	1490
Isoamyl alcohol	645	0·020	0·305	1420

The use of isobutyl alcohol was adopted, this being the more convenient solvent. Extraction of up to 60 μg of nitrogen is complete with a single 10-ml portion of isobutyl alcohol under the experimental conditions eventually established.

Absorbance curve

The coloured solution obtained from 35 μg of nitrogen submitted to the above procedure, was extracted with isobutyl alcohol and the absorbance measured at wavelengths between 320 and 800 mμ. Below 400 mμ the blank values tended to increase towards the shorter wavelength region and no absorption of nitrogen was observed. Blank values were small in the region of 400–500 mμ, and again no absorption of nitrogen was observed. The absorbance curve above 500 mμ is shown in Fig. 1, the absorption maximum being at 655 mμ.

Effect of pH

The same procedure was carried out with 30 μg of nitrogen and with the added quantity of 1*M* sodium hydroxide solution or 1*M* hydrochloric acid varied to adjust the solution to different pH. As shown in Fig. 2, a constant absorbance is observed in the pH range 11·4–12·5. This pH corresponds to 0·05–0·15*M* in free sodium hydroxide when no other salts are present in large quantity.

Effect of amount of phenol

In the next experiments, only the amount of phenol solution added was varied, and the results are shown in Fig. 3. The absorbance becomes constant with above 0·5 ml of phenol solution present and it was, therefore, decided to add 1·0 ml of phenol.

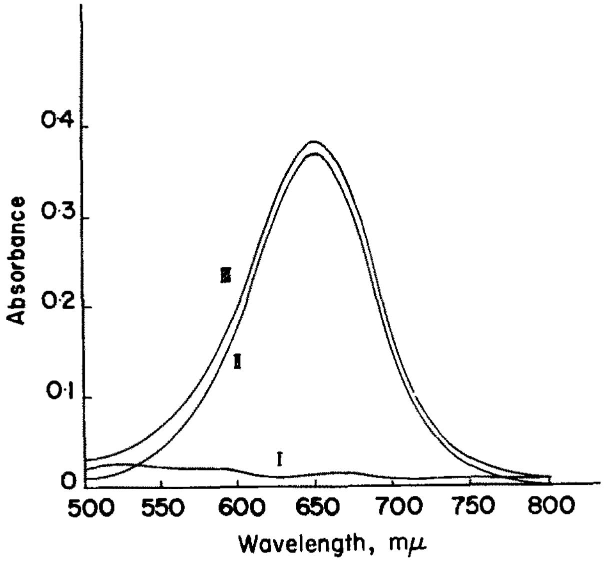

FIG. 1.—Absorbance curves using isobutyl alcohol:
I—reagent blank,
II—3·5 μg of nitrogen/ml of extract,
III—3·5 μg of nitrogen/ml of extract plus reagent blank.

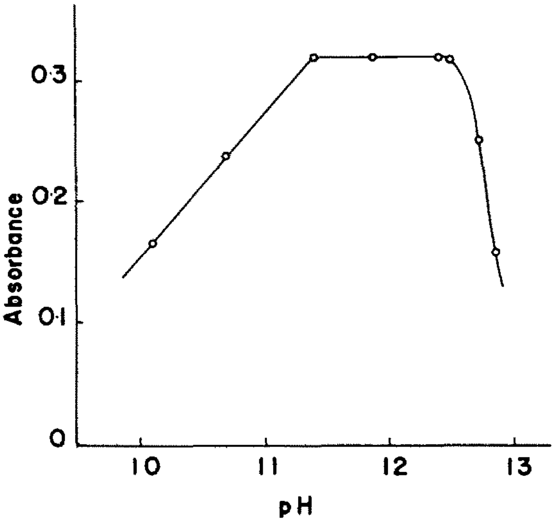

FIG. 2.—Effect of pH on absorbance (3 μg of nitrogen/ml of extract).

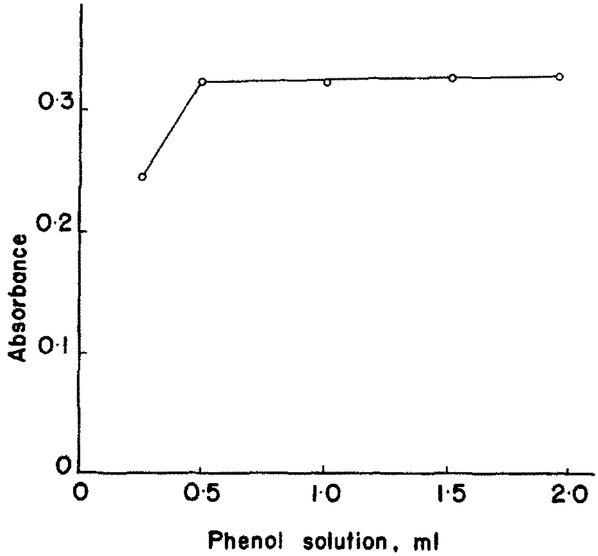

FIG. 3.—Effect of amount of phenol on absorbance (3 μg of nitrogen/ml of extract).

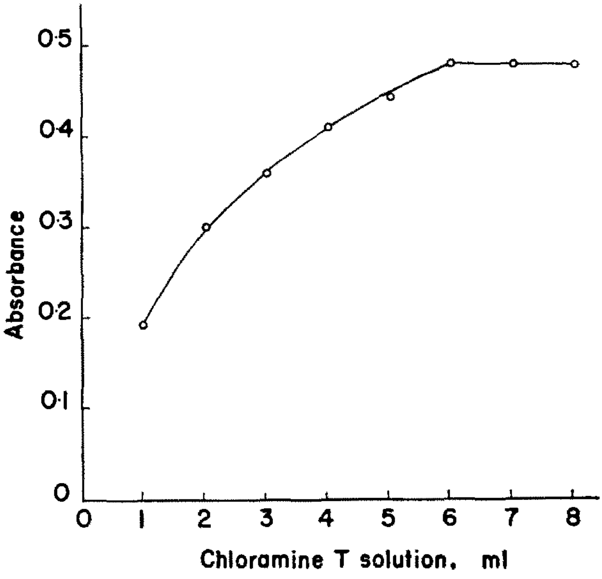

FIG. 4.—Effect of amount of chloramine-T on absorbance (4·5 μg of nitrogen/ml of extract).

Effect of amount of chloramine-T

The amount of chloramine-T solution added was varied with 45 μg of nitrogen present and keeping the other factors unchanged. From Fig. 4, a constant absorbance is obtained by the addition of over 6 ml of 5% chloramine-T solution and it was, therefore, decided to use 7 ml. There is a variation of absorbance according to the chloramine-T used and it is necessary to use a good quality product.

Effect of heating time

The same procedure was carried out as described above to ascertain the effect of the time of heating and the extraction temperature. From the experiments it was found that it is necessary to

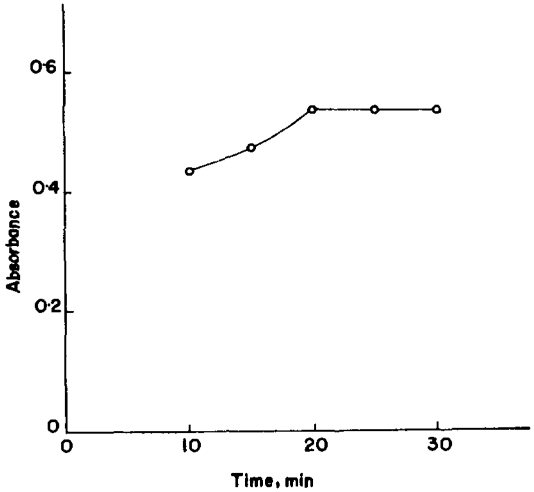

FIG. 5.—Effect of heating time on absorbance (5 μg of nitrogen/ml of extract).

heat the mixture in a boiling water bath for more than 20 min (see Fig. 5); also the absorbance of the extract solutions is constant when extracted between 10° and 25°, but it decreases when extracted at 30°.

Effect of amount of sodium chloride

Preliminary experiments (see below) with various salts as salting-out agents showed that sodium chloride was the most suitable. The same procedure as described before was carried out with 30 μg of nitrogen, but various quantities of sodium chloride were added after the cooling period. As shown in Fig. 6, it is necessary to add more than 8 g of sodium chloride. Addition of 8 g of sodium chloride brings the solution to saturation and some solid sodium chloride remains undissolved when more than 9 g of the salt is added. Because it is necessary to obtain a completely saturated solution of sodium chloride, 9 g of the salt was added henceforth.

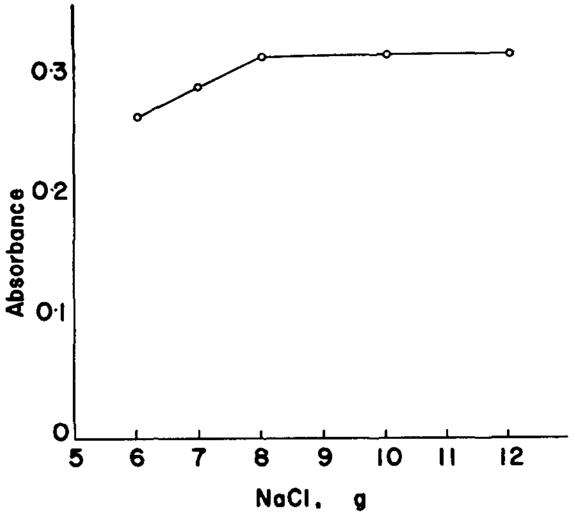

FIG. 6.—Effect of amount of sodium chloride on absorbance (3 μg of nitrogen/ml of extract).

Effect of other salting-out reagents

The same procedure as described above was employed to investigate the effects of potassium chloride, sodium sulphate, potassium sulphate, sodium nitrate and potassium nitrate as salting-out reagents. The solution was cooled to 15° after coloration, and each salt was added to more than saturation, then extraction was carried out. As indicated in Table II, the absorbance was greatest with sodium chloride and lower with all other salts.

TABLE II.—EFFECT OF VARIOUS SALTING-OUT REAGENTS ON EXTRACTION OF 30 μg OF NITROGEN

Salting-out reagent	Amount added, *g*	Absorbance	
		Blank	Corrected for blank
NaCl	9	0·035	0·320 0·322
KCl	9	0·033	0·284 0·285
Na_2SO_4	10	0·020	0·210 0·211
K_2SO_4	5	0·020	0·190 0·188
$NaNO_3$	20	0·022	0·182 0·183
KNO_3	9	0·020	0·168 0·138

Calibration curve

There is a linear relationship between the quantity of nitrogen and the absorbance over the range 0·1–60 μg of nitrogen/10-ml extract.

Effect of various ions and organic acids

Metal ions. Various metal ions were added to 30 μg of nitrogen and the same procedure carried out as above. The effect of copper is remarkable and the determination becomes impossible when 5 μg of copper is present (Table III). Other metal ions, such as 100 mg of Mo and W; 10 mg of Al, Zn, V, Ni and Sn; 2 mg of Fe; 1 mg of Co, Mg, Mn, Cd, Bi, U, Hg, Ag, Cr, Pb, Be, Se, Te, Zr and Ce; and 0·1 mg of Sb, Ti, Nb, and Ta do not affect the reaction.

Anions and organic acids. Various salts and organic acids were added to 30 μg of nitrogen and the solution was submitted to the determination of nitrogen as described above. These results are shown in Table III and Fig. 7. Organic acids which form complex salts interfere in the determination. Although sodium chloride, fluoride, nitrate and perchlorate and potassium chloride do not affect the reaction, sodium sulphate* and phosphate show characteristic effects.

Determination of Nitrogen in Iron, Steel and Aluminium

The developed procedure was applied to the determination of nitrogen in iron, steel and aluminium. Because the reaction was carried out at around pH 12, iron and most other metals will precipitate as their hydroxides. Coloration in the presence of a large amount of precipitate was not desirable because adsorption of nitrogen might occur; also, the extraction procedure was inconvenient. Consequently, steam distillation was used in the case of iron and steel to separate the ammonia before the photometric procedure. Aluminium did not precipitate under these conditions when the quantity was small, but it formed some precipitate when the quantity became larger. However, the amount of the precipitate was smaller than in the case of iron and steel samples and the number of impurities present in the metal was smaller. Therefore, the problem was only to remove copper (see above) and the determination was carried out without removal of other ions.

Determination of nitrogen in iron and steel

Procedure. The sample was placed in a beaker and heated with 40–60 ml of hydrochloric acid (1 + 1) until in solution.† The distillation apparatus (conventional type) was thoroughly steamed out, 20 ml of 0·1*M* sulphuric acid placed in the receiver and the tip of the condenser tube dipped

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* A direct extraction procedure on a neutralised Kjeldahl digest of organic material may be possible, provided the calibration curve is produced under the same conditions.

† When it was necessary to determine acid-soluble and acid-insoluble nitrogen separately, the residue was collected by filtration through asbestos, decomposed by the usual Kjeldahl method, then submitted to distillation for separate determination of nitrogen.

TABLE III.—EFFECTS OF COPPER AND ORGANIC ACIDS ON DETERMINATION OF 30 μg OF NITROGEN

Additive	Amount added	Absorbance		Nitrogen found, μg	
		Blank	Corrected for blank		
Cu	3 μg	0·027	0·322	30·4	
			0·321	30·3	
	5 μg	0·026	0·315	29·7	Green extract
			0·312	29·5	
	10 μg	0·022	0·238	22·5	Green extract
			0·267	25·3	
	30 μg	0·015	0·115	10·8	Precipitate
			0·097	9·2	
EDTA	0·05 g	0·095	0·155	14·5	
			0·182	17·2	
Tartaric acid	0·1 g	0·030	0·318	30·0	
			0·321	30·3	
	0·2 g	0·030	0·267	26·3	
			0·295	28·2	
	0·5 g	0·032	0·006	0·5	
			0·008	0·8	
Citric acid	0·2 g	0·030	0·318	30·0	
			0·313	29·3	
	0·3 g	0·030	0·296	28·0	
			0·306	28·7	
	0·5 g	0·095	0·025	2·4	
			0·065	6·2	
NaF	0·2 g	0·046	0·320	30·0	
			0·322	30·3	
	0·5 g	0·051	0·289	27·5	
			0·278	26·5	
$NaNO_3$	2·0 g	0·329	0·313	29·3	
			0·316	29·5	
$NaClO_4$	2·5 g	0·075	0·320	30·0	
			0·319	30·0	
	4·0 g	0·100	0·285	27·0	
			0·289	27·5	
NaCl	4·0 g	0·038	0·322	30·2	
			0·324	30·5	
	8·0 g	0·046	0·324	30·5	
			0·322	30·2	
KCl	8·0 g	0·230	0·320	30·0	
			0·323	30·3	

inside the solution. In the distillation flask, 50–75 ml of 12*M* sodium hydroxide solution were placed and the sample solution added from the funnel placed over it. The funnel must be thoroughly washed before use. Steam was then passed through the flask while heating the solution. When the distillate was around 90 ml, the receiver was lowered to raise the tip of the condenser tube above the solution and distillation was continued for 3–4 min. The tip of the condenser tube was washed with water, the receiver solution transferred to a 100-ml calibrated flask and diluted to the mark. From this solution a 20-ml aliquot was transferred to a glass-stoppered conical flask, 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution were added and the volume brought to 25 ml with water.

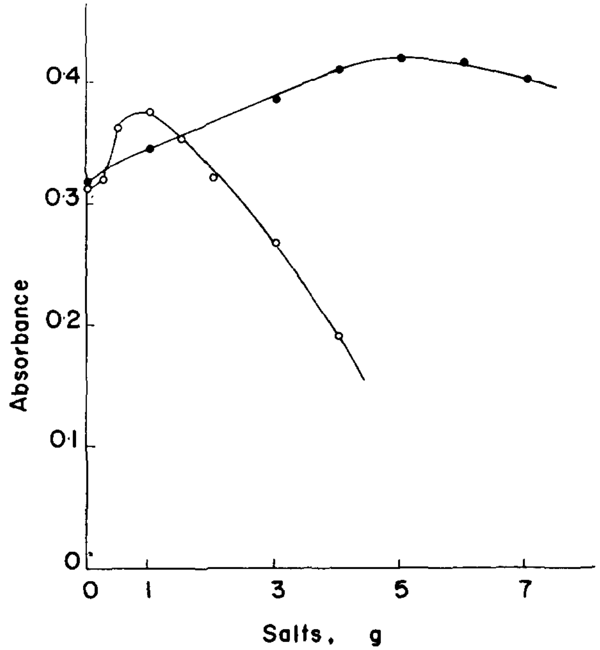

FIG. 7.—Effect of amount of sodium sulphate (●) and disodium hydrogen phosphate (○) on absorbance (3 μg of nitrogen/ml of extract).

This solution was submitted to the procedure described above and the quantity of nitrogen obtained from a calibration curve.

Examination of distillation method. Experiments were carried out to find whether nitrogen was completely recovered as ammonia by steam distillation with the apparatus used. To remove any nitrogen contained in electrolytic iron, 1 g of electrolytic iron was dissolved in 40 ml of hydrochloric acid (1 + 1), 50 ml of 12*M* sodium hydroxide solution added and the mixture boiled on a hot-plate for over 30 min. The nitrogen-free electrolytic iron solution thus obtained was transferred to a distillation flask, various amounts of standard nitrogen solution added and the mixture submitted to distillation as described above. Results of the determination of nitrogen by this procedure are shown in Table IV, and they indicate that the recovery of nitrogen is complete.

Analysis of samples. Several samples of iron and steel were submitted to determination of nitrogen by the above procedure and the results obtained are listed in Table V. Some results for the separate determination of acid-soluble and acid-insoluble nitrogen are given in Table VI.

TABLE IV.—RECOVERY OF NITROGEN AFTER DISTILLATION

Nitrogen added,[a] μg	Absorbance (corrected for blank)[c]	Total nitrogen found,[b] μg
50	0·112	50·0
	0·111	50·0
100	0·219	102·5
	0·215	100·0
150	0·326	152·5
	0·320	150·0
200	0·426	200·5
	0·424	199·5
250	0·534	252·5
	0·530	250·5

[a] 1 g of electrolytic iron taken.
[b] One-fifth of distillate used for spectrophotometry.
[c] Blank absorbance: 0·034.

TABLE V.—RESULTS OF THE DETERMINATION OF NITROGEN IN SOME CARBON STEELS

Sample	Amount taken, *g*	Absorbance (corrected for blank)	Total nitrogen found	
			By proposed method,[a] %	By Nessler method, %
No. 1	3·000	0·101	0·0016	0·0014
		0·100	0·0016	
No. 2	3·000	0·090	0·0014	0·0012
		0·085	0·0013	
No. 3	3·000	0·117	0·0018	0·0019
		0·117	0·0018	
No. 4	1·000	0·367	0·017	0·015
		0·360	0·017	
No. 5	1·000	0·275	0·013	0·012
		0·288	0·014	

[a] One-fifth of distillate used for spectrophotometry.

TABLE VI.—RESULTS OF THE DETERMINATION OF NITROGEN IN SOME IRONS AND STEELS

Sample	Amount taken, *g*	Soluble or insoluble nitrogen	Aliquot	Absorbance (corrected for blank)	Nitrogen found in sample	
					By proposed method,[a] %	By titrimetric method,[b] %
Cast		Sol.	1/5	0·027	0·0003	
iron	4·000			0·032	0·0004	
		Insol.	1/10	0·332	0·0078	0·007
				0·335	0·0079	
Pig		Sol.	1/5	0·035	0·0005	
iron	3·000			0·035	0·0005	
		Insol.	1/5	0·154	0·0024	0·004
				0·166	0·0026	
18–8		Sol.	1/20	0·413	0·0390	0·038
Stainless	2·000			0·414	0·0391	
steel		Insol.	1/5	0·010	0·0002	
				0·008	0·0002	
13-Chrome		Sol.	1/20	0·310	0·0293	0·0298
steel	2·000			0·299	0·0283	
		Insol.	1/5	0·036	0·0008	
				0·038	0·0009	

[a] One-fifth of distillate used for spectrophotometry.

[b] The ammonia is steam distilled into standard sulphuric acid solution, the excess of which is eventually titrated with standard sodium hydroxide using methyl red-methylene blue as indicator.

Determination of nitrogen in aluminium

Procedure. A solution of 1–2 g of the aluminium sample in a mixture of 20 ml of hydrochloric acid and 20 ml of water was diluted to about 70 ml with water and cooled to room temperature. About 10 g of granulated zinc were added and the mixture allowed to stand at room temperature with occasional shaking, when copper precipitated out on the surface of the zinc. After about 2 hr a piece of fresh zinc was added to see if its surface also blackened. When blackening no longer occurred, the solution was filtered through paper into a 100-ml calibrated flask. The filter paper and zinc were washed with water and the combined filtrate and washings diluted to the 100-ml mark with water. Ten ml of this solution were transferred to a beaker, neutralised with $3M$ sodium hydroxide solution (litmus paper), and 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution added. The pH of the solution was adjusted to about 12 (pH-meter) by the addition of $3M$ sodium hydroxide solution and the volume brought to about 25 ml with water. The total volume of $3M$ sodium hydroxide solution used in this procedure was recorded.

To a second 10-ml aliquot of the sample solution the same amount of 3*M* sodium hydroxide solution as used in the preceding experiment was added, followed by 1 ml of phenol solution and 3·5 ml of 10% chloramine-T solution. The volume was adjusted to about 25 ml and the determination of nitrogen completed as previously. The quantity of nitrogen was obtained from a calibration curve.

Examination of method for removal of copper. Only a small quantity of copper is generally present in aluminium. Preliminary experiments were carried out on its removal because copper interferes in the colour reaction (see above). The most simple method was to add zinc to the dilute hydrochloric acid solution of aluminium at room temperature to precipitate out metallic copper on the zinc.

One g of aluminium foil (0·011% of copper) was dissolved in a mixture of 20 ml each of hydrochloric acid and water, then standard nitrogen solution added. Copper was added and precipitated with zinc as described above. The solution was filtered, the filtrate diluted to 100 ml in a calibrated flask and 10 ml of this solution submitted to the determination of nitrogen.

As shown in Table VII removal of copper by the use of zinc has no effect, the added nitrogen being determined completely. Determination of nitrogen in the granulated zinc used showed that it contained $0{\cdot}001_2$% of nitrogen. The amount of zinc dissolved by this procedure was extremely small, but in any case, a blank test was always carried out at the same time.

Analysis of samples. The developed procedure was applied to the analysis of several samples of aluminium and the results obtained are shown in Table VIII.

TABLE VII.—RECOVERY OF NITROGEN AFTER REMOVAL OF COPPER BY ZINC[a]

Copper added, *mg*	Nitrogen added, *μg*	Absorbance		Total nitrogen found,[b] *μg*
		Measured	Corrected for blank	
0	0	0·054	—	—
		0·055	—	—
2·5	0	0·056	—	—
		0·056	—	—
0	300	0·375	0·320	301
		0·373	0·318	300
2·5	150	0·220	0·164	151
		0·218	0·162	150
2·5	300	0·373	0·317	299
		0·376	0·320	301

[a] 1·000 g of aluminium, containing 110 μg of copper as impurity, taken.

[b] One-tenth of solution, after removal of zinc, used for spectrophotometry.

TABLE VIII.—DETERMINATION OF NITROGEN IN ALUMINIUM

Sample	Amount taken, *g*	Absorbance (corrected for blank)	Total nitrogen found in sample	
			By proposed method,[a] %	By Nessler method, %
1st grade	2·1619	0·067	0·0029	0·0027
		0·066	0·0029	
2nd grade	2·1516	0·074	0·0033	0·0030
		0·074	0·0033	
3rd grade	2·1441	0·076	0·0035	0·0036
		0·078	0·0035	
Special grade	2·1376	0·041	0·0018	0·0019
		0·042	0·0018	
Foil	2·4658	0·068	0·0026	0·0025
		0·067	0·0026	

[a] One-tenth of solution, after removal of zinc, used for spectrophotometry.

Zusammenfassung—Die spektralphotometrische Bestimmung von Stickstoff als Ammoniak mit Extraktion in organisches Lösungsmittel wurde untersucht. Die blaue Verbindung aus Ammoniak, Phenol und Hypochlorit (Chloramin T) läßt sich durch Aussalzen völlig in Isobutyl- oder Isoamylalkohol extrahieren. Die günstigsten Bedingungen wurden ermittelt und das Verfahren auf Stickstoffbestimmungen in Eisen, Stahl und Aluminium angewandt.

Résumé—On a étudié un dosage spectrophotométrique de l'azote, à l'état d'ammoniac, par extraction avec un solvant organique. Le composé coloré en bleu que forme l'ammoniac avec le phénol et un hyperchlorite (chloramine-T) est extrait complètement à l'alcool isobutylique ou isoamylique, en utilisant seulement un réactif relargant, et on a établi les conditions optimales. Cette méthode a été appliquée au dosage de l'azote dans le fer, l'acier et l'aluminium.

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

TITRIMETRIC DETERMINATION OF CERIUM^{III}

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Summary—The use of potassium dichromate for the potentiometric titration of cerium^{III} in 12–13·5M phosphoric acid at room temperature has been investigated. The method, which is accurate to ±0·35% for 30–120 mg of cerium/50 ml of titration solution, has been applied to the determination of cerium in monazite sand and technical cerium carbonate. Methods have also been developed for the differential potentiometric titration of iron^{II} plus cerium^{III}, vanadium^{IV} plus cerium^{III}, and iron^{II} plus vanadium^{IV} plus cerium^{III} in the same solution.

MANY of the procedures for the titrimetric determination of cerium^{III} are indirect, involving oxidation to cerium^{IV}. Several oxidising agents have been tried, including atmospheric oxygen, potassium or ammonium persulphate, lead dioxide, bismuth tetroxide or sodium bismuthate, potassium hexacyanoferrate(III), potassium chlorate, ozone and silver^{II} oxide.

Von Knorre[1] appears to have been the earliest to apply himself to the titrimetric determination of cerium. He proposed the oxidation of cerium^{III} to cerium^{IV} with atmospheric oxygen in a basic medium. The resulting cerium^{IV} was treated in an acid medium with a known excess of hydrogen peroxide, the excess of which was back-titrated with standard potassium permanganate. Atmospheric oxidation of cerium^{III} was also resorted to by Barthauer and Pearce,[2] who reacted the cerium^{IV} formed with potassium iodide in an acid medium and titrated the liberated iodine with standard sodium thiosulphate. Lessnig[3] treated the cerium^{IV} formed with a known excess of iron^{II} and titrated the unreacted iron^{II} with standard potassium permanganate. The heterogeneous oxidation of cerium^{III} hydroxide by atmospheric oxygen in an alkaline medium must necessarily be incomplete.

The earliest investigator to employ potassium persulphate for the oxidation of cerium^{III} in sulphuric acid appears to have been Von Knorre.[4] After decomposing the excess persulphate by boiling, he determined the cerium^{IV} formed through the hydrogen peroxide-potassium permanganate method. Sterba-Boehm and Matula[5] also employed potassium persulphate for the oxidation of cerium^{III}, but they determined the resulting cerium^{IV} iodimetrically. Weiss and Sieger[6] reported that this method gives results 10–20% high. They also stated that a similar oxidation by persulphate in an alkaline medium in the presence of a nickel catalyst and titration of the cerium^{IV} with arsenite (according to the procedure of Lang and Zwerina[7]) gives low results (0–3·4%). Willard and Young[8] improved the method by using silver nitrate as a catalyst during the oxidation of cerium^{III} by persulphate.

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* Part II: See reference 29.

Job[9] achieved the oxidation of cerium^{III} with excess of lead dioxide in a strong nitric acid medium; after the excess of oxidising agent is removed by filtration, cerium^{IV} in the filtrate is determined by the hydrogen peroxide-permanganate method. Weiss and Sieger[6] stated that the method of Job gives inaccurate results. Gordon and Feibush[10] recently employed lead dioxide for the oxidation of small amounts of cerium^{III} in sulphuric acid. The cerium^{IV} is filtered into a known excess of iron^{II}, and the unreacted iron^{II} determined by a spectrophotometric method, after complexation with 1,10-phenanthroline.

Waegner and Muller[11] oxidised cerium^{III} by treatment with excess of bismuth tetroxide in a strong nitric acid solution. The excess of bismuth tetroxide is filtered off and the cerium^{IV} in the filtrate determined by the hydrogen peroxide-permanganate method. Weiss and Sieger[6] stated that this method gives about 10% low results. Metzger[12] used sodium bismuthate in sulphuric acid solution at boiling temperature in place of bismuth tetroxide, and determined the cerium^{IV} by the iron^{II} sulphate-permanganate method. The method is not precise, giving results with an error of 2%. Moreover, the method is cumbersome, because it requires a filtration and washing.

Browning and Palmer[13] treated cerium^{III} in an alkaline medium with an excess of hexacyanoferrate(III), the hydrated cerium^{IV} oxide being filtered off and the hexacyanoferrate(IV) in the filtrate titrated in an acid medium with standard potassium permanganate. Unless every precaution is taken to exclude air during the treatment of the cerium^{III} in alkaline solution with excess potassium hexacyanoferrate (III), the results will be low because part of the cerium^{III} is oxidised by atmospheric oxygen.

Strobasch[14] employed potassium chlorate as an oxidant for cerium^{III} in sulphuric acid. The excess oxidant is decomposed by boiling and the cerium^{IV} formed determined by the hydrogen peroxide-permanganate method.

Willard and Merritt[15] used ozone as the oxidising agent. When cerium^{III} is treated with 5% ozone for 60 min in a medium containing both sulphuric and phosphoric acids, cerium^{III} phosphate is oxidised to cerium^{IV} phosphate which separates as a thick white gel, it being more insoluble than the cerium^{III} phosphate. Unless the cerium^{IV} phosphate is precipitated in this way the oxidation is reported to be incomplete. After the reaction is completed, the cerium phosphate is dissolved in sulphuric acid until a clear yellow-orange solution results. The excess of ozone is driven out from the mixture by passing carbon dioxide or nitrogen for 15 min, then the cerium^{IV} titrated with a standard solution of iron^{II} sulphate using ferroïn as indicator. It is obvious that the method is tedious, although it is reported to give precise results. All substances which are oxidised by ozone in acid solution and reduced by iron^{II} sulphate must be absent. These include manganese^{II}, cobalt^{II}, vanadium^{IV} and large amounts of chromium^{III} salt. Chlorides and large concentrations of nitrates also interfere.

Kimura and Murakimi[16] and Lingane and Davis[17] carried out the indirect titrimetric determination of cerium^{III} using silver^{II} oxide as oxidant in nitric acid at room temperature; the redox potential[18] of the silver^{II}/silver^{I} couple is very high, being 1·929 V in 4*M* nitric acid and 2·00 V in 4*M* perchloric acid. Excess oxidant is easily removed by warming for a few min. The solution is then diluted, treated with excess standard iron^{II} solution, and the unreacted iron^{II} titrated with standard cerium^{IV} sulphate or permanganate solution. Chromium^{III}, manganese^{II} and other substances which are also oxidised by silver^{II} interfere; although cobalt^{II} is also oxidised, it does not interfere because the cobalt^{III} is decomposed during the process of heating. However, it is undesirable to titrate cerium^{IV} salt or any other oxidant with iron^{II} solution in the presence of nitric acid.

Mention may also be made of the procedure developed by Lang[19] which is of considerable theoretical interest. Cerium^{III} is treated with a sufficient excess of potassium dichromate in the presence of a larger excess of arsenic^{III} in a medium containing 3–40 ml of sulphuric acid and 4–5 g of metaphosphoric acid/200 ml. The reaction between dichromate and arsenic^{III} is believed to induce the oxidation of cerium^{III} by dichromate; the resulting cerium^{IV} is determined by titration with standard iron^{II} solution using diphenylamine as indicator. Evidently the concentrations of all of the reactants should be so arranged that when all of the cerium^{III} is oxidised, there should be no dichromate left.

Recently, Issa and Allam[28] have proposed the use of potassium permanganate in an alkaline medium for the oxidation of cerium^{III}. To a known excess of standard permanganate solution, add excess of telluric acid (sufficient to keep the tellurium^{VI}/manganese^{VII} ratio greater than 5). The mixture is now treated dropwise with sodium hydroxide solution to give a concentration of 1·0–2·0*M*, followed by an aliquot of the cerium^{III} solution. After waiting for 5–10 min the excess permanganate is back-titrated with a standard solution of thallium^{I}. The permanganate is reduced only to manganese^{IV}, which is stabilised by the telluric acid present. In the direct titration of cerium^{III} in an alkaline medium with potassium permanganate in the presence of a large excess of telluric acid, the time required for equilibrium potentials is about 1 min at the beginning of the titration and 9 min near the equivalence point. The method is only of theoretical interest because the reagents involved, namely telluric acid and thallium^{I}, are expensive.

Besides the indirect methods discussed above, several direct methods have also been proposed. As early as 1916, Lenher and Meloche[20] titrated cerium^{III} nitrate solution, in the presence of an excess of zinc oxide paste, with potassium permanganate solution, first in the cold, then at the boiling temperature towards the end-point. Milk of magnesia (but no calcium carbonate) was also found suitable in place of zinc oxide. Goffart[21] has shown that cerium^{III} is oxidised to the quadrivalent state (in a neutral sodium pyrophosphate medium) by titration with standard potassium permanganate. The visual end-point is obscured by the colour of the product of the reaction, manganese^{III} pyrophosphate complex. The potentiometric end-point method is also unsatisfactory, because the potential break is very small (15–25 mV). Hence, Goffart suggested amperometric end-point detection. The reaction becomes very slow near the end-point and vigorous agitation is necessary.

Marple, Przybylowicz and Hume[22] employed photometric titration for the determination of submilligram to decigram amounts of cerium^{III} with potassium permanganate in a neutral pyrophosphate medium. Arsenic^{III}, vanadium^{IV}, antimony^{III}, thallium^{I}, mercury^{I} and iodide are reported to interfere. In the photometric method chromium^{III}, fluoride and other substances which form precipitates should also be absent.

Tomiček[23] carried out the titration of cerium^{III} with potassium hexacyanoferrate (III), in a medium containing a high concentration of potassium carbonate, under a carbon dioxide atmosphere, with a potentiometric end-point. Air must be rigorously excluded because the complex carbonates of cerium^{III} are easily oxidised by atmospheric oxygen. Moreover, the alkaline condition results in the precipitation of many metals. The position of the inflection point on the potential-concentration curve depends on the concentration of the carbonate, being shifted towards more negative potentials as the carbonate concentration increases. This indicates that the cerium^{IV} carbonates are more complex than the cerium^{III} carbonates. This method gives poor inflection points when the cerium^{IV}/cerium^{III} ratio is large.

Bricker and Loeffler[24] recommended the titration of cerium^{III} solution in 1*M* sulphuric acid with a standard cobalt^{III} solution using a photometric end-point, following the absorption at 400 mμ (where the formation of cerium^{IV} is observed) or at 610 mμ (where the excess cobalt^{III} is detected). Because the reaction between cobalt^{III} and cerium^{III} is very slow in the vicinity of the equivalence point, the addition of silver nitrate is recommended to serve as a catalyst. The authors have stated that the reproducibility of the method is about 5 parts per 1,000; the disagreement between the values obtained by the sodium bismuthate and cobalt^{III} methods is about 1·5%. Manganese^{II}, chromium^{III}, vanadium^{IV} and other elements which are oxidised by cobalt^{III} interfere. Chloride, bromide and iodide are rapidly oxidised by cobalt^{III}. Hence their presence vitiates the results, as does that of acetic acid, acetic anhydride, glycerol, *etc.*, which are also rapidly oxidised. In view of the difficulties involved in the preparation of cobalt^{III} sulphate and the very poor stability of the reagent, it is doubtful whether the reagent can attain sufficient vogue.

Recently, Doležal, Rössler and Zýka[25] reported that cerium^{III} can be titrated potentiometrically in 0·2*M* sodium carbonate under an atmosphere of nitrogen with 0·01*M* potassium periodate solution. When the equivalence point is approached, it is necessary to wait for 15–30 sec until the potential becomes constant. The end-point is indicated by a potential change of 170 mV/0·02 ml of titrant at about 0·1 V *versus* a saturated calomel electrode. It is reported that the determination of 1–10 mg and 10–50 mg of cerium gave an average deviation of ±1·8% and ±1·0%, respectively, in 50 titrations. Bismuth^{III}, cobalt^{II}, chromium^{III}, iron^{III}, nickel^{II} and zinc^{II} interfere when present in concentrations greater than 1% of the cerium. Lanthanum, europium and yttrium do not interfere. The low degree of reproducibility of the method, interference of atmospheric oxygen, large number of other interferences and high cost of the reagent are some of the disadvantages attendant on the use of potassium periodate for the determination of cerium^{III}.

From the foregoing it is evident that the only precise method for the determination of cerium^{III} now available is the indirect procedure of Willard and Young[8] involving heating of cerium^{III} with excess of persulphate in the presence of silver nitrate as catalyst.

We have now developed a direct titration method with potassium dichromate. Making use of our observation that cerium^{III} is rapidly oxidised to cerium^{IV} by potassium dichromate in 10·5–13·5*M* phosphoric acid, conditions have been established under which cerium^{III} can be titrated directly with a standard solution of potassium dichromate at room temperature with a potentiometric end-point. It has already been reported[26] that the formal redox potential of the chromium^{VI}/chromium^{III} couple increases with increasing phosphoric acid concentration, from 1·016 V in 1·0*M* phosphoric acid to 1·483 V in 12*M* phosphoric acid. The formal redox potential of the cerium^{IV}/cerium^{III} couple has now been determined in media of varying phosphoric acid concentration. From the data presented in Table I and the curves given in Fig. 1, it will be seen that the potential of the chromium^{VI}/chromium^{III} couple has a value lower than that of the cerium^{IV}/cerium^{III} couple in phosphoric acid of concentration less than 6·6*M*, but has a higher value above this concentration. In 12*M* phosphoric acid the potential of the chromium^{VI}/chromium^{III} couple is greater than that of the cerium^{IV}/cerium^{III} couple by 0·248 V. The formal redox potential of the cerium^{IV}/cerium^{III} couple could not be determined in a medium containing phosphoric acid at a concentration lower that about 6*M*, because cerium^{IV} phosphate is insoluble under such conditions.

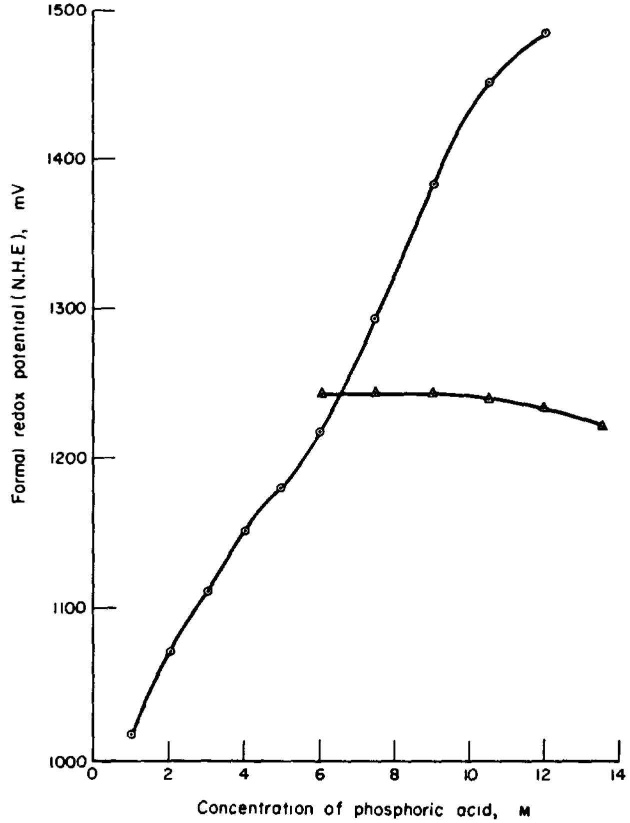

Fig. 1.—Formal redox potentials in a medium of varying phosphoric acid concentration:

○—○—chromium^{VI}/chromium^{III} couple,
△—△—cerium^{IV}/cerium^{III} couple.

In our experiments, phosphoric acid plays a two-fold role: firstly, it lowers the redox potential of the cerium^{IV}/cerium^{III} couple by complexing cerium^{IV} more strongly than cerium^{III}; secondly, it increases the potential of the chromium^{VI}/chromium^{III} couple. Thus in a suitable phosphoric acid medium cerium^{III} is oxidised to cerium^{IV} by chromium^{VI}, a reaction which is the reverse of the usual redox reaction in sulphuric or nitric acid media, namely, the oxidation of chromium^{III}

to chromium^{VI} by cerium^{IV}. Willard and Young[27] determined chromium^{III} by treatment with excess of cerium^{IV} sulphate in hot solution, followed by back-titration of the unreacted cerium^{IV} with standard sodium oxalate or sodium nitrite solution.

From the known difference in the redox couples in 12*M* phosphoric acid, the equilibrium constant of the following reaction is calculated to be $8{\cdot}318 \times 10^{24}$ at 28°:

$$6Ce^{3+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Ce^{4+} + 2Cr^{3+} + 7H_2O.$$

EXPERIMENTAL

Determination of Formal Redox Potential of Cerium^{IV}/Cerium^{III} Couple in a Medium of Varying Phosphoric Acid Concentration

Reagents

Cerium^{IV} solution. An approximately 0·1*M* solution is prepared from "Pro Analysi" grade cerium^{IV} sulphate (E. Merck, Germany) in 1*M* sulphuric acid and standardised against sodium oxalate.

Cerium^{III} solutions. An approximately 0·1*M* solution is prepared from cerium^{IV} sulphate by reduction with hydrogen peroxide in 1*M* sulphuric acid and boiling down to crystallisation. The solution is then cooled, made up to desired volume and standardised according to the method of Willard and Young.[8]

Syrupy phosphoric acid. Syrupy phosphoric acid of "Pro Analysi" grade supplied by E. Merck, Germany, is used in this investigation. This sample of phosphoric acid is free from impurities which can react with cerium^{IV} within the time of the experiment. The strength of phosphoric acid is ascertained after suitable dilution, by titration with a standard solution of sodium hydroxide using a mixture (1:1) of phenolphthalein and α-naphtholphthalein as indicator.

Apparatus

As described before.[26]

Procedure

Volumes corresponding to 2·50 ml of 0·1*M* cerium^{IV} solution and to 2·50 ml of 0·1*M* cerium^{III} are mixed. After adding enough phosphoric acid to reach the required strength, the mixture is diluted to 50 ml. The rest of the procedure is as described before.[26] The potentials attain equilibrium values immediately.

The values of the cerium^{IV}/cerium^{III} redox potential at different phosphoric acid concentrations are given in Table I (uncorrected for liquid-liquid junction potential).

TABLE I.—FORMAL REDOX POTENTIAL OF CERIUM^{IV}/CERIUM^{III} COUPLE IN A MEDIUM OF VARYING PHOSPHORIC ACID CONCENTRATION

Concentration of phosphoric acid, *M*	Formal redox potential (N.H.E.), *V*
6·0	1·244
7·5	1·244
9·0	1·244
10·5	1·239
12·0	1·235
13·5	1·222

Temperature 28°; total cerium concentration: 0·01*M*.

Oxidation of Cerium^{III} to Cerium^{IV} with Potassium Dichromate in a Strong Phosphoric Acid Medium

We have observed that the reaction between cerium^{III} and chromium^{VI} is so fast in 10·5–13·5*M* phosphoric acid that a direct potentiometric titration of cerium^{III} is possible with potassium dichromate at room temperature. When the concentration of phosphoric acid is 10·5*M* at the end of the titration, the reaction is somewhat slow so that near the equivalence point it is necessary to wait for about 6 min to obtain steady potentials. Hence we carried out the electrometric titration of cerium^{III} with potassium dichromate at room temperature maintaining the concentration of phosphoric acid at about 12*M* at the equivalence point.

Several experiments have shown that "Pro Analysi" grade phosphoric acid works quite satisfactorily as a titration medium. The potential break is about 50–60 mV/0·04 ml of 0·2*N* potassium dichromate when the titration solution is about 50 ml. AnalaR phosphoric acid of British Drug Houses Ltd., England, and reagent-grade acid of May and Baker, England, have also been found to give correct equivalence points, but the potential breaks are about 10 mV less.

Procedure

About 2–10 ml of solution, containing about 30–120 mg of cerium^{III}, are taken in a 150-ml Pyrex beaker and treated with the requisite volume (40–50 ml) of 90% phosphoric acid. The rest of the procedure is similar to that already described for manganese^{II}.[26] Near the equivalence point the potentials are noted after waiting for 3 min.

Because the potential break at the equivalence point is not very high, the equivalence point of the titration is best read from the curve obtained by plotting ΔE/ΔV against V. A representative curve of this type is shown in Fig. 2. A large number of determinations of cerium^{III} have been carried out in this manner and some typical results are given in Table II. The results show that the error of the determination is less than ±0·35%.

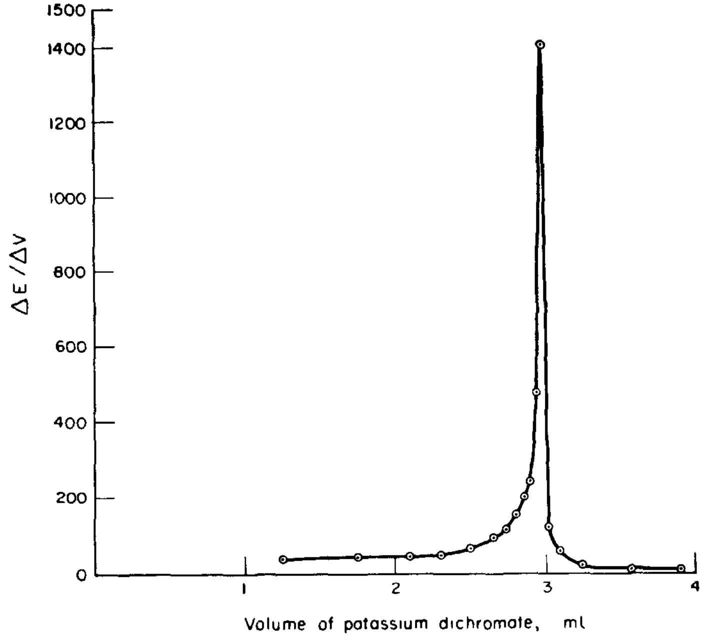

FIG. 2.—Potentiometric titration of cerium^{III} (83·50 mg) with potassium dichromate in 12*M* phosphoric acid.

Interferences

Interference from chloride and nitrate is similar to that found in the determination of manganese^{II}.[26] Fluoride interferes because it forms a precipitate with cerium^{III}, with a consequent slowing down of the reaction between cerium^{III} and chromium^{VI}. Iron^{II}, uranium^{IV}, vanadium^{IV},[29] molybdenum^{V}, arsenic^{III}, antimony^{III}, manganese^{II},[26] and lower valency states of tungsten are also oxidised by potassium dichromate under the conditions proposed for the titration of cerium^{III}. However, iron^{II} does not interfere in the determination of cerium^{III} by this method, because two different breaks in the potential *versus* volume curve are obtained, one corresponding to the oxidation of iron^{II} to iron^{III} and the other corresponding to the oxidation of cerium^{III} to cerium^{IV}. Cobalt^{II}, nickel^{II}, iron^{III}, tungsten^{VI}, molybdenum^{VI}, uranium^{VI}, chromium^{III}, cerium^{IV}, copper^{II}, zinc^{II},

TABLE II.—POTENTIOMETRIC TITRATION OF CERIUM$^{\mathrm{III}}$ WITH POTASSIUM DICHROMATE IN 12*M* PHOSPHORIC ACID

Cerium$^{\mathrm{III}}$ taken, *mg*	Cerium$^{\mathrm{III}}$ found, *mg*
31·54	31·65
45·85	45·74
51·29	51·29
69·18	68·96
72·88	72·88
92·06	91·94
95·06	95·06
113·4	113·6

thorium$^{\mathrm{IV}}$ and vanadium$^{\mathrm{V}}$ do not interfere (see Table III). Calcium, magnesium and aluminium also do not interfere. Sulphuric and perchloric acids do not interfere up to an over-all concentration of 1*N*. In the presence of thallium$^{\mathrm{I}}$ the potential break at the equivalence point is considerably reduced (from about 60 mV to about 10 mV/0·04 ml of 0·2*N* potassium dichromate solution), but the equivalence point is not affected.

TABLE III

Addenda	Amount added, *mg*	Cerium$^{\mathrm{III}}$ found, *mg*
Cobalt$^{\mathrm{II}}$	64·45	83·28
Cobalt$^{\mathrm{II}}$	32·22	83·50
Nickel$^{\mathrm{II}}$	65·73	83·50
Nickel$^{\mathrm{II}}$	32·86	83·28
Cobalt$^{\mathrm{II}}$	32·22	83·50
Nickel$^{\mathrm{II}}$	32·86	
Iron$^{\mathrm{III}}$	55·85	83·50
Iron$^{\mathrm{III}}$	27·92	83·50
Chromium$^{\mathrm{III}}$	20·80	83·50
Chromium$^{\mathrm{III}}$	10·40	83·28
Iron$^{\mathrm{III}}$	50·26	
Molybdenum$^{\mathrm{VI}}$	95·95	83·50
Uranium$^{\mathrm{VI}}$	59·90	83·50
Uranium$^{\mathrm{VI}}$	35·70	83·28
Molybdenum$^{\mathrm{VI}}$	57·57	
Cerium$^{\mathrm{IV}}$	70·05	83·50
Tungsten$^{\mathrm{VI}}$	86·80	83·50
Copper$^{\mathrm{II}}$	253·0	83·50
Zinc$^{\mathrm{II}}$	264·0	83·50
Copper$^{\mathrm{II}}$	253·0	83·72
Zinc$^{\mathrm{II}}$	264·0	
Thorium$^{\mathrm{IV}}$	116·0	83·50
Vanadium$^{\mathrm{V}}$	25·50	83·50

Cerium$^{\mathrm{III}}$ taken: 83·50 mg.

Determination of Iron$^{\mathrm{II}}$ and Cerium$^{\mathrm{III}}$ in Mixtures

When a mixture of iron$^{\mathrm{II}}$ and cerium$^{\mathrm{III}}$ is titrated with potassium dichromate in 12*M* phosphoric acid under a carbon dioxide atmosphere, two breaks are obtained, the first corresponding to the oxidation of iron$^{\mathrm{II}}$ to iron$^{\mathrm{III}}$ and the second corresponding to the oxidation of cerium$^{\mathrm{III}}$ to cerium$^{\mathrm{IV}}$. At the equivalence point for iron$^{\mathrm{II}}$ one has to wait for 6 min for the attainment of stable potential, the potential break being about 500 mV/0·04 ml of 0·2*N* potassium dichromate solution. Precautions must be taken to expel even traces of oxygen from all solutions and to prevent oxygen leaking into the titration vessel during the titration, iron$^{\mathrm{II}}$ being very much more susceptible to aerial oxidation in 12*M* phosphoric acid. If there is any doubt, the result for iron$^{\mathrm{II}}$ can be checked on a separate aliquot of the mixture by titration with potassium dichromate in 0·*SM* sulphuric acid either with a potentiometric or a visual end-point using diphenylamine sulphonic acid as indicator. The determination of cerium^{III} is not affected by the presence of oxygen, unlike that of iron^{II}.

Some typical results for the determination of iron^{II} and cerium^{III} in the same aliquot of solution are presented in Table IV. These show that the error of determination of iron^{II} is not greater than −0·5% and that for cerium^{III} ±0·3%. A typical curve showing the relation between potential and volume of oxidant is shown in Fig. 3. Because the potential break for the cerium part is not high, a plot of ΔE/ΔV *versus* V is recommended (Fig. 3 inset) for the cerium part of the titration. If it is required to determine iron^{III} and cerium^{IV} in admixture, the solution can be passed through a Jones reductor and the resulting iron^{II} and cerium^{III} assayed more conveniently by the above method than by any of the existing procedures.

TABLE IV.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND CERIUM^{III}

Iron,^{II} *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found
23·34	23·24	46·20	46·26
55·37	55·25	54·51	54·64
61·81	61·57	44·81	44·81
33·55	33·43	67·69	67·79
25·22	25·10	92·17	92·40
28·74	28·63	51·14	51·26

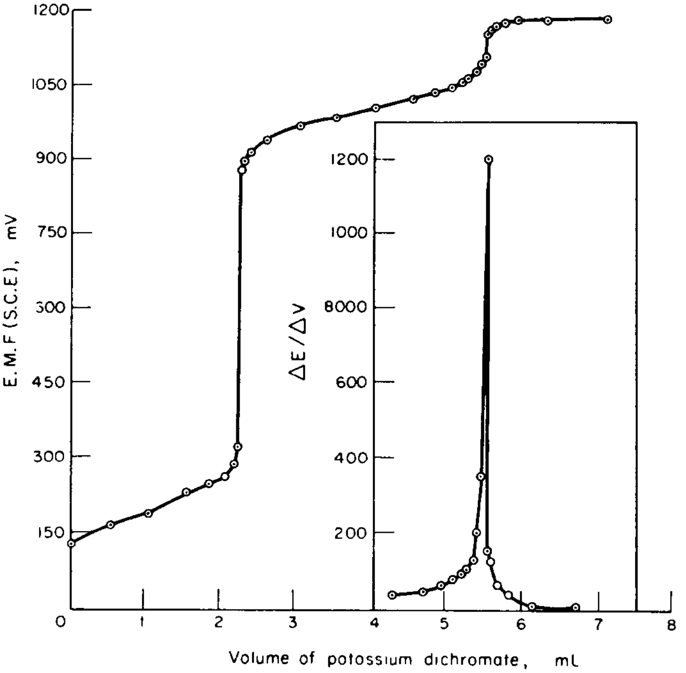

FIG. 3.—Potentiometric titration of a mixture of iron^{II} (25·10 mg) and cerium^{III} (92·40 mg) with potassium dichromate in 12*M* phosphoric acid.

Determination of Vanadium^{IV} and Cerium^{III} in Mixtures

We have observed that only one break is observed in the potential *versus* volume curve when a mixture of cerium^{III} and vanadium^{IV} is titrated potentiometrically with potassium dichromate in 12*M* phosphoric acid. This break corresponds to the simultaneous oxidation of cerium^{III} and vanadium^{IV} to cerium^{IV} and vanadium^{V}, respectively. When an excess of iron^{II} (sufficient to reduce vanadium^{IV} to vanadium^{III}), is added to the mixture of cerium^{III} and vanadium^{IV} and the titration carried out in 12*M* phosphoric acid in air with potassium dichromate, however, three different breaks are obtained. The first break corresponds to the oxidation of unreacted iron^{II} to iron^{III}, the second break to the oxidation of vanadium^{III} to vanadium^{IV} and the third break to the simultaneous oxidation of vanadium^{IV} and cerium^{III} to vanadium^{V} and cerium^{IV}, respectively. From these three titres the amounts of vanadium^{IV} and cerium^{III} present in the mixture can be calculated.

Procedure

An aliquot of the mixture of vanadium^{IV} and cerium^{III} is taken in a 150-ml Pyrex beaker and an excess of approximately 0·2*M* iron^{II} solution is added. The mixture is then treated with an amount of syrupy phosphoric acid such that its concentration is 12*M* at the third potential break in the titration. The mixture is stirred by means of an electromagnetic stirrer and titrated with potassium dichromate, using the potentiometric assembly already described. The potential obtained at the first break shows considerable drift and becomes stable only after 8 min. At the second and third breaks, however, the potential attains a fairly stable value in about 3 min. The potential jump at the first break amounts to about 120 mV, at the second to about 160 mV and at the third break to about 40 mV/0·04 ml of 0·2*N* potassium dichromate solution, when the total volume of the titration solution is about 50 ml.

Some typical results given in Table V show that the method gives quite precise results for both vanadium^{IV} and cerium^{III}, the error for vanadium^{IV} being ±0·3% and that for cerium^{III} ±0·38%.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF VANADIUM^{IV} AND CERIUM^{III}.

Vanadium^{IV}, *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found
20·38	20·38	45·95	45·95
25·60	25·60	47·82	47·93
26·93	26·89	38·12	38·12
14·88	14·90	57·75	57·95
11·16	11·19	43·89	44·00
31·24	31·32	28·87	28·76

Determination of Iron^{II}, Vanadium^{IV} and Cerium^{III} in Mixtures

From the foregoing it will be obvious that iron^{II}, vanadium^{IV} and cerium^{III} can be determined potentiometrically in the same solution with potassium dichromate in a strong phosphoric acid medium (12*M* at the third inflection point) at room temperature, provided an inert atmosphere is maintained during the titration and provided the amount of iron^{II} is greater than that of vanadium^{IV}. However, if the mixture contains insufficient iron,^{II} a known excess of iron^{II} may be added to the mixture before the titration is carried out. The first break in potential corresponds to the oxidation of iron^{II} to iron^{III}, the second break in potential to the oxidation of vanadium^{III} to vanadium^{IV} and the third break in potential to the simultaneous oxidation of vanadium^{IV} and cerium^{III}. From these three titres the amounts of iron^{II}, vanadium^{IV} and cerium^{III} present in the mixture can be calculated. Phosphoric acid should be added to the mixture only after it is freed from dissolved oxygen by passage of an inert gas and all necessary precautions are taken to prevent the leakage of air during titration. The potentiometric assembly and titration are the same as before.

A typical potentiometric titration curve is shown in Fig. 4. Because the third break in potential is not high, a plot of $\Delta E/\Delta v$ *versus* V is recommended (Fig. 4 inset) for the vanadium^{IV} and cerium^{III} part of the titration. Iron^{II} can be determined with an error not exceeding −0·5%, vanadium^{IV} ±0·3% and cerium^{III} ±0·38% (Table VI).

TABLE VI.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II}, VANADIUM^{IV} AND CERIUM^{III}.

Iron^{II}, *mg*		Vanadium^{IV}, *mg*		Cerium^{III}, *mg*	
Taken	Found	Taken	Found	Taken	Found
42·95	42·74	20·38	20·38	45·95	45·95
46·62	46·40	25·60	25·60	47·82	47·93
53·95	53·87	26·93	26·89	38·12	38·12
32·16	32·00	14·88	14·90	57·75	57·95
62·59	62·27	11·16	11·19	43·89	44·00
41·02	41·02	31·24	31·32	28·87	28·76

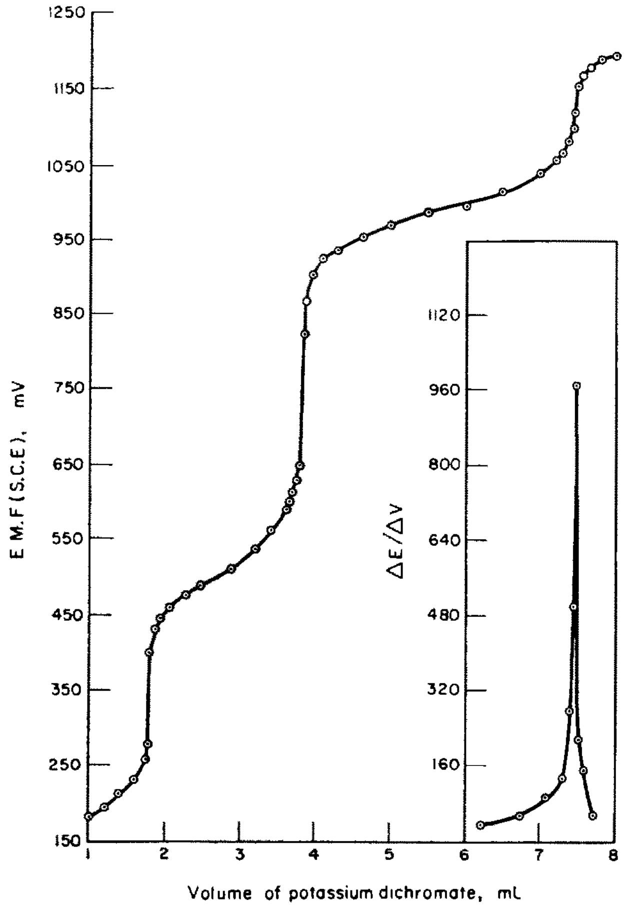

FIG. 4.—Potentiometric titration of a mixture of iron^{II} (42·74 mg), vanadium^{IV} (20·38 mg) and cerium^{III} (45·95 mg) with potassium dichromate in 12*M* phosphoric acid.

Analysis of Cerium in Minerals and Technical Products

Monazite (Travancore, India)

About 10 g of the monazite sand is digested in a porcelain evaporating basin with 25 ml of concentrated sulphuric acid on a sand bath until most of the sulphuric acid is evaporated. It is then cooled and the mass leached with 1*M* sulphuric acid, filtered and made up to 250 ml in a volumetric flask. Ten-ml portions are withdrawn and titrated by the procedure already described for the determination of cerium^{III}. None of the rare earths and thorium present in the sample interfered (Table VII).

Technical Cerium Carbonate (Indian Rare Earths Ltd., Alwaye, India)

About 6 g of sample is treated in a 600-ml Pyrex beaker with 25 ml of sulphuric acid (1 : 1). After the reaction is complete, make up to 250 ml in a volumetric flask. The solution contains mostly cerium^{III} and some cerium^{IV}. The cerium^{III} present is determined by treating 10 ml of the solution with 50 ml of syrupy phosphoric acid and titrating potentiometrically with potassium dichromate solution. The total cerium in the sample is determined by treating 10 ml of the solution with an excess of iron^{II}, then with phosphoric acid so that the over-all concentration is 12*M* at the end-point and titrating in air with potassium dichromate using a potentiometric end-point. The first break is neglected; the volume of titrant added between the first and second breaks corresponds to the cerium^{III}. Results are presented in Table VII.

Table VII

Sample	Cerium found by new method, %	Cerium found by method of Willard and Young[8], %
Monazite	24·12, 24·20, 24·12 Av. = 24·15	24·09, 24·20, 24·16 Av. = 24·15
Technical cerium carbonate	46·03, 46·15, 46·09 Av. = 46·09 (total cerium)	46·14, 46·10, 46·20 Av. = 46·15 (total cerium)
	39·96, 40·10, 39·96 Av. = 40·00 (cerium^{III} only)	

Acknowledgement—Two of us (P. K. R. and S. B. R.) thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Der Gebrauch von Kaliumdichromat zur potentiometrischen Bestimmung von Cer^{III} in 12 bis 13,5 M Phosphorsäure bei Zimmertemperatur wurde untersucht. Die Methode, die bei 30–120 mg Cer in 50 ml Titrationslösung auf ±0,35% genau ist wurde auf die Bestimmung von Cer in Monazitsand und in technischem Cercarbonat angewandt. Es wurden auch Methoden zur potentiometrischen Differenzbestimmung von Eisen^{II} und Cer^{III}, Vanadium^{II} und Cer^{III} sowie von Eisen^{II}, Vanadium^{II} und Cer^{III} in derselben Lösung entwickelt.

Résumé—On a étudié l'emploi du bichromate de potassium pour le dosage potentiométrique du cérium(III) en acide phosphorique 12–13,5 M à température ambiante. La méthode, qui est précise à ±0,35% pour 30–120 mg de cérium/50 ml de solution à doser, a été appliquée au dosage du cérium dans le sable de monazite et dans le carbonate de cérium technique. On a aussi élaboré des méthodes de dosage potentiométrique différentiel de fer(II) plus cérium(III), vanadium(IV) et cérium(III), et fer(II) plus vanadium(IV) plus cérium(III) dans le même solution.

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STUDIES IN THE RELATIONSHIP BETWEEN MOLECULAR STRUCTURE AND CHROMATOGRAPHIC BEHAVIOUR—I*

BEHAVIOUR OF SOME NITROPHENOLS CHROMATOGRAPHED ON ALUMINA-IMPREGNATED SURFACES

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Summary—A series of nuclear-substituted nitrophenols has been chromatographed on various papers (cellulose, alumina-impregnated cellulose and alumina-impregnated glass fibre), using a simple non-polar developing solvent (anhydrous cyclohexane). From a consideration of the R_f values obtained, it is suggested that these compounds are mainly chromatographed by an adsorption process. As a first approximation the mechanism postulated is one of intermolecular hydrogen bonding between the nitro, phenolic and/or halogen groups of the molecule and the hydroxyl groups considered to cover the impregnation. This bonding is modified by the intramolecular hydrogen bonding of the nuclear substituents. The significance of electronic and steric effects is considered. It is suggested that because of the ease of delocalisation of electronic effects in these nuclear systems, no group or atomic chromatographic parameters can be assigned.

In the general field of chromatographic separation of phenols several techniques have been used, *viz.*, gas chromatography,[1,2] electrophoresis,[3] paper chromatography,[4,5] column chromatography with silica gel as the adsorbent,[6,7] thin-layer chromatography[8,9] and paper impregnated with polyamides[10] and formamide.[11]

Work relating structure and chromatographic behaviour has been mainly concerned with alkylated phenols chromatographed on paper,[5] although Carlton and Bradbury[6] separated alkyl phenols on silica gel and showed that the adsorption of these phenols is considerably influenced by the size and position of the alkyl group.

Very little work has previously been done on the effect of nuclear substituents, except for that of Smith[7] who investigated a small number of phenols containing halogen, nitro, amino and oxygen groups. He suggested modes of adsorption, but these could not be adequately substantiated on the relativity haphazard choice of phenols used, although there is no doubt that hydrogen bonding between the silica gel and the phenol plays a dominant role in the chromatography of these compounds.

The polyamides and formamide used to impregnate some papers studied, also bind the phenols through hydrogen bonds and using both 10% and 15% nylon-impregnated papers, Martin and Husband[10] showed that the R_f values decreased with increase in the nylon percentage when the phenols were eluted with a cyclohexane/acetic acid mixture or with dilute aqueous acetic acid.

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Both Marcinkiewicz and coworkers[5] and Martin and Husband[10] have been able to show that the number of carbon atoms in the side chain of a single unknown alkyl phenol or the several homologues of a mixture of straight chain alkyl phenols may be determined from R_f or R_M values of related compounds, because each methylene group has a definite parameter in a particular chromatographic system. Marcinkiewicz and coworkers were able to calculate ΔR_M values for branched side chains and whilst it was noted that the change in R_M or R_f caused by nuclear substitution was less than that caused by side-chain substitution, very few phenols were studied to substantiate or extend this correlation.

The present authors have investigated 38 nitrophenols with various nuclear substituents, and have chromatographed them on papers impregnated with different amounts of alumina in a standard solvent system. The effect of these various substituents on the hydrogen bonding in the system has been studied and to simplify the over-all system and minimise hydrogen bonding between the phenols and the development solvent, anhydrous cyclohexane was chosen as the solvent.

EXPERIMENTAL

The surfaces used were:

(1) cellulose paper (Whatman No. 1),
(2) cellulose paper (Whatman No. 1) impregnated with 2% of alumina,
(3) cellulose paper (Whatman No. 1) impregnated with 7·5% of alumina,
(4) glass fibre "paper" (Whatman) impregnated with 7·5% of alumina,
(5) cellulose paper (Schleicher and Schull No. 288) impregnated with 25% of alumina.

Each type of paper was from one particular manufactured batch and was supplied impregnated by the manufacturer. All papers were stored under the same conditions.

In order to obtain accurate and reproducible results, all other necessary conditions were standardised as previously discussed.[18]

Pretreatment of papers

Because the papers are hygroscopic, to ensure a standard moisture content, all papers were dried at 110° for 15 min, allowed to cool in an evacuated desiccator for 20 min, then the vacuum slowly released with dried air.

Application of phenols and development conditions

All papers were run in the "machine direction" of the fibres. To ensure that the original solvent front was a known and fixed distance from the point of application of all spots, the position of the starting point of each substance was first marked on every paper used.

2·5 μl of a 0·25% w/v solution of the chromatographically pure phenol in n-butanol were applied as quickly as possible. To prevent dispersion of the solute, a current of warm air was blown onto the paper during application. The loaded papers were then placed at a fixed position over a solvent trough in a tank thermostatted at 25° ± 0·5°. The tank atmosphere had been previously saturated with solvent vapour by keeping approximately 100 ml of solvent in two small beakers in the tank, and hanging strips of filter paper, wet with the solvent, on the inside walls of the tank. The papers were allowed to stand for 10 min to enable saturation conditions to be regained, then a standard volume (200 ml) of the anhydrous cyclohexane was placed in the solvent trough and the phenols chromatographed by an ascending technique.

The length of run from each line of application to the solvent front was 22–23 cm. The time of each run varied, depending on the amount of impregnation and the type of support fibre. The greater the amount of impregnation, the longer the time required for the solvent to move the standard distance. On the glass fibre paper, which had a noticeably more open weave than the cellulose papers, the solvent moved fairly rapidly.

Solvent

Cyclohexane (MFC grade, Hopkin and Williams Ltd., U.K.) was dried over sodium wire, then fractionally distilled. The fraction boiling at 83–4° at 760 mm of pressure was collected. This treatment ensured that the solvent was anhydrous. The purity was further assessed by gas-liquid chromatography, using a Celite column and a dinonyl phthalate stationary phase, at a column temperature of 80°. A Pye Argon chromatograph was employed. Only one peak was obtained on the record chart, indicating only cyclohexane to be present.

Phenols

All crude phenols were purified by recrystallisation from a suitable solvent until the melting point agreed with literature values and only one spot appeared on any chromatographic run.

Detection of spots

Although the nitrophenols are coloured, irradiation with ultraviolet light sharply defined the spot perimeters, enabling accurate measurement to be made.

RESULTS

The results are shown in Table I. Each result is the average of at least three runs, the difference between the R_f values of any two runs being not more than ±0·01 of an R_f unit, except where stated. In these cases (marked * in all tables) the difference is not more than ±0·02 of an R_f unit.

On untreated cellulose paper it can be seen that the number of nitro groups in the phenol has a profound effect on the chromatographic behaviour.

Mononitro compounds having the nitro group in the 2-position and one or two other substituents all travelled to the solvent front, discrete spots, slightly elongated in a direction parallel to the solvent front, being formed. Mononitro compounds with the nitro group in the 3- or 4- position and with no more than one other substituent, gave discrete spots elongated in the direction of the solvent flow. Mononitro compounds with the nitro group in the 4-position and with two other substituents may be classified into:

(a) Those having 2,6-substituents with one electronegative group. These all gave discrete spots in the solvent front.

(b) Those having 2,6-substituents with two electronegative groups. These were badly streaked, giving a distinct main spot not separated from the streak. The R_f value of these main spots was fairly high in all cases.

For dinitro compounds with a substituent in the 2-position, the spot moved, but was badly streaked. The amount of movement depended on the electronegative character of the other substituents, the more electronegative substituents giving compounds with low R_f values. The 3,5-dinitro compound had a low R_f value. The spot was small and discrete. Only one trinitro compound was chromatographed. This had a very low R_f value.

On alumina-impregnated papers the R_f values rapidly decreased with increase in the amount of impregnation; with 25% of alumina only four phenols (2-nitrophenol, 2-nitro-4-methylphenol, 2-nitro-6-methylphenol and 2-nitro-4-tert-butyl-6-methylphenol) moved and the greatest R_f recorded (for the latter two) was only 0·06 R_f unit.

There was, in general, a slightly lower R_f value for phenols chromatographed on the alumina-impregnated glass fibre paper. Slight variations are thought to be caused by variations in the texture of the glass fibre paper, which was not of as uniform an appearance as the cellulose papers.

The area of the spots diminished with increase in the amount of impregnation. Compounds which gave streaks on the untreated cellulose paper gave discrete spots on the 2% alumina-impregnated papers.

TABLE I.—R_f VALUES ON THE VARIOUS SURFACES INVESTIGATED

Phenol	R_f				
	(1)	(2)	(3)	(4)	(5)
2-Nitro-	1·00	1·00	0·28	0·28	0·04*
3-Nitro-	0·13#	0·04	0·02	0·00	0·00
4-Nitro-	0·08#	0·04	0·02	0·00	0·00
2,4-Dinitro-	0·9[a]	0·08	0·04	0·00	0·00
2,6-Dinitro-	0·9[a]	0·04	0·00	0·00	0·00
3,5-Dinitro-	0·05[d]	0·02	0·00	0·00	0·00
2,4,6-Trinitro-	0·02[d]	0·00	0·00	0·00	0·00
2-Nitro-4-chloro-	1·00	0·82*	0·21	0·14	0·00
2-Nitro-4-bromo-	1·00	0·83*	0·24	0·17	0·00
2-Nitro-4-methyl-	1·00	0·92	0·51	0·50	0·03
2-Nitro-5-methyl-	1·00	1·00	0·43	0·29	0·00
2-Nitro-6-methyl-	1·00	1·00	0·30*	0·33	0·06
4-Nitro-2-chloro-	0·3[d]	0·08	0·04	0·00	0·00
4-Nitro-2-methyl-	0·3[d]	0·05	0·01	0·00	0·00
4-Nitro-2-sec-butyl-	0·3[d]	0·08	0·02	0·00	0·00
4-Nitro-2-cyclohexyl-	0·2	0·06	0·02	0·02	0·00
2-Nitro-4-chloro-6-bromo-	0·5	0·56	0·05	0·05	0·00
2-Nitro-4,6-dibromo-	1·00	0·60	0·06	0·04	0·00
2-Nitro-4,6-di-iodo-	1·00	0·79	0·08	0·00	0·00
2-Nitro-4-methyl-6-bromo-	1·00	0·89	0·10	00·6	0·00
2-Nitro-4-bromo-6-methyl-	1·00	0·96	0·25	0·23	0·00
2-Nitro-4-chloro-5-methyl-	1·00	0·94	0·27	0·14	0·00
2-Nitro-4-tert-butyl-6-methyl-	1·00	1·00	0·77	0·79	0·06
4-Nitro-2,6-dibromo-	0·75[c]	0·10	0·00	0·00	0·00
4-Nitro-2,6-di-iodo-	0·8[c]	0·11	0·02	0·02	0·00
4-Nitro-2-chloro-6-bromo-	0·75[c]	0·10	0·00	0·00	0·00
2,4-Dinitro-6-chloro-	0·7[a]	0·04	0·00	0·00	0·00
2,4-Dinitro-6-bromo-	0·8[a]	0·04	0·00	0·00	0·00
2,4-Dinitro-6-iodo-	1·00[a]	0·07	0·00	0·00	0·00
2,4-Dinitro-6-methyl-	1·00[a]	0·58	0·10	0·07	0·00
2,6-Dinitro-4-methyl-	1·00[b]	0·16	0·02	0·02	0·00
2,6-Dinitro-4-tert-butyl-	1·00[b]	0·20	0·04	0·02	0·00
2-Bromo-4-nitro-6-methyl-	1·00	0·50	0·12	0·06	0·00
2-Bromo-4-nitro-6-ethyl-	1·00	0·64	0·19	0·10	0·00
2-Bromo-4-nitro-6-isopropyl-	1·00	0·75	0·29	0·13	0·00
2-Bromo-4-nitro-6-sec-butyl-	1·00	0·72	0·33	0·05	0·00
2-Bromo-4-nitro-6-tert-butyl-	1·00	0·88	0·56	0·38	0·00
2-Bromo-4-nitro-6-cyclohexyl-	1·00	0·73	0·28	0·10	0·00

[a] Spots badly streaked, with streak from starting point to an area of greatest spot density at value indicated.

[b] Spot mainly reached solvent front, but also badly streaked.

[c] Spot badly streaked; all has moved from starting point.
Main spot density clearly visible with centre at value given.
There was no separation of spot and streak.

[d] Discrete spots of relatively small area, but base of spot on starting line.

DISCUSSION

It is thought that the mechanism of the chromatographic separation of the phenols studied is essentially a two-stage process:

(i) Dissolution of the phenol in the non-polar cyclohexane. This will be favoured by the formation of internal hydrogen bonds with the hydrogen of the phenolic group and an electronegative atom of a group in the 2-position, which will reduce the over-all polarity of the phenol.

(ii) Adsorption of the phenol onto the substrate by means of hydrogen bonds formed between electronegative groups or atoms of the phenol and hydrogen atoms of hydroxyl groups of the surface.

If either of these processes predominates then the spot will be discrete. If neither predominates, the spot will streak. If the polarity of the system is increased by increasing the polarity of the substrate, then the spots which previously streaked will appear as discrete spots.

Because a small increase in the amount of impregnation of the cellulose greatly decreases the R_f values of the phenols, it is suggested that in this fairly simple polar/non-polar system, the partition of the phenols between these two phases on impregnated papers, is mainly caused by the adsorption onto the alumina.

The glass fibre paper generally shows more adsorption of the phenols than does the cellulose paper with the same amount of alumina impregnation. It is, however, less uniform in texture than the cellulose paper and this may account for some non-parallelism of the results. The silica skeleton of the glass fibre paper may account for some of the increased adsorption.

For a detailed study of the mechanism of the chromatographic process it was decided to use mainly the results from the 2% and 7·5% impregnated papers (cellulose and glass fibre), but to consider for 'trend' purposes the over-all behaviour of the phenols compared.

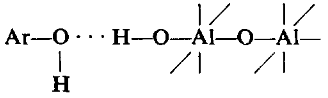
We think that the main mechanism of the process will be essentially adsorption chromatography, because it is not possible that the papers will have a sufficiently high water content to enable a surface layer of water to be obtained on the fibres. The mechanisms which are responsible for adsorption by solids from liquids are:

(i) non-polar van der Waal's forces,
(ii) formation of hydrogen bonds or operation of other non-ionic polar forces,
(iii) covalent bond formation,
(iv) ion exchange.

In any system more than one of these may operate, but we are concerned only with the forces listed under (ii); of these, hydrogen bond formation is the most important. There is little evidence that other non-ionic polar forces have much influence on adsorption processes from dilute solutions.[13] Some attempts have been made to demonstrate their operation but the evidence is equivocal.

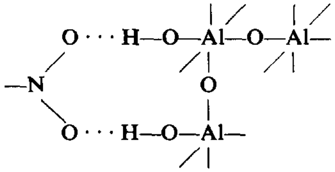
Hydrogen bonding in adsorption of phenols from solution by solids has been reasonably well established for various adsorbates, including alumina.[13] Bernal[14] has stated that many, if not all, so called oxide surfaces are effectively hydroxyl covered at ordinary temperatures, and that relatively stringent conditions of high temperatures and low pressures do not completely remove the hydroxyl groups. We consider that with the conditions used for this work, the impregnated papers must be impregnated with alumina which is wholly or substantially hydroxylated and this phenomenon will give rise to the following possible hydrogen bond systems with the phenolic group, the nitro group and probably some halogen groups:

(i)

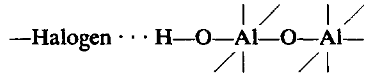


$Ar{-}O \cdots H{-}O{-}Al{-}O{-}Al{-}$

(ii)

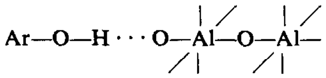


(iii)



$-Halogen \cdots H{-}O{-}Al{-}O{-}Al{-}$

(iv)



$Ar{-}O{-}H \cdots O{-}Al{-}O{-}Al{-}$

Graham and Stone[16] have shown that (iv) is unlikely and may be considered to make an insignificant contribution to the complete system.

Desorption takes place primarily as a breaking of these hydrogen bonds by the forces of dissolution of the non-polar part of the molecule in the non-polar phase (anhydrous cyclohexane) of the system.

Because each phenol has two possible points of attachment to the hydroxylated surface, it is likely that if the phenol can lie in the plane of the adsorbent surface, then the R_f value will be low because of the high probability of adsorption on the polar phase.

The factors which may affect the adsorption (and hence the R_f values) of these phenols are:

(i) Internal hydrogen bonding of the phenolic group with a nitro group, or a halogen group, in the 2-position, decreasing the probability of external hydrogen bonding by any of the groups. This internal hydrogen bonding will decrease the adsorption and hence increase the R_f value.

(ii) Electronic or steric effects altering the strength of this internal hydrogen bonding. The effect on the adsorption will depend upon the nature of the group.

(iii) Bulk effects—the effects of groups causing some of the non-polar part of the molecule to be held away from the polar surface and hence held in the non-polar phase. This effect will decrease the adsorption.

(iv) The bonding of the molecule to the polar layer by a nitro group or halogen group, not involved in internal hydrogen bonding with the phenolic group.

These factors may not always be acting alone and it is very unlikely that steric and electronic effects can be entirely separated.

Consider internal hydrogen bonding between the phenolic group and a nitro group in the 2-position. The results in Table II show that chelation of the 2-nitro group with the phenolic group greatly reduces the availability of either for bonding to the polar layer.

The effect of internal hydrogen bonding between the phenolic group and a halogen atom may be seen by a consideration of the results in Table III.

TABLE II

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-	1·00	0·28
3-Nitro-	0·04	0·02
4-Nitro-	0·04	0·02
2,4-Dinitro-	0·08	0·04

TABLE III

Phenol	$R_{f(2)}$	$R_{f(3)}$
4-Nitro-	0·04	0·02
2-Chloro-4-nitro-	0·08	0·04
2-Methyl-4-nitro-	0·05	0·01

The 2-chloro group is apparently involved in hydrogen bonding with the phenolic group, because when a methyl group replaces a chloro group there is a consequent decrease in the R_f value. A comparison of the results obtained from 4-nitrophenol and 2-methyl-4-nitrophenol indicates that a methyl group, substituted in the 2-position, has very little effect on the adsorption of the phenol.

The effect of substituents on the bonding between the phenolic group and the 2-nitro group may be seen by considering the series 2-nitro-4-(R)-phenol (see Table IV).

TABLE IV

R	$R_{f(2)}$	$R_{f(3)}$	$R_{f(4)}$
Hydrogen	1·00	0·28	0·28
Chloro	0·82*	0·21	0·14
Bromo	0·83*	0·24	0·17
Methyl	0·92	0·51	0·50

For comparison purposes, other than to show trends, R_f values above 0·80 are ignored. Hence, considering values obtained on 7·5% alumina-impregnated paper and ignoring (for simplification) any possible mutual attachment of the 4-group and the polar adsorbent, the results shown in Table IV may be explained as follows. In spite of the greater inductive effect of the 2-nitro group, the presence of a 4-halogeno substituent must slightly weaken the intramolecular hydrogen bonding, and hence slightly enhance the availability of the nitro and phenolic groups for intermolecular hydrogen bonding with the hydroxyl covered surface. The presence of a 4-methyl group will have an opposite effect.

The nitro group has a strong inductive effect, and whilst the variation in the results from the phenols shown in Table V may be considered to be partly because of the electronic effects of the substituents, it is considered that in this case the electronic effect of the methyl substituent is probably very small in comparison to the effect of the second nitro group placed in the nucleus and giving a further position of attachment to the polar surface.

A consideration of steric models indicates that substitution of a methyl group in the 6-position does not affect the ease of rotation of the phenolic group. When the phenol is attached to the polar adsorbent by the nitro and bromine groups, the

6-methyl group can lie in the plane of the organic molecule and hence the bulk effect, which may increase dissolution in the non-polar phase of the system, can be considered to be negligible.

TABLE V

Phenol	$R_{f(2)}$	$R_{f(3)}$	$R_{f(2)}$
2-Nitro-	1·00	0·28	0·28
2-Nitro-6-methyl-	1·00	0·30*	0·33
2,6-Dinitro-	0·04	0·00	0·00

Consideration of the results obtained with the series 2,4-dinitro-6-R-phenol (see Table VI), indicates that the same reasoning may be applied to slightly more complex molecules.

TABLE VI

R	$R_{f(2)}$	$R_{f(3)}$
Hydrogen	0·08	0·04
Chloro	0·04	0·00
Bromo	0·04	0·00
Iodo	0·07	0·00
Methyl	0·58	0·10

In a phenol having more than one such group, the effects may be additive, if similar, but if they are in opposition then the position of the group relative to the chelate system becomes important.

Consider groups having the same effect (Table VII).

TABLE VII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-4-chloro-	0·82*	0·21
2-Nitro-4-chloro-6-bromo-	0·56	0·05
2-Nitro-4-bromo-	0·83*	0·24
2-Nitro-4,6-dibromo-	0·60	0·06
2-Nitro-4,6-di-iodo-	0·79	0·08

Here the effect of two halogen atoms is apparent.

With 2 alkyl groups, as in Table VIII, the large increase in R_f values with the substitution of a 4-tert-butyl group is probably caused by the bulk effect of this group. Steric models indicate that a large proportion of this hydrocarbon group is held out of the plane of the polar adsorbent, and hence in the non-polar phase of the system.

TABLE VIII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-6-methyl-	1·00	0·30*
2-Nitro-4-tert-butyl-6-methyl-	1·00	0·77

With substituents having opposing electronic effects (Table IX), the relative positions of all groups must be considered. It is improbable that the 6-bromo group takes part in internal hydrogen bonding, so that the 2-nitro group will effectively capture the phenolic hydrogen. Although the position of the substituent plays a part in determining the total effect, each group will still give (qualitatively) the expected result.

TABLE IX

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-4-methyl-6-bromo-	0·89	0·10
2-Nitro-4-bromo-6-methyl-	0·96	0·25

The bulk effect may be both electronic and steric in origin. Whilst there is a difference in the atomic sizes of the halogen atoms, their electronic effects are very closely related to the size effect, and in nuclear-substituted phenols, because of the close proximity of the substituents to the nucleus, there is probably interaction between the nuclear π-electronic orbitals and the d-orbitals of the halogen. We suggest, therefore, that independent steric effects of the halogens cannot be considered. With alkyl substituents this electronic interaction with the benzene nucleus will be much reduced, and the steric effects are relatively more pronounced.

Consider the results (Table X) obtained from phenols held in the plane of the adsorbent by intermolecular hydrogen bonding between the hydroxyl of the polar surface and both the phenolic group and the 4-nitro group.

TABLE X

Phenol	$R_{f(2)}$	$R_{f(3)}$	$R_{f(4)}$
4-Nitro-	0·04	0·02	0·00
4-Nitro-2-methyl-	0·05	0·01	0·00
4-Nitro-2-sec-butyl-	0·08	0·02	0·00
4-Nitro-2-cyclohexyl-	0·06	0·02	0·02
4-Nitro-2-bromo-6-methyl-	0·50	0·12	0·06
4-Nitro-2-bromo-6-ethyl-	0·64	0·19	0·10
4-Nitro-2-bromo-6-isopropyl-	0·75	0·29	0·13
4-Nitro-2-bromo-6-sec-butyl-	0·72	0·33	0·05
4-Nitro-2-bromo-6-tert-butyl-	0·88	0·56	0·38
4-Nitro-2-bromo-6-cyclohexyl-	0·73	0·28	0·10

The adsorption and the amount of hydrocarbon held in the non-polar phase is generally reflected in the R_f values obtained. Models indicate that the tert-butyl group is by far the bulkiest group, but a study of models alone cannot give the complete explanation. In 2,6-dinitro-4-tert-butylphenol and 2,6-dinitro-4-methylphenol, models indicate that the tert-butylphenol should have a much greater solubility in the non-polar phase and hence a correspondingly higher R_f value than the methyl compound. The values in Table XI indicate that other effects must play a part, the R_f value of the methyl compound being higher than expected. It is suggested that the results may be explained by considering the inductive effect caused by the hyperconjugation of the 4-methyl group with the benzene nucleus. This will tend to increase the amount of internal hydrogen bonding between the 2-nitro group and the phenolic group and reduce the availability of either for intermolecular hydrogen bonding. The tert-butyl group cannot hyperconjugate with the nucleus and the main effect to be considered for this compound will be the bulk effect.

TABLE XI

Phenol	$R_{f(2)}$	$R_{f(3)}$
2,6-Dinitro-4-methyl-	0·16	0·02
2,6-Dinitro-4-tert-butyl-	0·20	0·04

The relatively large effect of an additional nitro group, the smaller effect of the halogens and the effect of variation in the polar nature of the substituent may be seen in Table XII.

TABLE XII

Phenol	$R_{f(2)}$	$R_{f(3)}$
2-Nitro-	1·00	0·28
2,4-Dinitro-	0·08	0·04
2,4,6-Trinitro-	0·00	0·00
2-Nitro-4-methyl-	0·92	0·51
2-Nitro-4-chloro-	0·82*	0·21
2-Nitro-4-bromo-	0·83*	0·24
4-Nitro-2-chloro-6-bromo-	0·10	0·00
4-Nitro-2,6-dibromo-	0·10	0·00
4-Nitro-2,6-di-iodo-	0·11	0·02
2,4-Dinitro-6-methyl-	0·58	0·10
2,4-Dinitro-6-chloro-	0·04	0·00
2,4-Dinitro-6-bromo-	0·04	0·00
2,4-Dinitro-6-iodo-	0·07	0·00

CONCLUSIONS

We think that, as a first approximation, the chromatographic behaviour of the nitrophenols is dependent on the amount of internal hydrogen bonding between the phenolic group, the nitro group and/or the halogens present, and the intermolecular hydrogen bonding between these groups and the hydroxyl groups of the substrate. This intermolecular bonding may be modified by the electronic effects of substituent groups.

Whilst it may be possible to calculate chromatographic parameters (ΔR_M values) for groups or atoms in simple alkylated phenols chromatographed in relatively non-polar systems, where the system is essentially polar such parameters are not readily attainable. We suggest that because of the ease of delocalisation of electronic effects in a benzene nucleus, substitution of any group into this electronic system affects the whole molecule. The effect on the intermolecular bonding group or groups depends not only on the nature of the substituent but also on its position relative to theses bonding groups. This has been shown for other systems—phenoxyacetic acids chromatographed in butanolic systems[15]—where the effects were not so apparent because of the insulating effect of the ether oxygen. We consider that it may be possible to deduce approximate values for compounds from a knowledge of their structure and the behaviour of related compounds and so to construct a chromatographic system of solvent and support to give effective separation of closely related compounds of known structure.

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Zusamenfassung—Eine Anzahl kernsubstituierter Nitrophenole wurde an verschiedenen Trägern (Cellulose, Aluminiumoxyd auf Cellulose und Aluminiumoxyd auf Glasfaser) mit einem einfachen unpolaren Lösungsmittel (wasserfreiem Cyclohexan) zur Entwicklung chromatographiert. An Hand einer Betrachtung der R_f-Werte wird wahrscheinlich gemacht, daß diese Verbindungen im wesentlichen durch einen Adsorptionsprozeß chromatographiert werden. In erster Näherung beruht der vorgeschlagene Mechanismus darauf, daß zwischen Nitro- und Phenolgruppen und/oder Halogenen im Molekül und den Hydroxylgruppen an der Oberfläche des Adsorbens Wasserstoffbrücken ausgebildet werden. Diese Bindung wird durch innermolekulare Wasserstoffbrücken beeinflußt. Die Bedeutung elektromerer und sterischer Effekte wird betrachtet. Wegen der leichten Delokalisation elektromerer Effekte in diesen aromatischen Kernen lassen sich keine Atom- oder Gruppenparameter für das chromatographische Verhalten angeben.

Résumé—On a chromatographié une série de nitrophénols substitués au noyau sur divers supports (cellulose, cellulose imprégnéé d'alumine et fibre de verre imprégnée d'alumine) en utilisant pour le développement un solvant simple non polaire (cyclohexane anhydre). A partir des considérations sur les valeurs de R_F obtenues, on suggère que ces composés sont principalement chromatographiés par un processus d'adsorption. En première approximation, on suppose un mécanisme de liaison hydrogène intermoléculaire entre le groupe nitro, le groupe phénolique et/ou les groupes halogènes de la molécule, et les groupes hydroxylés dont on considère recouverte l'imprégnation. Cette liaison est modifiée par la liaison hydrogène intramoléculaire des substituants nucléaires. Par suite de la facilité de délocalisation des effets électroniques dans ces systèmes nucléaires, il semble qu'on ne puisse attribuer de paramètres chromatographiques de groupes ou atomiques.

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PRECIPITATION OF ZINC 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—Zinc 8-hydroxyquinaldate can be precipitated quantitatively from homogeneous solution with 8-hydroxyquinaldine generated by the hydrolysis of 8-acetoxyquinaldine. Separation studies indicate the superiority of this method over the conventional procedure using 8-hydroxyquinaldine.

8-HYDROXYQUINALDINE was first reported in 1944 by Merritt and Walker[1] as an analytical reagent for the determination of several metallic ions; since then several investigators have used 8-hydroxyquinaldine in analytical applications. 8-Hydroxyquinaldine exhibits a significant difference in behaviour as compared with 8-hydroxyquinoline, *e.g.*, it will not precipitate aluminium whereas 8-hydroxyquinoline does. However, these two precipitants are similar enough chemically to have suggested the use of appropriate PFHS reagents[2,3] for the generation of 8-hydroxyquinaldine in much the same way that 8-hydroxyquinoline has been generated.[4–10] Thus, it was the purpose of this investigation to use 8-acetoxyquinaldine as a source of 8-hydroxyquinaldine in the precipitation of zinc from homogeneous solution.

EXPERIMENTAL

Reagents

Zinc: A stock solution of zinc^{II} was prepared by dissolving 2·0011 g of pure zinc sheet, 99·998%, in 20 ml of 1:1 hydrochloric acid and diluting with water to one litre. The concentration of this solution was confirmed by EDTA titration, using Eriochrome Black T indicator. Solutions containing 10·00, 25·01, and 50·03 mg of zinc per 50 ml were prepared by further dilution.

8-Acetoxyquinaldine: The reagent (Burdick and Jackson Laboratories, 1953 South Harvey St., Muskegon, Mich., U.S.A.) was stored in a desiccator, in a refrigerator, to minimise reagent hydrolysis. An acetone solution of the reagent was also kept in the refrigerator; 5 ml of this solution contained 1·5 × the theoretical quantity of reagent required to precipitate 50 mg of zinc.

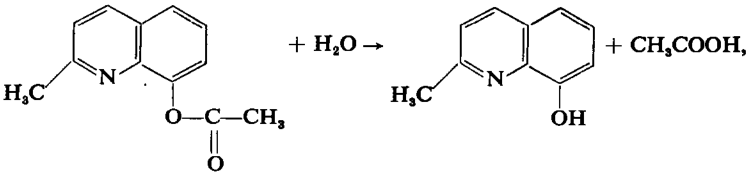
8-Hydroxyquinaldine: The stock solution was prepared by dissolving 5 g of the reagent (G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio, U.S.A.) in 12 g of glacial acetic acid, and diluting to 100 ml with distilled water. Such a solution, kept in a refrigerator, is stable for at least 2 months.

Diverse ions: Solutions of aluminium and magnesium were prepared by dissolving their sulphates in dilute sulphuric acid. The concentration of the aluminium^{III} solution was determined by precipitation with 8-hydroxyquinoline, and that of the magnesium^{II} solution by EDTA titration.

All other chemicals used were analytical-reagent grade.

Precipitation of zinc

In the reaction



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the rate of hydrolysis of 8-acetoxyquinaldine increases with either increasing pH or increasing temperature of the reaction mixture.

Preliminary investigations were undertaken to determine the optimum conditions of pH, concentration of reagents and temperature of reaction which would result in a precipitate with desirable physical characteristics (*cf.* Fig. 1). Precipitation was carried out in the pH range 4·5–7·0, with ammonium acetate as buffer. Below pH5·0, the precipitation of zinc^{II} was incomplete; anomalous results were obtained in the pH range 5·5–6·0; *i.e.*, some were low and some high. Desirable results were obtained at pH 6·5, with 1·5 × the theoretical quantity of 8-acetoxyquinaldine and the use of a temperature of 60–70°.

TABLE I.—DETERMINATION OF ZINC BY PRECIPITATION AS THE 8-HYDROXYQUINALDATE

Method of precipitation	PFHS	PFHS	PFHS	PFHS	PFHS	Conventional	PFHS	Conventional	PFHS
Reagent used[a]	8-AQD	8-AQD	8-AQD	8-AQD	8-AQD	8-HQD	8-AQD	8-HQD	8-AQ
Zn taken, *mg*	1·00	5·00	10·00	25·01	50·03	50·03	100·06	100·06	50·03
Zn found, *mg*	−0·07	+0·03	−0·05	+0·03	+0·08	−0·26	−0·27	+0·54	−0·03
Difference, *mg*	−0·04	−0·02	−0·05	−0·01	+0·11	−0·33	−0·17	+0·58	0·00
	−0·06	+0·02	−0·05	−0·02	−0·03	−0·37	−0·25	+0·58	−0·03
					+0·03[b]				
					−0·13[b]				
					−0·11[b]				
Zn found in fillrate,[c] *mg*	<0·01	<0·01	<0·01	<0·01	<0·01	~0·05	<0·01	<0·01	<0·01

[a] 8-AQD = 8-acetoxyquinaldine; 8-HQD = 8-hydroxyquinaldine; 8-AQ = 8-acetoxyquinoline.

[b] 10 ml of 20% ammonium tartrate added to the solution before adding 8-AQD.

[c] Determined by photometric titration with 0·001*M* EDTA solution after treating the filtrate with nitric-perchloric acid.

Recommended procedure

Dilute the solution, containing 10 to 50 mg of zinc, to about 175 ml, add 10 ml of 20% ammonium acetate solution, and adjust the pH of the solution to 6·5 with either 1*M* aqueous ammonia or 1*M* acetic acid. Add slowly, with stirring, 5 ml of an acetone solution containing 0·462 g of 8-acetoxyquinaldine, and dilute to 200 ml with water. Heat the solution for 2 hr at 70°, and filter hot, using about 100 ml of hot water (*ca.* 80°) to transfer the precipitate to a medium-frit glass filter. Dry the precipitate at 130° to constant weight (~6 hr), and weigh as $Zn(C_{10}H_8ON)_2$; the gravimetric factor for zinc is 0·17125. (Note. When aluminium is present, add 10 ml of 20% ammonium tartrate solution before adjusting the pH.)

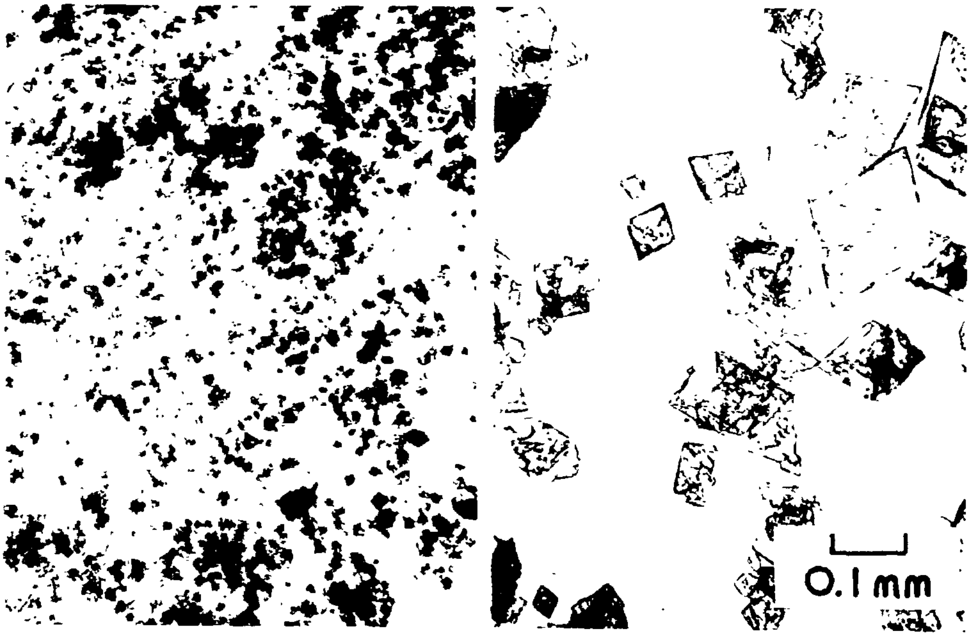
Drying of zinc 8-hydroxyquinaldate

The precipitate contains 1 molecule of water, which is removed by heating at 130°. However, it requires 5–6 hr to obtain constant weight. Attempts to reduce the drying time, *e.g.*, by drying the precipitate for 2 hr at 130° and then for 30 min periods at either 250°, 200° or 160°, were unsuccessful. Thermogravimetric study

TABLE II.—DETERMINATION OF ZINC BY THE RECOMMENDED PROCEDURE

8-AQD used[a]	1·5×	3×	7·5×	15×	75×
Zn taken, *mg*	50·03	25·01	10·00	5·00	1·00
Zn found, *mg*	−0·08	−0·03	−0·05	−0·15	−0·09
Difference, *mg*	−0·12	−0·05	−0·05	−0·15	−0·09
	+0·03	−0·02	−0·07	−0·17	−0·03

[a] 0·462 g of reagent used in all precipitation experiments; in each case, this corresponds to the theoretical quantity of reagent required for the precipitation of the zinc multiplied by a factor which is the number preceding the ×.



(a)

(b)

Fig. 1.—Photomicrographs of zinc 8-hydroxyquinaldate (both photomicrographs are at same magnification):

(a) left panel: conventional precipitation.

(b) right panel: PFHS.

TABLE III.—DETERMINATION OF ZINC IN THE PRESENCE OF DIVERSE IONS

Method of Precipitation	PFHS	Con-ventional	PFHS	PFHS	PFHS	PFHS	Con-ventional	PFHS	PFHS	Con-ventional	PFHS
Zn taken, *mg*	50·03	50·03	50·03	25·01	50·03	50·03	50·03	50·03	50·03	50·03	50·03
Al added, *mg*	50	50	100	—	—	—	—	—	50	50	100
Mg added, *mg*	—	—	—	10	25	50	50	100	100	50	100
20% Ammonium tartrate added, *ml*	10	10	20	—	—	—	—	—	10	10	10
Zn found, *mg*,	0·06	+0·20	−0·14[c]	−0·03	+0·52[c]	+0·66[c]	+1·10[c]	+0·76[c]	+0·64[c]	+0·78	+0·61
Difference, *mg*	−0·08[c]	+0·13	−0·13	+0·02	+0·76 +0·25 −0·04[a] −0·11[a]	+0·61	+1·15	+0·73	+0·25	+0·80	+0·23
Diverse metal found[b] in precipitate, *mg*	Al none		Al <0·01		Mg 0·2	Mg 1·4	Mg 1·2	Mg <0·2	Al <0·02 Mg 1·2		

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[a] 10 ml of 20% ammonium tartrate added.

[b] Diverse metals determined or detected in the precipitate as follows: (1) Al with Alizarin S;[11] (2) Mg fluorometrically with *o*,*o*′-dihydroxyazobenzene[12] (organic material in precipitate decomposed in oxygen flask and magnesium and aluminium then separated from zinc by ion-exchange with IRA-400[13,14]).

[c] Diverse metal determined in this precipitate.

also indicated that 130° was an appropriate drying temperature for zinc 8-hydroxyquinaldate, and that it appeared to be somewhat critical. Alternatively, the determination of zinc can be concluded by titrimetric analysis.[1]

RESULTS AND DISCUSSION

Table I shows that satisfactory results could be obtained with from 1 to 100 mg of zinc using the procedure given, but modified in that 1·5 × the theoretical amount of 8-acetoxyquinaldine required was used for each precipitation. Results obtained by conventional precipitation are also shown for comparison.

As shown in Table II, satisfactory results were also obtained in the range 1–50 mg of zinc with a constant amount of 8-acetoxyquinaldine, *i.e.*, 0·462 g, which corresponds to the 1·5 × quantity for 50 mg of zinc. Because of the slightly lower results obtained with the smaller amounts of zinc, the recommended procedure is limited to 10–50 mg of zinc.

The results of the separation of zinc from aluminium and magnesium are shown in Table III. Aluminium did not coprecipitate; however, high results were obtained in the presence of magnesium. In general, more satisfactory results were obtained by PFHS than by conventional precipitation.

Acknowledgment—The authors wish to acknowledge the support in part of the United States Atomic Energy Commission under Contract AT(11-1)-582.

Zusammenfassung—Zink-8-hydroxychinaldat kann quantitativ aus homogener Lösung mit durch Hydrolyse von 8-Acetoxychinaldin erzeugtem 8-Hydroxychinaldin gefällt werden. Abtrennungsversuche zeigen die Überlegenheit dieser Methode gegenüber der gebräuchlichen mit 8-Hydroxychinaldin.

Résumé—Le 8-hydroxyquinaldinate de zinc peut être précipité quantitativement d'une solution homogène au moyen de 8-hydroxyquinaldine générée par l'hydrolyse de 8-acétoxyquinaldine. Des études de séparation montrent la supériorité de cette méthode sur le procédé habituel utilisant la 8-hydroxyquinaldine.

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PRECIPITATION OF METAL 8-HYDROXYQUINOLATES FROM HOMOGENEOUS SOLUTION—VII*

INDIUM AND GALLIUM

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Summary—The precipitation from homogeneous solution of indium and gallium, using 8-acetoxyquinoline, has been investigated. It has been established that the method cannot be recommended for the determination of either metal, although under certain rigorously controlled conditions indium 8-hydroxyquinolate precipitates quantitatively and stoichiometrically. The conventional precipitation of indium 8-hydroxyquinolate has also been found to give erroneous analytical results.

INTRODUCTION

FROM an investigation of the precipitation from homogeneous solution of indium, using 8-acetoxyquinoline, it became evident that the experimental conditions need to be rigorously controlled in order to obtain, simultaneously, a precipitate of stoichiometric composition, and complete separation of the indium. A subsequent investigation of the conventional method[1] of precipitating indium with 8-hydroxyquinoline also indicated the difficulty of obtaining quantitative precipitation. It became the purpose of this investigation, therefore, to evaluate critically the analytical aspects of the precipitation of indium 8-hydroxyquinolate. The similar precipitation of gallium was also the subject of a brief investigation.

EXPERIMENTAL

Reagents

Indium solution: Indium metal of high purity (Indium Corp. of America, Utica, N.Y.) was dissolved in dilute hydrochloric acid, and the solution was diluted to the required volume with distilled water.

Gallium solution: High purity gallium (99·99%, Fisher Scientific Co.) was dissolved in a 1:2 mixture of 70% perchloric acid and 95% sulphuric acid, and the solution was diluted to the required volume with distilled water.

8-Acetoxyquinoline: For indium, PF/HS grade 8-acetoxyquinoline (Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich.) was dissolved in acetone; 5 ml of this solution contained 4 times the stoichiometric quantity of reagent needed to precipitate 50 mg of indium.

For gallium, 1·0 g of 8-acetoxyquinoline was dissolved in 1:1 acetic acid (25 ml); this solution contained 2·5 times the stoichiometric quantity of reagent required to precipitate 50 mg of gallium.

All other chemicals used were reagent-grade.

RESULTS

Conventional precipitation of indium with 8-hydroxyquinoline

Geilmann and Wrigge[1] recommended a sodium acetate-acetic acid medium for the precipitation of indium with 8-hydroxyquinoline. The pH of the medium was about 4·5. Table I shows typical results obtained when this procedure was used. Low

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* Part VI: See *Talanta*, 1963, **10**, 111.

TABLE I.—PRECIPITATION OF INDIUM BY THE METHOD OF GEILMANN AND WRIGGE[1]

Indium taken, *mg*	Indium in precipitate, *mg* (difference[a])	Indium in filtrate, *mg*[b]
24·31	−0·21	>0·4
	−0·35	>0·4
	−0·20	0·2
50·62	−0·48	1·1
	−0·47	0·4
76·52	−0·25	>0·4
	−0·08	>0·4
	−0·37	>0·4

[a] Difference = found − taken.

[b] Determined polarographically in an aqueous perchloric acid-potassium chloride medium.[8]

gravimetric results were also obtained in the mineral acid medium recommended by Geilmann and Wrigge.[1]

Conventional precipitation of gallium with 8-*hydroxyquinoline*

The method of Geilmann and Wrigge[1] and that of Moeller and Cohen[3] gave slightly low recoveries of gallium.

PFHS of indium with 8-*acetoxyquinoline*

Experiments were carried out to study the effects of (*a*) different wash solutions, (*b*) pH in the range 2·0–5·0, (*c*) various sodium acetate-acetic acid and ammonium acetate-acetic acid buffers, (*d*) absence of buffers, and (*e*) quantity of 8-acetoxyquinoline, on the PFHS of indium 8-hydroxyquinolate. Some results are shown in Table II. It became evident that indium could be precipitated quantitatively, as a stoichiometric 8-hydroxyquinolate, under closely controlled conditions.

Procedure: The starting solution should contain 15–75 mg of indium as the chloride. To this are added 2·0 ml of glacial acetic acid and 2·0 g of sodium acetate, and the resulting solution is diluted to 180 ml. The pH is adjusted to 4·5 with either hydrochloric acid or aqueous ammonia, and a two-fold excess* of 8-acetoxyquinoline is added. The solution is heated at 80° for 2 hr, and is allowed to cool to room temperature before filtering. The solution is filtered through a medium-porosity filtering crucible, and the precipitate is washed with distilled water, dried to constant weight at 130°, and weighed as $In(C_9H_6NO)_3$.

Table III shows the results obtained using this procedure. Also shown are the results obtained with smaller quantities of indium.

PFHS of gallium with 8-*acetoxyquinoline*

The procedure was similar to that used for the corresponding determination of aluminium,[4] except that the pH was adjusted to 3·7, 3·9 or 4·1. The precipitates were dried to constant weight at 112 ± 2° (*ca.* 2 hr) and weighed as $Ga(C_9H_6NO)_3$. Table IV shows the results obtained using this procedure.

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* A two-fold excess indicates 2 times the stoichiometric amount.

TABLE II.—PRECIPITATION OF INDIUM WITH 8-ACETOXYQUINOLINE: INITIAL RESULTS

Number	1	2	3	4	5	6	7	8	9	10	11	12
Indium taken, *mg*	24·40	24·40	24·31	48·62	72·93	73·20	73·20	76·57	51·04	25·52	25·48	25·48
Indium in precipitate, *mg* (difference[a])	+0·03, +0·09	−0·05, +0·04	−0·07, −0·11	−0·70, −0·75	−1·37, −1·25	−0·08, −0·05	+0·02, 0·00	+0·25, +0·71	+0·09, +0·09	+0·37, +0·39	−0·04, −0·06	+0·05, +0·05
Indium in filtrate, *mg*	0·36, 0·21	0·17, 0·22	0·22, 0·20	0·06, 0·07	0·08, 0·03	0·18, 0·18	0·08, 0·13	0·05, 0·09	<0·1, <0·1	0·10, 0·10	0·16, 0·18	0·15, 0·22
Conditions of precipitation	b,e,m	b,d,m	b,h,m	b,h,m	b,h,m	b,f,i,m	c,f,i,m	c,f,j,m	c,f,j,k	c,f,j,k	c,g,j,k	c,g,j,l

[a] Difference = found − taken
[b] pH = 4·0
[c] pH = 4·5
[d] 0·5 ml of glacial acetic acid
[e] 1·0 ml of glacial acetic acid
[f] 1·5 ml of glacial acetic acid
[g] 2·0 ml of glacial acetic acid
[h] 0·6 g of sodium acetate
[i] 1·2 g of sodium acetate
[j] 2·0 g of sodium acetate
[k] 0·5 g of 8-acetoxyquinoline
[l] 0·75 g of 8-acetoxyquinoline
[m] 1·0 g of 8-acetoxyquinoline

TABLE III.—PFHS OF INDIUM 8-HYDROXYQUINOLATE USING A TWO-FOLD EXCESS OF 8-ACETOXYQUINOLINE

Number	1			2			3		
Indium taken, *mg*	75·93			50·62			25·31		
Indium in precipitate, *mg* (difference[a])	+0·01	+0·01	−0·05	+0·10	+0·14	+0·05	+0·07	+0·05	+0·03
Indium in filtrate, *mg*	0·06	0·06	0·06	0·06	0·04	0·12	0·04	0·05	0·03

Number	4			5			6		
Indium taken, *mg*	15·29			10·19			5·10		
Indium in precipitate, *mg* (difference[a])	+0·09	+0·11	+0·13	−0·31	−0·29	−0·19	−0·44	−0·21	−0·90
Indium in filtrate, *mg*	0·03	0·03	0·03	0·56	0·55	0·27	0·60	0·32	0·90

[a] Difference = found − taken

Table IV.—PFHS of gallium with 8-acetoxyquinoline

Gallium taken, *mg*	4·55				11·37				22·74	
Gallium in precipitate, *mg* (difference[a,b])	−0·05	−0·20	−0·15	−0·12	−0·01	−0·06	−0·08	−0·17	−0·08	−0·09
Gallium in filtrate, *mg*[c]	0·16	0·16	0·22	0·28	0·22	0·26	0·10	0·16	0·18	0·17
Initial pH	3·9		3·7		3·9		4·1		3·9	

[a] Difference = found − taken

[b] A loss of gallium was also experienced in numerous other experiments

[c] Determined spectrophotometrically after extraction of its 8-hydroxyquinolate into chloroform

DISCUSSION

Indium

The results shown in Table I clearly indicate a large solubility loss when indium is precipitated by the direct addition of 8-hydroxyquinoline. Moreover, the results shown in Table II demonstrate the difficulty of obtaining a quantitative precipitate of stoichiometric composition when PFHS is used.

Further experiments using the procedure recommended in this paper established that it was possible to precipitate the indium quantitatively as $In(C_9H_6NO)_3$ (*cf.* Table III). However, the precipitation conditions require rigorous control, *e.g.*, a two-fold excess of 8-acetoxyquinoline, which, of course, would be impractical in analysis. Furthermore, the results obtained by this procedure were satisfactory only for 15–75 mg of indium; as can be seen in Table III, unsatisfactory results were obtained in the 5–10 mg range.

To ascertain whether the non-stoichiometric composition of the precipitate resulted from the formation of a small amount of indium hydroxide, two precipitates, prepared similarly to No. 5 of Table II and No. 1 of Table III, were examined in the infrared spectral region in KBr discs carefully prepared to exclude moisture. Conclusions from the results about the presence of hydroxide were inconclusive.

It is apparent that indium can be quantitatively precipitated from homogeneous solution as a stoichiometric compound using 8-acetoxyquinoline; the experimental conditions of the method are, however, impractical for analysis, although the process is useful for preparative purposes. The conventional method of precipitating indium 8-hydroxyquinolate, as described in the existing literature, gives erroneous analytical results, and therefore it is not recommended for use. It is worthy of mention that precipitates obtained by PFHS and by direct mixing of reagents do not differ in physical appearance.

Gallium

The precipitation of gallium was also unsatisfactory. Although Hollingshead[5] suggested that the low recoveries of gallium obtained by conventional precipitation[1,3] may have resulted from the sublimation of the precipitate at 120°, the present investigation does not indicate this to be a factor. At pH 3·7 and 3·9, although apparent recoveries are slightly low, the amount of gallium in the filtrates indicates that the precipitates must contain some coprecipitated reagent to make up their weight. At pH 4·1, when the weight deficiency of the precipitate agrees with the amount of gallium found in the filtrate, the precipitate weight is low in gallium by *ca.* 0·12 mg. The low recoveries, therefore, result from the incomplete precipitation of gallium. In consequence, neither the conventional nor the PFHS methods for gallium can be recommended for use.

Acknowledgment—The authors thank N. Haberman and S. R. Smith for preliminary work on the PFHS of indium, D. B. de Oliveira for initial studies on the PFHS of gallium, and R. J. Magee for the interpretation of the infrared spectra and for his interest generally. They also acknowledge the partial assistance of the United States Atomic Energy Commision under Contract AT(II-I)-582.

Zusammenfassung—Die Fällung von Indium und Gallium aus homogener Lösung mit 8-Acetoxychinolin wurde untersucht. Es wurde festgestellt, daß die Methode für beide Metalle nicht zu empfehlen ist, obwohl unter bestimmten, scharf kontrollierten Bedingungen Indium-8-hydroxychinolat quantitativ und stöchiometrisch ausfällt. Auch die konventionelle Fällung von Indium-8-hydroxychinolat gibt falsche Analysenergebnisse.

Résumé—On a étudié la précipitation de l'indium et du gallium en solution homogène au moyen de 8-acétoxyquinoline. On a établi que la méthode ne peut être recommandée pour le dosage de ces deux métaux, bien que, dans certaines conditions rigoureusement contrôlées, le 8-hydroxyquinolinate d'indium précipite quantitativement et stoechiométriquement. On a trouvé que la précipitation ordinaire du 8-hydroxyquinolinate d'indium donne aussi des résultats analytiques erronés.

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PRECIPITATION OF INDIUM 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—The precipitation of indium from homogeneous solution as the 8-hydroxyquinaldate, with 8-acetoxyquinaldine as a source reagent, provides a quantitative procedure, and a satisfactory separation from lead, calcium and magnesium.

INTRODUCTION

IN a previous investigation, Jones *et al.*[1] concluded that 8-hydroxyquinoline was not a satisfactory reagent for the determination of indium. The present investigation was therefore undertaken to study the precipitation of indium from homogeneous solution (PFHS) with 8-hydroxyquinaldine, using 8-acetoxyquinaldine[2,3] as the parent reagent.

EXPERIMENTAL

Reagents

Indium: Indium metal of high purity (Indium Corp. of America, Utica, New York) was dissolved in dilute hydrochloric acid.

8-*Acetoxyquinaldine:* PF/HS grade 8-acetoxyquinaldine (Burdick and Jackson Laboratories, 1953 S. Harvey St., Muskegon, Mich.).

All other chemicals used were reagent-grade.

Procedure

To 25–50 mg of a nearly neutral solution of indium, contained in a 250-ml beaker, add 2·0 g of sodium acetate; dilute to 180 ml and adjust the pH to 4·5 with filtered aqueous ammonia (1:1). Add 10 ml of an acetone solution containing 1·0 g of 8-acetoxyquinaldine (5 times the stoichiometric quantity of reagent needed to precipitate 37·5 mg of indium). Heat the solution at 80° for 2 hr, allow it to cool to room temperature, and filter through a medium-porosity filter, transferring and washing the precipitate with water at room temperature. Dry to constant weight at 130°, and weigh as $In(C_{10}H_8NO)_3$; the gravimetric factor for indium is 0·1948.

RESULTS AND DISCUSSION

Initial investigations showed that if 1·0 g of 8-acetoxyquinaldine were used, 25–75 mg of indium could be quantitatively precipitated in the pH range 4·3–4·7; when a smaller quantity of reagent, *i.e.*, 0·33 g, was used to precipitate 25 mg of indium, the filtrate was found consistently to contain about 0·3 mg of indium. Table I shows that gravimetric results, correct to within about 0·5%, can be obtained with 25–75 mg of indium. Coprecipitation of reagent probably accounts for the slightly high results. With 5- to 10-mg samples of indium there were significant losses of indium to the filtrates. Thermogravimetric analysis of the precipitate showed 130° to be a satisfactory drying temperature. Table I also shows that indium can be satisfactorily separated from lead, calcium and magnesium, but not from aluminium; when tartaric acid was used to complex aluminium, it apparently also complexed indium, thus leading to low results.

A brief investigation of the PFHS of gallium indicated that only after about half of the gallium can be precipitated as the 8-hydroxyquinaldate by the method described.[2]

Table I.—Precipitation of indium 8-hydroxyquinaldate from homogeneous solution

Indium taken, *mg*	Diverse element taken, *mg*	Indium found, *mg* (difference[a])	Indium in filtrate,[b] *mg*
75·93	None	0·37, 0·25, 0·32	0·06, 0·06, 0·06
50·62	None	0·16, 0·14, 0·26	0·07, 0·07, 0·05
25·31	None	0·13, 0·15, 0·20	0·05, 0·08, 0·05
10·12	None	0·16, 0·10	0·14, 0·12
5·06	None	−0·08, −0·06, −0·02	0·14, 0·18, 0·16
25·48	Ca-100	0·19, 0·15, 0·21	c
	Pb-25	0·23, 0·17, 0·19	c
	Mg-25	0·23, 0·35, 0·39	c
	Al-25	5·0, 2·1, 5·3	c

[a] Difference = found − taken.

[b] Determined polarographically in an aqueous perchloric acid-potassium chloride medium.[4]

[c] Not determined.

Zusammenfassung—Die Fällung von Indium aus homogener Lösung als 8-Hydroxychinaldat mit 8-Acetoxychinaldin zur Bildung des Reagens stellt brauchbares quantitatives Verfahren dar; die Trennung von Blei, Calcium, Magnesium und Aluminium ist gut.

Résumé—La précipitation de l'indium en solution homogène, à l'état de 8-hydroxyquinaldate, avec la 8-acétoxyquinaldine comme source de réactif, est une méthode quantitative satisfaisante. L' indium est bien séparé de plomb, calcium, magnésium et aluminium.

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POTENTIOMETRIC DETERMINATION OF VANADIUM AS SILVER ORTHOVANADATE

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Summary—A rapid and accurate electrometric method for the determination of vanadium as silver orthovanadate has been investigated. It consists in titrating sodium orthovanadate solution potentiometrically at pH 11·5 against standard $AgNO_3$, using a silver indicator electrode in conjunction with S.C.E., connected by a KNO_3 bridge. Either of the reagents may be used as titrant. A marked change in e.m.f. is observed at the end-point. corresponding to the precipitation of Ag_3VO_4 in the pH range 8–9. The curves have a regular form; a pronounced maximum in dE/dV occurs at the end-point; and the accuracy and reproducibility of the electrometric results has been found to be excellent even at low concentrations ($1 \times 10^{-3}M$) of the reactants. Potentiometric titration offers a simple, rapid and accurate method for the determination of vanadium as silver orthovanadate.

BROWNING and Palmer[1] and Moser and Brandl[2] have reported an accurate gravimetric method for determining vanadium as silver vanadate. No reference has been found in the literature regarding the determination of vanadium by electrometric methods other than polarographic ones. The present investigation involves a potentiometric study of the reaction between silver nitrate and sodium orthovanadate, and has been undertaken to investigate the process as a possible analytical method for the determination of vanadium.

EXPERIMENTAL

Merck guaranteed extrapure reagents, $AgNO_3$, V_2O_5 and NaOH, were used and their solutions prepared in air-free conductivity water.

Standard solutions of sodium orthovanadate were prepared by dissolving calculated amounts of V_2O_5 in a boiling solution of NaOH of the required strength.

The pH of the sodium orthovanadate solution thus obtained was measured by means of a glass electrode and found to be about 11·5. Different concentrations of $AgNO_3$ and Na_3VO_4 were taken and a series of potentiometric titrations was carried out both by the direct and the inverse method, *i.e.*, $AgNO_3$ solution being added from a microburette to the Na_3VO_4 solution in the electrode cell, and *vice versa*. Titrations were also performed in the presence of varying concentrations of ethanol. For precise and steady measurements of e.m.f., a platinum gauze electrode was used. This was electrolytically coated with silver at a low current density (a current strength of the order of 2–10 mA) in a bath of pure silver cyanide. It was dipped in the titre solution and used as an indicator electrode in conjunction with a standard calomel electrode. The connection between the calomel half cell and the titration vessel was made with saturated KNO_3 solution. The electrode cell was immersed in an electrically maintained thermostat at 40 ± 0·1°. The e.m.f. was measured on a Cambridge (null-deflection type) pH meter. The titration solution was continuously stirred by an electrically-driven stirrer. Curves were plotted of the E (obs.) *vs.* the volume of the titrant added in ml, and from the sharp jump in potential indicated by the titration curves the equivalence point was obtained. This was further checked by calculating the maximum value of dE/dV in each case. Twenty ml of the reagent were taken in the cell each time. (See Table I.) Two typical sets of curves are illustrated (Figs. 1 and 2).

DISCUSSION

An examination of the results reveals that the reaction between $AgNO_3$ and Na_3VO_4 can be successfully followed potentiometrically using silver as an indicator

TABLE I.—SUMMARY OF THE RESULTS OF POTENTIOMETRIC TITRATIONS

Concentration of solutions		Point of equivalence: $3Na_2O.V_2O_5$ or $AgNO_3$ required for the formation of Ag_3VO_4, *ml*	
$AgNO_3$	$3Na_2O.V_2O_5$	Calculated	Observed from max. dE/dV.
		Direct titrations, Fig. 1	
M/10	*M*/250	4·80	4·80
M/15	*M*/500	3·60	3·60
M/20	*M*/750	3·18	3·20
M/50	*M*/1000	6·0	5·95
		Reverse titrations, Fig. 2	
M/50	*M*/30	2·00	2·00
M/100	*M*/80	2·66	2·70
M/250	*M*/250	3·33	3·30
M/750	*M*/500	2·22	2·20

TABLE II.—POTENTIOMETRIC DETERMINATION OF VANADIUM

V^{5-} present, *mg*	V^{5-} found, *mg*	Error, *mg*
8·1520	8·1520	0·0
2·7160	2·7330	0·0170
1·3573	1·3450	0·0123
0·4524	0·4483	0·0041

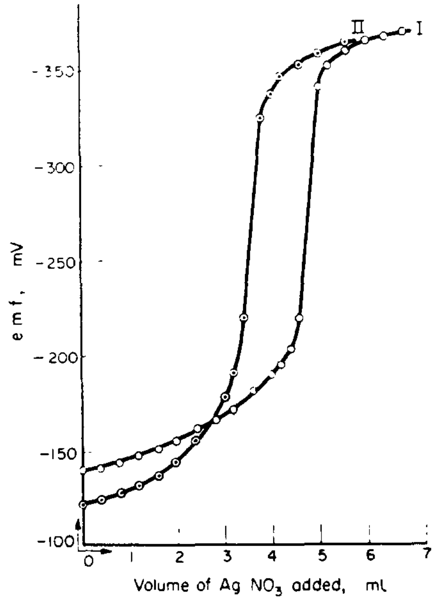

FIG. 1.—Direct potentiometric titrations between silver nitrate and sodium orthovanadate: (I) *M*/10 $AgNO_3$ *vs.* *M*/250 $3Na_2O.V_2O_5$: (II) *M*/15 $AgNO_3$ *vs.* *M*/500 $3Na_2O.V_2O_5$.

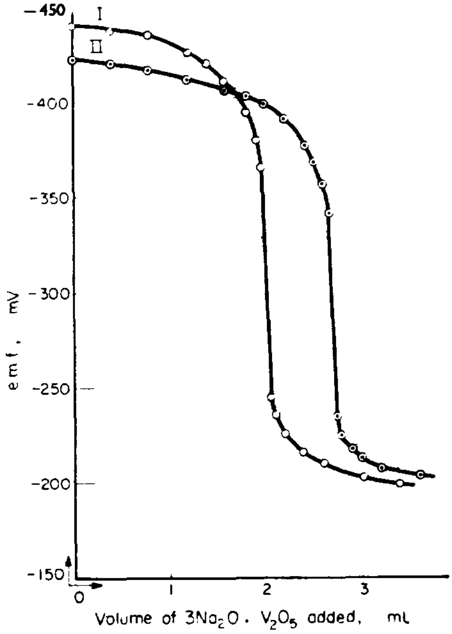

FIG. 2.—Reverse potentiometric titrations between silver nitrate and sodium orthovanadate: (I) *M*/30 $3Na_2O.V_2O_5$ *vs.* *M*/50 $AgNO_3$: (II) *M*/80 $3Na_2O.V_2O_5$ *vs.* *M*/100 $AgNO_3$.

electrode with either of the reactants used as the titrant. The end-point obtained from the max. dE/dV and deflection in titration curves occurs at a point where the molecular ratio $Ag^-:VO_4^{3-}$ is 3:1, corresponding to the formation of silver orthovanadate, Ag_3VO_4, at pH range 8–9. The compound has been found to be highly insoluble, and therefore suitable for precipitation. The titration curves are symmetrical on both sides of the stoichiometric end-point, which is marked by a sharp change in e.m.f. and the results are accurate and reproducible.

In the direct titration curves (Fig. 1), when Na_3VO_4 is being titrated, the e.m.f. gradually increases with the start of the reaction and a marked upward jump is obtained at the equivalence point, after which the potential assumes a constant value. In the case of inverse titrations, when the silver electrode is dipped in $AgNO_3$ solution, the e.m.f. assumes a steady value rapidly after each addition of the alkali vanadate solution, till at the stoichiometric end-point a sharp fall in potential is observed, after which the e.m.f. becomes almost constant. Continuous stirring in the vicinity of electrode has a favourable effect on the titrations. Each titration takes about half an hour for completion. The addition of ethanol has hardly any effect on the accuracy of the end-point or on the magnitude of the break in potential.

The present investigation confirms the formation and precipitation of Ag_3VO_4 in the pH range 8–9. The potentiometric method is much more convenient than the methods currently available. It is simple because it does not require costly chemicals or complicated apparatus or procedure. Furthermore, it has the advantages of great rapidity and excellent precision. The method can therefore be recommended for the quantitative determination of even low concentrations of vanadium.

Acknowledgement—One of us (O. P. S.) is thankful to the authorities of the Council of Scientific and Industrial Research, India, for the award of Junior Fellowship.

Résumé—On a étudié une méthode électrométrique rapide et précise de dosage du vanadium à l'état d'orthovanadate d'argent. Elle consiste en un titrage potentiométrique d'une solution d'orthovanadate de sodium à pH 11,5 au moyen d'une solution titrée de $AgNO_3$, en employant une électrode indicatrice d'argent, reliée à une électrode étalon par un pont de KNO_3. Chacun des deux réactifs peut être utilisé comme agent de titrage. On observe un changement net de la f.é.m. au point final, correspondant à la précipitation de Ag_3VO_4 à pH 8–9. Les courbes ont une forme régulière, il apparaît un maximum prononcé de dE/dV au point final, et la précision et la reproductibilité des résultats électrométriques se sont révélées satisfaisantes, même aux faibles concentrations ($1 \times 10^{-3}M$) des réactifs. Les titrages potentiométriques offrent une méthode simple, rapide et précise de dosage de vanadium à l'état d'orthovanadate d'argent.

Zusammenfassung—Eine schnelle und genaue elektrometrische Method zur Vanadinbestimmung als Silber-Orthovanadat wurde erforscht. Man titriert Natrium-Orthovanadatlösung bei pH 11,5 potentiometrisch gegen eingestelltes Silbernitrat unter Verwendung einer Silber-Indikatorelektrode, Als Vegleichselektrode ist mit einer Kaliumnitratbrücke eine gesättigte Kalomelektrode angeschlossen. Beide Reagentien konnen als Titrierlösung verwendet werden. Ein ausgeprägter Sprung der EMK wird am Endpunkt beobachtet, der der Fallung von Silberorthovanadat bei pH 8–9 entspricht, Die Kurven haben die normale Form, in der differenzierten Kurve tritt am Endpunkt ein ausgeprägtes Maximum auf und die elektrometrischen

Ergebnisse sind auch bei niedrigen Konzentrationen ($1 . 10^{-}M^{3}$) der Reaktanten sehr genau und reproduzierbar. Potentiometrische Titrationen bieten eine einfache, schnelle und genaue Methode zur quantitativen Vanadinbestimmung als Silberorthovanadat.

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SEPARATION OF EUROPIUM$^{\text{III}}$ AND AMERICIUM$^{\text{III}}$ BY SOLVENT EXTRACTION OF THEIR METAL CHELATE COMPLEXES

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Summary—Separation of Eu^{3+} and Am^{3+} by solvent extraction has been studied. The distribution of chelate complexes of these metal ions between $0{\cdot}1M$ sodium perchlorate and chloroform or methylisobutylketone with nineteen chelating acids has been determined. Among these acids it was observed that some extract Eu^{3+} into the organic phase better than Am^{3+}, some extract Am^{3+} better, and some extract them equally well. The separation factor, $SF = D_{Eu}/D_{Am}$, was determined for twelve of these acids by the extraction of Eu^{3+} and Am^{3+} from $0{\cdot}1M$ (H,Na)ClO_4. The values of log SF are as follows: dibutylphosphate (DBP), $+1{\cdot}36$; dioctylphosphate (DOP), $+1{\cdot}15$; 1-phenyl-3-methyl-4-acetylpyrazolone-5, $+0{\cdot}54$; 2-thenoyltrifluoracetone (TTA), $+0{\cdot}48$; neocupferron, $+0{\cdot}24$; *N*-benzoylphenylhydroxylamine, $+0{\cdot}22$; *N*-2,4-dichlorobenzoylphenylhydroxylamine, $+0{\cdot}12$; β-isopropyltropolone (IPT), $-0{\cdot}01$; 1-hydroxy-2-naphthoic acid, $+0{\cdot}03$; 2-hydroxy-1-naphthoic acid, $+0{\cdot}01$; 3-hydroxy-2-naphthoic acid, $-0{\cdot}02$; 5,7-dichloroxine, $-0{\cdot}99$. From these results it follows that dialkylhydrogenphosphates and 5,7-dichloroxine are the most suitable chelating acids for the separation of Eu^{3+} and Am^{3+} by solvent extraction.

INTRODUCTION

THE separation of tervalent lanthanide and actinide ions is usually difficult because of the similarity of these ions. Their chemical properties have been studied extensively, and various types of separations such as the group separation of gross actinide ions from lanthanide ions or the separation of an individual ion from others in the same group have been investigated. Among many separation methods, anion exchange was reported[1] to be very effective for the gross separation of tervalent actinide from tervalent lanthanide ions when concentrated hydrochloric acid or thiocyanate solution was used as the aqueous medium to form adsorbable complex ions on the anion-exchange resin.

In the present laboratory extensive work has been carried out to find out the conditions for the separation of lanthanide and actinide ions by solvent extraction, and various metal extracting ligands, organic solvents and aqueous solution systems have been investigated for this purpose.

Dyrssen and Liem[2] studied the solvent extraction of Eu^{3+} and Am^{3+} by dibutylphosphate (DBP) in different organic solvents, and they reported that the extraction of Eu^{3+} and Am^{3+} with DBP is quite different in n-hexane, carbon tetrachloride, chloroform, isopropyl ether, hexone and hexol. They showed that the distribution ratio of the metal ions between the organic phase and $0{\cdot}1M$ nitric acid, log D_{Eu},

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ranges between −2·60 (in hexane) to −3·34 (in hexol) with 0·1*M* DBP; and moreover, the separation factor, log *SF*(= log D_{Eu}/D_{Am}), ranges between 1·36 (in $CHCl_3$) to 0·33 (in hexol).

The present study was made to find the most effective extracting ligand for the separation of Eu^{3+} and Am^{3+}. To fix conditions we used 0·1*M* $(H,Na)ClO_4$ and $CHCl_3$ or hexone as organic solvents. The paper gives the experimental results for the distribution of metal chelate complexes of Eu^{3+} and Am^{3+} between the organic and the aqueous phase, and presents a short discussion on the separation of these two metal ions by solvent extraction of their chelate complexes. Short reports of our results have been presented earlier.[3,4]

RESULTS

Nineteen acids were investigated, and our experimental results show that different chelating acids (HA) give different separation factors.

In the present study, only the variation of the net distribution ratio of Eu^{3+} and Am^{3+} with the hydrogen ion concentration ($-\log [H^+]$) was determined. Even though no information on the hydrolysis of tracer concentrations of tervalent lanthanide or actinide elements is available, it may be concluded from studies at higher metal concentrations[5–7] that no hydrolysis occurs below pH 5-6. All experiments were therefore carried out at a pH below 5·5. The net distribution ratio, *D*, was determined between 0·01 and 100.

Assuming that the extraction of Eu^{3+} and Am^{3+} takes place by the following reaction:

$$M^{3+}(aq) + (3 + n)HA(org) \rightleftharpoons MA_3(HA)_n(org) + 3H^+(aq)$$

and that the distribution ratio is given by

$$D = [MA_3(HA)_n]_{org}/[M^{3+}]$$

we may express the extraction constant as follows:

$$K_{ex} = D[H^+]^3[HA]_{org}^{-(3+n)}$$

Since $[HA]_{org}$ is constant for each reagent (0·05*M* for dichloroxine and 0·1*M* for the other acids) we could not determine the composition of the extracted complexes.* Therefore $D[H^+]^3$ was calculated instead of K_{ex}.

The values of $D[H^+]^3$ for Eu^{3+} and Am^{3+} with twelve ligands are listed in Table I, together with the separation factors, the acid dissociation constants, and the distribution constants of the acids between chloroform or hexone and 0·1*M* $NaClO_4$.

Table II shows the results of the extraction with three ligands, which formed aqueous complexes to such an extent that the slope of the plots log *D versus* $-\log [H^+]$ was always less than 3. Table III shows the results for four ligands which showed too small extraction to determine the net distribution ratio *D*, or the separation factor *SF*, under the experimental conditions.

DISCUSSION

As shown in Table I, the separation of Am^{3+} and Eu^{3+} is most effective with the dialkylhydrogenphosphate, which extracts Eu^{3+} better than Am^{3+}, and with

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* For 0·1*M* IPT in chloroform, for example, we observed that EuA_3HA is the main complex in the organic phase.

TABLE I.—SEPARATION OF Eu^{3+} AND Am^{3+} IN 0·1M $NaClO_4$ BY SOLVENT EXTRACTION WITH VARIOUS CHELATING ACIDS*

Reagent (HA)	Organic solvent	pK_a	$\log K_d$	$\log SF$	$\log D_{Eu}[H^+]^3$	$\log D_{Am}[H^+]^3$
Dibutylhydrogenphosphate (DBP)†	$CHCl_3$	1·00	0·24	+1·36	2·91	- 4·27
Dioctylhydrogenphosphate (DOP)	$CHCl_3$	(≈ 1·5)[a]	(≈ 4·9)[a]	+1·15	4·86	6·01
1-Phenyl-3-methyl-4-acetylpyrazolone-5	$CHCl_3$	b	b	+0·54	- 6·33	6·87
2-Thenoyltrifluoroacetone (TTA)	$CHCl_3$	6·23(4·43)[c]	1·81	+0·48	11·68	12·20
Neocupferron	$CHCl_3$	(≈ 3·7)[a]	(≈ 2·8)[a]	+0·24	8·90	9·14
N-Benzoylphenylhydroxylamine	$CHCl_3$	8·15	2·33	+0·22	14·39	14·61
N-2-4-Dichlorobenzoylphenylhydroxylamine	$CHCl_3$	(≈ 8)[a]	(≈ 3·3)[a]	+0·12	- 13·92	14·04
β-Isopropyltropolone (IPT)	$CHCl_3$	7·04	3·37	- 0·01	9·90	- 9·89
1-Hydroxy-2-naphthoic acid	hexone	d	d	+0·03	13·24	13·27
2-Hydroxy-1-naphthoic acid	hexone	d	d	+0·01	12·12	12·13
3-Hydroxy-2-naphthoic acid	hexone	d	d	0·02	12·27	12·25
5,7-Dichloroxine	$CHCl_3$	7·47	3·80	0·99	13·73	12·74

* The concentration of HA is 0·1M except for 5,7-dichloroxine (0·05M).

† The constants for DBP were taken from Dyrssen and Liem.[8]

[a] Estimated value.

[b] The value of $pK_a + \log(1 + K_d)$ was determined by Jensen[10] as 7·1 ± 0·1.

[c] Enol form.

[d] cf. the values for salycylic acid; $pK_{a1} = 2{\cdot}82$, $pK_{a2} = 13$ $\log K_D = 2{\cdot}51$.

5,7-dichloroxine, which extracts Am^{3+} better than Eu^{3+}. At present it would be difficult to draw any general conclusions about the influence of the chelating acid on the separation factor. It is also difficult to predict whether a chelating acid will form extractable complexes with the rather inert tervalent lanthanide and actinide ions.

However, some conclusions may be reached on the basis of our investigation. Thus, chelating acids with the same reacting groups seem to give separation factors close to each other. Examples of such groups are =POOH (in dialkylphosphates), —COCHC(OH)— (in acetylpyrazolone and TTA), —N(OH)NO and —N(OH)CO— (in cupferron, neocupferron and the benzoylhydroxylamines), —COOH (in the hydroxynaphthoic acids). The extraction is generally poor if the chelating acid is too weak, and a substitution which increases the acid strength of a reagent will usually improve the extraction properties. Thus, dichloroxine extracts better than oxine, TTA better than acetylacetone, and 2-hydroxy-1-naphthoic acid better than 1-naphthoic acid. The extraction may also be poor because of the formation of MA_n complexes in the aqueous phase if the hydrophobic part of the chelating acid is too small in relation to the hydrophilic groups; thus, neocupferron is better than cupferron, the 2-chloromethyl derivative of kojic acid better than kojic acid itself (2-hydroxymethyl) and naphthoic acid better than benzoic acid. In the case of DBP and DOP practically no MA_n complexes are formed in the aqueous phase, because the hydrophobic groups are large enough for both acids. The difference of $D[H^+]^3$ for the two acids is rather difficult to explain.

TABLE II.—EXTRACTION OF Eu^{3+} AND Am^{3+} WITH VARIOUS CHELATING ACIDS WHICH GAVE NO CONSTANT VALUES OF $D[H^+]^3$

Chelating acid	Separation	log *SF*
1-Nitroso-2-naphthol	$D_{Eu} \ll D_{Am}$	not constant
2-Hydroxyl-1,4-naphthoquinone	$D_{Eu} > D_{Am}$	$\approx +0{\cdot}4$
2-Chloromethyl-5-hydroxyl-γ-pyrone	$D_{Eu} < D_{Am}$	$\approx -0{\cdot}4$

TABLE III.—RESULTS WITH VARIOUS CHELATING ACIDS WHICH GAVE VERY POOR EXTRACTION

Chelating acid	Approximate tendency for separation
Isatin-β-oxime	$D_{Eu} < D_{Am}$
Kojic acid (2-hydroxymethyl-5-hydroxy-γ-pyrone)	$D_{Eu} \simeq D_{Am}$
2-Methyl-5-hydroxy-γ-pyrone	$D_{Eu} \simeq D_{Am}$
1-Naphthoic acid	$D_{Eu} \simeq D_{Am}$

The separation factor of these metal ions is sometimes also influenced by the organic solvent, perhaps because of the interaction between the solvent molecule and the metal chelate MA_3.

The addition of some water-soluble ligands (masking agents like citrate) to the aqueous phase may also shift the separation factor. If $SF > 0$, a complexing ligand with a larger stability constant for Am^{3+} should increase the separation factor. If $SF < 0$ (i.e., Am^{3+} is extracted better) the stability constant of the masking agent should be larger for Eu^{3+}. Otherwise, the separation gained by the extraction is decreased by the addition of the masking agent.

There have been some reports[12–14] on the extraction of various rare earth elements with some of the ligands in the present study. Figure 1 summarises the results with IPT and DBP.

From this work we suggest in Table IV a selection of extracting ligands for the separation of the combination of ions listed below.

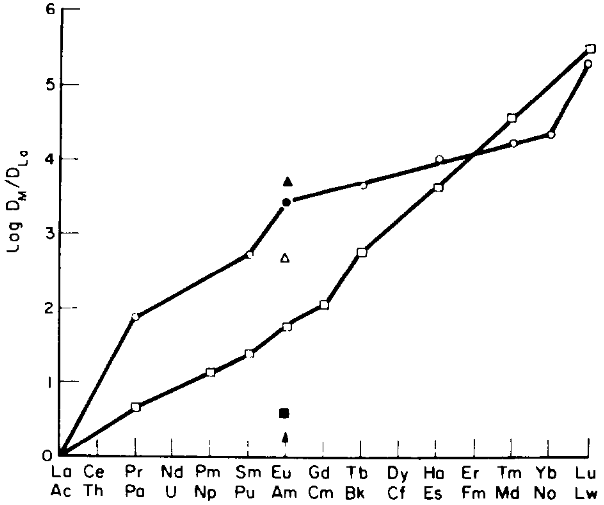

FIG. 1.—Separation of trivalent lanthanide ions and Am^{3+}. Values of log D_M/D_{La}.
□—The DBP-dibutylether system reported by Duyckaerts and Drèze[14]:
○—The IPT-chloroform system reported by Dyrssen[12]:
△—Values of Eu^{3+} and Am^{3+} for 5,7-dichloroxine in chloroform:
(■, ●, ▲—Am^{3+}).

TABLE IV.—SUITABLE EXTRACTING LIGANDS

Separation	Extracting ligand (in $CHCl_3$)
Am^{3+} from Eu^{3+}	DOP(Eu^{3+} in the organic phase) or 5,7-dichloroxine (Am^{3+} in the organic phase)
Am^{3+} from $La^{3+} - Sm^{3+}$	5,7-dichloroxine (Am^{3+} in the organic phase) or IPT (Am^{3+} in the organic phase)
Am^{3+} from Gd^{3+}—Lu^{3+}	DOP(Gd—Lu in the organic phase).

EXPERIMENTAL

Tracers

Tracer amounts of β,γ-active $^{152}Eu + {}^{154}Eu$ and α,γ-active ^{241}Am were obtained from Harwell, England. The tracers were dissolved in 0·1*M* $HClO_4$ to prepare the stock solution. The experiments were carried out one year after the preparation and so, even if there were some short-lived radioactive impurities in the radioactive samples, they should have decayed.

Reagents

All reagents used in this study were of analytical grade. Chloroform was shaken three times with the same amount of water to remove alcohol in it. Sodium perchlorate was prepared from Na_2CO_3 and $HClO_4$ and was twice recrystallised. Dioctylphosphate was washed with dilute NaOH and 0·1*M* $HClO_4$. Other reagents were used without further purification.

Procedures

All experiments in this study were carried out in a thermostatted room at 25°. The initial volumes of the organic and the aqueous phase were each 10·0 ml. The ionic strength of the aqueous phase was always kept as 0·1*M* with 0·1*M* $NaClO_4$ and 0·1*M* $HClO_4$. The aqueous phase was prepared as follows: 0·1 ml of Eu and Am mixed tracer solution in 0·1*M* $HClO_4$, 1·0 ml of Y^{3+} carrier solution ($10^{-4}M$ Y^{3+}) in 0·01*M* $HClO_4$ + 0·09*M* $NaClO_4$ and 2·0 ml of buffer solution (0·05*M* solution of sulphanilic acid or pyridine in 0·1*M* $NaClO_4$) were added in 40-ml stoppered glass tubes. The hydrogen ion concentration of the solution was adjusted by the addition of various amount of 0·1*M* $HClO_4$ or NaOH solution into the bottles and, finally, 0·1*M* $NaClO_4$ solution was added until the volume became 10·0 ml. The organic solutions of the chelating acids were left standing overnight after the dissolution to ensure that the system was in an equilibrium state before the experiments were started. Ten ml of organic solution thus prepared were added to the aqueous solution in the bottles. The tracers were always added in the aqueous phase.

The bottles were then placed in a machine with a rotating framework, and agitation was continued until extraction equilibrium was achieved (usually, 1 hr was sufficient). In some cases, for example 1-nitroso-2-naphthol in $CHCl_3$, the system was shaken by hand for about 3 min to avoid any effects of the decomposition of the organic substance. The results for two systems which had been agitated for different intervals were always compared to check if the extraction equilibrium had been reached.

The whole system was then centrifuged, and some portion of both phases were taken to measure the radioactivities, which was done as follows: 0·2 ml of the organic phase (except for dioctylphosphate) was transferred to a stainless steel dish (2 cm in diameter). The dish was first placed under an infrared lamp to evaporate the solvent ($CHCl_3$ or hexone) gradually, and then it was placed on a hot plate at 250°. To the residue thus obtained in the dish was added a small amount of concentrated nitric acid, and it was heated on the hot plate again to complete the decomposition of the organic substance. When the organic phase contained dioctylphosphate, it was shaken with the same amount of nitric acid to back-extract the metal ion into the acid, and 0·2 ml of this nitric acid solution was transferred to the stainless steel dish and heated on the hot plate. Two ml of the aqueous phase [0·1*M* $(H,Na)ClO_4$] were transferred into another stoppered glass tube, and a small amount of ammonia was added to make the pH high enough for the extraction with β-isopropyltropolone (IPT). IPT-chloroform solution was then added, and the metal ions were extracted into the aqueous phase, agitating by hand. The organic phase thus obtained was treated as above to get samples for the radioactivity measurements.

To measure the hydrogen ion concentration, 5 ml of the aqueous phase were transferred to a small plastic vessel. The hydrogen ion concentration ($-\log[H^+]$) was measured potentiometrically using 0·0100*M* $HClO_4$ and 0·090*M* $NaClO_4$ mixture solution as the standard of $\log[H^+] = -2·00$ but when $-\log[H^+]$ was lower than 2, $[H^+]$ was calculated from the known composition of the aqueous phase.

The radioactivities of the sample in the dish (α-activity of ^{241}Am and β-activity of $^{152}Eu + ^{154}Eu$) were measured as follows: the sample on the stainless steel dish was placed in a gas-flow type proportional counter (Tracerlab SC-16). The α-activity was first measured in the proportional region (where 10^6 dpm of β-activity gives less than one cpm). Then the β-activity was measured in the Geiger region applying an aluminium foil (6 mg per cm^2) to absorb the α-particles and to count only the β-activity. The background from ^{241}Am (which may result from γ-rays), was corrected from the values obtained from samples which contained only ^{241}Am under the same experimental conditions.

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Zusammenfassung—Die Trennung von Europium(III) und Americium(III) durch flüssig-flüssig-Extraktion wurde untersuckt. Die Verteilung der Chelate dieser Ionen zwischen 0,1 m Natriumperchlorat und Chloroform oder Methylisobutylketon wurde mit 19 chelatbildenden, Säuren geprüft, Unter diesen Säuren extrahieren einige Eu^{3+} besser in die organische Phase als Am^{3+}, einige Am^{3+} besser als Eu^{3+}, weider andere extrahieren beide in gleichem Maße. Der Trennfaktor SF = D_{Eu}/D_{Am} wurde für 12 Säuren durch Extraktion von Eu^{3+} und Am^{3+} aus 0.1 m $(H, Na)ClO_4$ ermittelt. Die Werte von log SF sind folgende: Dibutylphosphat (DBP) +1,36, Dioctylphosphat (DOP) +1,15, 1-Phenyl-3-methyl-4-acetylpyrazolon-5 +0,54, 2-Thenoyltrifluoraceton (TTA) +0,48, Neocupferron +0,24, N-Benzoylphenylhydroxylamin +0,22, N-2,4-dichlorbenzoyl-phenylhydroxylamin +0,12, β-Isopropyltropolon (IPT) −0,01, 1-Hydroxy-2-naphthoesäure +0,03, 2-Hydroxy-1-naphthoesäure +0,01, 3-Hydroxy-2-naphthoesäure −0,02, 5,7-Dichloroxin −0,99. Hieraus folgt, daß Dialkylhydrogenphosphate und 5,7-Dichloroxin die besten Chelatbildner zur Trennung von Eu^{3+} und Am^{3+} durch flüssig-flüssig-Extraktion darstellen.

Résumé—On a étudié la séparation de Eu^{3+} et Am^{3+} par extraction aux solvants. On a déterminé la distribution des complexes chélatés de ces ions métalliques entre le perchlorate de sodium 0,1 M et le chloroforme ou la méthylisobutylcétone avec dix neuf acides chélatants. On a observé que, parmi ces acides, certains extraient mieux Eu^{3+} que Am^{3+} dans la phase organique, certains extraient mieux Am^{3+}, et d'autres extraient également ces deux ions. Le facteur de séparation, $SF = D_{Eu}/D_{Am}$, a été déterminé pour 12 de ces acides, par extraction de Eu^{3+} et Am^{3+} à partir de (H,Na) ClO_4 0,1 M. Les valeurs de log SF sont les suivantes: dibutylphosphate (DBP) +1,36; dioctylphosphate (DOP) +1,15; 1-phényl-3-méthyl-4-acétylpyrazolone-5 +0,54; 2-thénoyltrifluoracétone (TTA) +0,48; néocupferron +0,24; N-benzoylphénylhydroxylamine +0,22; N-2,4-dichlorobenzoylphénylhydroxylamine +0,12; β-isopropyltropolone (IPT) −0,01; acide 1-hydroxy-2-naphthoïque +0,03; acide 2-hydroxy-1-naphtoïque +0,01; acide 3-hydroxy-2-naphtoïque −0,02; 5,7-dichloroxine −0,99. De ces résultats, il découle que les dialkylhydrogènephosphates et la 5,7-dichloroxine sont les acides chélatants les plus convenables pour la séparation de Eu^{3+} et Am^{3+} par extraction aux solvants.

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THEORETICAL CONSIDERATIONS ON THE INDIRECT DETERMINATION OF ANIONS

DETERMINATION OF SULPHATE WITH BARIUM CHLORANILATE

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Summary—Some anions (sulphate) may be determined by their reaction with a slightly dissociated or slightly soluble compound (barium chloranilate), another anion (chloranilate ion) being liberated and its extinction measured. An equation is given in this paper for the relationship between the concentration of sulphate and the extinction. For low concentrations the equation is non-linear. A calibration curve, prepared under standardised conditions, agrees well with theory. It shows a precision of about 5% at 20 μg of sulphate. At higher levels the precision is slightly better. It is proved that many interferences of foreign ions may be explained quantitatively by consideration of the activity coefficients. The scope of this method is discussed.

INTRODUCTION

FOR the quantitative determination of anions with organic reagents, indirect methods often have to be used. Many of them are based on reactions of the following type (charges have been omitted for simplicity):

$$M_pC_q + rA \rightarrow M_pA_r + qC$$

where A is the anion to be determined. C may represent any anion which can be easily determined, for example, by spectrophotometry. M_pC_q and M_pA_r are slightly soluble or slightly dissociated compounds. Several applications[1-9] of this principle have been described for the case when C represents the bivalent anion of $C_6H_2Cl_2O_4$ (H_2C), 2,5-dichloro-3,6-dihydroxybenzoquinone (chloranilic acid). In this paper the use of salts of this reagent will be discussed, but similar results may be expected for some other reagents.

The dissociation constants of H_2C are given by Schwarzenbach and Suter:[10] $pK_1 = 0{\cdot}85$ and $pK_2 = 3{\cdot}18$. Other authors give slightly different values.[11,12] The differences may arise from differences in ionic strength. The anion C is violet and has a strong absorption at 332 mμ; ε is about $27{\cdot}5 \times 10^3$ litre. mol^{-1} . cm^{-1}. Salts of the acid have been used for the determination of sulphate, [1,3,4,6,8] fluoride,[5,7] chloride,[2,3] phosphate[13] and other ions.

It seems to be generally assumed that a linear relationship exists between the concentration of A and the extinction E. In the first part of the present paper a more exact relationship between these quantities is given for the case when $p = q = r = 1$ and MC and MA are slightly soluble salts. In the second part of the paper the interference by foreign compounds (sodium chloride, potassium nitrate), not reacting *chemically* with M, C and A, is calculated from activity considerations. In the third part some results are given of experiments in which $M = Ba^{2+}$ and $A = SO_4^{2-}$, *i.e.*, in the case of the determination of sulphate with barium chloranilate.

THEORETICAL DISCUSSION

Relationship between extinction and unknown concentration

The symbol $[X]_i$ is used for the moles of component X, present in phase i, not calculated for 1 litre of solution but for 1 litre of the complete system: solid compounds (MA and MC) plus liquid. This notation simplifies the calculations, because the difference between total volume and volume of the liquid alone is neglected. The difference is so small, however, that the error made may certainly be neglected. The index t indicates the total amount of a substance present.

Furthermore, it should be noted that s_1 and s_2 have been defined in equations (6) and (8) as the products of the ionic concentrations, not of the ionic activities. The influence of this difference will be discussed in the section on the causes of error.

We define:

$$x = [C]_{sol} + [HC]_{sol} + [H_2C]_{sol} \tag{1}$$

$$y = [A]_{sol} + [HA]_{sol} + [H_2A]_{sol} + [A]_{MA} \tag{2}$$

$$A' = [A]_{sol} + [HA]_{sol} + [H_2A]_{sol} \tag{3}$$

$$\alpha = \frac{[C]_{sol}}{x} \tag{4}$$

$$\beta = \frac{[A]_{sol}}{A'} \tag{5}$$

s_1 and s_2 are the "solubility products" of MC and MA, respectively, ε is the molar extinction coefficient of C, and d is the path length of the light in the spectrophotometer cell.

From these definitions we see that, if no A is added and there is only a saturated solution of MC:

$$[M]_{sol} \cdot [C]_{sol} = s_1 \tag{6}$$

and because $x = [M]_{sol}$, substitution of equation (4) gives $\alpha x^2 = s_1$ and

$$x = \sqrt{\frac{s_1}{\alpha}} \tag{7}$$

If so much A is added that the solution is saturated with respect to MA, but no solid MA is formed, it is seen from

$$[M]_{sol} \cdot [A]_{sol} = s_2 \tag{8}$$

that

$$[A]_{sol} = \frac{s_2}{[M]_{sol}} .$$

Combination with equations (2), (4), (5), (6) and (7) gives:

$$y = \frac{s_2}{\beta} \cdot \sqrt{\frac{\alpha}{s_1}} \tag{9}$$

This value gives the amount of y which is at least necessary to give an extinction larger than the blank.

If solid MC and MA are both present, equations (10)–(14) are valid:

$$[C]_t = x + [C]_{MC} \qquad (10)$$

$$[M]_t = [M]_{sol} + [M]_{MC} + [M]_{MA} \qquad (11)$$

$$[M]_{MC} = [C]_{MC} \qquad (12)$$

$$[A]_{MA} = [M]_{MA} \qquad (13)$$

$$[M]_t = [C]_t \qquad (14)$$

Substitution of equations (10) and (11) in (12) and subtraction of (14) gives:

$$x = [M]_{sol} + [M]_{MA} \qquad (15)$$

From equations (2), (3), (5) and (13) we find:

$$[M]_{MA} = y - \frac{[A]_{sol}}{\beta} \qquad (16)$$

and from (4), (6), (8) and (16):

$$[M]_{MA} = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x \qquad (17)$$

From equations (4), (6) and (15) we see:

$$[M]_{MA} = x - \frac{s_1}{\alpha x} \qquad (18)$$

Combination of (17) and (18) gives:

$$x = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x + \frac{s_1}{x\alpha} \qquad (19)$$

After rearrangements we find the quadratic equation:

$$x^2 \left\{1 + \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta}\right\} - yx - \frac{s_1}{\alpha} = 0 \qquad (20)$$

Solution of this equation gives:

$$x = \frac{y + \sqrt{y^2 + \dfrac{4 \cdot s_1}{\alpha} + \dfrac{4 \cdot s_2}{\beta}}}{2 + 2 \cdot \dfrac{s_2}{s_1} \cdot \dfrac{\alpha}{\beta}} \qquad (21)$$

For many practical cases $\frac{s_2}{\beta} \ll \frac{s_1}{\alpha}$, *i.e.*, the apparent (conditional) solubility constant of MA is much smaller than that of MC. Therefore in those cases equation (21) simplifies to:

$$x = \frac{y + \sqrt{y^2 + \dfrac{4 \cdot s_1}{\alpha}}}{2} \qquad (22)$$

The extinction measured, however, is caused by one of C, HC or H_2C, and not by their sum x. Therefore, the relation between x and this specimen should be used. In this paper the extinction of C is measured, and equation (4) gives the relation required.

From Beer's law:

$$E = \varepsilon \, . \, c \, . \, d. \tag{23}$$

and from equations (4) and (22) it now follows that

$$E = \frac{\varepsilon \, . \, d \, . \, \alpha}{2} \left(y + \sqrt{y^2 + \frac{4 \, . \, s_1}{\alpha}} \right) \tag{24}$$

where E is written for the extinction from C. We assume that the contribution of HC and H_2C to the extinction may be neglected.

It is necessary at this point to stress the fact that the values of α and s_1 may vary with the experimental conditions. The variation of α is caused especially by the pH and also by the dissociation constants, which vary with the composition (including ionic strength) of the solution. The variation of s_1 is caused especially by the composition of the solution. For these reasons the indices b and s are used below, b indicating the blank and the calibration solution, which generally will have the same over-all composition, and s indicating the sample solution.

In this way we find for the difference between the extinction of the sample solution and the blank, the value

$$\Delta E_s = \frac{\varepsilon \, . \, d \, . \, \alpha_s}{2} \left(y + \sqrt{y^2 + \frac{4 s_{1,s}}{\alpha_s}} \right) - \frac{\varepsilon \, . \, d \, . \, \alpha_b}{2} \sqrt{\frac{4 s_{1,b}}{\alpha_b}} \tag{25}$$

The difference between the extinction of the calibration solution and the blank solution is given by:

$$\Delta E_b = \frac{\varepsilon \, . \, d \, . \, \alpha_b}{2} \left(y + \sqrt{y^2 + \frac{4 s_{1,b}}{\alpha_b}} \right) - \frac{\varepsilon \, . \, d \, . \, \alpha_b}{2} \sqrt{\frac{4 s_{1,b}}{\alpha_b}} \tag{26}$$

The equations are simplified if $\alpha_s = \alpha_b = 1$.
This was the case in our experiments. The relative error:

$$F = \frac{\Delta E_s - \Delta E_b}{\Delta E_s}$$

is now given by:

$$F = \frac{\sqrt{y^2 + 4 s_{1,s}} - \sqrt{y^2 + 4 s_{1,b}}}{y + \sqrt{y^2 + 4 s_{1,s}}} \tag{27}$$

Causes of error

The main causes of error are:

(a) Errors caused by foreign compounds reacting chemically with one of the components of the solutions or absorbing at the wavelength used. They are not discussed in this paper.

(b) Photometric errors. They are discussed briefly in the discussion on the scope of the method

(c) Errors caused by different conditions and compositions in calibration and sample solutions. They are discussed below.

Errors from different conditions. It is clear that α is a function of the dissociation constants and of the pH. In the case when H_2C is chloranilic acid, with $pK_1 = 0{\cdot}85$ and $pK_2 = 3{\cdot}18$, a pH above about 5 is necessary to ensure that small differences in pH do not give large differences in α. Regarding β, a lower pH value may be used if $A = SO_4^{2-}$. In non-aqueous media the calculation of the desirable pH region is complicated by the fact that K values are not generally known in those media, and that pH values measured in the conventional way may be seriously in error because the diffusion potential between reference electrode and sample solution is often unknown. Fortunately, it is possible to find conditions, which have not to be kept rigorously constant, without danger for changes in α and β.

More serious, however, is the variation of s_1 with the experimental conditions. This is now treated in some detail.

If the symbol s is used for the product of *ionic concentrations* in the saturated solution, a for activities, c for concentrations, f for activity coefficients and ω for ionic strength, we see that

$$s_\omega = c_C \, . \, c_M = \frac{a_C \, . \, a_M}{f_C \, . \, f_M} \tag{28}$$

It should be noted that for calculations of ω, concentrations have to be expressed in moles/kg of solvent and not moles/litre of solution.
Now

$$s_{\omega=0} = a_C \, . \, a_M \tag{29}$$

and combination of equations (28) and (29) gives:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f_C \, . \, f_M} \tag{30}$$

The values of f_C and f_M are approximately equal if both ions have the same charge. Writing $f = f_C = f_M$, we find:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f^2} \tag{31}$$

The values of f are found approximately from:[14]

$$-\log f = \frac{z^2 A \sqrt{\omega}}{1 + \delta b \sqrt{\omega}} \tag{32}$$

In this equation b is the ionic radius of M^{2+} and C^{2-}; z is their charge. The values of A and δ depend on factors of which only the dielectric constant of the medium is important to us. The exact value of b is not known, but at low values of ω, $\delta b \sqrt{\omega} \ll 1$, and therefore the exact value is not very important. We used $b = 5 \times 10^{-8}$. Values of A and δ were calculated for some cases of practical importance: (1) water, (2) water-ethanol mixture containing 50 ml of 95·5% ethanol in a 100-ml total volume (*i.e.*, 43% ethanol), and (3) the same but 75 ml of 95·5% ethanol in 100 ml (*i.e.*, 69% ethanol). For water $D = 80$, and for the mixtures $D = 54$ and 40, respectively.[15] Inserting these values and $z = 2$ or -2 in the formulae for A and δ found in the literature,[14] we find:

for water:
$$-\log f = \frac{2{\cdot}00 \sqrt{\omega}}{1 + 1{\cdot}64\sqrt{\omega}} \tag{33a}$$

for 43% ethanol:
$$-\log f = \frac{3{\cdot}65 \sqrt{\omega}}{1 + 2{\cdot}00\sqrt{\omega}} \tag{33b}$$

for 69% ethanol:
$$-\log f = \frac{5{\cdot}65 \sqrt{\omega}}{1 + 2{\cdot}34\sqrt{\omega}} \tag{33c}$$

Table I gives some values of f for various values of ω. It is clear that for low values of ω, the value of f is chiefly determined by the numerator. Therefore about the same value of f is found in water and in 69% ethanol if $(2{\cdot}00\sqrt{\omega})_{\text{water}} = (5{\cdot}65\sqrt{\omega})_{69\%\ \text{ethanol}}$, *i.e.*, the ionic strength in water may be eight times as high as in the mixture to give the same effect. From this we may conclude that in this respect water is a more favourable solvent than the mixtures.

More generally, the relative influence of ionic strength in various media may be approximated by the fact that A is proportional to $D^{3/2}$.

TABLE I.—VALUES OF f FOR BIVALENT IONS

Ionic strength (ω)	Activity coefficient (f)		
	Water	43% Ethanol	69% Ethanol
10^{-5}	0·986	0·974	0·960
$1{\cdot}1 \times 10^{-5}$	0·985	0·973	0·958
10^{-4}	0·956	0·921	0·881
$1{\cdot}1 \times 10^{-4}$	0·954	0·917	0·875
10^{-3}	0·871	0·779	0·682
$1{\cdot}1 \times 10^{-3}$	0·865	0·770	0·670
10^{-2}	0·673	0·496	0·348
$1{\cdot}1 \times 10^{-2}$	0·662	0·482	0·334
10^{-1}	0·383	0·196	0·094
$1{\cdot}1 \times 10^{-1}$	0·371	0·187	0·088

CONCLUSIONS FROM THEORETICAL DISCUSSION

Calibration curve

A calibration curve was calculated from equation (26). The values used were $y = 10^{-6}$ to 3×10^{-5}, $s_1 = 6 \times 10^{-11}$, $\varepsilon = 27{\cdot}5 \times 10^3$, $d = 4$ and $\alpha = \beta = 1$. In Table II the results are given and compared with those obtained, assuming every ion of A^{2-} liberates one ion of C^{2-}. The table shows that the extinction values, calculated in the first way, are much lower, and that the deviation from linearity is large.

TABLE II.—RELATIONSHIP BETWEEN SULPHATE CONCENTRATION (y) AND EXTINCTION (E)

y	E^a	E^b
10^{-6}	0·055	0·110
3×10^{-6}	0·180	0·330
10^{-5}	0·710	1·10
3×10^{-5}	2·65	3·30

[a] Calculated from equation (26).
[b] Assuming 1 SO_4^{2-} gives 1 C^{2-}.

Consequences of variation of s_1 with ω

The error F was calculated from equation (27) for the case when $\omega = 0{\cdot}01$, both in blank and calibration solution, and $\omega = 0{\cdot}011$, $0{\cdot}013$ and $0{\cdot}020$ in the sample solution (69% ethanol). It was found from experiments that when $\omega = 0{\cdot}01$, $s_1 = 6 \times 10^{-11}$. From this value and equations (31) and (33c) the values $6{\cdot}5 \times 10^{-11}$, $7{\cdot}6 \times 10^{-11}$ and $11{\cdot}9 \times 10^{-11}$ were calculated for the solubility product at $\omega = 0{\cdot}011$, 0·013 and 0·020. Table III shows that at $\omega = 0{\cdot}01$, the ionic strength of the sample solution should not differ more than about 10 or 20% from the ionic strength of the blank and calibration solutions.

TABLE III.—ERROR (F) RESULTING FROM A DIFFERENCE IN IONIC STRENGTH (ω) BETWEEN BLANK AND SAMPLE SOLUTION AT VARIOUS SULPHATE CONCENTRATIONS (y)

y	ω_b	ω_s	F, %
10^{-6}	0·010	0·011	4
10^{-6}	0·010	0·013	11
10^{-6}	0·010	0·020	28
3×10^{-6}	0·010	0·011	3
3×10^{-6}	0·010	0·013	9
3×10^{-6}	0·010	0·020	25
10^{-5}	0·010	0·011	2
10^{-5}	0·010	0·013	6
10^{-5}	0·010	0·020	16

EXPERIMENTAL

Barium chloranilate was prepared by slowly adding, at room temperature, with stirring, a slight excess of H_2C in 4 litres of water to 250 ml of 0·04*M* barium chloride solution. A fine purple precipitate is formed. After standing overnight the liquid is decanted, and the BaC is filtered by suction through a porcelain filter. After washing with ethanol and ether, the product is dried at 100°. Some water is retained unless the product is dried for some considerable time. A less satisfactory brown product was obtained when the directions of Bertolacini and Barney[1] were followed, *i.e.* when a large excess of barium chloride was added to the H_2C solution.

For preparation of the calibration curve, the sample, containing very little free hydrogen ion, is transferred to a 100-ml calibrated flask. Five ml of 10% urotropine solution, 10 ml of 0·1*M* sodium chloride solution and 75 ml of 95·5% ethanol are added exactly, followed by water to just below the calibration mark. This causes a rise in temperature of about 5°. The flask is placed in a thermostat bath at 20° for 10 min, the volume adjusted with water, 50 mg of BaC added and the flask again placed in the thermostat bath for at least 1 hr with occasional shaking. The suspension is filtered through a G4 filter (Fig. 1) by application of gentle pressure. Part of the filtrate is collected in a spectrophotometer cell and sucked from it with a polythene tube. This filling and suction procedure is repeated twice. In this way the cell is cleaned and filled with the required solution without risk that any liquid touches the outside of the walls, and that change of the absorption results from complete purification of the walls. The blank and calibration solution were measured in the same cells. As reference an approximately 10^{-4}*M* potassium dichromate solution in 0·02*M* sulphuric acid was used.

RESULTS

Some extinction measurements were made of aqueous solutions of chloranilic acid at various pH. The results at pH 3–9 agreed with the values of pK_2 given in the literature and gave a value of 28×10^3 for ε. At pH <3 the extinction was slightly higher than expected, probably because of the extinction of H_2C or HC^-. The difference was so small, however, that no interference from H_2C and HC^- may be expected at the pH used for the measurements.

In 69% ethanol the value for ε was $27{\cdot}5 \times 10^3$. No measurement of the dissociation constant was made in this solvent, for the reason given above, but it was found that at an apparent pH of 6–6·5 (measured with the glass electrode), prepared with urotropine, small changes in pH did not influence the results. The solubility product of BaC was calculated from measurements of C^{2-} with the assumption that BaC is completely dissociated.

In 69% ethanol in 0·01*M* (0·0115 molal) solution of sodium chloride the value

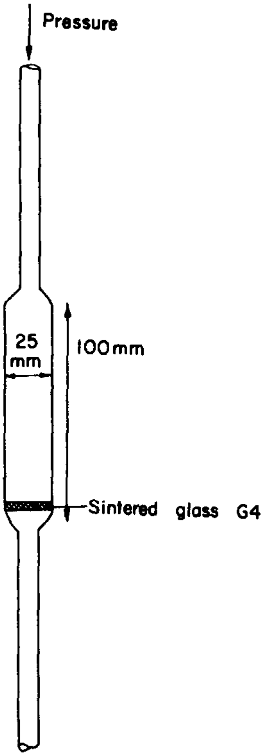

FIG. 1.—Filtration apparatus.

found was $s_1 = 6 \times 10^{-11}$. In 43% ethanol and $\omega = 0{\cdot}01$ the value was about 16×10^{-10} (20°). The large difference of these values makes it necessary for the ethanol concentration to be controlled rigorously.

The validity of equations (31) and (33c) was tested by measuring the extinction of saturated solutions of BaC to which different monovalent salts were added. The agreement of the results with theory is good (Table IV). Some experiments showed that slightly different results were found if sodium chloride was replaced by potassium nitrate in the same concentrations (the values in the presence of potassium nitrate were corrected for nitrate extinction, $\varepsilon = 0{\cdot}6$). This proves that not only the ionic strength but also the type of ion present influences the results.

A calibration curve was prepared for quantities of sulphate ranging from 18 to 108 μg in 69% ethanol and $\omega = 0{\cdot}0115$ in sodium chloride. The agreement with the theoretical curve is satisfactory. For s_2 the value 3×10^{-16} was used. It has been calculated from the value 4×10^{-17}, found by interpolation from the data given in the literature[16] and correction of this value for $\omega = 0{\cdot}0115$. The agreement with theory is very bad if it is assumed that one C^{2-} is liberated for each SO_4^{2-} added. (Fig. 2). In later experiments the curve was extended up to 400 μg of sulphate. The theoretical curve was also followed closely in this region.

For large values of y the difference between both curves corresponds to a difference in concentration of $\sqrt{s_1} = 7{\cdot}7 \times 10^{-6}$ moles/litre, *i.e.*, with 74 μg of sulphate/100 ml.

TABLE IV.—RELATIONSHIP BETWEEN IONIC STRENGTH AND EXTINCTION OF SOLUTIONS OF BARIUM CHLORANILATE IN 69% ETHANOL

Ionic strength	Salt	Extinction	
		Calculated	Found
$1·71 \times 10^{-4}$	NaCl	0·086	0·075
$3·42 \times 10^{-4}$	NaCl	0·095	0·088
$8·55 \times 10^{-4}$	NaCl	0·106	0·096
$1·71 \times 10^{-3}$	NaCl	0·122	0·108
$5·88 \times 10^{-3}$	$NaNO_3$	0·177	0·174
$8·55 \times 10^{-3}$	NaCl	0·203	0·220
$1·22 \times 10^{-2}$	$NaNO_3$	0·242	0·267
$1·72 \times 10^{-2}$	$NaNO_3$	0·280	0·339
$2·57 \times 10^{-2}$	NaCl	0·358	0·395

Therefore, a calibration curve constructed for high sulphate concentrations extrapolated to low sulphate concentrations suggests zero extinction for 47 μg of sulphate/100 ml.

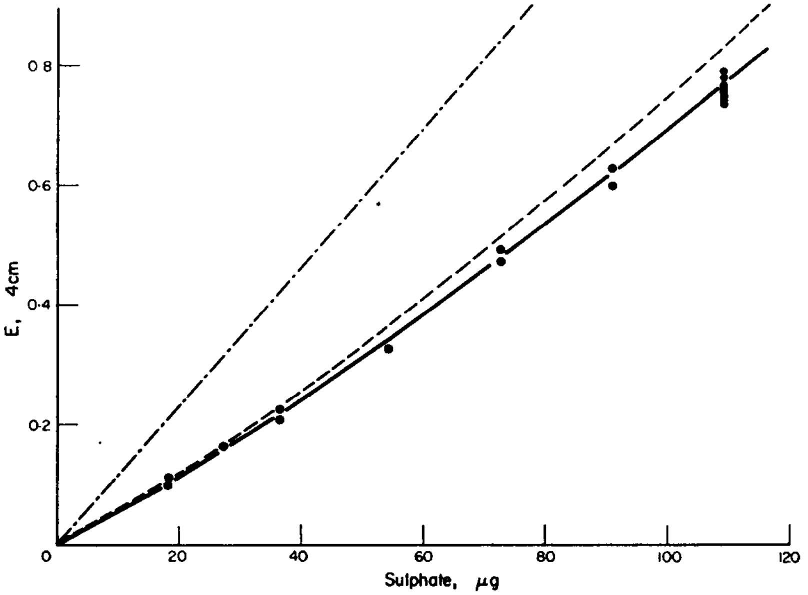

FIG. 2.—Calibration curve at 332 mμ in 100 ml of final solution (69% ethanol):
—— experimental,
– – – calculated from equation (26),
— · — · calculated by assuming 1 SO_4^{2-} gives 1 C^{2-}.

SCOPE OF METHOD

The sensitivity of a colorimetric method may be limited by two factors: chemical and instrumental. The latter factor is caused by the fact that at low extinction readings the percentage error is greatly increased. Assuming the Ringbom curve to be valid and accepting a value of 0·2% for the standard deviation in the transmission measurements, the percentage error in E from the instrument is 1% at E = 0·10, 2% at E = 0·05, 4·5% at E = 0·02 and 9% at E = 0·01.

The chemical error probably arises largely from the uncertainty in the blank (salt concentration).

The total error is found by quadratic addition of both errors. In the present example it seems that the instrumental error is of minor importance, but if the chemical error is reduced, the instrumental one may become the limiting factor.

One way to achieve this reduction seems to be a decrease in the value of the blank itself, which, probably, will give improvement in the reproducibility. In our experiments this was performed by the addition of ethanol, but the blank remained too large.

A disadvantage, however, of this change in the procedure will be that with constant sample volume the final volume will be increased considerably.

In any case, it is necessary that the ionic composition is controlled between narrow limits. It seems, therefore, that the practical application of the procedure will be limited to those problems in which good control of the ionic composition of the sample is possible.

The chloranilic acid method has also been used with other metal salts of the same anion. In some cases the solubility is less and it is an important consequence that it makes the control of the ionic composition less stringent. For the solubility product of the lead salt in 69% ethanol we found $2{\cdot}5 \times 10^{-12}$. Unfortunately, however, the solubility of lead sulphate in this medium is too large to make this favourable aspect useful for the determination of sulphate. Similar unfavourable results were obtained with 50% dioxan and 50% methylcellosolve solutions.

This consequence that a less soluble product (or a stronger complex) is required, may be a disadvantage of the use of a less soluble metal chloranilate.

Another possibility for increasing the sensitivity seems to be the replacement of the chloranilate ion by another ion giving less soluble salts. The value of ε, though theoretically limited,[17] may also be higher than in our case.

Zusammenfassung—Die Bestimmung von einigen Anionen (z.B. das Sulfat) kann durchgeführt werden durch die Reaktion mit einer wenig dissozierte oder wenig lösliche Verbindung (z.B. Bariumchloranilat). Von dieser Reaktion wird ein anderes Anion (z.B. Chloranilation) freigesetzt, dessen Extinktion gemessen wird. In dieser Arbeit ist eine Gleichung abgeleitet worden für die Beziehung zwischen der Sulfatkonzentration und der Extinktion. Für niedrige Konzentrationen ist die Beziehung nicht linear. Eine Eichkurve wurde hergestellt und zeigte gute Übereinstimmung mit der Theorie. Die Genauigkeit war ungefähr 5% bei 20 μg Sulfat, etwas besser bei grösseren Mengen. Es wird nachgewiesen dass viele Störungen erklärt werden können durch Berücksichtiging der Aktivitätskoeffizient. Die Möglichkeiten dieses Verfahrens werden erörtert.

Résumé—La détermination de certains anions (par example le sulphate) peut être exécutée a l'aide de la réaction avec une substance peu dissociée ou peu soluble (par example le chloranilate de baryum). Par cette réaction un autre anion (l'ion de chloranilate) est libéré et son extinction est mesuré. Dans notre publication une équation est derivée, exprimant la relation entre la concentration de sulphate et l'extinction mesuré. A concentrations basses la relation n'est pas linéaire. Une courbe d'étalonage est en bon rapport avec la théorie. Elle montre une précision de 5%, quand 20 μg de sulphate sont determinés. Avec des quantités plus élevées, la précision est meilleure. Nous avons demontré que beaucoup d'erreurs sont explicables, considérant les coefficients d'activité. Les possibilités de cette méthode sont discutées.

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PRELIMINARY COMMUNICATION

Extractive titrations using metallochromic indicators

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During recent years many new complexans as well as metallochromic indicators have been investigated to try and obtain higher selectivity, reproducibility and simplicity in the complexometric determination of various metals.

On the other hand, organic reagents forming metal chelates extractable into organic solvents, such as carbon tetrachloride and chloroform, *etc.*, have only been used as titrants to a small extent. Although such extractive titrations have been known for quite a long time,[1] they are limited to the case when the chelate formed is intensely coloured and the colour of the reagent used differs from that of the metal chelate (dithizone extraction). For this reason a great number of organic reagents forming slightly coloured or colourless metal chelates soluble in an organic solvent cannot be used as titrants, although their extraction properties are well known and systematically studied.[2] It has now been shown that the application of metallochromic indicators enables these organic reagents also to be used for extractive titrations.

It is evident that extractive titration with a metallochromic indicator can be successfully carried out only if the following conditions are fulfilled:

1. Neither the metallochromic indicator nor its metal chelate is extracted into the organic solvent.
2. The organic reagent forms extractable chelates the extraction constants of which are sufficiently high and whose solubility in organic solvents is of the order of >0·1 g/litre.
3. The extraction constant of the metal chelate is higher than the stability constant of the metallochromic indicator with the same metal.
4. The time of reaching equilibrium is not greater than 1 min.
5. The stock solution of the organic reagent is sufficiently stable.

Further discussion of these conditions, especially points 2 and 3, will be given in a subsequent paper. Although the above limitations are fairly restrictive, from among the great number of organic reagents and metallochromic indicators now available many will undoubtedly be suitable for this type of titration.

Experimental verification of extractive titrations using metallochromic indicators was made as follows. Iron^{III} was titrated at pH 3–4 using acetate buffer and 2 drops of 2% aqueous Tiron as indicator. The titrant was $1{\cdot}5 \times 10^{-2}M$ aqueous cupferron stabilised according to Kolthoff and Liberti[3] by ammonium carbonate. Chloroform was used as the organic solvent. Under these conditions Tiron forms with tiron a blue-coloured chelate soluble in water. At the equivalence point the blue colour in the aqueous phase disappears. If the equivalence point has to be observed precisely, the organic layer can be discharged and a fresh portion of chloroform added before the end of the titration. When the titrated solution is shaken in a separatory funnel, the time for reaching equilibrium is a maximum of 20–30 sec. In the case of determining milligram amounts of iron (volume: 20 ml) the precision of titration is satisfactory, the relative error being ±0·5%.

Compared with normal complexometric titration the advantage of extractive titration lies in the fact that the tested metal is not only determined but also separated from the treated solution, which remains free also from an excess of the titrant. As the extraction constants of many metals differ considerably from the stability constants of many of their chelates, new types of selective determinations may become possible. A disadvantage of this type of titration compared with normal complexometry is that stock solutions of the organic reagents involved are often less stable than those of complexans.

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Summary—The possibilities of extractive titrations using metallochromic indicators are discussed.

Zusammenfassung—Die Möglichkeiten extraktiver Titrationen mit Metallfarbindikatoren werden diskutiert.

Résumé—On discute des possibilités de dosages par extraction au moyen d'indicateurs métallochromes.

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SHORT COMMUNICATIONS

Spectrophotometric determination of hydrogen peroxide in alkaline solution

(*Received* 11 *September* 1963. *Accepted* 6 *February* 1964)

SEVERAL methods[1-9] are available for the spectrophotometric determination of hydrogen peroxide, the situation up to 1953 having been reviewed by Duval.[10] Except for the method of Erdey and Inczédy,[9] in which hydrogen peroxide is determined at pH 12, all procedures are either for acidic or neutral solutions.

A simple spectrophotometric method for the determination of concentrations of about $10^{-4}M$ of hydrogen peroxide in $0{\cdot}1M$ potassium hydroxide solution has now been developed. It is based on the decrease in absorbance of potassium hexacyanoferrate(III) in alkaline solution:

$$2K_3Fe(CN)_6 + H_2O_2 + 2KOH \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2 \,.$$

A similar reduction of hexacyanoferrate(III) by hydrogen peroxide in 30% alkaline solution has previously been used to determine hydrogen peroxide ($6 \times 10^{-3}M$) by potentiometric titration.[11]

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III). Analytical-grade reagent was dried at 60° for 20 hr, then cooled in a desiccator.

Potassium hexacyanoferrate(II). Analytical-grade reagent was dehydrated by heating at 110° for 24 hr, then cooled in a desiccator.

Hydrogen peroxide. 50% H_2O_2 solution was used as received from the Food Machinery and Chemical Corporation, U.S.A.

Distilled water. Redistilled from alkaline potassium permanganate in a stream of oxygen.

Potassium hydroxide. Standard ($1M$) solution as supplied by British Drug Houses Ltd., England.

Procedure

The absorption spectra of potassium hexacyanoferrate(III) and hexacyanoferrate(II) at room temperature (29°), as measured with a Beckman DU spectrophotometer in a 1-cm silica cell, are shown in Fig. 1. Potassium hexacyanoferrate(III) shows absorption maxima at 260, 302 and 418 mμ, the absorbance being identical in aqueous and $0{\cdot}1M$ potassium hydroxide solution. Potassium hexacyanoferrate(II) has no maxima in its absorption spectrum. Its absorbance is slightly less in $0{\cdot}1M$ potassium hydroxide solution than in aqueous solution.

Aqueous solutions of potassium hexacyanoferrate(III) obey the Beer-Lambert Law up to quite high concentrations (Fig. 2).* The absorbance at 418 mμ of a mixture of potassium hexacyanoferrate(III) and hexacyanoferrate(II) (each approximately $10^{-3}M$) is a direct measure of the hexacyanoferrate(III) concentration. The absorption peaks at 260 and 302 mμ for hexacyanoferrate(III) are not useful for the analysis of mixtures of hexacyanoferrate(III) and hexacyanoferrate(II) because hexacyanoferrate(II) has an appreciable absorbance at these wavelengths.

Aqueous solutions of potassium hexacyanoferrate(II) develop a yellow colour on standing, but solutions in $0{\cdot}1M$ potassium hydroxide are stable. Therefore, determination of hydrogen peroxide by the decrease in absorbance it causes of a solution of potassium hexacyanoferrate(III) is best carried out in $0{\cdot}1M$ potassium hydroxide.

The rate of reduction of potassium hexacyanoferrate(III) by hydrogen peroxide is dependent on the hydroxyl ion concentration of the solution (see Table I). It becomes sufficiently rapid for analytical purposes in $0{\cdot}1M$ potassium hydroxide.

Various volumes (1–15 ml) of $3{\cdot}23 \times 10^{-3}M$ hydrogen peroxide solution were added to 20 ml of $5 \times 10^{-3}M$ potassium hexacyanoferrate(III) solution and 10 ml of $1M$ potassium hydroxide. The mixtures were diluted to 100 ml and allowed to stand for 25 min, then compared at 418 mμ in

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* The results at 302 mμ are included for anyone interested in determining hexacyanoferrate(III) alone, in which case measurements at 302 mμ will be more sensitive than those at 418 mμ.

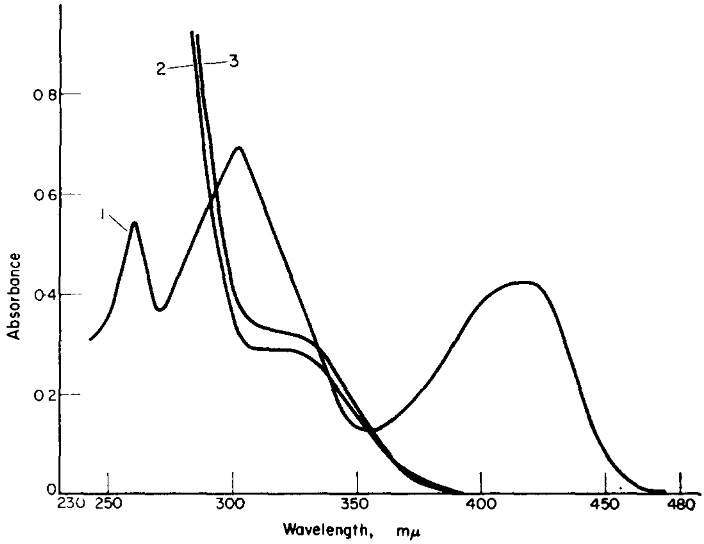

FIG. 1.—Absorption spectra:

1. 4·19 × $10^{-4}M$ $K_3Fe(CN)_6$ in water or 0·1*M* KOH.
2. 9·54 × $10^{-4}M$ $K_4Fe(CN)_6$ in 0·1*M* KOH.
3. 9·54 × $10^{-4}M$ $K_4Fe(CN)_6$ in water.

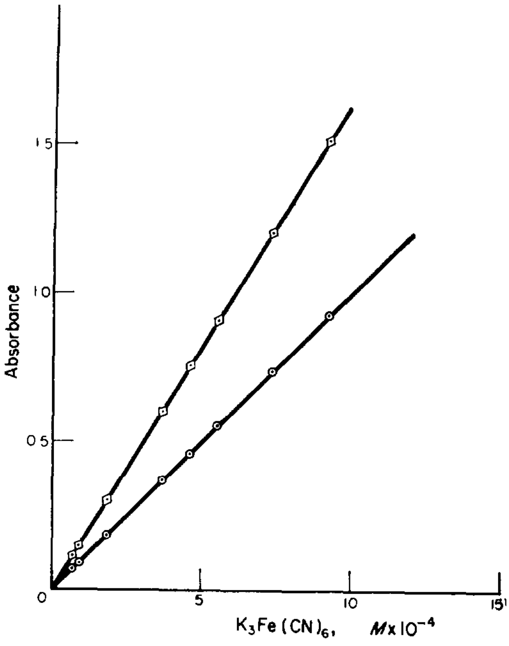

FIG. 2.—Conformity to Beer-Lambert Law of $K_3Fe(CN)_6$ at 29°:

◇ aqueous solution at 302 mμ: ϵ_{302} = 1648 mole^{-1}. cm^{-1},
○ aqueous solution at 418 mμ: ϵ_{418} = 1012 mole^{-1}. cm^{-1}.

1-cm silica cells with a blank prepared from potassium hexacyanoferrate(III) and potassium hydroxide solutions alone. The sample was placed in the "check" position and the blank in the "measure" position of the spectrophotometer. This arrangement gave absorbances which were a direct measure of the hexacyanoferrate(III) reduced by hydrogen peroxide. A comparison of the concentrations of hydrogen peroxide expected with those found on the basis of the hexacyanoferrate(III) reduced is shown in Table II. The standard deviation of the results is $\pm 2{\cdot}4\%$.

Many common ions, such as chloride, bromide, sulphate and phosphate, are stable towards hexacyanoferrate(III) and hexacyanoferrate(II); therefore they will not interfere in the determination of hydrogen peroxide. Obviously, the method will not be directly applicable in the presence of ions which react with hexacyanoferrate(III), with hexacyanoferrate(II) or with both. The authors have used the method with good results to measure hydrogen peroxide in irradiated alkaline solutions of potassium bromide in studies of aqueous radiolysis in the alkaline region.

TABLE I.—DEPENDENCE OF THE RATE OF REDUCTION OF $1{\cdot}000 \times 10^{-3}M$ POTASSIUM HEXACYANOFERRATE(III) BY $3{\cdot}336 \times 10^{-4}M$ HYDROGEN PEROXIDE ON THE HYDROXYL ION CONCENTRATION OF THE SOLUTION

KOH, *M*	0·0	0·0001	0·0005	0·001	0·005	0·01	0·1
H_2O_2 reacted with hexacyanoferrate(III) in 18 hr, $M \times 10^{-4}$	Nil	0·198	1·54	2·63	3·31	3·31	3·34
Approximate time for reaction completion, *min*	← not measured →				50	15	13

TABLE II.—A COMPARISON OF THE CONCENTRATIONS OF HYDROGEN PEROXIDE EXPECTED WITH THOSE FOUND ON THE BASIS OF HEXACYANOFERRATE(III) REDUCED IN ALKALINE SOLUTION

H_2O_2 expected, $M \times 10^{-4}$	4·84	4·20	3·55	3·23	2·91	2·26	1·62	0·969	0·323
H_2O_2 found, $M \times 10^{-4}$	4·94	4·34	3·65	3·35	2·95	2·25	1·65	0·959	0·311

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Summary—A method of analysis of hydrogen peroxide in concentrations of about $10^{-4}M$, applicable to solutions which are stable towards alkaline hexacyanoferrate(III) and hexacyanoferrate(II), is suggested. The hydrogen peroxide is determined spectrophotometrically at 418 mμ from the decrease in absorbance it causes in a $1 \times 10^{-3}M$ potassium hexacyanoferrate(III) in $0{\cdot}1M$ potassium hydroxide.

Zusammenfassung—Eine Methode zur Bestimmung von Wasserstoffperoxyd in Konzentrationen von etwa 10^{-4}m wird vorgeschlagen. Sie läßt sich auf Lösungen anwenden, die gegen alkalisches Hexacyanoferrat(III) und -(II) stabil sind. Das Wasserstoffperoxyd wird spekralphotometrisch bei 418 mμ bestimmt an Hand der Extinktionsabnahme, die es an einer $1{\cdot}10^{-3}$m Kaliumhexacyanoferrat(III)-Lösung in 0,1m Kaliumhydroxyd hervorruft.

Résumé—On propose une méthode de dosage de l'eau oxygénée à des concentrations d'environ 10^{-4}M, applicable aux solutions qui sont stables vis-à-vis des hexacyanoferrate(III) et hexacyanoferrate(II) alcalins. L'eau oxygénée est dosée spectrophotométriquement à 418 mμ, par la diminution d'absorbance qu'elle apporte à une solution 1×10^{-3}M d'hexacyanoferrate(III) de potassium en potasse 0,1M.

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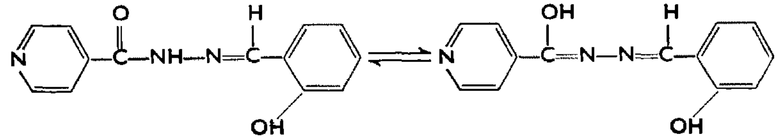
1-Isonicotinoyl-2-salicylidenehydrazine as a new chelatometric reagent

(*Received* 25 *October* 1962. *Accepted* 17 *February* 1964)

THE development of chelatometry in recent years has been responsible for the introduction of a number of organic reagents and new indicators. It has been observed in the case of certain reagents that their condensation with other compounds containing complex-forming groups (or even sometimes the self-coupling product[1]) becomes a specific reagent for some cations. In the course of development of new reagents which may exhibit specific reactions with some cations we have examined the complex-forming properties of 1-isonicotinoyl-2-salicylidenehydrazine.[2] While much work on the reagent remains to be done, the present paper briefly reports some of its possible applications for the determination and detection of cations.

The reagent was prepared by refluxing about equimolar quantities of isonicotinic acid hydrazide (isoniazid) and salicyladehyde (this being in slight excess) in 95% ethanol.[2] The product, after washing with water and ethanol to remove any unchanged reactants, had a m.p. of 265°. A 0·1% solution of the reagent in 99·9% ethanol is a very light yellow in the pH range 1–7, but deepens in the pH range 8–13. The change of colour can probably be attributed to the following two forms of the reagent



The reagent solution was investigated for metallochromic and chelatometric properties with the following 31 cations: $\mathrm{Ag^{I}}$, $\mathrm{Na^{I}}$, $\mathrm{K^{I}}$, $\mathrm{Rb^{I}}$, $\mathrm{Cs^{I}}$, $\mathrm{Hg^{II}}$, $\mathrm{Pb^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Sn^{II}}$, $\mathrm{Fe^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Mn^{II}}$, $\mathrm{Ca^{II}}$, $\mathrm{Sr^{II}}$, $\mathrm{Ba^{II}}$, $\mathrm{Mg^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{TiO^{II}}$, $\mathrm{VO^{II}}$, $\mathrm{UO_2^{II}}$, $\mathrm{Sb^{III}}$, $\mathrm{Al^{III}}$, $\mathrm{Fe^{III}}$. $\mathrm{Cr^{III}}$, $\mathrm{Au^{III}}$, $\mathrm{Ce^{IV}}$, $\mathrm{Th^{IV}}$, $\mathrm{Zr^{IV}}$ and $\mathrm{Pt^{IV}}$. The experiments were carried out with 2 ml of 0·01*F* and 0·1*F* solutions of suitable salts of the cations and 10 ml of the reagent. Any colour developed and/or the appearance of a precipitate was noted. The important observations are presented in Tables I and II.

TABLE I—CATIONS FORMING PRECIPITATES WITH 1-ISONICOTINOYL-2-SALICYLIDENEHYDRAZINE

Cation	Salt used	Colour of precipitate
$\mathrm{Cu^{II}}$	$\mathrm{CuSO_4{\cdot}5H_2O}$	Green
$\mathrm{Ni^{II}}$	$\mathrm{NiSO_4{\cdot}7H_2O}$	Orange
$\mathrm{Zn^{II}}$	$\mathrm{Zn(CH_3COO)_2{\cdot}2H_2O}$	Bright yellow
$\mathrm{Pd^{II}}$	$\mathrm{PdCl_2}$	Deep yellow
$\mathrm{Ce^{IV}}$	$\mathrm{2(NH_4)_2{\cdot}Ce(SO_4)_2{\cdot}2H_2O}$	Light yellow

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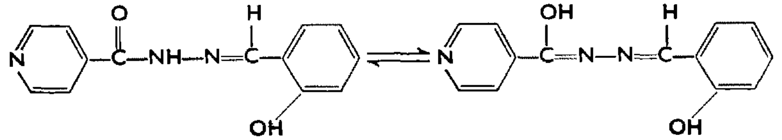

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Pd^{II}	$PdCl_2$	Deep yellow
Ce^{IV}	$2(NH_4)_2{\cdot}Ce(SO_4)_2{\cdot}2H_2O$	Light yellow

TABLE II—CATIONS FORMING SOLUBLE COMPLEXES WITH 1-ISONICOTINOYL-2-SALICYLIDENEHYDRAZINE

Cation	Salt used	Colour	Colour change on addition of excess EDTA
Pb^{II}	$Pb(NO_3)_2$	Deep yellow	Very light yellow
Fe^{II}	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Brown	Very light yellow
Co^{II}	$CoCl_2 \cdot 6H_2O$	Yellow	Very light yellow
Sn^{II}	$SnCl_2$	Deep yellow	Colourless
TiO^{II}	$K_2TiO(C_2O_4)_2 \cdot 2H_2O$	Orange-yellow	Yellow
VO^{II}	$VO(SO_4)$	Deep yellow	Greenish yellow
$UO_2{}^{II}$	$UO_2(CH_3COO)_2 \cdot 2H_2O$	Orange-yellow	Yellow
Sb^{III}	$Sb_2(SO_4)_3$	Yellow	Very light yellow
Al^{III}	$AlCl_3 \cdot 6H_2O$	Deep yellow	Very light yellow on heating
Fe^{III}	$Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$	Brown	Very light yellow
Th^{IV}	$Th(NO_3)_4 \cdot 4H_2O$	Deep yellow	Very light yellow
Zr^{IV}	$Zr(NO_3)_4 \cdot 5H_2O$	Deep yellow	Yellow

It is evident from Table I that Cu^{II}, Ni^{II}, Zn^{II}, Pd^{II} and Ce^{IV} give distinctly coloured precipitates with the reagent. The precipitation of Cu^{II} is quantitative and has been utilised for its gravimetric determination. The reagent presents some difficulty in gravimetry because of its low solubility; its sodium salt serves as a better precipitant. Furthermore, because Cd^{II}, Co^{II}, Mn^{II}, Th^{IV} and Zr^{IV} are not precipitated by the reagent, its utility for the following separations seems to merit investigation:

Cu^{II} in presence of Cd^{II},

Ni^{II} in presence of Co^{II},

Zn^{II} in presence of Mn^{II},

Ce^{IV} in presence of Th^{IV} and Zr^{IV}.

These investigations are in progress and the results will be published in due course.

Acknowledgement—The authors wish to thank Professor P. K. Kelkar, Director, Indian Institute of Technology, Kanpur, for providing facilities and for his interest in the work.

Summary—1-Isonicotinoyl-2-salicylidenehydrazine, prepared by the condensation of isonicotinic acid hydrazide and salicylaldehyde, has been examined for chelatometric properties with a number of cations. It precipitates Cu^{II}, Ni^{II}, Zn^{II}, Pd^{II} and Ce^{IV}, and forms soluble complexes with Pb^{II}, Fe^{II}, Co^{II}, Sn^{II}, TiO^{II}, VO^{II}, $UO_2{}^{II}$, Sb^{III}, Al^{III}, Fe^{III}, Th^{IV} and Zr^{IV}.

Zusammenfassung—Durch Kondensation von Isonicotinsäurehydrazid und Salicylaldehyd hergestelltes 1-Isonicotinoyl-2-salicylidenhydrazin wurde mit einigen Kationen auf seine chelatometrischen Eigenschaften geprüft. Es gibt Fallungen mit Cu^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+} und Ce^{4+} und lösliche Komplexe mit Pb^{2+}, Fe^{2+}, Co^{2+}, Sn^{2+}, TiO^{2+}, VO^{2+}, UO_2^{2+}, Sb^{3+}, Al^{3+}, Fe^{3+}, Th^{4+}, und Zr^{4+}.

Résumé—La 1-isonicotinoyl 2-salicylidène hydrazine a été préparée par condensation de l'isoniazide avec le salicylaldéhyde. On a étudié ses propriétés chélatométriques avec un certain nombre de cations. Elle précipite Cu(II), Ni(II), Zn(II), Pd(II) et Ce(IV) et forme des complexes solubles avec Pb(II), Fe(II), Co(II), Sn(II), TiO(II), VO(II), UO_2(II), Sb(III), Al(III), Fe(III), Th(IV) et Zr(IV).

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[2] Flavio Mattu and Renzo Pirisi, *Chimica* (*Milan*), 1952, **7**, 239.

Determination of tetra-ethylthiuram disulphide and elemental sulphur in organic extracts using cathode-ray polarography

(*Received* 1 *November* 1963. *Accepted* 15 *February* 1964)

INTRODUCTION

A NUMBER of polarographic methods have been described previously for the determination of thiuram disulphides[1,2,3] and free sulphur[4] and in many circumstances these appear to have appreciable advantages over colorimetric or other methods, particularly for micro or semi-micro amounts. However, no methods have appeared in the literature for the determination of these compounds using the linear-sweep cathode-ray polarograph (CRP), and because organic methods are not always equally applicable to conventional polarographs and the CRP, the following are described for the latter instrument.

The method for tetra-ethylthiuram disulphide (TETDS) is based on that of Belitskaya[1], who examined the polarographic waves of TETDS in an ammoniacal, partly ethanolic, buffer. It was found that, using the CRP, the current/concentration relationship for TETDS in this buffer was very non-linear in the concentration range studied by Belitskaya (150–600 ppm), but by reducing the concentration to a level of 1·5–15·0 ppm, a linear relationship was obtained. Working in this range, it is possible to add a small aliquot of the sample solution directly to the polarographic cell containing an aliquot of partially deoxygenated base electrolyte. This procedure minimises any modification of the base electrolyte by the solvent used in the sample preparation, prevents any oxidation of the TETDS which might occur at such low concentrations, and increases the speed of the method. Depending on which solvent has been used in the extraction of the synthetic rubber and on the nature of the synthetic, the rubber itself may be more or less dissolved in the extraction solvent. On addition to the base electrolyte, the rubber will then be reprecipitated, but this does not appear to lead to entrainment of the TETDS, possibly because of the very small amounts involved. This is shown by the results given in Table I. The ethyl acetate/isopropanol solvent does not dissolve a significant proportion of the rubber which was being analysed. Therefore, no precipitation occurs when this

TABLE I—EXTRACTION OF TETDS BY DIFFERENT SOLVENT SYSTEMS

Sample	TETDS, %	
	Chloroform[a]	Ethyl acetate/isopropanol[b]
A	1·48	$1{\cdot}40_0$
B	$1{\cdot}20_0$	$1{\cdot}11_1$

[a] 0·5 g of rubber dissolved in 24·5 ml of chloroform.
[b] 1·0 g of rubber extracted with 2 × 20 ml of 3:1 v/v ethyl acetate/isopropanol mixture and the combined extracts made to 50 ml.

Résumé—La 1-isonicotinoyl 2-salicylidène hydrazine a été préparée par condensation de l'isoniazide avec le salicylaldéhyde. On a étudié ses propriétés chélatométriques avec un certain nombre de cations. Elle précipite Cu(II), Ni(II), Zn(II), Pd(II) et Ce(IV) et forme des complexes solubles avec Pb(II), Fe(II), Co(II), Sn(II), TiO(II), VO(II), UO_2(II), Sb(III), Al(III), Fe(III), Th(IV) et Zr(IV).

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[b] 1·0 g of rubber extracted with 2 × 20 ml of 3:1 v/v ethyl acetate/isopropanol mixture and the combined extracts made to 50 ml.

solvent is used. In fact, although two extractions were made with it, the result is appreciably lower than that obtained using chloroform as the solvent, probably because of incomplete extraction of the TETDS by the ethyl acetate/isopropanol mixture. A third extraction of the rubber usually contains 0·02–0·04% of TETDS.

The determination of sulphur caused rather more difficulty. A number of base electrolytes have been suggested in the literature for the conventional polarography of sulphur, *e.g*., pyridine-sodium acetate in acetic acid, pyridinium hydrochloride in methanol, and sulphuric acid in methanol. However, in all of these base electrolytes, using the CRP the wave-form from the sulphur discharge was found to be complex, with several major peaks situated close together. The relative heights of these peaks varied with sulphur concentration and also with the presence or absence of TETDS, although the latter is discharged at a more negative potential. With none of these previously mentioned base electrolytes was it possible to obtain anything approaching a linear current/concentration relationship, at least in the presence of TETDS. The sensitivity was, however, very high, as little as 0·5 ppm of sulphur giving a peak current of the order of 2 μA.

The sharp, wedge-shaped peaks obtained in the above-mentioned base electrolytes suggest that the polarographic current for sulphur using the CRP is considerably modified by an adsorption process. It was thought, therefore, that the addition of a powerful surface-active agent to the base electrolyte might cause a major alteration in the appearance of the wave-form, possibly leading to a reduction in sensitivity of the method, which would be tolerable, but also leading to a simplification of the wave-form, which was the desired effect. When a considerable quantity of cetrimide (a mixture of dodecyl-, tetradecyl- and hexadecyl-trimethylammonium bromides) was incorporated into a pyridine-pyridinium chloride in methanol base electrolyte, only one major peak was in fact observed for sulphur, and it was possible to obtain a reasonably linear current/concentration relationship, although only over a narrow range of sulphur concentration, 0·06–0·60 ppm. However, the sensitivity was enhanced, rather than decreased. The calibration was found to be still a little dependent on the TETDS concentration, but by preparing the calibration graph in the presence of TETDS at about the concentration it would be present in the solution from the sample, the effect was minimised.

RESULTS AND DISCUSSION

It is not possible to ascertain the over-all accuracy of the method as applied to synthetic rubbers, because of the uncertainty in the final amounts of sulphur and TETDS in the dry rubber, even when measured amounts have been added to the lattices. No other methods have been tried for comparison, but it is unlikely that they would give any clearer picture of the accuracy of the polarographic method. However, the reproducibilities of the methods have been determined by calculating the standard deviation of a series of replicates on the same batch of rubber. In this test, 0·5-g samples of the rubber, each cut into 10–15 pieces, were dissolved in 24·5 ml of chloroform by shaking for about 2 hr. The results were as follows:

Tetra-ethylthiuram disulphide (10 determinations): mean = 1·61% w/w,
standard deviation = 0·02;

Elemental sulphur (10 determinations): mean = 0·30% w/w,
standard deviation = 0·01.

EXPERIMENTAL

A solution or extract of the synthetic rubber is prepared using, for example, a 0·5- or 1·0-g sample and ending with a final solution volume of 25 or 50 ml. The solvent used will depend on the synthetic under investigation; we have used both chloroform and an ethyl acetate/isopropanol mixture. The solution should contain 20–1500 ppm of TETDS and 5–150 ppm of sulphur.

Polarograph. K1000 cathode-ray polarograph of Southern Analytical Ltd., Camberley, Surrey, England.

Determination of TETDS

Base electrolyte. A mixture of 30 ml of 95% ethanol, 15 ml of aqueous 1*M* ammonia:1*M* ammonium chloride buffer, and 5 ml of 10% w/v sodium sulphite solution. (This latter solution should be prepared fresh daily).

Procedure. A suitable aliquot (0·05–0·50 ml) of the sample solution is added to 5 ml of partially deoxygenated base electrolyte in the polarographic cell, so that the final concentration is in the range 3–15 ppm of TETDS. The deoxygenation is completed and the peak height of the TETDS wave read off in the usual manner, using the settings: $E_{start} = -0·40$ V versus the SCE, $E_{peak} = -0·63/-0·65$ V. The current may be referred to a calibration graph prepared by adding suitable concentrations of an ethanolic solution of pure TETDS to aliquots of base electrolyte, provided that an internal standard is used at the time of sample measurement and its value compared with the value obtained when the calibration graph was prepared. If the values are not in agreement, the sample current must be suitably adjusted before reading the TETDS concentration from the graph.

Determination of elemental sulphur

Base electrolyte. Dissolve 1 g of cetrimide (Cetavlon) in 50 ml of methanol, add 9·4 ml of analytical reagent grade pyridine and 0·6 ml of concentrated hydrochloric acid.

Procedure. Pipette 5 ml of the base electrolyte into a polarographic cell and start deoxygenation. After about 2 min, introduce a suitable aliquot (0·02–0·05 ml) of sample solution into the base electrolyte. Continue deoxygenation for a further 1–2 min, then read off the peak current at a suitable scale factor, using the instrument setting $E_{start} = -0·3$ V versus the SCE. The peak should appear on the screen at a potential of $-0·15$ to $-0·20$ V. The sulphur concentration may be obtained from a calibration graph, provided that an internal standard is used as mentioned in the TETDS procedure.

A suitable calibration graph may be obtained by weighing out 5·00 mg of micronised sulphur, dissolving in 80 ml of benzene and adjusting to 100 ml in a graduated flask. Aliquots of this solution (0·005–0·05 ml) are added with an Agla micrometer syringe (Burroughs Welcome and Co., London, England) to 5 ml of base electrolyte and the peak currents recorded as in the sample procedure. The peak current of an internal standard should also be recorded on the calibration graph.

Acknowledgements—I should like to thank Mrs. S. Martin and I. Carpenter for carrying out the experimental work and the Directors of The Distillers Company Limited for permission to publish the paper.

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Summary—A cathode-ray polarographic method is described for the determination of free sulphur and tetra-ethylthiuram disulphide in a synthetic rubber extract. The method appears to have a higher sensitivity and better reproducibility than is obtained by conventional polarographic methods, particularly in the case of the thiuram, although the range in which a linear current/concentration relationship is obtained is rather limited.

Zusammenfassung—Bestimmung von Tetraäthylthiuramdisulfid und elementarem Schwefel in organischen Extrakten mit dem Kathodenstrahlpolarographen. Die Arbeit beschreibt eine kathodenstrahlpolarographische Bestimmungsmethode für freien Schwefel und Tetraäthylthiuramdisulfid in einem Extrakt aus synthetischem Gummi. Die Methode ist offenbar empfindlicher und besser reproduzierbar als herkommliche polarographische Methoden, besonders im Falle des Disulfids; allerdings ist der Bereich der linearen Abhängigkeit des Stromes von der Konzentration ziemlich beschränkt.

Résumé—Le mémoire décrit une méthode oscillopolarographique de dosage du soufre libre et du disulfure de tétraéthylthiurame dans un extrait de caoutchouc synthétique. La méthode se révèle être d'une plus grande sensibilité et d'une meilleure reproductibilité que les méthodes polarographiques usuelles, particulièrement dans le cas du thiurame, bien que le domaine dans lequel une relation linéaire courant-concentration est observée soit assez limité.

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Talanta, 1964, Vol. 11, pp. 897 to 899. Pergamon Press Ltd.

LETTERS TO THE EDITOR

Correction for the separation of hydrogen isotopes during distillation in the determination of tritium

SIR:

In the determination of tritium in tritiated water, it is frequently necessary to distil the sample as a purification stage, either to separate from large amounts of interfering ions, or to separate from other β-emitters which would interfere in the liquid β-scintillation counting finish. As is well-known, the concentration of tritium in the distillate will be less than in the residue. For accurate work, it is necessary to correct for this factor. This note shows one of the many ways in which this correction can be calculated, and gives the results in a form which is of immediate use to the analyst.

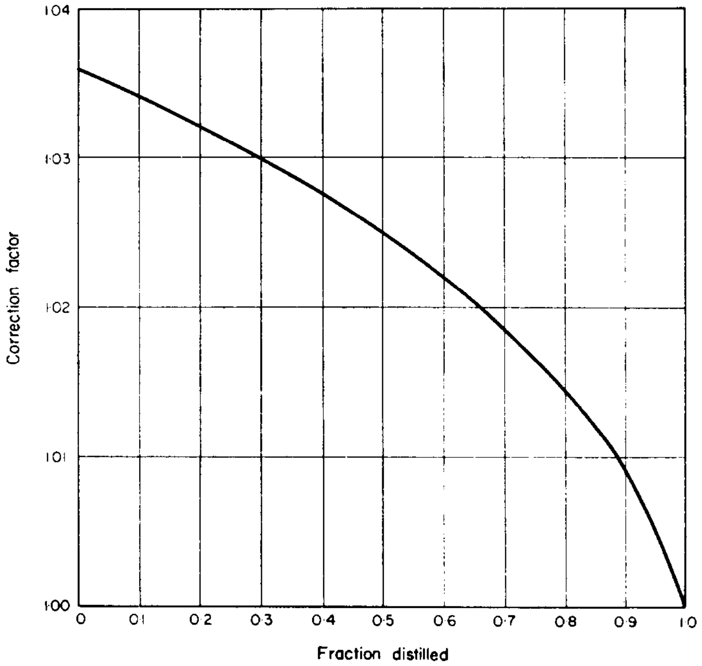

FIG. 1.—Correction factor for depletion of tritium on distillation.

The basis of the calculation is the results of Avinur and Nir;[1] they state that the ratio of the concentration of tritium, in tritiated, water in the liquid phase to that in the vapour phase at equilibrium is 1·036 ± 0.001 at 760 mm pressure.

Consider a weight of tritium, T, in a weight of water, W. T is very small in comparison with W. Distil a weight of water, δW, containing a weight of tritium, δT.

From the information of Avinur and Nir:

$$(T/W) \div (\delta T/\delta W) = 1{\cdot}036$$

$$\delta T/T = \delta W/(1{\cdot}036 W).$$

Integrating,

$$\log T = (\log W/1{\cdot}036) + \log C.$$

Hence

$$\log (T_0/T) = \log (W_0/W) \div 1{\cdot}036$$

or

$$(T_0/T) = (W_0/W)^{\frac{1}{1\cdot036}}.$$

Because W_0, T_0, are the original amounts of water and tritium, and W, T, are the amounts of water and tritium remaining, therefore $(W_0 - W)$, $(T_0 - T)$ are the amounts in the distillate.

One measures, by counting, $(T_0 - T)/(W_0 - W)$, and wishes to know (T_0/W_0).

That is,

$$\frac{(T_0 - T)}{(W_0 - W)} \times F = \frac{T_0}{W_0},$$

where F is a factor which varies with

$$\left(1 - \frac{W}{W_0}\right),$$

the fraction distilled. This factor F has been calculated, and is given in Fig. 1.

The calculation assumes that the distillation is carried out under perfect equilibrium conditions to ensure maximum isotope separation. This, in most cases, is certainly not true, but subsidiary calculations have shown that the graph is reasonably valid for non-equilibrium conditions.

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2 *January* 1964.

C. J. Riley
H. Brooks

REFERENCE

[1] P. Avinur and A. Nir, *Nature*, 1960, **188**, 652.

The photosensitivity of the complex of iron^{III} with 1,10-phenanthroline

SIR:

Photochemical reduction of the iron^{III} complex of α,α-dipyridyl has been known for several years.[1] The corresponding iron^{III} complex with 1,10-phenanthroline might also be expected to be photosensitive. We have now confirmed this fact and used it in the study of some problems in analytical chemistry.

Photoreduction of the iron^{III}-1,10-phenanthroline complex only becomes appreciable at wavelengths shorter than 590 mμ. A very strong development of the red iron^{II}-1,10-phenathroline colour was observed after irradiation by ultraviolet rays. Practically no photoreduction occurs at pH less than 1·4. Above this value the rate increases, becoming constant between pH 4·0 and 6·0. At higher pH a decrease in photoreduction is again observed. Photoreduction is not prevented by the presence of complexing agents, such as citric, tartaric, oxalic, boric, phosphoric, acetic, iminodiacetic and nitriloacetic acids and EDTA. In fact, many of these reagents accelerate the reaction. DCyTA has a strong retarding action and fluoride completely prevents photoreduction.

Traces of iron have been determined in sodium citrate and sodium tartrate by a method based on the above findings. Chemical reduction with hydroxylamine or hydroquinone, as recommended for determination of total iron content using 1,10-phenanthroline,[2] is slow and often incomplete. It can be accelerated photochemically or complete reduction can be achieved photochemically ($>$10 min, 200 W mercury lamp) in the absence of chemical reductants.

In the determination of iron^{II} in haematite with 1,10-phenanthroline, photoreduction of any iron^{III} must be prevented. Elimination of interference from iron^{III} by addition of fluoride[3] is only possible over a very narrow range of pH, which is, moreover, very close to the lower limit of applicability of 1,10-phenathroline. Further, the slight colour from the iron^{III} increases the blank value. Reliable results have now been obtained by dissolving the haematite under non-oxidising

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$$\log T = (\log W/1{\cdot}036) + \log C.$$

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the fraction distilled. This factor F has been calculated, and is given in Fig. 1.

The calculation assumes that the distillation is carried out under perfect equilibrium conditions to ensure maximum isotope separation. This, in most cases, is certainly not true, but subsidiary calculations have shown that the graph is reasonably valid for non-equilibrium conditions.

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17 *January* 1964.

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DETERMINATION OF THE METHYLOL GROUP IN PHENOLIC RESINS

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Summary—An accurate and simple method for determination of the methylol group in phenolic resins is described. The phenolic hydroxyl group is determined by titration with sodium methoxide in non-aqueous solvent, and total hydroxyl group (phenolic hydroxyl plus alcoholic hydroxyl) is found by calculation of the integrated absorption intensity from the infrared spectrum observed between 3600 and 3000 cm^{-1}. The alcoholic hydroxyl group (methylol group) is calculated as the difference between the total and the phenolic hydroxyl group. In contrast to customary techniques, this method is simple, direct and provides a satisfactory precision (± 8%).

INTRODUCTION

SEVERAL techniques have recently been described for determination of the methylol group in phenolic resins, but they have not been found generally satisfactory.

Stenmark and Weiss[1] reported an accurate and simple method for determination of the methylol group in resins. Methylol groups and phenol condense in the presence of acid catalyst to form water which is titrated directly with Karl Fischer reagent. This method provided an accurate value with small samples and thus facilitated experiments on laboratory scale preparations. However, the reaction is slow, requiring as long as 3 hr for completion.

Motoyoshi[2] reported the determination of methylol groups in resins by the following method. The resin, dried in vacuum at 50°, is extracted by methanol, the phenolic hydroxyl group in the extracted resin methylated by methyl iodide-potassium hydroxide solution, and the alcoholic hydroxyl group determined by phthalic anhydride. The precision of this method was not quoted.

Somiya *et al.*[3] measured the infrared spectra of methylol derivatives of phenol, *o*-, *m*- and *p*-cresol, 2,4-dimethylphenol and 2,4-dibromophenol, and determined the intensity of the methylol group absorption at 10 μ by the potassium bromide disc process. They proved that methylol groups in novolaks can be determined with satisfactory precision by their method. However, methylol groups of phenolic alcohols absorb between 9·5 and 10·5 μ and these absorptions are not always constant in position. For this reason, methylol groups of resoles are difficult to determine with sufficient precision.

In this paper, a comparatively accurate, rapid and simple method for the determination of methylol groups in phenol-formaldehyde resins is proposed. Phenolic hydroxyl groups are titrated directly with sodium methoxide, and total hydroxyl group (phenolic hydroxyl group plus alcoholic hydroxyl group) is determined from infrared absorption spectrum between 3600 and 3000 cm^{-1}. The methylol group is calculated as the difference between the total and phenolic hydroxyl groups.

EXPERIMENTAL

Determination of Phenolic Hydroxyl Group

In 1948, Moss, Elliott and Hall[4] pointed out that phenols behave as moderately strong acids in anhydrous ethylenediamine. They were unable to find a satisfactory visual indicator, but carried out potentiometric titrations successfully using sodium aminoethoxide in ethylenediamine-ethanolamine as the titrant.

Fritz and Lisicki[5] titrated phenols potentiometrically in butylamine with sodium methoxide, but found no successful visual indicator. Later, Fritz and Keen[6] reported that phenol and alkyl-substituted phenols were somewhat weaker acids but could be titrated in ethylenediamine using *o*-nitroaniline as the indicator.

In the present work, essentially the same procedure as that of Fritz and Keen was used.

Reagents

Benzene. Extra pure (Kanto Chemical Co., Japan)

Methanol. Extra pure (Kanto Chemical Co., Japan)

Ethylenediamine (anhydrous). Guaranteed reagent (Kanto Chemical Co., Japan)

Phenol samples. Commercial samples (98–100% purity)

Benzyl alcohol. Guaranteed reagent (Daiichi Pure Chemicals Co., Japan)

o-Hydroxybenzyl alcohol (saligenine). Guaranteed reagent (Tokyo Kasei Kogyo Co., Japan)

p-Hydroxybenzyl alcohol. Prepared by hydrogenation of *p*-hydroxybenzaldehyde (Tokyo Kasei Kogyo Co., Japan) and recrystallised from water, m.p. 123°

p-Cresol dialcohol. Prepared by Auwer's Method,[9] m.p. 128·5°

o-Cresol dialcohol. Prepared by Hanus's Method,[10] m.p. 92·5°

o-Nitroaniline. Guaranteed reagent, 0·15 g dissolved in 100 ml of benzene.

Benzoic acid. Guaranteed reagent (Kanto Chemical Co., Japan)

Sodium methoxide (0·1–0·2 *M*). About 0·6 g of freshly cut sodium metal is added to 10 ml of methanol in a loosely covered flask. When the reaction is complete, 15 ml of methanol and 150 ml of benzene are added with stirring until the solution becomes homogeneous and clear. This is stored in a glass bottle protected from moisture and carbon dioxide. The titrant solution is standardised against benzoic acid.

Apparatus

The titration assembly consists of a 10-ml burette, a 50 to 100-ml titration vessel (covered to prevent absorption of carbon dioxide from the air), and a magnetic stirrer (equipped with a small stirring bar sealed in glass).

Procedure

About 25 ml of ethylenediamine, with 3–4 drops of *o*-nitroaniline as the indicator, is titrated with sodium methoxide to a red colour. The neutralised solvent is combined with the sample solution and titrated with sodium methoxide, the end-point being the change from clear yellow to orange-red. The weight of sample taken is so selected that 1–5 ml of the methoxide will be consumed.

Determination of Phenolic and Alcoholic Hydroxyl Group

From infrared studies on the association of phenol with several ketones Widom *et al.*[7] reported that the phenol-acetone complex has a great association effect. In general,[8] the intensity is greatly increased in solvents in which the association effect occurs.

In the present work, acetone was used as a solvent that not only dissolves phenols and resins but also increases the association effect, and the total hydroxyl group (phenolic hydroxyl plus alcoholic hydroxyl) was determined quantitatively by infrared absorption spectra between 3600 and 3000 cm^{-1}.

Reagents

Acetone. Extra pure (Kanto Chemical Co., Japan) distilled in an all-glass apparatus from phosphorus pentoxide immediately before use.

Phenols and phenolic alcohols. As above.

Apparatus

The absorption was measured using a Nihon Bunko Model 301 infrared spectrophotometer. Two 0·100-mm cells having sodium chloride plates were used.

Procedure

In actual measurements, a solution in which 5–30 mg of sample is dissolved in 1 ml of acetone is placed in the sample beam and acetone in the reference beam of the instrument. Examples of the spectra obtained are given for the phenol-acetone solution in Fig. 1.

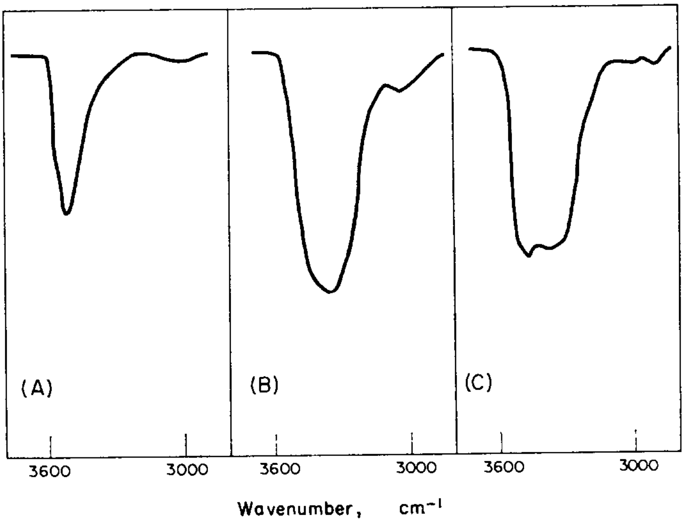

FIG. 1.—Infrared spectra of samples:
(A) benzyl alcohol,
(B) phenol,
(C) *p*-methylol phenol.

Because the phenolic and alcoholic hydroxyl absorptions occur at somewhat different wavelengths, integrated absorption intensities were calculated by dividing the range 3000 to 3600 cm^{-1} into fifteen equal parts using the following equation

$$A = 1/c, l \left(\sum_{n=1}^{15} \log (To/T)\, \Delta\nu \right)$$

where c is the concentration (mole/l.), l is the cell length (cm) and $\Delta\nu$ is the width of each part (40 cm^{-1}).

Determination of Methylol Group

The methylol content (mole/g) of the samples was calculated from the expression

$$\frac{A' - B \times D}{C}$$

where A′ = the integrated absorption intensity of total hydroxyl group/g (1/g. cm^2),
B = the mean integrated absorption intensity of phenolic hydroxyl group/molecule (1/mole. cm^2),
C = the mean integrated absorption intensity of alcoholic hydroxyl group/molecule (1/mole. cm^2),
D = phenolic hydroxyl group (mole/g).

RESULTS AND DISCUSSION

Data for determination of phenolic hydroxyl groups are given in Table I.

TABLE I.—TITRATION OF PHENOLS IN ETHYLENEDIAMINE
(Indicator: *o*-nitroaniline)

Compound	Taken, *mg*	MeONa, *ml*	MeONa, *M*	Found, %
Phenol	53·98	4·79	0·1206	100·5
o-Hydroxybenzyl alcohol	20·36	1·23	0·1331	100·0
p-Hydroxybenzyl alcohol	28·18	1·81	0·1231	97·5
p-Cresol dialcohol	23·33	1·23	0·1124	100·0
o-Cresol dialcohol	22·97	1·22	0·1124	98·5
2,6-Xylenol	40·19	2·91	0·1124	99·5
Phenol + benzyl alcohol	36·16 37·94	3·12	0·1212	98·5
Phenol + water	54·73 14·25	4·78	0·1218	100·0

This method gave satisfactory results for the titration of this type of phenolic hydroxyl group. The precision was within ±1 % and the bias was not significant. However, this method possessed the defect that high molecular weight substances precipitated in the course of titration, obscuring the end-point. The presence of a small amount of water in the sample did not interfere.

The integrated absorption intensities of phenols and phenolic alcohols are given in Table II. The intensity of aromatic CH was neglected because it was less than 1 % of the intensity of phenolic hydroxyl group in the samples.

TABLE II.—INTEGRATED ABSORPTION INTENSITY OF PHENOLIC AND ALCOHOLIC HYDROXYL GROUPS

Compound	Integrated absorption intensity, $\times 10^4$ litre. mole^{-1}. cm^{-2}
Phenol	3·35
o-Cresol	3·37
p-Cresol	3·34
2,4-Xylenol	3·35
2,6-Xylenol	2·37
Benzyl alcohol	1·35
o-Hydroxybenzyl alcohol	4·69
p-Hydroxybenzyl alcohol	4·62
o-Cresol dialcohol	5·66
p-Cresol dialcohol	6·10

The data were arranged by least squares, supposing that the following equation was applicable to them

$$A_{\mathrm{total}} = \mathrm{m}B + \mathrm{n}C$$

where A_{total} is the integrated absorption intensity of total hydroxyl/mole, B and C are as before, m is the number of phenolic hydroxyl groups/molecule, and n is the number of alcoholic hydroxyl groups/molecule.

The results were as follows: $B = 3{\cdot}35 \times 10^4$, $C = 1{\cdot}29 \times 10^4$, standard deviation $\sigma = 0{\cdot}11 \times 10^4$.

Because the hydroxyl absorption of water and alcohol occurs in the same region, the presence of small amounts of water and alcohol in the sample interferes. While the presence of lower polyoxymethylene glycols (formaldehyde polymers) is to be avoided, small amounts do not interfere.

Data of determination of methylol groups in phenolic alcohols are shown in Table III.

The precision of the method is about 8 %, with a daily error of determination of about 4 %. This is considered to be satisfactory.

Analysis of Phenol-Formaldehyde Resins

The method was applied to three phenolic resins of the resol type with the results shown in Table IV. These resins were prepared with varied concentrations of formaldehyde under alkaline conditions and were freeze-dried two or three times from benzene–methanol to eliminate water.

TABLE III.—DETERMINATION OF METHYLOL GROUPS IN PHENOLIC ALCOHOL

Compound	A′, l/g. cm^2	D, × 10^{-3} mole/g	Alcoholic OH, × 10^{-3} mole/g	
			Found	Theoretical
o-Hydroxybenzyl alcohol	378	8·01	8·5	8·1
p-Hydroxybenzyl alcohol	372	7·87	8·4	8·1
o-Cresol dialcohol	362	5·95	10·7	11·9
p-Cresol dialcohol	337	5·85	12·9	11·9

TABLE IV.—DETERMINATION OF METHYLOL GROUPS IN PHENOLIC RESINS

Resin	A′, l/g. cm^2	D, × 10^{-3} mole/g	Alcoholic OH, × 10^{-3} mole/g
1	351	7·13	8·7
2	321	5·98	9·4
3	385	5·44	15·7

The methylol content was determined under the conditions outlined above; satisfactory results were obtained.

Acknowledgement—The authors thank Professor H. Kamada of Tokyo University for advice and Vice-President T. Kikuchi of Fudow Chemical Company for permission to publish this paper.

Zusammenfassung—Eine genaue und einfache Methode zur Bestimmung der Methylolgruppe in Phenolharzen wird beschrieben. Die phenolische Hydroxylgruppe wird durch Titration mit Natriummethylat in einem nichtwäßrigen Lösungsmittel bestimmt, die Gesamtmenge an OH-Gruppen (phenolische und alkoholische) findet man aus der integrierten Absorptionsintensität im Infrarotspektrum zwischen 3600 und 3000 cm^{-1}. Der Gehalt an alkoholischen (Methylol-) Hydroxylgruppen wird als Differenz zwischen Gesamt- und phenolischen Hydroxylgruppen berechnet. Im Gegensatz zu herkömmlichen Vorschriften ist die Methode einfach und direkt und liefert zufriedens tellende Genauigkeit (±8%).

Résumé—On décrit une méthode précise et simple de sodage du groupe méthylol dans les résines phénoliques. Le groupe hydroxyle phénolique est dosé volumé-triquement au moyen de méthylate de sodium en solvant non aqueux, et l'hydroxyle total (hydroxyle phénolique plus hydroxyle alcoolique) est trouvé par calcul de l'intensité d'absorption intégrée à partir du spectre infra-rouge observé entre 3600 et 3000 cm^{-1}. Le groupe hydroxyle alcoolique (groupe méthylol) est calculé en tant que différence entre l'hydroxyle total et l'hydroxyle phénolique. Par opposition à la technique usuelle, cette méthode est simple, direct, et fournit une précision satisfaisante (±8%).

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PAPER CHROMATOGRAPHY IN INORGANIC QUALITATIVE ANALYSIS

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Summary—A two-dimensional paper chromatographic method for the separation and identification of several metal ions is described. After preparation, the sample is run with an ethanol:hydrochloric acid:water (75 : 20 : 5) mixture, and later in a second dimension with a tetrahydrofuran: nitric acid: water (85: 5: 10) mixture. The chromatogram can be developed with a 0·2% ethanolic solution of Morin, and is examined both in sunlight and in ultraviolet light, in acidic conditions and after alkalisation with ammonia vapour. Those metal ions which migrate together in the first solvent will be separated in the second one, and can be identified reliably. The composition of the original sample can be deduced from the R_f values, colours and fluorescences of the various spots.

IN a previous paper a general method for orientative qualitative analysis has been described.[1] This was not suitable for the simultaneous detection of the following combinations: Zr-Th, Sc-Al, Co-V-Ti, Cu-U, Bi-Pd, Zn, and Sn. A further development of the method, by which any of these ions in admixture can be detected reliably, is based on the use of a solvent in a second dimension, with an appreciably lower dielectric constant than the first. Tetrahydrofuran (THF) was found to be suitable. THF has already been used chromatographically by Specker and Hartkamp.[2]

Pure THF is generally unsuitable as a chromatographic solvent, because the cations, used in the form of chlorides, sulphates or nitrates, remain at the starting point of the chromatogram. If, however, inorganic acids and water are added to the solvent, migration of the ions takes place. To find the optimal composition of the solvent mixture, thorium and zirconium, which generally show a marked difference in behaviour in this type of chromatography, were examined. If the amount of electrolyte in the solvent is increased, thorium migrates with the front, and even zirconium moves from the origin. Both ions, however, form extended spots. If the composition of the solvent is within the limits by volume of 80–85% of THF, 5–10% of nitric acid and 10–15% of water, thorium migrates exactly along with the front. In those cases where the solvent forms two fronts in the chromatographic process, thorium is found in the second front. Zirconium migrates only slightly, and although its spot may extend up to an R_f value of 0·5, it can be reliably distinguished from thorium. In addition, other metal ions, which cannot be separated with an ethanol-hydrochloric acid solvent, are separated with this solvent to such an extent that individual qualitative test can be carried out without difficulty.

Specker and Hartkamp[2] investigated the dependence of R_f values of cations on the composition of solvent mixtures. Burstall and co-workers[3] separated thorium from rare earths with 2-methyltetrahydrofuran (tetrahydrosylvan), containing 10%

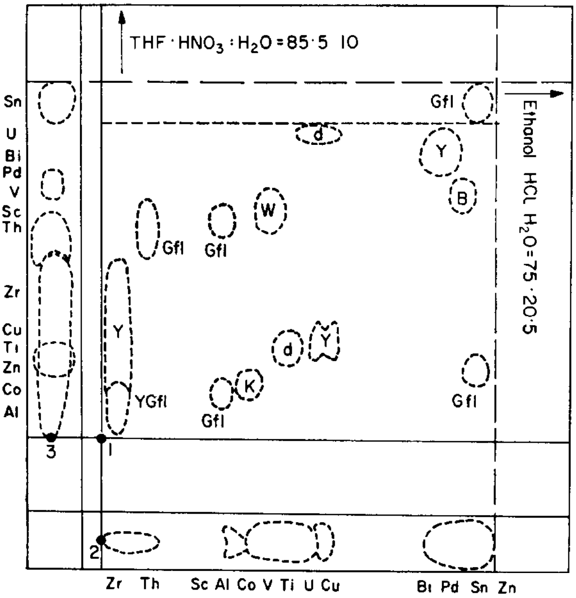

FIG. 1

by volume of nitric acid and 5% of water. For the present purpose a mixture of THF: nitric acid:water (85:5:10) is the most suitable one. Using this solvent in a second dimension, after a run with a hydrochloric acid-ethanol solvent, and drying, all those ions which were not separated by the first solvent will form clearly discernable spots in the chromatogram.

TABLE I.—R_f VALUES IN THE SOLVENT THF:HNO_3:H_2O (85:5:10)

Element	R_f value
Zr	Yellow strip extending from the origin to approximately R_f 0·5: green fluorescence at the origin.
Th	In Front 2 (R_f value in relation to Front is 1:0:9)
Al	0·14
Sc	0·65
Co	0·14
V	0·65
Ti	0·23
U	In Front 2 (R_f related to Front is 1:0:9)
Cu	0·25
Bi	0·88
Pd	0·72
Zn	0·20
Sn	0·94

If, after drying, the chromatogram is sprayed with a 0·2% ethanolic solution of Morin, the spots will appear as indicated in Fig. 1. The R_f values in the solvent mixture of the pairs and the triplet are presented in Table I.

In Table I the R_f values are related to the first Front. The distance of the two Fronts, if the first Front has migrated approximately 20 cm from the origin, is about 20 mm; the R_f value of the second Front therefore is about 0·90.

EXPERIMENTAL

Reagents

Tetrahydrofuran (THF): Puriss

Ethanol: 96%

Hydrochloric acid: S.g. = 1·19

Nitric acid: S.g. = 1·42

Morin (3,5,7,2′,4′-pentahydroxyflavone): 0·2% in ethanol

*Solvent I (ethanol:*HCl:H_2O = 75:20:5): Mix 5 ml of water with 20 ml of concentrated hydrochloric acid, and pour this solution into 75 ml of ethanol.

Solvent II (THF:HNO_3:H_2O = 85:5:10): Mix 5 ml of concentrated nitric acid with 10 ml of water and pour this with constant stirring into 85 ml of THF.

Paper: Schleicher and Schull No. 2043/A, size 58 × 60 cm.

Procedure

Prepare the solution to be analysed, using the procedure described elsewhere,[1] by boiling with H_2O_2 and HCl. Place a drop of the solution on a 29 × 30 cm (quarter) sheet of Schleicher-Schüll No. 2043/A paper. The origin must be chosen as follows (see Fig. 2). First draw two base-lines at right angles to each other, 30 mm from the original (machine-cut) edges of the paper. These lines act as the boundaries of the two test-strips which will later be cut from the chromatogram. Now ascertain the direction of the fibres of the paper; they appear in normal cases to be parallel to the longer side. Draw two starting lines at distances of 10 and 30 mm from the base-lines, one parallel and one perpendicular to the fibres. The origin is the point of intersection of these last lines (Point 1 on Fig. 2). Place a further drop of the sample at Point 2 (15 mm from the edge of the paper). Dip the paper, at right angles to the fibres, in Solvent I, and let the solvent run overnight, using ascending technique. During this time the front travels about 20 cm from the start. Dry the chromatogram under an infrared lamp, and remove traces of hydrochloric acid as completely as possible by an air stream. Cut off the 30-mm test strip (which is parallel to the shorter edge of the paper), and store for further experiments (Test strip of Solvent I).

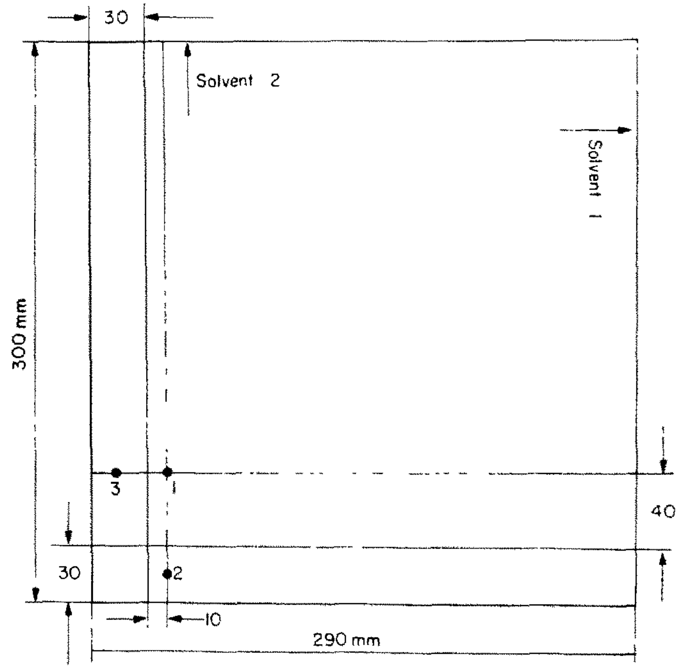

FIG. 2

Place a further drop of the original solution on Point 3 (see Fig. 3), 40 mm from the freshly-cut edge and 15 mm from the original edge of the paper. (Test strip of Solvent II). Dip the freshly-cut edge of the paper in Solvent II and let the solvent run for 4–5 hr, during which time the front migrates about 20 cm from the start. (This distance can be marked on the paper previously.) Dry the paper, remove the traces of nitric acid by an air stream, and spray the paper with a 0·2% ethanolic Morin solution.

Examine the paper in sunlight, and in transparent and reflected ultraviolet light. Mark the coloured spots and the green or yellow fluorescent ones on one side of the paper. Hold the paper over ammonia vapour and examine once more. Mark any spots on the other side of the paper. This examination shows whether spots corresponding to ions which are not separated by Solvent I contain one or more components. R_f values for Solvent II are presented in Table I, and a typical chromatogram is shown in Fig. 1. The notations are those used in an earlier paper.[1]

It is very important to remove hydrochloric acid as completely as possible from the paper after the first run by thorough drying and ventilation. Otherwise the formation of the thorium-nitrate complex (which is soluble in THF) will not be achieved. If it is not, thorium shows an R_f value of about 0·5–0·6. If the chromatographic separation is interrupted after the run with Solvent I, and the dry paper is placed over ammonia vapour, thorium will then have an R_f value higher than 0·5 in Solvent II, but it does not reach the second front. It can still, however, be reliably identified in the presence of zirconium. If only THF is used, thorium migrates along with the second Front. The R_f values for the other metal ions are not affected by previous treatment with the hydrochloric acid solvent, and therefore the same results will be obtained if only Solvent II is used for the chromatographic separation. Uranium, as opposed to thorium, will be found in either case in the second Front.

There are difficulties in identifying those ions which have high R_f values in both solvent systems (0·9 to 1·0); these will be concentrated on the diagonally opposite corner of the chromatogram from the origin. The difficulties occur because impurities dissolved from the paper (particularly iron) are concentrated on this part of the chromatogram, and the resulting dark spot will hide the spots being sought, both in sunlight and in ultraviolet radiation. However, most of these ions, *e.g.*, antimony, tin and gallium, can be identified easily in Solvent I, and of the unresolved zinc-tin pair, zinc migrates more slowly in Solvent II than does tin.

Sensitivities for the qualitative tests on the single ions are about the same as described previously;[1] if the ions are in mixtures, the sensitivities are generally lower by 1–2 magnitudes. Morin is not a very sensitive reagent for most of the metal ions. The sensitivities can be increased as follows: examine the chromatogram after the run with Solvent I, and then from the information gained in this way, apply specific reagents, after the run with Solvent II, on the spots in which any given ion is suspected.

Acknowledgement—The authors wish to express their thanks to Prof. B. Lengyel, Head of the Research Group, for having kindly permitted this work to be carried out in his Institute.

Zusammenfassung—Eine zweidimensionale papierchromatographische Methode zur Trennung und Identifikation mehrerer Metallionen wird vorgeschlagen. Nach geeigneter Vorbereitung lässt man die Probe mit einem Äthanol-Salzsäure-Wasser-Gemisch 75:20:5 laufen, anschliessend in der zweiten Dimension mit Tetrahydrofuran-Salpetersäure-Wasser 85:5:10. Das Chromatogramm kann mit einer 0·2% igen alkoholischen Morinlösung entwickelt werden und wird im Tageslicht und unter einer Ultraviolettlampe betrachtet, sowohl im sauren Zustand als auch nach Behandlung mit Ammoniakgas. Die Metallionen, die im ersten Laufmittel zusammen wandern, werden im zweiten getrennt und können zuverlässig identifiziert werden. Die Zusammensetzung der Probe kann aus R_f-Wert, Farbe und Fluoreszenz der einzelnen Flecke ermittelt werden.

Résumé—On présente une méthode de chromatographie sur papier à deux dimensions pour séparer et identifier plusieurs ions métalliques. Après une préparation convenable, l'échantillon est entraîné par un mélange éthanol—acide chlorhydrique—eau (75:20:5) puis, dans la seconde dimension, par un mélange tétrahydrofuran—acide nitrique—eau (85:5:10). Le chromatogramme peut être révélé par une solution alcoolique a 0·2% de morin, et doit être examiné à la lumière solaire et en lumière ultra-violette, tant à l'état acide qu'après alcalinisation aux vapeurs d'ammoniac. Les ions métalliques qui migrent ensemble dans le premier solvant seront séparés dans le second, et peuvent être identifiés de facon certaine. One peut estimer la composition de l'échantillon original à partir des valeurs des R_f, des couleurs et de la fluorescence des diverses taches.

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THERMOANALYTICAL PROPERTIES OF ANALYTICAL-GRADE REAGENTS

AMMONIUM SALTS

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Summary—Twenty-six ammonium salts have been investigated derivatographically. The weight change, rate of weight change and enthalpy change of the salts have been measured as a function of temperature. From the results the temperatures at which the salts may be dried without decomposition are given.

DUVAL and his coworkers[1] studied nearly one thousand analytical precipitates by the method of thermal gravimetry. The intention was to establish the temperature at which the analytical precipitate is of stoichiometric composition and the temperature interval over which the precipitate is suitable for weighing. Berg[2] and Smothers and Chiang[3] introduced the method of differential thermal analysis in their books and treated in detail its most important fields of application. Few workers have used the two methods in conjunction with each other. Erdey, Paulik and Paulik combined the methods of thermal gravimetry (TG) and differential thermal analysis (DTA) with the method of derivative thermal gravimetry (DTG) elaborated by themselves.[4] TG, DTA and DTG curves were recorded automatically on an apparatus designated a derivatograph.[5,6] The derivatograph can measure simultaneously, for a single sample, change of weight (TG), rate of change of weight (DTA) and enthalpy change (DTG), as a function of temperature, at a heating rate of 1–20°/min.

Twenty-six ammonium salts have now been investigated derivatographically (Table I). We have attempted to explain the results in terms of the Lewis electron theory previously applied to acid-base reactions.[7,8] The various decomposition processes can be interpreted satisfactorily on the basis of the derivatograms. Where intermediate plateaux occur on the TG curves, they correspond to the formation of definite compounds, the formulae of which have been marked on the appropriate figures. Experimental weight losses agree well in most cases with the theoretical losses expected for the formation of such compounds. In those cases where agreement was not so good, the deviation could be attributed to two processes occurring at about the same temperature. Not all of the decomposition products were examined.

EXPERIMENTAL

The studies were carried out using a Paulik-Paulik-Erdey type 676 derivatograph manufactured by Orion-Gyem, Budapest, Hungary. The sample (100–200 mg) was weighed in the platinum crucible of the instrument. Gaseous decomposition products were pumped off from the air space of the furnace. A heating rate of 5°/min was employed. Samples were pulverised in a porcelain mortar and passed through a sieve of the same mesh-size in every case before being weighed.

The reagents used in the experiments were made available to us by E. Merck (Darmstadt, Germany), for which we would like to express our thanks.

TABLE I

Figure	Ammonium salt	Formula	DTA peaks, °C	DTG peaks, °C	Temperature of drying,[a] °C
1	Fluoride	NH_4F	Endothermic: 145, 220	145, 225	<50
2	Hydrogen fluoride	$NH_4F.HF$	Endothermic: 125, 240	235	<60
3	Chloride	NH_4Cl	Endothermic: 185, 345	345	110–120
4	Bromide	NH_4Br	Endothermic: 150, 415	410	<200
5	Iodide	NH_4I	Endothermic: 390	400	<200[b]
6	Perchlorate	NH_4ClO_4	Endothermic: 250; exothermic: 400	400	<200[c]
7	Sulphate	$(NH_4)_2SO_4$	Endothermic: 330, 410	410	<200
8	Thiosulphate	$(NH_4)_2S_2O_3$	Endothermic: 140, 225, 400; exothermic: 350	220, 245, 350, 400	<80
9	Persulphate	$(NH_4)_2S_2O_8$	Endothermic: 370; exothermic: 170	180, 365	<100[c]
10	Thiocyanate	NH_4SCN	Endothermic: 90, 115, 150, 245; exothermic: 525	245, 290, 515	<100[c]
11	Nitrate	NH_4NO_3	Endothermic: 45, 84, 130, 166; exothermic: 285	285	100–110
12	Molybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	Endothermic: 120, 235, 350	110, 230, 350	<100
13	Metavanadate	NH_4VO_3	Endothermic: 240, 375	230, 375	<100
14	Monohydrogen phosphate	$(NH_4)_2HPO_4$	Endothermic: 170; exothermic: 280	150, 170, 260, 760	<100
15	Dihydrogen phosphate	$NH_4H_2PO_4$	Endothermic: 200	230, 730	<150
16	Chromate	$(NH_4)_2CrO_4$	Endothermic: 130; exothermic: 245, 405	125, 236, 405	<40
17	Dichromate	$(NH_4)_2Cr_2O_7$	exothermic: 230, 390	230, 395	<200
18	Pentaborate	$NH_4B_5O_8.4H_2O$	Endothermic: 160, 280, 400	160, 280, 400, 430	—
19	Sulphamate	$NH_4SO_3NH_2$	Endothermic: 135, 475	225, 290, 465	
20	Carbonate	$(NH_4)_2CO_3$	Endothermic: 80	75	—
21	Acetate	NH_4OOCCH_3	Endothermic: 100, 115, 155	150	30–40
22	Oxalate	$(NH_4)_2(COO)_2.H_2O$	Endothermic: 115, 235	115, 235, 300	<150[d]
23	Citrate	$(NH_4)_2C_6H_6O_7$	Endothermic: 195	195	<100
24	Benzoate	$NH_4C_7H_5O_2$	Endothermic: 195, 250	235	<50
25	Salicylate	$NH_4C_7H_5O_3$	Endothermic: 200	190	<100
26	Tartrate	$(NH_4)_2C_4H_4O_6$	Endothermic: 185, 245	180, 245	<100

[a] Without decomposition.

[b] Sample is hygroscopic.

[c] If pure.

[d] This temperature is for anhydrous ammonium oxalate. The monohydrate can be dried at 30–40°.

RESULTS AND DISCUSSION

Ammonium fluoride

It can be seen from the derivatogram (Fig. 1) that the mechanically bound water content of the sample is lost at about 50°. The peak on the DTA and DTG curves at 145° indicates a maximal rate of removal of ammonia according to

$$2NH_4F \rightarrow NH_4F.HF + NH_3.$$

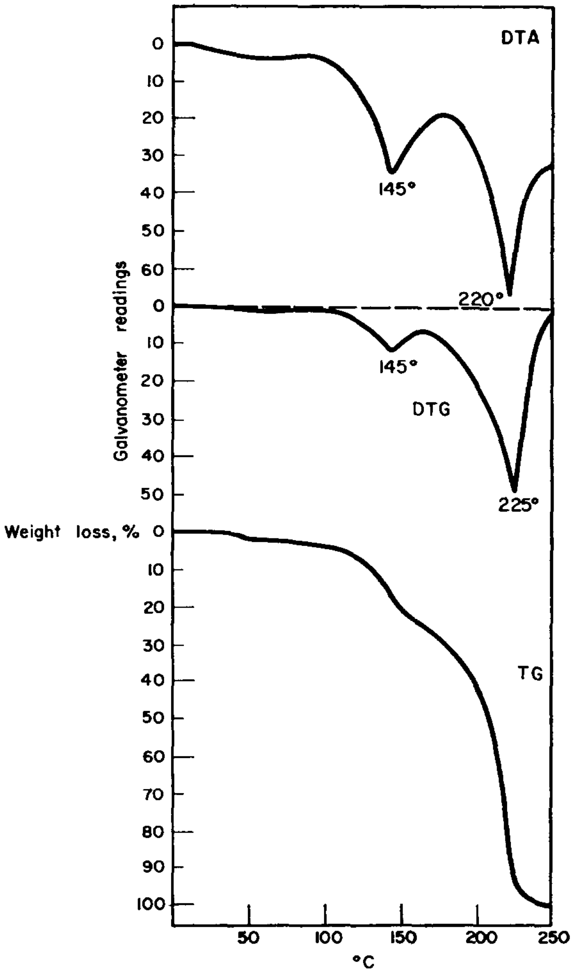


FIG. 1.—Ammonium fluoride.

The ammonium hydrogen fluoride formed begins to decompose to a small degree at this temperature. This decomposition proceeds at a maximal rate at 225°, ammonia and hydrogen fluoride being obtained.

Ammonium hydrogen fluoride

The sample melts at 125° (DTA curve in Fig. 2). The rate of decomposition—beginning at 80°—increases and the rate of weight decrease is maximal at 235°. Ammonium hydrogen fluoride is more stable than the neutral salt.

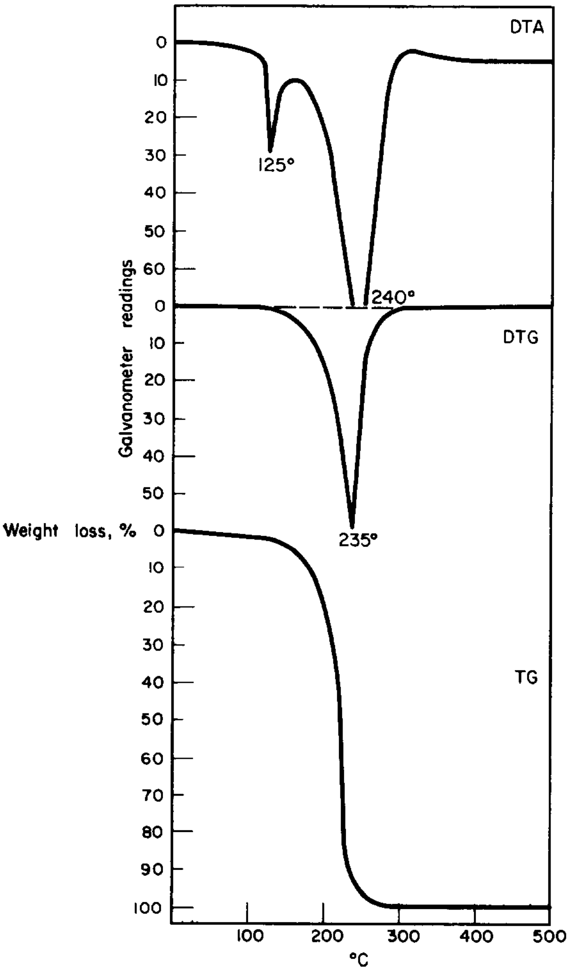


FIG. 2.—Ammonium hydrogen fluoride.

Ammonium chloride

Ammonium chloride shows little change in weight up to 200° (Fig. 3). The endothermic DTA peak at 185° indicates a change of crystal structure of ammonium chloride. Above 200° the substance sublimes, the sublimation rate being maximal at 345°. After sublimation it dissociates completely in the gaseous phase into ammonia and hydrochloric acid

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

On cooling, the reaction is reversed and ammonium chloride condenses from the gaseous phase.

Hydrochloric acid formed during the decomposition is very active and reacts with various metal oxides or carbonates at a temperature above 300° to form chlorides, water and carbon dioxide. Thus, aluminium oxide can be fused in this way.

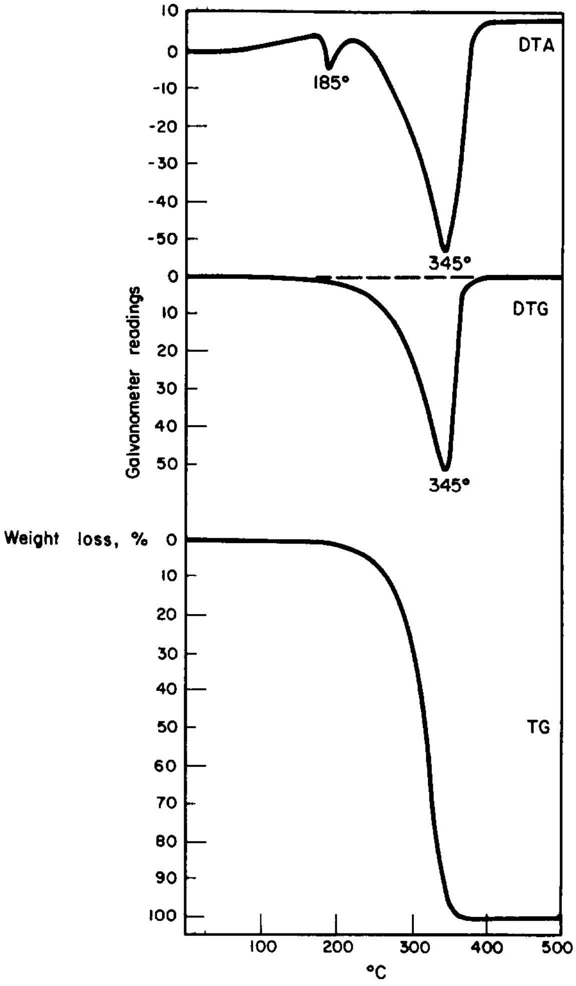


FIG. 3.—Ammonium chloride.

Ammonium bromide

Ammonium bromide shows a change in crystal structure at 150° (DTA curve in Fig. 4). Decomposition only begins to any marked extent above 250°. The salt does not melt at atmospheric pressure, but sublimes and decomposes completely in the gaseous phase to form ammonia and hydrogen bromide

$$NH_4Br \rightleftharpoons NH_3 + HBr$$

On cooling, ammonium bromide condenses, *i.e.*, the reaction is reversible. Sublimation proceeds at the highest rate at 410°.

Ammonium iodide

Sublimation of ammonium iodide proceeds over nearly the same temperature interval as that of ammonium bromide (Fig. 5). Also, the ammonium iodide sublimes and decomposes in the gaseous phase to ammonia and hydrogen iodide

$$NH_4I \rightleftharpoons NH_3 + HI.$$

On cooling, ammonium iodide condenses.

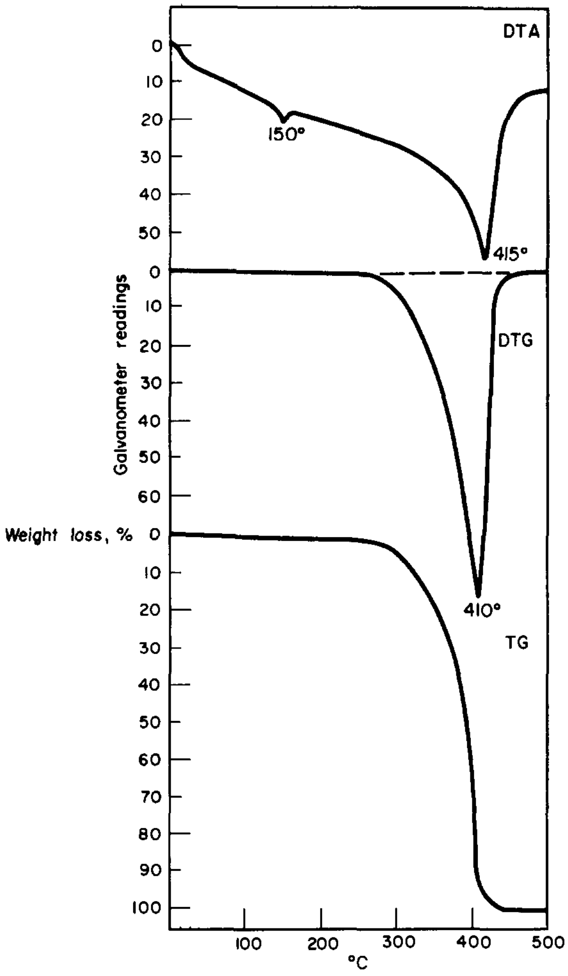


FIG. 4.—Ammonium bromide.

Ammonium perchlorate

An endothermic process can be observed on the DTA curve at 250° (Fig. 6), which accompanies a change in crystal structure of the ammonium perchlorate. Thereafter a decrease of weight begins. This decrease of weight is caused by decomposition and sublimation of the salt. Decomposition begins at a much lower temperature if there are small amounts of metal oxide or organic substance contamination. The sample studied is of analytical-grade material and is, therefore, very stable. The decomposition beginning above 250° is an exothermic process, as shown by the DTA peak at 400°. As the temperature of the sample reaches 400° decomposition proceeds explosively.

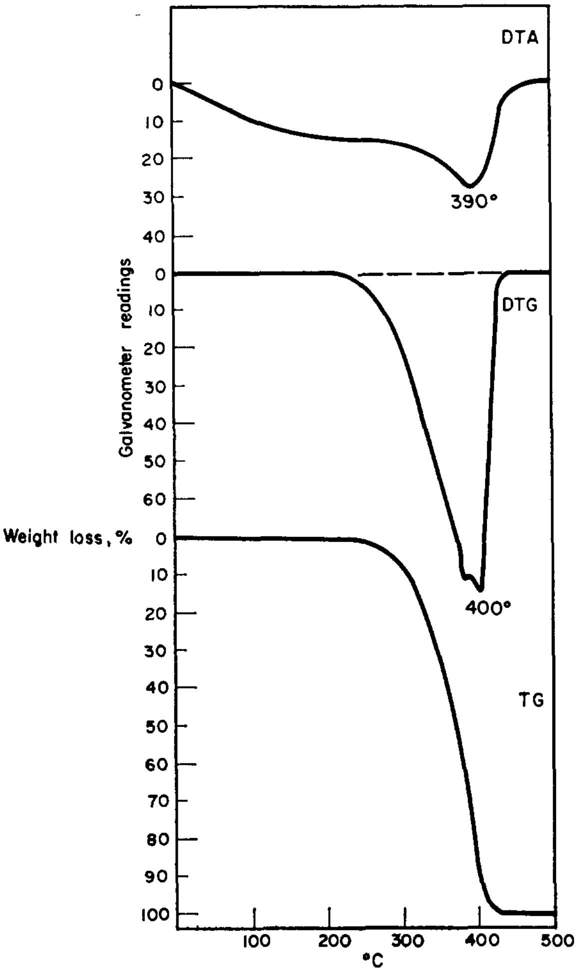


FIG. 5.—Ammonium iodide.

In the gaseous phase quite different reaction products are present depending on the temperature of decomposition. Below 300°, the reaction products are gaseous nitrogen, oxygen, chlorine and water vapour. Above 300°, various nitrogen oxides are also present besides gaseous nitrogen

$$2NH_4ClO_4 \rightarrow 2NO + O_2 + Cl_2 + 4H_2O.$$

At the temperature of the reaction the nitrogen monoxide reacts with oxygen and chlorine to form nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3) and nitrosyl chloride (NOCl). The temperature of decomposition and composition of decomposition products varies according to the nature and amount of contaminants.

Ammonium sulphate

The ammonium sulphate sample contains neither mechanically bound nor water of crystallisation. The substance begins to decompose above 250° (Fig. 7). In the

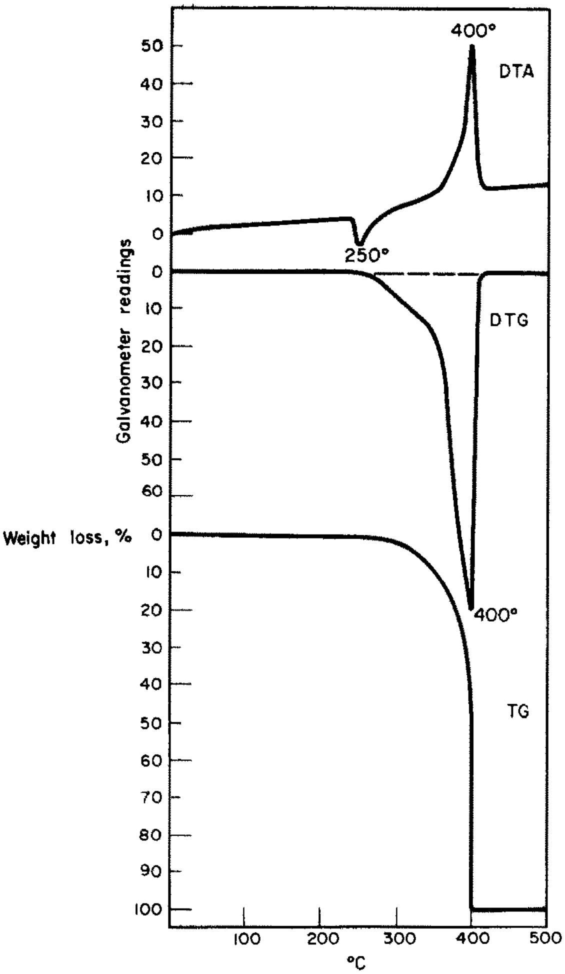


FIG. 6.—Ammonium perchlorate.

first step of the decomposition the molecule loses ammonia and ammonium hydrogen sulphate is formed

$$(NH_4)_2SO_4 \xrightarrow{230\text{-}350^\circ} NH_4HSO_4 + NH_3.$$

This reaction seems to be quantitative according to the derivatogram. The reaction is indicated by the endothermic DTA peak at 330°. Ammonium sulphate itself does not melt, although the ammonium hydrogen sulphate formed during the decomposition does. The ammonium hydrogen sulphate decomposes at 410° at a maximal rate and the process is completed at 450°

$$NH_4HSO_4 \xrightarrow{350\text{-}450^\circ} NH_3 + H_2SO_4.$$

Sulphuric acid formed during the decomposition is very active and fuses various metal oxides.

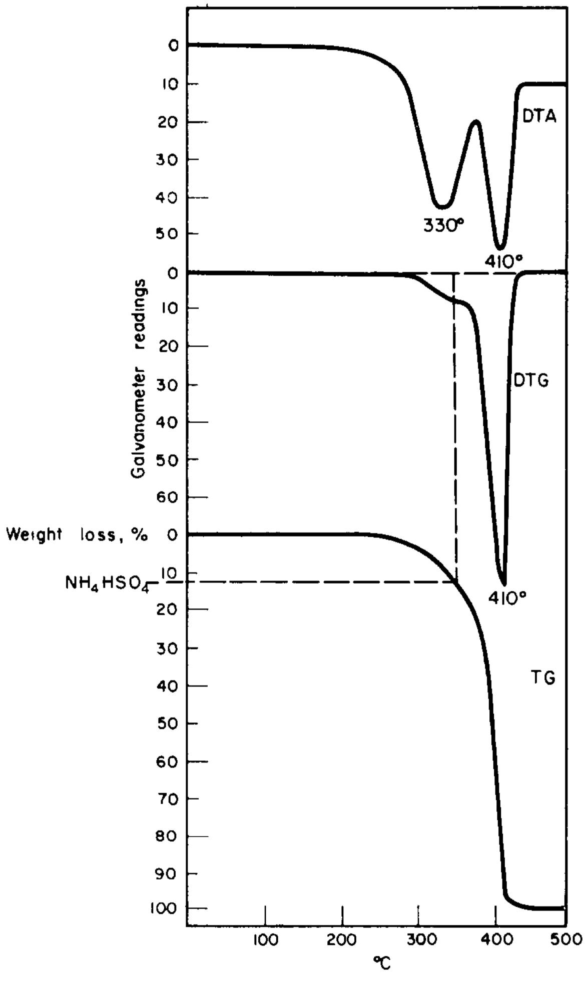


Fig. 7.—Ammonium sulphate.

Ammonium thiosulphate

The thermal decomposition of ammonium thiosulphate is complicated (Fig. 8). Up to 100° neither weight nor enthalpy change can be observed. The endothermic DTA peak at 140° indicates a change of crystal structure. Above 100° decomposition begins, ammonium sulphite and sulphur being formed

$$(NH_4)_2S_2O_3 \xrightarrow{>100^\circ} (NH_4)_2SO_3 + S.$$

Part of the ammonium sulphite immediately decomposes, the maximal rate being at 230–245°

$$(NH_4)_2SO_3 \rightarrow 2NH_3 + SO_2 + H_2O.$$

The rest of the ammonium sulphite is oxidised to ammonium sulphate. The net effect of the enthalpy changes of the two processes is endothermic. Above 275° the sulphur burns exothermically and ammonium hydrogen sulphate is formed from the ammonium sulphate. Above 360° the ammonium hydrogen sulphate decomposes, the rate being maximal at 400°.

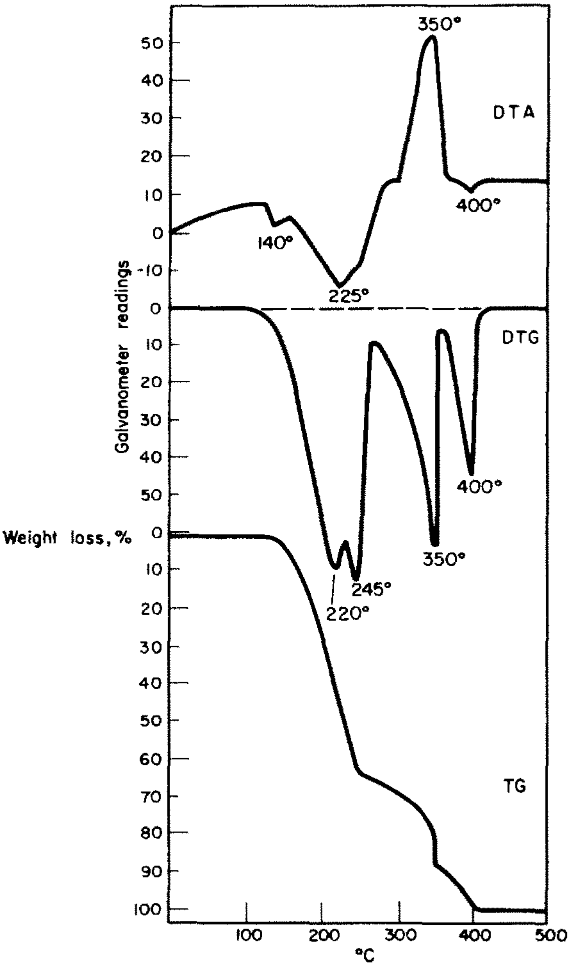


FIG. 8.—Ammonium thiosulphate.

Ammonium persulphate

Pure ammonium persulphate decomposes explosively at 180° according to the derivatographic curves (Fig. 9), ammonium pyrosulphate being formed and oxygen liberated

$$2(NH_4)_2S_2O_8 \rightarrow 2(NH_4)_2S_2O_7 + O_2.$$

As shown by the TG curve, the exothermic reaction proceeds quantitatively. If water vapour is present in the furnace air space or the sample contains any organic matter, this reaction proceeds at a lower temperature. Ammonium pyrosulphate begins to decompose above 250°, sulphur trioxide being lost and ammonium sulphate remaining

$$(NH_4)_2S_2O_7 \rightarrow (NH_4)_2SO_4 + SO_3.$$

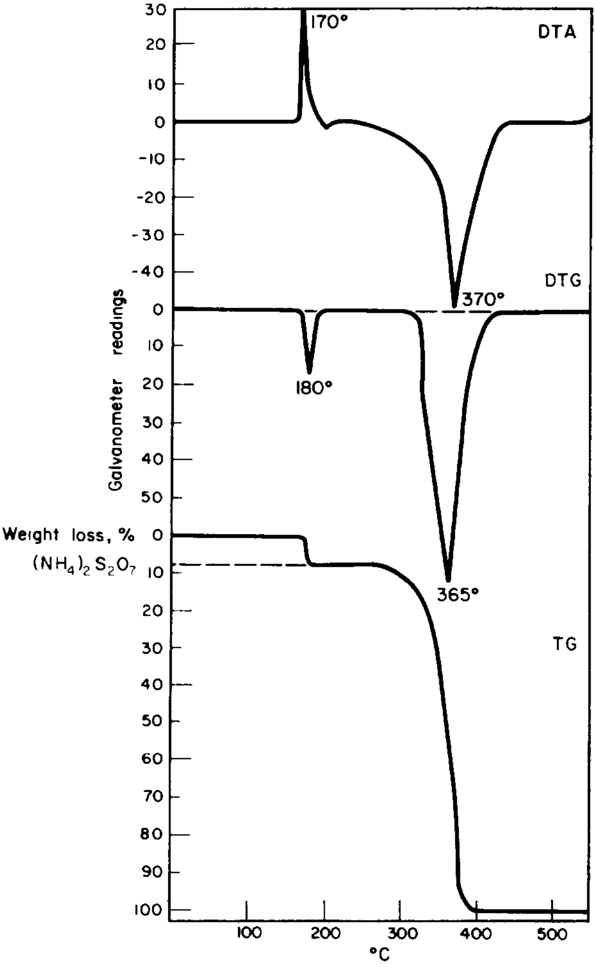


FIG. 9.—Ammonium persulphate.

This process is, however, very slow and not quantitative, because at the same time the ammonium sulphate formed decomposes to ammonium hydrogen sulphate, which in turn decomposes to ammonia and sulphuric acid

$$(NH_4)_2SO_4 \rightarrow NH_3 + NH_4HSO_4$$

$$NH_4HSO_4 \rightarrow NH_3 + H_2SO_4.$$

The above three decomposition processes proceed between 300 and 400° and are maximal in rate at 365°. All three decomposition processes are endothermic. Pure ammonium persulphate can be dried to about 100° without decomposition and heating it to 200° ammonium pyrosulphate can be obtained.

Ammonium thiocyanate

The endothermic peaks on the DTA curve (Fig. 10) of ammonium thiocyanate at 90 and 115° are characteristic of changes of crystal structure of the sample. These changes are reversible. The endothermic DTA peak at 150° is characteristic of melting of the sample; the break in the curve at about 170° shows that after the melting another process accompanied by an enthalpy change proceeds. This region of the DTA curve shows the transformation of the ammonium thiocyanate into thiourea

$$NH_4SCN \rightarrow CS(NH_2)_2.$$

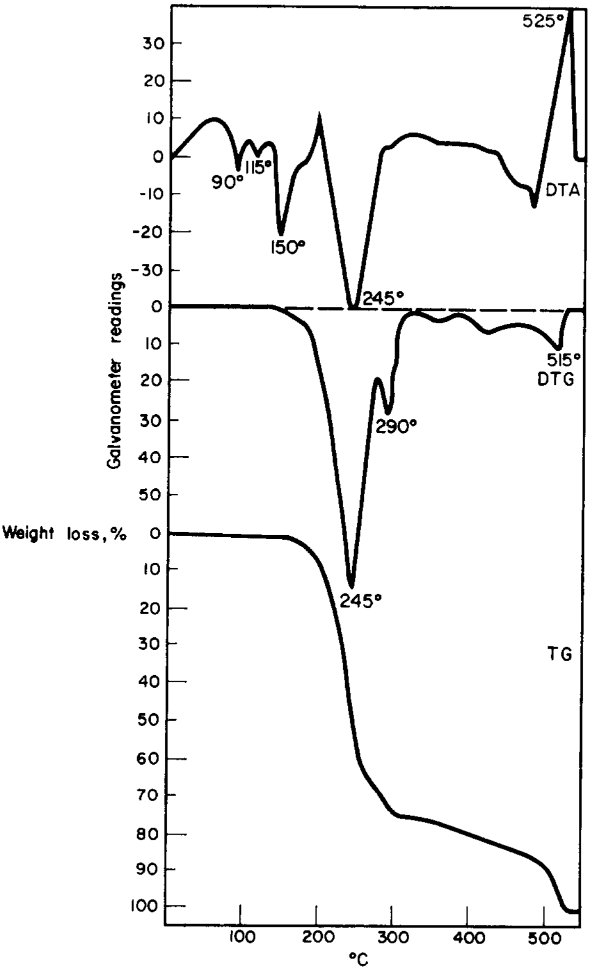


FIG. 10.—Ammonium thiocyanate.

The transformation proceeds only partially and on further increase of temperature the amount of the thiourea formed decreases. After melting and partial transformation the substance decomposes, ammonia, carbon disulphide and hydrogen sulphide being removed, while guanidine thiocyanate and melamine thiocyanate remain. The first decomposition process is complete at about 300°, while the thiocyanates formed, having a higher decomposition temperature, are removed at a maximal rate only at 515°. This process is exothermic.

Ammonium nitrate

The derivatographic curve (Fig. 11) of ammonium nitrate provides a good illustration of the advantage of a multifunctional apparatus (TG, DTG and DTA).

Ammonium nitrate has three transformation points above room temperature.

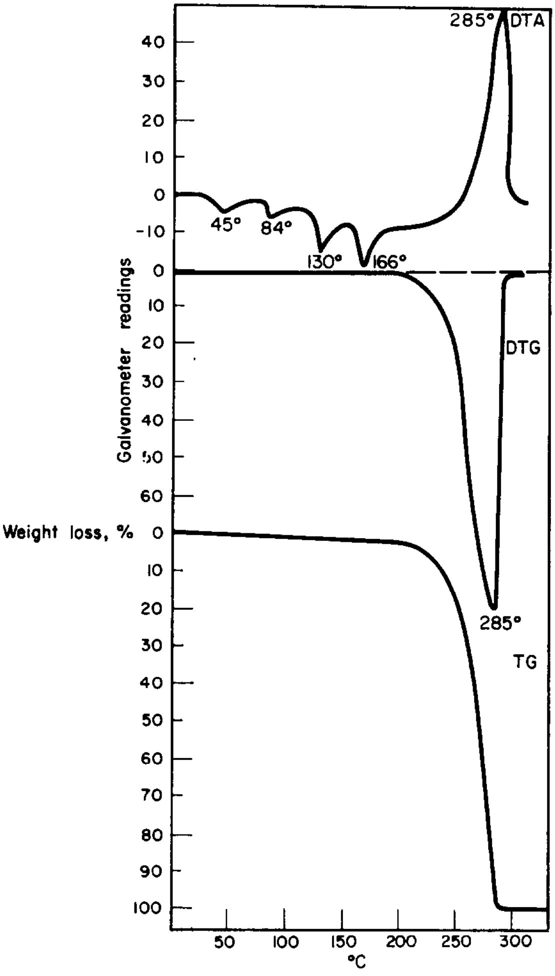


FIG. 11.—Ammonium nitrate.

The three changes of crystal structure are well shown on the DTA curve by the endothermic peaks at 45, 84 and 130°. The sample melts at 166° (DTA curve). Decomposition and decrease in weight of ammonium nitrate begin above 150°. Up to 200° the decomposition is of small extent, and above 220° it becomes exothermic. Between 220 and 260° dinitrogen oxide (N_2O) is formed in 98% yield:

$$NH_4NO_3 \xrightarrow{220\text{–}260°} 2H_2O + N_2O.$$

The decomposition proceeds explosively between 260 and 290° and on further rise in temperature the amount (previously very small) of poisonous nitrogen monoxide (NO) and nitrogen dioxide (NO_2) increases. Care should be taken in drying large amounts of ammonium nitrate not to raise the temperature above 100–110° because explosion then becomes possible.

Ammonium molybdate tetrahydrate

The sample weight begins to decrease above 40°. In the first step (Fig. 12) it loses its four molecules of water of crystallisation

$$(NH_4)_6Mo_7O_{24}.4H_2O \xrightarrow{40\text{–}170^\circ} (NH_4)_6Mo_7O_{24} + 4H_2O.$$

This process is shown by the DTG peak at 110° and the endothermic DTA peak at 120°.

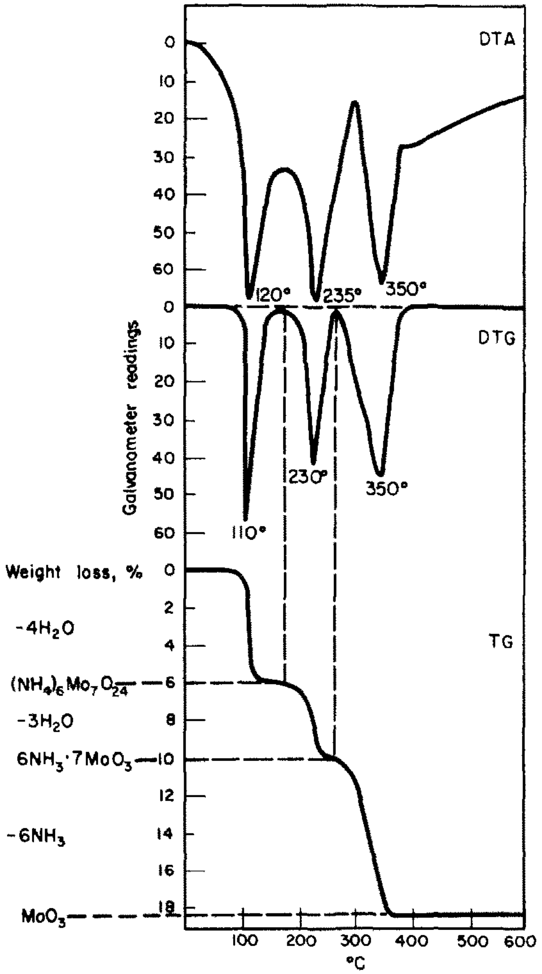


Fig. 12.—Ammonium molybdate tetrahydrate.

The sample weight then decreases further, the rate of decrease being a minimum at 170°. Above 170° the weight of the sample decreases more quickly, the weight decrease, corresponding to the removal of three molecules of water, being at a maximal rate at 230° (TG curve):

$$(NH_4)_6Mo_7O_{24} \xrightarrow{170\text{–}260^\circ} 6NH_3.7MoO_3 + 3H_2O.$$

The next decomposition process lasts from 260 to 400°, while six molecules of ammonia are removed and a residue of molybdenum trioxide remains

$$6NH_3.7MoO_3 \xrightarrow{260-400^\circ} 7MoO_3 + 6NH_3.$$

The composition of the sample, calculated on the basis of the TG curve, is exactly identical with the above formula. The weight of the molybdenum trioxide residue slowly decreased above 600°, because at this temperature molybdenum trioxide sublimes. Material free from water of crystallisation can be produced by careful drying below 100°.

Ammonium metavanadate

The sample begins to decompose above 130° (Fig. 13), the decomposition proceeding in two well separated steps. In the first step, which is indicated by the endothermic DTA peak at 240° and the DTG peak at 230°, ammonia splits off

$$NH_4NO_3 \xrightarrow{130-270^\circ} HVO_3 + NH_3.$$

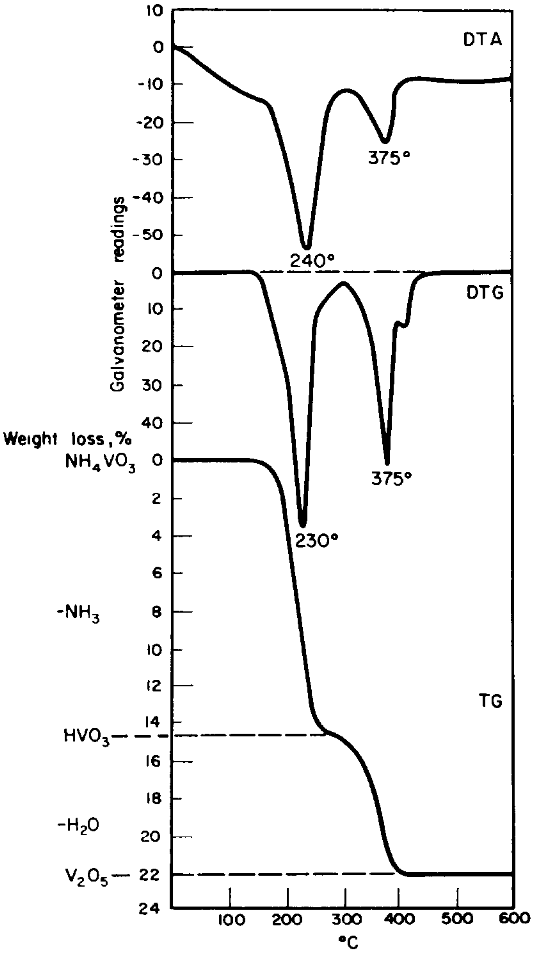


Fig. 13.—Ammonium metavanadate.

After the removal of ammonia, water starts to be lost, and above 470° only vanadium pentoxide remains

$$2HVO_3 \xrightarrow{270-470^\circ} V_2O_5 + H_2O.$$

Diammonium monohydrogen phosphate

There is no weight change up to 100° (Fig. 14). Above this temperature loss of weight begins, proceeding at 150, 170 and 260° at a maximal rate. The three peaks observed on the DTG curve indicate that several decomposition processes proceed simultaneously. In the first step ammonium dihydrogen phosphate is formed by removal of one mole of ammonia

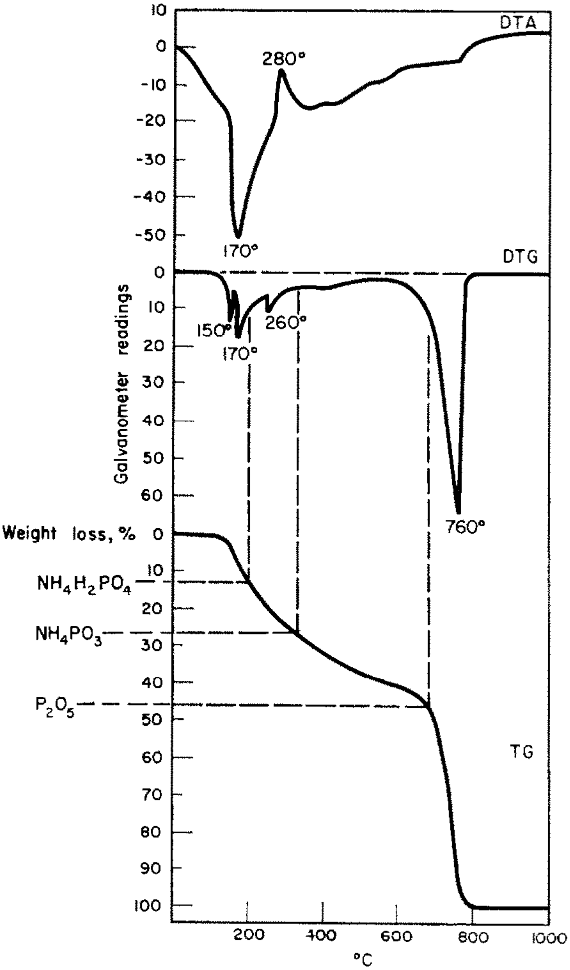


FIG. 14.—Diammonium monohydrogen phosphate.

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3.$$

After this loss of ammonia (at about 150°), the sample melts and diammonium dihydrogen pyrophosphate is formed by removal of one mole of water

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O.$$

On further heating the pyrophosphate loses a further molecule of water and ammonium metaphosphate is formed

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O.$$

This ammonium metaphosphate melt is water-soluble up to 280°, then an exothermic transformation takes place and a glassy metaphosphate melt, insoluble in water, remains. Further ammonia and water are removed from the ammonium metaphosphate between 600 and 800° (maximal rate at 760°), leaving a residue of phosphorus pentoxide

$$2NH_4PO_3 \rightarrow P_2O_5 + 2NH_3 + H_2O.$$

During the experiment the various decomposition processes proceed simultaneously and may not be distinguished from each other. However, levels corresponding to the various compositions are drawn on Fig. 14, calculated on the basis of the weight of the sample, in order to make the decomposition processes clear. The various acidic pyro and metaphosphates formed from diammonium monohydrogen phosphate are very active and fuse different metal oxides, the phosphates of the metals being formed.

Monoammonium dihydrogen phosphate

It can be seen in Fig. 15 that weight loss only starts above 150°. The sample melts at 200°, which is indicated by an endothermic DTA peak. Above 200° decomposition proceeds in the same way as was described in Fig. 14 for diammonium monohydrogen phosphate. The individual decomposition processes also cannot be separated from each other here.

Ammonium chromate

The weight of the sample decreases above 50° (Fig. 16), the first decomposition process having a maximal rate at 125°. Ammonia and water are released and ammonium dichromate is formed

$$2(NH_4)_2CrO_4 \xrightarrow{50\text{–}150^\circ} (NH_4)_2Cr_2O_7 + 2NH_3 + H_2O.$$

At this temperature, however, the ammonium dichromate is unstable and it slowly decomposes above 160°. The exothermic decomposition process proceeding at about 230–240° indicates the simultaneous splitting off of water, ammonia and oxygen

$$2(NH_4)_2Cr_2O_7 \xrightarrow{160\text{–}450^\circ} 2Cr_2O_3 + 4NH_3 + 2H_2O + 3O_2.$$

The decomposition finishes at about 405°, oxygen being lost in an exothermic process. The various stages show that the decomposition proceeds explosively and this fact causes a weight loss 2% more than the theoretical value, because the gaseous decomposition products carry away solid particles.

Ammonium dichromate

Ammonium dichromate is of constant weight up to 200° in air. Above this temperature the weight of the sample slowly begins to decrease, and between 240 and 250° decomposition proceeds explosively (Fig. 17)

$$2(NH_4)_2Cr_2O_7 \xrightarrow{240\text{–}250^\circ} 2Cr_2O_3 + 4NH_3 + 2H_2O + 3O_2.$$

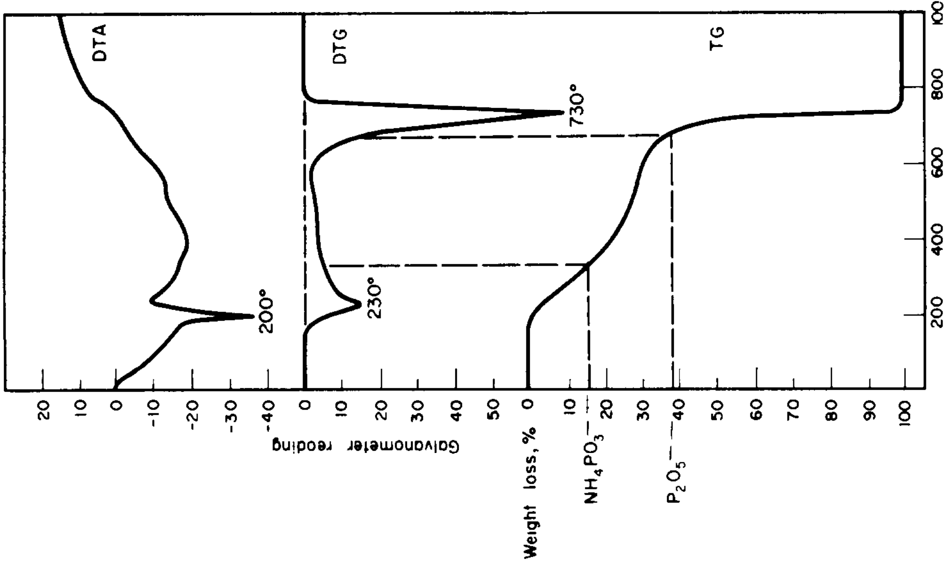


Fig. 15.—Monoammonium dihydrogen phosphate.

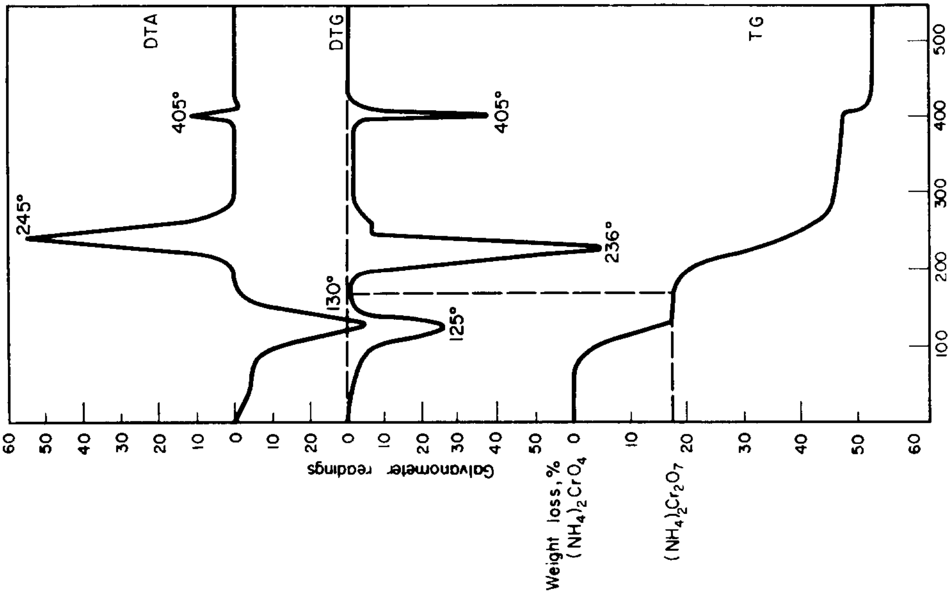


Fig. 16.—Ammonium chromate.

The decomposition proceeds in a single step when more than 100 mg of ammonium dichromate are involved (curve 1, Fig. 17). If the amount involved is decreased, decomposition proceeds in three steps. Curves 2 and 3 (Fig. 17) are thermograms of initial sample weights of 60 and 30 mg, respectively. The heating rate and other experimental conditions were the same for all three measurements. The shape of curve 1 (TG curve) agrees well with that published by Duval;[9] that of curves 2 and 3 is, however, markedly different.

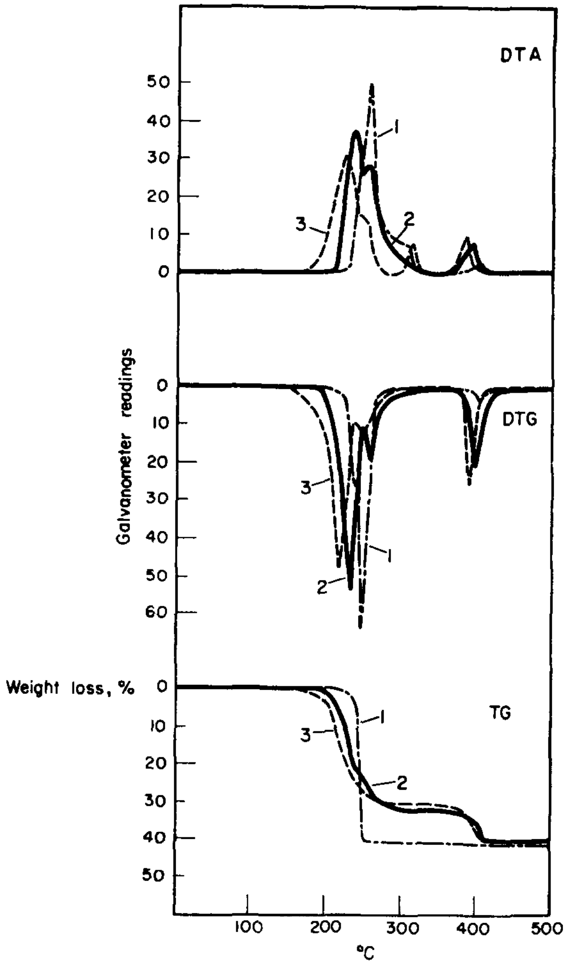


FIG. 17.—Ammonium dichromate.

Ammonium pentaborate tetrahydrate

Ammonium pentaborate tetrahydrate begins to loose weight above 100° (Fig. 18). The DTG maximum at 160° indicates a maximal rate of removal of three moles of water of crystallisation

$$NH_4B_5O_8.4H_2O \xrightarrow{100\text{-}230^\circ} NH_4B_5O_8.H_2O + 3H_2O.$$

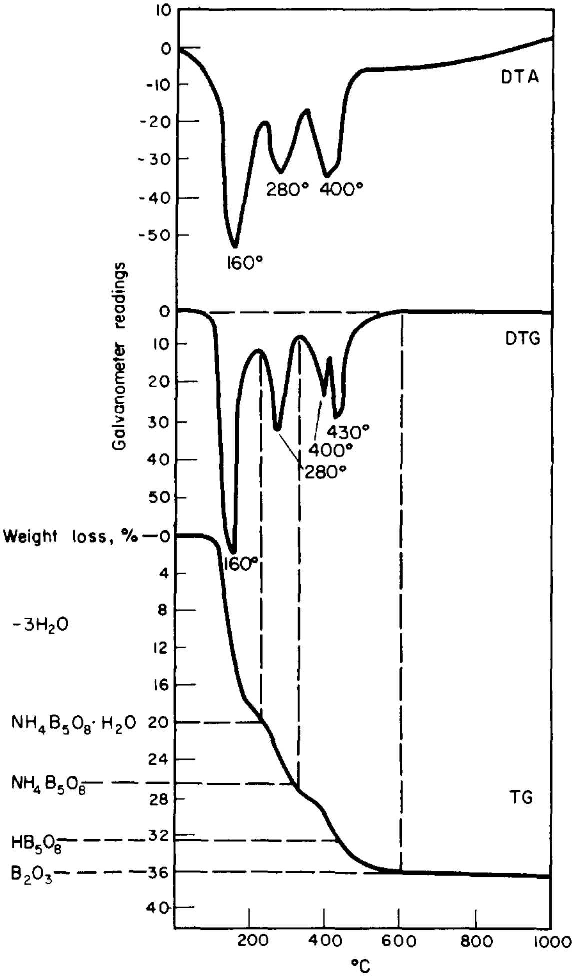


FIG. 18.—Ammonium pentaborate tetrahydrate.

Above 230° the fourth water molecule begins to be lost, the rate being maximal at 280°

$$NH_4B_5O_8.H_2O \xrightarrow{230\text{–}330^\circ} NH_4B_5O_8 + H_2O.$$

The fourth water molecule is bound more strongly than are the other three. After removal of the fourth molecule, ammonia splits off and pentaboric acid is formed

$$NH_4B_5O_8 \xrightarrow{330\text{–}440^\circ} HB_5O_8 + NH_3.$$

The pentaboric acid is, however, unstable at this temperature, immediately losing water to yield boric oxide

$$2HB_5O_8 \xrightarrow{440\text{–}460^\circ} 5B_2O_3 + H_2O.$$

On the DTG and DTA curves a peak corresponds to each of the described processes. The individual decomposition processes are more separated at a lower heating rate.

Water-free ammonium pentaborate cannot be produced by drying because loss of the fourth water molecule proceeds simultaneously with decomposition of the substance.

Ammonium sulphamate

The sample melts at 135°, as indicated by the endothermic peak on the DTA curve (Fig. 19). The weight of the sample does not change until 200°, then decomposition begins and is a maximum at 225 and 290°. Ammonia is removed and ammonium sulphamate is formed

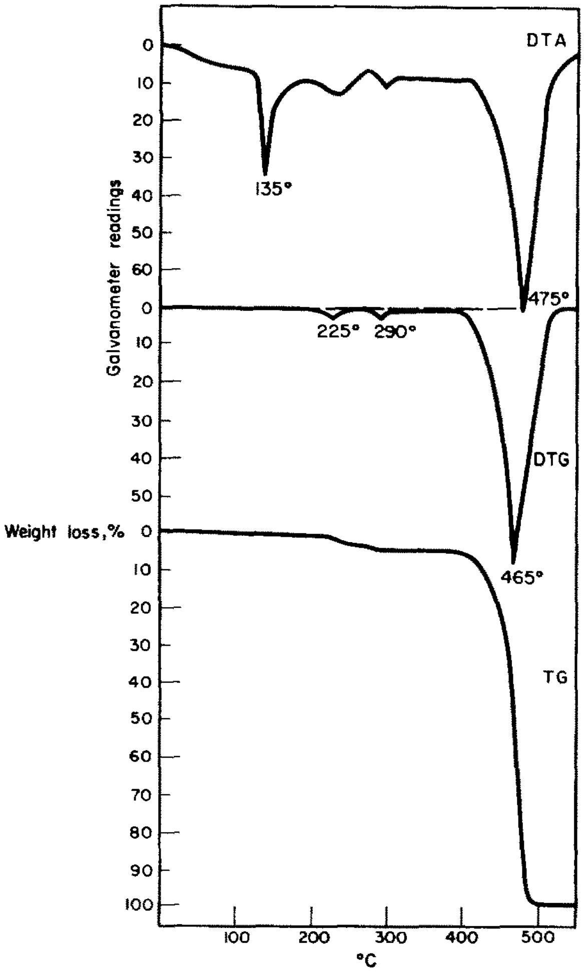


FIG. 19.—Ammonium sulphamate.

$$2NH_4SO_3NH_2 \rightarrow (NH_4SO_3)_2NH + NH_3.$$

According to our experimental conditions the reaction is not quantitative, because on raising the temperature decomposition of the ammonium sulphamate also starts. This decomposition is maximal in rate at 465° and is an endothermic process.

Ammonium carbonate

Decomposition of the sample has already begun at 20° and reaches its maximal rate at 75° (Fig. 20). Ammonia, carbon dioxide and water are formed

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O.$$

The sample does not melt, but sublimes, and in the meantime decomposes. The endothermic peak at 80° is the enthalpy change of the decomposition. The DTG peak at 105° indicates that water remaining in the crucible during the decomposition is a little overheated and evaporated quickly. The decomposition is practically finished at 100°. By decreasing the partial pressure of the decomposition products, the decomposition can be completed at lower temperatures. According to our measurements ammonium carbonate cannot be dried without decomposition.

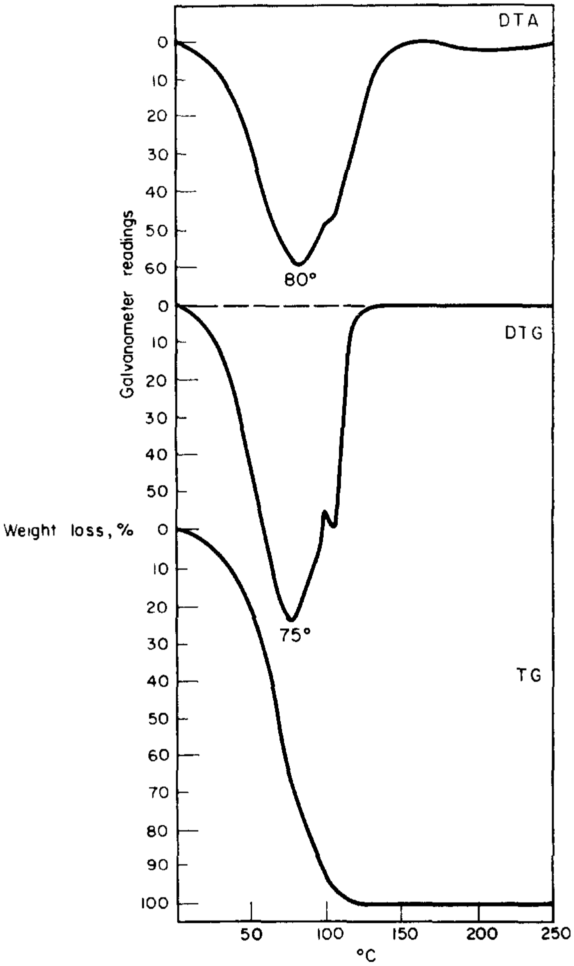


FIG. 20.—Ammonium carbonate.

Ammonium acetate

The decomposition of ammonium acetate starts above 60° (Fig. 21). The maximum on the DTA curve at 100° shows partly the decomposition and partly the onset

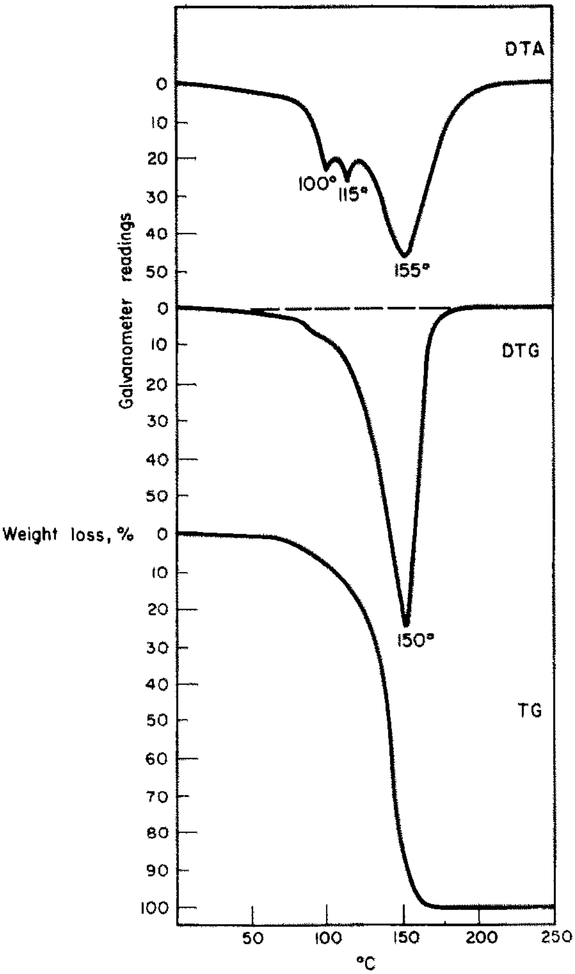


FIG. 21.—Ammonium acetate.

of melting. The sample melts at 115° (DTA curve). Ammonia is lost first during the decomposition and acetic acid is formed. On raising the temperature acetamide results and water splits off

$$NH_4OOCCH_3 \rightarrow NH_3 + CH_3COOH$$

or

$$NH_4OOCCH_3 \rightarrow H_2NOCCH_3 + H_2O.$$

The acetamide distils at about 150°. The decomposition is an endothermic process.

Ammonium oxalate monohydrate

Ammonium oxalate begins to decompose above 70° (Fig. 22). In the first stage it loses its molecule of water of crystallisation (maximal rate at 115°). The anhydrous ammonium oxalate is of constant weight between 120 and 200°, then decomposes above 200°. Decomposition proceeds in two stages. The first process is at a maximal

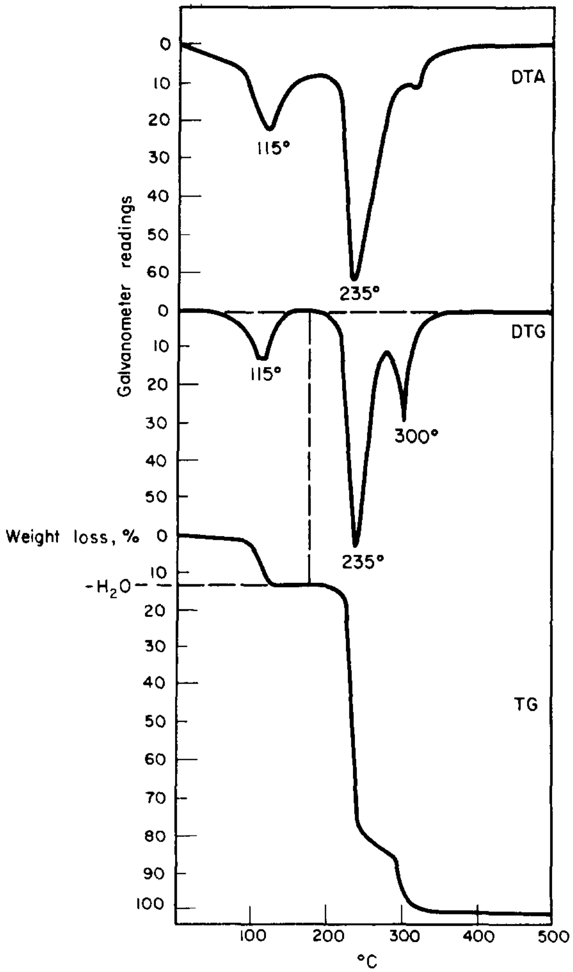


FIG. 22.—Ammonium oxalate monohydrate.

rate at 235° and the second one at 300°. The DTG peak at 235° indicates decomposition of oxalate. Carbon monoxide, carbon dioxide, ammonia, formic acid and oxamide are formed during the decomposition

$$(NH_4)_2(COO)_2 \rightarrow H_2N\text{—}CO\text{—}CO\text{—}NH_2 + H_2O.$$

The decomposition products are in the gaseous state at this temperature, except for oxamide, the composition varying according to the experimental conditions.

Ammonium citrate

The weight of the sample begins to decrease at about 150° (Fig. 23) in an endothermic process, the maximal rate being at 195°. Meanwhile, the sample cracked; the carbon residue was oxidised quantitatively only above 800°.

Ammonium benzoate

The weight of the sample scarcely changes before 100°, then it decreases and the substance sublimes. The endothermic DTA peak at 195° (Fig. 24) shows the melting

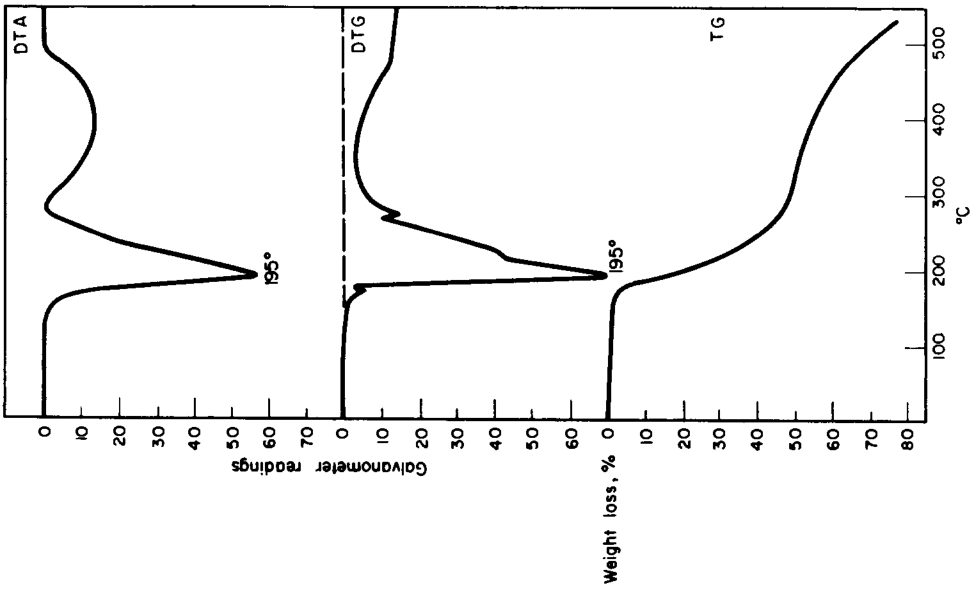


FIG. 23.—Ammonium citrate.

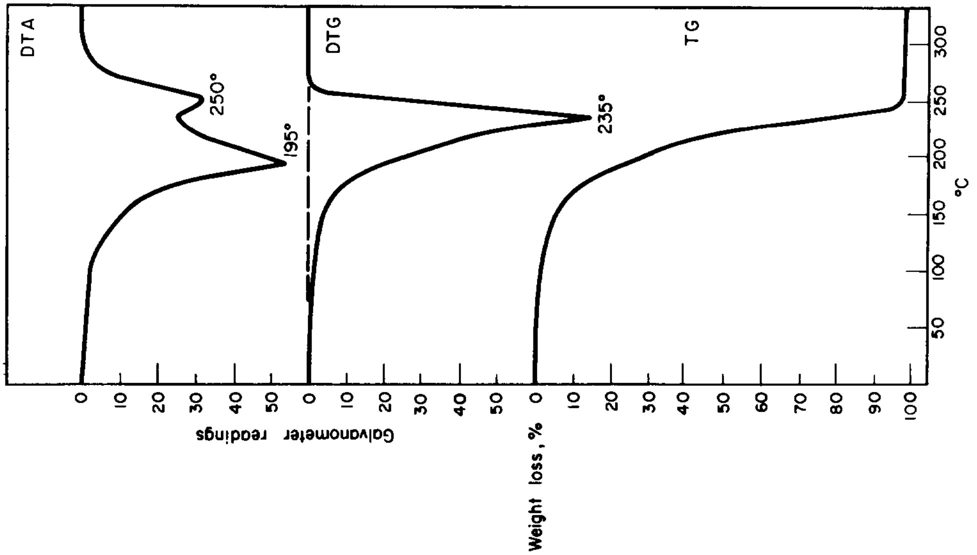


FIG. 24.—Ammonium benzoate.

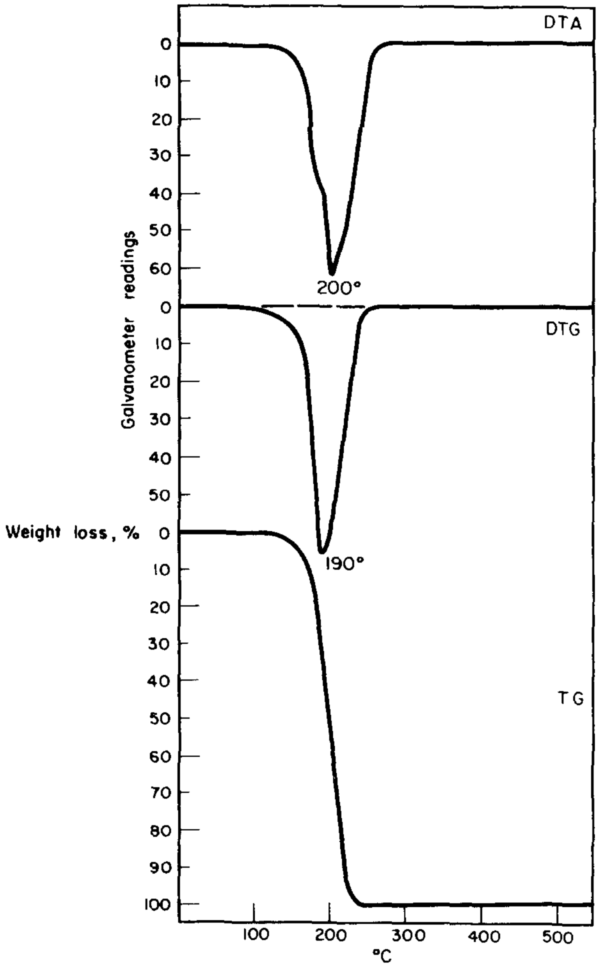


FIG. 25.—Ammonium salicylate.

of the sample (m.p.:[10] 190°). The rate of weight decrease is a maximum at 235° after the melting (DTG curve). The substance left the crucible without any change in composition. This was confirmed by the absence of any carbon residue.

Ammonium salicylate

There is no change in weight of the sample until 100°, when sublimation starts, its rate being maximal at 190°. Sublimation was complete at 250° and the crucible was empty.

Ammonium tartrate

Ammonium tartrate is of constant weight up to 100°, above which decomposition slowly starts. Ammonia is lost and ammonium hydrogen tartrate formed [maximal rate at 180° (Fig. 26)][11]

$$(NH_4)_2C_4H_4O_6 \xrightarrow{100\text{–}200^\circ} NH_4HC_4H_4O_6 + NH_3.$$

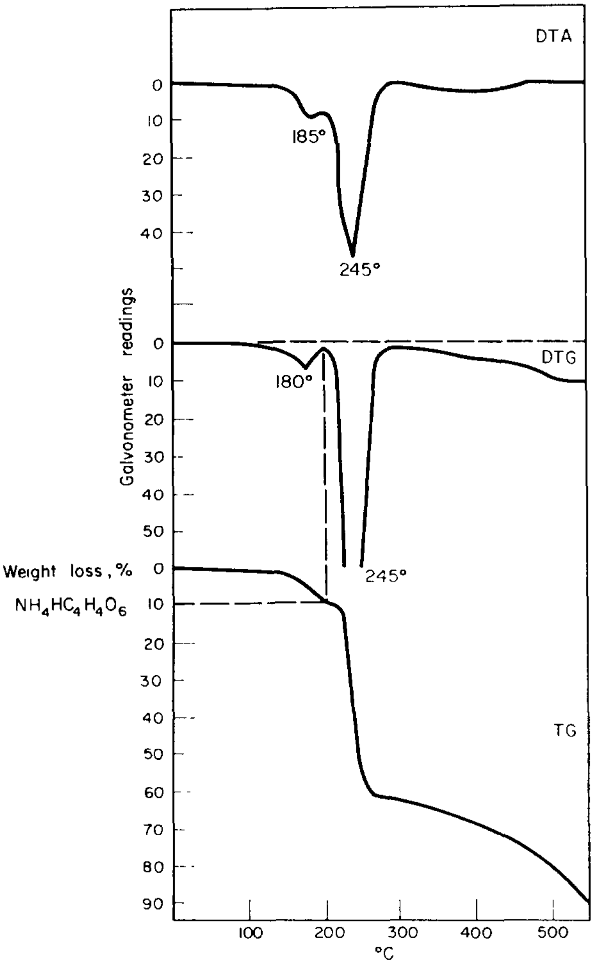


FIG. 26.—Ammonium tartrate.

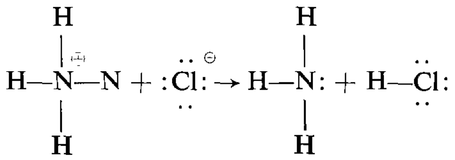
The ammonium hydrogen tartrate begins to decompose above 200°, the decomposition products varying according to the experimental conditions. They may include water, ammonium carbonate, ammonium acetate, formamide, *etc.* This process is maximal in rate at 245°. Above 300° there was a residue of decomposition products from the sample (about 30% of it).

CONCLUSIONS

It is important to follow exactly the prescribed experimental conditions. Thus, in the case of ammonium dichromate it was possible by decreasing the amount of the substance to avoid an explosive decomposition (Fig. 17). For initial amounts of 30 and 60 mg of material, the decomposition products do not carry away solid particles, so the amount of the residue is equal to the theoretical value; for 120 mg of material, however, the decomposition proceeds explosively and the weight of the residue is 2% less than the theoretical value.

The decomposition curves of ammonium salts of organic acids show well that the decomposition temperature increases with increasing molecular weight. Ammonium salicylate (Fig. 25) and ammonium benzoate (Fig. 26) sublime without decomposition.

On the basis of the high temperature acid-base theory, the decomposition of ammonium salts can be explained by the fact that the base strength of the anion increases with rise in temperature until it reaches the base strength of the ammonia molecule. At this temperature the anion base removes the proton from the ammonia.



$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}{}^{\oplus}{-}N} + :\overset{..}{\underset{..}{\mathrm{Cl}}}:^{\ominus} \rightarrow \mathrm{H{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}}: + \mathrm{H{-}}\overset{..}{\underset{..}{\mathrm{Cl}}}:$$

The weaker the anion base, the higher the temperature of the decomposition. Comparison of decomposition curves of the various ammonium salts gives information on the base strength of the anions. According to the measurements—in agreement with the known facts—the strongest anion base is the oxygen ion. The strongly basic character of the oxygen ion is shown by the fact that ammonium oxide [$(NH_4)_2O$] has never been made because of its instability. After the oxygen ion the halide ions follow in the order of decreasing base strength: F^-, Cl^-, I^-, Br^-. Under the given conditions iodide ion is a stronger base than bromide, which is connected with its higher deformability. On the DTA curves of ammonium salts temperatures of interconversion of different crystal modifications appear. During such conversions the more closely packed crystal structure is always formed on the higher temperature side, which is in agreement with the known fact that at higher temperatures the co-ordination number generally increases.

Zusammenfassung—26 Ammoniumsalze wurden derivatographisch untersucht. Gewichtsänderung und ihre Geschwindigkeit sowie die Enthalpieänderung der Salze wurden in Abhängigkeit von der Temperatur gemessen. An Hand der Ergebnisse werden die Temperaturen angegeben, bei denen die Salze unzersetzt getrocknet werden können.

Résumé—On a étudié vingt six sels d'ammonium par dérivatographie. La variation de poids, la vitesse de variation de poids et la variation d'enthalpie ont été mesurées en fonction de la température. A partir de ces résultats, on donne les températures auxquelles les sels peuvent être séchés sans décomposition.

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USE OF OXYCELLULOSE FOR COLLECTION OF TRACES OF METALS—II*

APPLICATION OF OXYCELLULOSE IN SOLVENTS AND IN SOLUTIONS OF DIFFERENT ORGANIC COMPOUNDS

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Summary—Oxycellulose has been applied as a collector for the following metal-ion contaminants of organic solvents and of different organic compounds: Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}. From 100 ml of solvent 1–20 μg of ions have been collected with 5 mg of oxycellulose. The solutions of the organic compounds were 1–3%. The water content of the solvents has a marked effect on the collection. By repeated collection an ion can be removed quantitatively.

INTRODUCTION

EARLIER investigations[1] showed that oxycellulose is a very suitable material for the collection and removal of traces of metals from distilled water and from highly diluted inorganic salt solutions. After collection, the metal ions are identified directly on the oxycellulose. The ionic strength of the solution has a marked effect on the metal-binding capacity of oxycellulose.

The detection and the quantitative determination of the metal contaminants of organic compounds is a frequent and an important task in analysis. The metal-binding capacity of oxycellulose in the presence of organic solvents and of different organic compounds has therefore been investigated. The collection of the following metal ions was studied: Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. For the collection of these ions the method described previously was used.[1] The fixation of lead ion on oxycellulose was followed quantitatively by the dithizone method.[2]

EXPERIMENTAL AND RESULTS

Qualitative investigations

Table I gives the minimum detectable quantity of the ions Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} and Zn^{2+} on oxycellulose, collected from water and from different solvents. The ions were added to the purified solvent in increasing quantity, and were tested for after collection on the oxycellulose disc. In most of the organic solvents the minimum detectable quantity of the ions was greater than in water. The greater the water content of the solution, the smaller was the quantity of metal ion that could be detected. With water-immiscible solvents, *e.g.*, chloroform, carbon tetrachloride, benzene, fatty acid salts of the metals were used.

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* Part I—See ref. 1.

TABLE I.—IONS COLLECTED ON OXYCELLULOSE FROM SOLVENTS

Solvent	Ion, μg				
	Cu^{2+}	Fe^{3+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
Acetone	5	5	5	10	10
Methyl alcohol	1	1	1	10	1
Ethyl alcohol	1	1	1	10	1
n-Propyl alcohol	15	10	5	20	5
n-Butyl alcohol	10	5	1	20	5
Isobutyl alcohol	5	5	1	10	5
Dioxan	15	5	5	20	20
Dimethylformamide	1	1	5	10	10
Chloroform	2	1	2	10	5
Carbon tetrachloride	2	1	2	10	5
Benzene	10	2	10	10	5
Water	1	1	1	1	1

The following list includes the various organic compounds from which more than 50% of the Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} and Zn^{2+} ion (up to 10 μg) could be collected on oxycellulose:

Acetamide
Acetanilide
Antipyrine
Aspirin
Benzoic acid
Bromacetocarbamide
Bromovalerocarbamide
Caffeine
Carbamide
Chloral hydrate
Cholesterol
5,5-Diethylbarbituric acid
5-Ethyl-5-butylbarbituric acid
Glucose
Methyl *p*-hydroxybenzoate
Hyoscine hydrobromide
Lactose
Mannite
2-Naphthol
Phenacetin
Phenol
2-Phenylcinchoninic acid
Pyrogallol
Raffinose
Phenyl salicylate
Santonin
Terpinal hydrate
Theophylline
Thymol
Urethane

All the commercially available materials were contaminated with heavy metals. Therefore, before the experiments, these materials were purified with oxycellulose. In the case of complex-forming compounds (citric, oxalic, succinic, thiobarbituric acids, *etc.*) oxycellulose could not remove the metal ion. With alkaloid salts the collection is effective only in dilute solution. The detection of the ion is not influenced by the colour of the sample, because the organic compounds can be washed out from the oxycellulose disc by water or by another solvent. The bound metal ion is not removed by this procedure.

For an indication of the metal ions likely to be present in various solutions or solvents this qualitative process, using oxycellulose, is a very suitable rapid method. By dividing the oxycellulose disc into pieces, more than one ion can be tested for without using the ring-oven method.

Quantitative investigations

In the quantitative investigations, the fixation of Pb^{2+} ion on oxycellulose, from water, from different solvents and from solutions of organic compounds, was followed by the dithizone method.[2]

One hundred ml of the solvent, containing 1–5 μg of Pb^{2+} ion, were shaken with 5 mg of oxycellulose for 5 min and the oxycellulose fibrils were collected as usual.[1] The oxycellulose disc was put into a volumetric flask, and the lead ion was extracted by a dithizone-carbon tetrachloride solution in the presence of potassium cyanide. The colour of the solution was compared with that of a lead-dithizone standard solution.

Table II shows the result of the collection of Pb^{2+} ion from water on oxycellulose. By repeated collection, 1–5 μg of Pb^{2+} ion could be removed quantitatively.

TABLE II.—QUANTITATIVE COLLECTION OF Pb^{2+} FROM WATER WITH OXYCELLULOSE AFTER REPEATED COLLECTION

Added Pb^{2+} ion, *μg/100 ml*	Pb^{2+} ion, μg, First collection	Second collection	Third collection	Arithmetical mean of Pb^{2+} ion found, μg
1·0	0·6 0·7 0·6	0·4 0·3 0·3		1·0
2·0	1·2 1·3 1·2	0·5 0·5 0·5	0·3 0·2 0·2	2·0
3·6	1·6 1·6 1·9	0·6 0·7 0·6	0·4 0·5 0·3	2·7
4·0	2·8 3·0 2·8	0·7 0·6 0·6	0·3 0·2 0·2	3·7
5·0	3·5 3·4 3·2	0·8 0·8 1·0	0·3 0·4 0·3	4·6

Table III indicates that there may be some relation between the amount of Pb^{2+} ion removed by oxycellulose and the dielectric constant of the solvent.

As mentioned earlier, the water content of the solvent has a marked effect on the collection. Only a few per cent of the added metal ions can be removed by oxycellulose from anhydrous solvents (water content less than $10^{-2} - 10^{-3}\%$). If the oxycellulose was swollen with water before adding it to the anhydrous solvents, the quantity of the bound ion increased. This suggests that swelling of the oxycellulose is of considerable importance in binding the metal ions. (According to results in the literature,[3] water has the greatest swelling effect on oxycellulose.)

TABLE III.—EFFECT OF DIELECTRIC CONSTANT ON THE COLLECTION OF Pb^{2+} ION
(Pb^{2+} ion: 5 μg/50 ml; oxycellulose: 5 mg)

Solvent	Dielectric constant, ε	Arithmetical mean of Pb^{2+} ion found, μg
Water	78	3·8
Dimethylformamide	37	2·7
n-Butyl alcohol	18	2·0
Methyl alcohol	32	1·5
Ethyl alcohol	24	0·9
n-Propyl alcohol	20	0·8
Ethyl acetate	6·0	0·5
Ether	4·0	0·4
Dioxan	2·2	0·3
Acetone	21	0·2

The results in Table IV show the extent of removal of Pb^{2+} ion from different solvent-water mixtures.

In Table V the results of the quantitative collection of 1 μg of Pb^{2+} ion from organic compounds are summarised. The compounds were dissolved in 30 ml of water.

TABLE IV.—COLLECTION OF Pb^{2+} BY OXYCELLULOSE FROM SOLVENT WITH DIFFERENT WATER CONTENTS

(Pb^{2+} ion: 5 μg/50 ml)

Solvent	Arithmetical mean of Pb^{2+} ion found, μg			
	Water content, v/v %			
	1·5%	10%	20%	50%
Acetone	0·2	0·4	1·1	2·2
Dimethylformamide	2·7	2·7	2·8	3·0
Dioxan	0·3	1·2	1·3	2·8
Ethyl alcohol	0·9	1·0	1·2	2·0
Methyl alcohol	1·5	1·7	1·6	3·0

TABLE V.—COLLECTION OF Pb^{2+} BY OXYCELLULOSE FROM ORGANIC COMPOUNDS

(Pb^{2+} ion: 1·0 μg/30 ml of water)

Compound	Compound in 30 ml of water, g	Arithmetic mean of Pb^{2+} ion found, μg
Acetamide	1	1·0
Antipyrine	1	1·0
Glucose	1	0·6
Hydroquinone	1	1·1
Carbamide	1	0·9
Thiocarbamide	1	0·7
Urethane	1	1·0
Atropine sulphate	0·1	0·6
Ephedrine hydrochloride	0·1	0·5
Hyoscine hydrobromide	0·1	0·7
Quinidine sulphate	0·1	0·5

CONCLUSIONS

From the results of experiments dealing with the collection of frequent metal contaminants of various organic solvents and organic compounds, it is apparent that oxycellulose is a suitable collector for metal ions, not only from aqueous but also from non-aqueous solutions.

Zusammenfassung—Oxycellulose wurde zur Anreicherung folgender Metallverunreinigungen in organischen Lösungsmitteln und verschiedenen organischen Verbindungen verwendet: Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} und Zn^{2+}. 1–20 μg dieser Ionen wurden aus 100 ml Lösungsmittel mit 5 mg Oxycellulose angereichert. Die Lösungen der organischen Verbindungen waren 1–3%. Der Wassergehalt der Lösungsmittel war von großem Einfluß auf die Anreicherung. Durch wiederholte Anreicherung konnte das Ion quantitativ entfernt werden.

Résumé—On a utilisé l'oxycellulose comme collecteur pour recueillir les ions métalliques suivants, contaminants de solvants organiques et de divers composés organiques: Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}. Avec

5 mg d'oxycellulose, on recueille 1–20 μg d'ions de 100 ml de solvants. La concentration des solutions de composés organiques est de 1–3%. La teneur en eau des solvants a une grande influence sur la séparation. Par traitements répétés, l'ion peut être séparé quantitativement.

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THE CHROMATOGRAPHY OF *p'*-SUBSTITUTED-*p*-HYDROXYAZOBENZENES ON ALUMINA-IMPREGNATED PAPER*

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Summary—R_f values of *p'*-substituted-*p*-hydroxyazobenzenes on paper, glass-fibre "paper", and these papers impregnated with different amounts of alumina are given. Results indicate that the alumina is primarily responsible for sorption. The effect of the electrical nature of the *p'*-substituent on sorption is small. Sorption is considered to be a result of hydrogen bonding between oxygen centres in the sorbed molecule and active hydrogen centres on the hydroxylated alumina.

INTRODUCTION

THE suggested relation between R values from column adsorption chromatography and linear adsorption isotherms has been substantiated by Claesson.[1] This worker successfully constructed linear adsorption isotherms for a number of homologous series of organic compounds from results obtained by using the interferometric method of Tiselius and Claessen[2] with the techniques of frontal analysis, displacement analysis and carrier-displacement analysis.

LeRosen and his coworkers[3] related the structure of a molecule to its sorption on silicic acid. Martin[4] established a theoretical relation between the chemical potential of a molecule and its partition coefficient for a two-phase system of ideal solutions when the two phases are in equilibrium, and derived the expression

$$\Delta\mu_{(F)}A = RT \ln \left(\frac{N_A{}^M}{N_A{}^S}\right)$$

where $\Delta\mu_{(F)}A$ = the free energy required to transport 1 mole of A from phase S to phase M,

$N_A{}^M$ = the mole fraction of A in phase M,

and $N_A{}^S$ = the mole fraction of A in phase S.

He also showed that where the molecule A is composed of the several groups X, Y and Z, then the free energy required to transport A from phase S to phase M is the sum of the free energies required to transport the individual groups X, Y and Z from phase S to phase M.

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* Presented at a joint meeting of the Institute of Chemistry of Ireland and the Scottish Section of the Society for Analytical Chemistry in Dublin, 5 September, 1963.

Later, Sporer and Trueblood[5] carried out a quantitative study of the relation between the molecular structure of a number of aromatic compounds and their adsorption affinities on silicic acid-celite columns using benzene as the eluent. These workers observed that Langmuir isotherms calculated from observed chromatographic development rates agreed with those evaluated from static adsorption studies determined for the same systems. They also suggested that the standard free energy change for a molecule on adsorption, as given by the equation

$$\Delta F^\circ = -RT \ln K$$

is, to a first approximation, the sum of the free energy changes for the component atoms which comprise the molecule. This established for adsorption chromatography a similar thermodynamic concept to that proposed by Martin[4] for partition chromatography.

Erió, Goode and Ibbitson[6] have carried out static adsorption studies of phenols from cyclohexane onto alumina, while Ibbitson, Jackson, McCarthy and Stone[7] have similarly investigated azobenzenes sorbed from benzene. In each case the free energy changes of sorption have been determined in terms of the equation

$$\Delta G^\circ = -RT \ln K.$$

Because of the foregoing we have sought to correlate data obtained from static sorption studies of hydroxyazobenzenes from benzene onto alumina by Stone,[8] with R_f values determined for the same compounds by adsorption chromatography on alumina-impregnated papers with benzene as the eluent, and with other known physical parameters. In each case the compounds were chromatographed on untreated paper of a comparable grade as control experiments. The compounds investigated were *p*-hydroxyazobenzenes with substituents of different electrical character in the *p*′-position.

EXPERIMENTAL

Five grades of paper were used in the investigation:

(a) untreated Whatman No. 1 paper,
(b) Whatman No. 1 paper impregnated with 2% of alumina,
(c) Whatman No. 1 paper impregnated with 7·5% of alumina,
(d) untreated glass-fibre paper,
(e) glass-fibre paper impregnated with 7·5% of alumina.

The papers were activated at 120° for 15 min (heating for longer periods caused yellowing of the paper), then cooled in a vacuum desiccator.

Samples (2.5 μl) of the hydroxyazobenzenes (1% w/v solutions) were applied at a point 6 cm from the base of a paper and at intervals of 2 cm from each other. The dispersing solvent was removed by a current of warm air directed at the point of application of the samples.

The eluent, M.F.C. grade benzene, was dried over sodium wire, redistilled, and the fraction boiling at 80·1° (760 mm pressure) collected. This gave a single peak when examined by gas-liquid chromatography on a dinonylphthalate column at 75°, using a Pye Argon Chromatograph.

The papers were conditioned in a tank saturated with benzene vapour for 15 min, then eluted by an ascending technique at a temperature of 25° ± 0·5°. The length of run was governed by the distance reached by the solvent front (*ca.* 22 cm from the point of application), rather than by time, because of the different rates of flow of the eluent through the different grades of paper. For both grades of glass-fibre paper the eluent rose to the desired height in 1 hr. The three grades of filter paper were slower, the solvent taking 3–5 hr to rise through the paper; the untreated paper was the fastest and the paper impregnated with 7·5% of alumina the slowest. After elution, the chromatograms were dried and viewed under an ultraviolet lamp to mark the positions of compounds.

RESULTS

The results collected in Table I represent the mean of 5 runs. The R_f values are reproducible to ±0·01 of an R_f unit.

DISCUSSION

From Table I it can be seen that on untreated glass-fibre paper the compounds travelled with the solvent front. Some sorption took place on untreated Whatman No. 1 papers but all of the compounds had high R_f values, there being little differentiation between the values for the different compounds. Impregnation of the papers with alumina resulted in a substantial increase in the degree of sorption, with R_f values ranging from 0·33 to 0·54 on the 2% alumina-impregnated paper, 0·08 to 0·15 on the 7·5% alumina-impregnated paper, and 0·03 to 0·05 on the 7·5% alumina-impregnated glass-fibre paper. Hence, it is concluded that the alumina surface is responsible for the sorption of the compounds, with the "paper" substrate playing little or no part in sorption.

TABLE I.—R_f VALUES OF *p*′-SUBSTITUTED-*p*-HYDROXYAZOBENZENES

	R_f*				
p′-Substituent	(a)	(b)	(c)	(d)	(e)
Nitro	0·95	0·37	0·09	1·0	0·02
Chloro	0·97	0·54	0·15	1·0	0·03
Bromo	0·96	0·52	0·14	1·0	0·03
Iodo	0·96	0·52	0·12	1·0	0·03
Hydrogen	0·96	0·52	0·13	1·0	0·04
tert-Butyl	0·95	0·48	0·13	1·0	0·04
Methyl	0·95	0·46	0·12	1·0	0·05
Methoxyl	0·94	0·33	0·08	1·0	0·04

* (a) Untreated Whatman No. 1, (b) Whatman No. 1 paper impregnated with 2% of alumina, (c) Whatman No. 1 paper impregnated with 7·5% of alumina, (d) untreated glass-fibre paper, (e) glass-fibre paper impregnated with 7·5% of alumina.

Three other factors may now be considered: (a) the effect of the electrical nature of the *p*′-substituent, (b) the mechanism of sorption, and (c) the alignment of the sorbed molecule onto the surface of the adsorbent.

(*a*) *Effect of electrical nature of p*′*-substituent*

Stone,[8] from static sorption studies, has suggested that compounds of this type are adsorbed from benzene onto alumina as a result of hydrogen bonding between the hydrogen atom of the hydroxyl group of the molecule and the active oxygen centres on the alumina surface. He found that though the free energy decrease of sorption could be correlated with the electrical character of the *p*′-substituent, those compounds with electron-attracting groups being more strongly adsorbed than those with electron-releasing groups, the magnitude of the free energy change is small.

This effect has been confirmed and explained by Catchpole, Foster and Holden[9] who determined the hydroxyl stretching frequencies for hydroxyazobenzenes, including a number of the compounds investigated here. A plot of the hydroxyl stretching frequencies for these compounds against Hammett σ functions,[10] was compared with a similar plot for comparable phenols using the data of Flynn, Werner and Graham.[11] Both plots were linear, with the former having a smaller slope than the latter. Catchpole, Foster and Holden[9] suggested, therefore, that the electronic effect of the *p*′-substituent in the one benzene ring suffers a decrease in intensity when transmitted across the azo group to the *p*-hydroxyl group in the other benzene ring of the conjugated system. Catchpole and coworkers[9,12] showed that the electrical effect of the p'-substituent on the acid dissociation constants of these hydroxyazobenzenes is also small.

From Table I it can be seen that for the 2% alumina-impregnated papers and the 7·5% alumina-impregnated papers the R_f values, in general, change with the electrical nature of the group but once again the magnitude of the change is small.

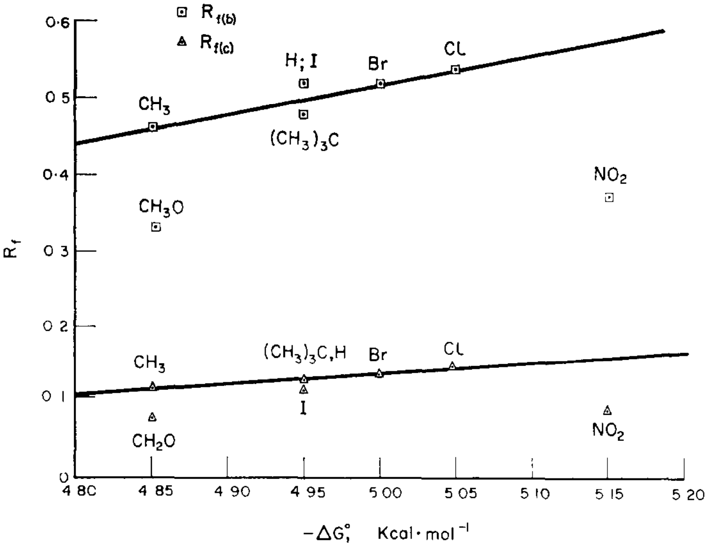

FIG. 1

(b) *Mechanism of sorption*

For the mechanism of sorption of the compounds onto alumina-impregnated paper to be the same as that proposed by Stone[8] for static sorption, one would expect that the order of R_f values would parallel the order of free energy changes of sorption and that a plot of R_f values against $-\Delta G^\circ$ values would be linear. Furthermore, one would expect plots of R_f values against hydroxyl stretching frequencies, Hammett σ functions and dissociation constants to be linear.

However, from Table I and from Fig. 1 it can be seen that the R_f values do not parallel the free energy changes. For substituents which do not contain an oxygen atom, the R_f values are lower, indicating stronger adsorption for electron-releasing groups than for electron-attracting groups, *i.e.*, the reverse of that expected from Stone's work. Those compounds in which the p'-substituent contains an oxygen atom are strongly adsorbed irrespective of whether the oxygen atom is part of the electron-attracting nitro group or of the electron-releasing methoxyl group.

Further, for compounds containing non-oxygenated substituents in the p'-position, the higher R_f values, relative to the values for the unsubstituted parent compound, in the presence of electron-attracting substituents are associated with (a) hypsochromic shifts of the hydroxyl stretching frequencies (Fig. 2), (b) positive Hammett σ functions (Fig. 3), and (c) stronger acid dissociation constants (Fig. 4), while the lower R_f values for the electron-releasing substituents are associated with (a) bathochromic shifts, (b) negative Hammett σ functions, and (c) weaker acid dissociation constants. As

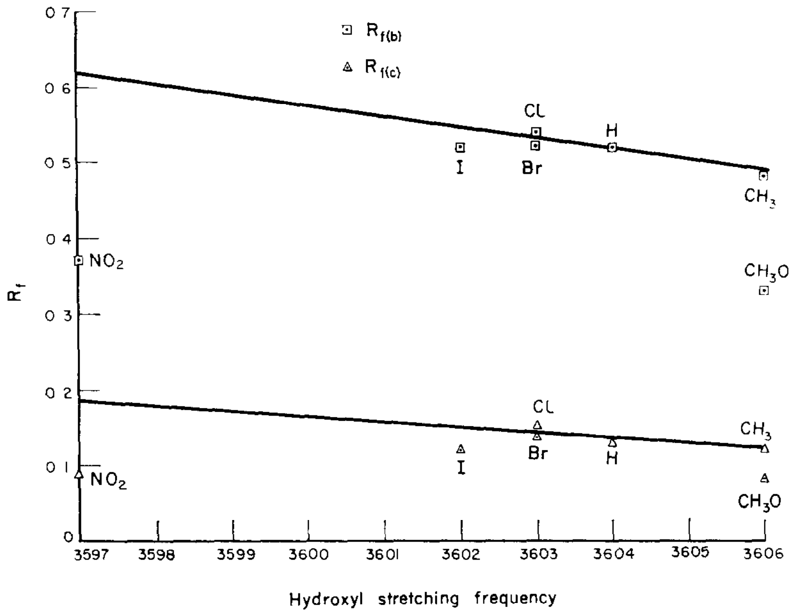
⊡ $R_{f(b)}$
△ $R_{f(c)}$
R_f
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Cl
H
I
Br
CH_3
NO_2
CH_3O
Cl
Br
H
I
CH_3
NO_2
CH_3O
3597
3598
3599
3600
3601
3602
3603
3604
3605
3606
Hydroxyl stretching frequency

FIG. 2

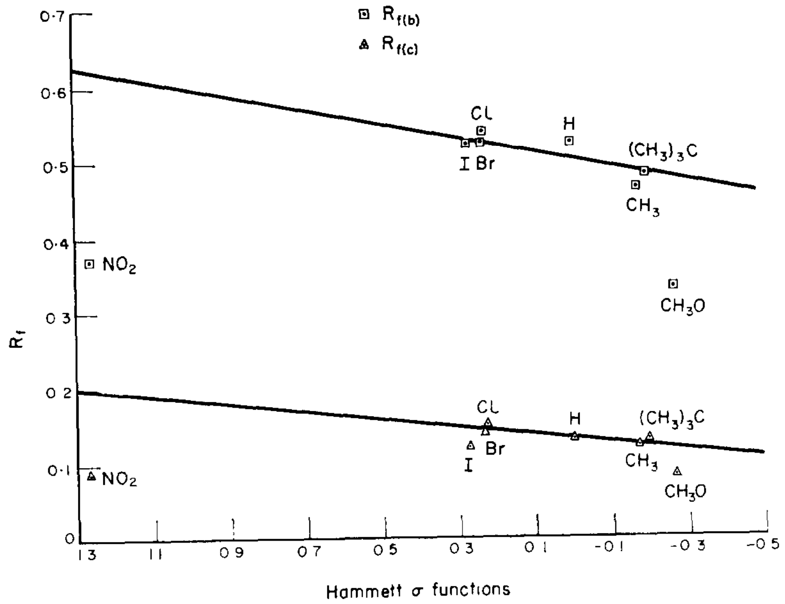
⊡ $R_{f(b)}$
△ $R_{f(c)}$
R_f
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Cl
H
I Br
$(CH_3)_3C$
CH_3
NO_2
CH_3O
Cl
H
$(CH_3)_3C$
Br
I
CH_3
CH_3O
NO_2
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
-0.3
-0.5
Hammett σ functions

FIG. 3

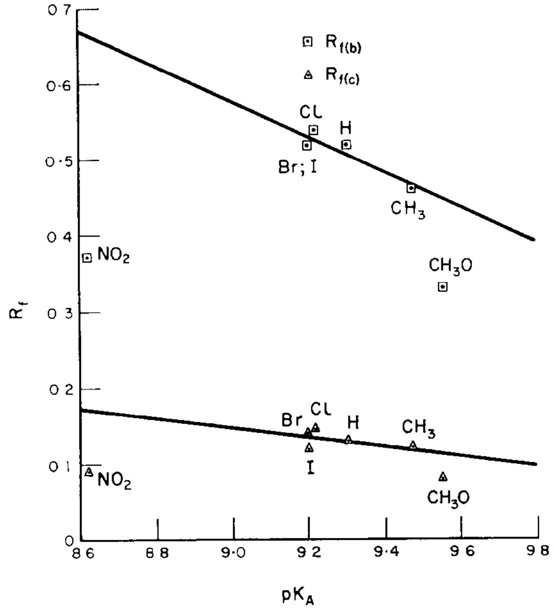

FIG. 4

in the case of the plot of the R_f values against $-\Delta G^\circ$ values, however, the positions of the compounds with oxygen atoms in the substituent groups are anomalous.

Because of these facts we consider that a different mechanism of bonding must operate on the alumina-impregnated papers from that on static beds of alumina.

We propose that, in accordance with the suggestion of Bernal,[13] the alumina is hydroxylated, presenting at its active sites not oxygen atoms but hydrogen atoms, and that the mechanism of sorption is hydrogen bonding *via* the phenolic oxygen and these active hydrogen sites. The electron-attracting halogen atoms decrease the electron density around the phenolic oxygen, thus resulting in a weakening of the hydrogen bond and an increase in the R_f values. The electron-releasing groups increase the electron density at the phenolic oxygen atom and hence increase the tendency to hydrogen bond with the proton-donating hydroxylated alumina. Compounds containing a nitro or methoxyl group hydrogen bond by the oxygen atoms at either end of the molecule. They are thus more strongly adsorbed, and hence have lower R_f values.

This view is substantiated by the results of other workers. Thus, Ibbitson, Jackson, McCarthy and Stone,[7] who observed an unexpectedly low free energy change for *p*-acetoxyazobenzene, proposed that the compound was sorbed by one of two mechanisms: either the carbonyl group activates a hydrogen atom of the methyl residue and this activated hydrogen atom bonds with the active oxygen of the alumina, or the acetyl group acts as an acceptor group for hydrogen bonding while the alumina acts as a proton donor. The latter of these two explanations is in accordance with our view.

Bark and Graham[14] observed that for substituted phenoxyacetic acids chromatographed on paper, those with oxygen atoms in the substituent groups had lower R_f values than the unsubstituted acid, whilst those with halogen or alkyl groups had higher R_f values. Sporer and Trueblood[5] concluded from their studies that the active sites on silicic acid were hydroxyl groups. Smith[15] observed that halogenated phenols had higher R_f values than alkyl phenols when sorbed from benzene onto silica gel. Bark and Graham[16] have similarly explained the behaviour of nitrophenols on alumina-impregnated papers.

(*c*) *Alignment of sorbed molecule onto surface of absorbent*

From column adsorption chromatography, Zechmeister,[17] Brockmann[18] and Sporer and Trueblood[5] have proposed the group anchoring site concept for attachment of the sorbed molecule to the surface. From studies of hydrocarbons and azobenzenes sorbed onto alumina-impregnated glass fibre paper, Klemm and coworkers[19] proposed a "flat-wise" π complex for the former and a partial "flat-wise" sorption through the π electrons of the benzene ring and the lone pair of electrons of the azo-nitrogen atoms.

The presence of a single spot and the absence of tailing for each compound on our chromatograms suggests the absence of the unstable cis isomers, and that the compounds migrate as the stable trans forms. Hence, for the proposed mechanism of bonding to occur, *i.e.*, the attachment of the phenolic oxygen to the substrate, the azo-skeleton is tilted slightly away from the substrate, into the organic mobile phase. Even so, the angle of the tilt is sufficiently small for the oxygen atoms of the nitro and methoxyl groups to be sufficiently close to the substrate surface for hydrogen bonding to occur.

Acknowledgement—We thank Messrs. Reeve Angel and Co. Ltd. for the gift of impregnated papers.

Zusammenfassung—R_f-Werte p'-substituierter p-Hydroxyazobenzole an Papier, Glasfasser-"papier" und mit verschiedenen Mengen Aluminiumoxyd imprägnierten Papieren werden angegeben. Di Ergebnisse zeigen, daß in erster Linie das Aluminiumoxyd für die Sorption verantwortlich ist. Der Einfluß des elektrometen Effekts des p'-Substituenten ist gering. Die Sorption wird als Ergebnis von Wassers tofibrücken zwischen Sauerstoffatomen im sorbierten Molekül und aktiven Wasserstoffatomen am hydroxylhaltigen Aluminiumoxyd angesehen.

Résumé—On donne les valeurs R_f de p-hydroxyazobenzènes p'-substitués, sur papier, papier en fibre de verre, et sur les mêmes papiers imprégnés de différentes quantités d'alumine. Les résultats indiquent que l'alumine est essentiellement responsable de la sorption. L'effect, sur la sorption, de la nature électrique du substituant en p′ est faible. On considère que la sorption est un résultat de la liaison hydrogène entre les centres oxygène dans la molécule sorbée et les centres hydrogène actif de l'alumine hydroxylée.

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AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT—III*

PHOTOMETRIC DETERMINATION OF MANGANESE^{II} THROUGH OXIDATION TO MANGANESE^{VII}

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Summary—Manganese^{II} is oxidised to permanganic acid by treatment with a slight excess of ammonium hexanitratocerate(IV) in a 0·5–2*M* nitric acid medium at room temperature. The reaction is markedly catalysed by silver nitrate, so that quantitative oxidation is possible within 1 min. Conditions have been developed for utilising the catalysed reaction for the colorimetric determination of manganese over the range 0·33–19·93 mg/litre. The new method has the advantage over those currently available in that the oxidation to manganese^{VII} is stoichiometric at room temperature. Under the conditions prescribed the permanganic acid formed is stable for at least 24 hr. Interference from sulphate and from chloride, bromide and iodide can be eliminated by treating the test solution with barium nitrate or silver nitrate, respectively, before the oxidation with cerium^{IV}. Application of the method to the determination of manganese in steel is considered.

The colorimetric determination of manganese has engaged the attention of chemists for over a century. Crum[1] appears to have been the first to observe the oxidation of manganese^{II} to permanganate by lead dioxide in nitric acid solution. Pichard[2] and a host of workers employed this reaction for the colorimetric determination of manganese. Reddrop and Ramage[3] as early as 1895 proposed the oxidation of manganese^{II} to permanganate with sodium bismuthate. The method seems to have been forgotten until Dufty[4] again drew attention to it in 1901. In the procedures employing both lead dioxide and sodium bismuthate, excess oxidising agent should be separated from the solution by filtration before the colour comparisons are made. Moreover, both methods suffer from the defect that a high temperature is necessary to complete the oxidation of manganese^{II} to permanganate. It is also possible that some of the permanganate may decompose at the high temperature and high acidities recommended. Marshall,[5] Von Knorre[6] and Walters[7] used potassium persulphate with a silver salt as catalyst in the oxidation of manganese^{II} to manganese^{VII} in the colorimetric determination of manganese. The general procedure that has been evolved as a result of the investigations of several workers is to heat the manganese^{II} in a sulphuric acid medium (containing some phosphoric acid) with excess persulphate and a trace of silver salt as catalyst. Phosphoric acid serves to prevent the precipitation of manganese dioxide. Gortner and Rost[8] and Applebaum[9] criticised the persulphate method, stating that the oxidation of manganese^{II} is often incomplete and that the permanganate colour frequently fades in a short time.

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* Part II: *Talanta*, 1963, **10**, 657.

In view of the erratic nature of the persulphate–manganese^{II} reaction, Willard and Greathouse[10] proposed the use of potassium periodate for the oxidation of manganese^{II} to manganese^{VII} in sulphuric, phosphoric or nitric acid or in a mixture of two or more acids. Chromium^{III}, cerium^{III}, *etc.*, are also oxidised by periodate in acid solution. A disadvantage is that a large excess (about fifty to one hundred times) of periodate has to be used. Koroleff[11] proposed the use of a silver salt to speed up the reaction and this also assists in economising on the amount of periodate. Although Willard and Greathouse proposed a minimum concentration of $1{\cdot}75M$ sulphuric acid, Richards[12] found that when the concentration of manganese is low (a few μg in 10 ml), a high concentration of phosphoric acid prevents the full development of the colour. Richards recommends an acidity of $2{\cdot}0N$ in sulphuric acid. While determining manganese^{II} in caustic soda, Williams and Andes[13] add sufficient phosphoric acid to produce a pH of 2 at which the oxidation by periodate is conducted. Nydahl[14] recently stated that the colorimetric determination of manganese according to the periodate method requires rather a long period of heating for the full development of colour, especially in very dilute solution, even when it is carried out as proposed by Richards or by Koroleff. When the amount of manganese is 1 μmole/100 ml, Nydahl observed the oxidation to take place only to 49% extent in 1 hr, on a steam bath, and to 57% in 2 hr when carried out under the optimum conditions prescribed by Richards. In the presence of 0·1 mmole of silver nitrate the corresponding figures were 86 and 91%, respectively.

Strickland and Spicer[15] carried out a fairly systematic study of the important factors governing a satisfactory analytical application of the periodate oxidation. They observed that

1. The extinction obtained from a given quantity of manganese can vary in magnitude and reproducibility according to the conditions.

2. The rate of oxidation is mainly dependent upon the acidity of the solution and has a minimum value when the reaction takes place (at 100°) in a nitric or sulphuric acid medium of $1{\cdot}5M$ concentration. At lower acidities the reaction becomes very rapid, but the extinctions are rather erratic and the use of a low acidity to increase the rate is not recommended. With more strongly acid solutions there is again an increase in the rate of the reaction, but the final extinction under these conditions decreases less rapidly and the extinctions are reproducible. Nevertheless, for several reasons, the acidity must not exceed certain approximate values. It is suggested that the most satisfactory acid range to use with sulphuric acid at 100° is 3–$6M$ and the corresponding range for nitric acid at 100° is 4–$7M$.

3. With sulphuric acid concentrations greater than $6M$ the decrease of extinction becomes very rapid, largely because of the formation of permanganic anhydride. The effect with nitric acid is not so pronounced and is mainly the result of the formation of quadrivalent manganese. If the acidity becomes too great in nitric acid media, manganese dioxide may precipitate. In view of the above effects, the acidity of sample and standard solutions should be reproduced to within at least $0{\cdot}5M$ and care should be taken to ensure that concentration changes from evaporation, *etc.*, do not exceed 5–10%.

4. If solutions are boiled, the additional complication of permanganic acid volatility is encountered in the case of sulphuric acid solutions. This can lead to appreciable errors in acid solutions more concentrated than $6M$.

5. Because the rate of oxidation increases two or three times for an increase in temperature of 20°, it is obvious that as high a temperature as practicable should be used. The maximum extinction from a given quantity of manganese can vary by a few per cent, however, according to the exact temperature and the latter should be controlled to within 10°. Superheating (which is marked with sulphuric acid) may be avoided by the addition of glass beads, *etc.*

6. The reaction does not depend to any appreciable extent on the concentration of periodate, provided that this exceeds the concentration of manganese some fifty or one hundred times. It is suggested that 0·5 g of potassium periodate is used for every 100 ml of solution in which the concentration of manganese^{II} should not exceed about $5{\cdot}10 \times 10^{-4}M$.

7. The nature of the reaction is such that complete oxidation is never theoretically achieved and the extinction-time curve approaches a maximum asymptotically. Although in practice the extinction rapidly attains a maximum value within the sensitivity of measurement of the absorptiometer, the relatively slow approach to this value makes a visual estimation deceptive and it is essential to allow further time to elapse after the colour appears to be fully developed.

Tomula and Aho[16] proposed a colorimetric method for the determination of manganese^{II} through its oxidation to manganese^{III} in a sulphuric acid medium by potassium bromate, the resulting manganese^{III} being stabilised by complexation with phosphoric acid. Purdy and Hume[17] in a recent communication criticised the method and stated "in attempting to study the reproducibility and sensitivity of their method, the authors were unable to obtain consistent results". The latter authors improved the method and determined manganese as the tervalent complex in strong sulphuric acid. As much as 70 mg of manganese/100 ml could be determined. The recommended procedure was to treat the sample solution with enough concentrated sulphuric acid to give an over-all $8M$ acidity on dilution to 100 ml, followed by the addition of 2 ml of $0{\cdot}5M$ potassium cyanide and 5 ml of $0{\cdot}17M$ potassium bromate. After diluting to 100 ml, the absorbance of the solution was measured at 500 mμ in a spectrophotometer. Working at such high acid concentrations is not, however, always convenient, and the use of potassium cyanide is associated with the obvious dangers.

In view of what has been said above it was considered advantageous to possess a reagent which can oxidise manganese^{II} to permanganate quantitatively at room temperature. We have observed that ammonium hexanitratocerate(IV) does this in a dilute nitric acid medium. Silver nitrate accelerates the reaction to such an extent that the oxidation is complete within 1 min at room temperature. We have developed conditions under which the reaction can be used for the colorimetric determination of manganese over the range 0·33 to 19·93 mg/litre. Nitrate, perchlorate and borate do not interfere. Interference from chloride, bromide and iodide can be eliminated by adding sufficient silver nitrate to precipitate the silver halide, which is filtered off. Sulphate is similarly removed by the addition of barium nitrate to the hot test solution. Nickel^{II}, iron^{III}, copper^{II}, calcium^{II}, barium^{II} and molybdenum^{VI} do not interfere even when present in large quantities; when cobalt^{II} is present a correction for its own colour becomes necessary. Chromium^{III} interferes because it is oxidised along with the manganese^{II}, but curiously enough the oxidation of manganese^{II} does not go to quantitative completion at room temperature in the presence of chromium^{III}.

EXPERIMENTAL

Reagents

Ammonium hexanitratocerate(IV). An approximately $0{\cdot}05M$ stock solution of this reagent was prepared as described in Part I of this series.[18] From this a $0{\cdot}01M$ solution is prepared by suitable dilution with $1{\cdot}0M$ nitric acid which has been previously boiled out to free it from any traces of nitrous acid. No standardisation of this reagent is required because it is added in excess to the manganese^{II} solution.

Manganese^{II} solution. An approximately $0{\cdot}025M$ solution of manganese^{II} was prepared by dissolving analytical reagent grade manganese^{II} sulphate (B.D.H. Ltd., England) in doubly distilled water and diluting to 1 litre. The solution was standardised potentiometrically by the methods of Lingane and Karplus[19] and Gopala Rao and Kanta Rao.[20] This standard solution is suitably diluted as required.

Nitric acid solution. An approximately $8M$ solution of nitric acid was prepared by twice diluting analytical reagent-grade nitric acid with doubly distilled water, was boiled out to drive off any oxides of nitrogen, and was stored in an amber coloured bottle protected from light.

Silver nitrate solution. A 5% solution of analytical reagent grade silver nitrate was used as catalyst.

All other reagents employed in this investigation were of analytical reagent quality.

Apparatus

A Klett-Summerson photoelectric colorimeter with optically matched tubes was generally used for colour comparison, with a green filter transmitting at a wavelength of 525–540 mμ. A Hilger Uvispek spectrophotometer with 1-cm cells was also used whenever necessary.

Influence of time

Five ml of $0{\cdot}001510M$ manganese^{II} solution were taken in a 50-ml calibrated flask, acidified with sufficient 1:1 nitric acid to give an over-all acid concentration of $1{\cdot}0M$ when diluted to 50 ml, then treated with 10 ml of $0{\cdot}01M$ ammonium hexanitratocerate(IV) and the mixture diluted to the mark. It was immediately transferred to the colorimeter and the absorption of the solution measured against a blank of ammonium hexanitratocerate(IV) solution of equivalent concentration. The dial readings of the instrument noted at different times are recorded in Table I. In these experiments the molar ratio of manganese^{II}:cerium^{IV} was 1:10.

TABLE I

Time, *min*	1	5	15	30	45	60	120	180	240	300
Dial reading of colorimeter	26	61	101	142	161	169	179	187	194	194

The results in Table I show that about 4 hr are required for complete oxidation of manganese^{II} at room temperature.

Influence of temperature

Somewhat similar experiments to those above, but carried out at the temperature of a boiling water bath yielded the observations recorded in Table II.

TABLE II

Time of heating, *min*	1	2	5	10	15	30	60
Dial reading of colorimeter	45	61	108	122	149	193	194

It is evident that the oxidation of manganese^{II} is complete in about 30 min.

Influence of cerium^{IV} concentration

Experiments made at room temperature by varying the ratio of manganese^{II}:cerium^{IV} yielded the observations presented in Table III. In these experiments the concentration of manganese^{II} was maintained constant and that of the cerium^{IV} varied. It may be noted that 1 mole of manganese^{II} requires 5 moles of cerium^{IV} for complete oxidation to manganese^{VII}.

TABLE III

Time, *min*	Molar ratio of manganese^{II}:cerium^{IV}				
	1:5	1:10	1:15	1:20	1:40
	Dial reading of colorimeter				
1	14	26	38	65	76
2	29	41	49	89	92
5	43	61	71	114	118
15	76	101	108	168	170
30	94	142	159	192	193
60	103	169	184	194	194
120	147	179	194	194	194
240	178	194	194	194	194
300	182	194	194	194	194

Manganese taken: 0·0075 mmole

From Table III the rate of oxidation of manganese^{II} at room temperature can be increased by increasing the concentration of cerium^{IV} relative to that of manganese^{II}. With a fairly large excess of cerium^{IV} (1:20) the time of reaction can be reduced to 1 hr.

Influence of catalysts

With a view to further reducing the time of reaction at room temperature the use of catalysts, such as cobalt^{II}, nickel^{II}, osmium^{VIII} and silver^{I} salts, was investigated. Of the substances tried, only silver^{I} nitrate markedly accelerated the reaction.

Experiments were made to ascertain the optimum concentration of catalyst required for rapid oxidation of manganese^{II} by cerium^{IV} in a nitric acid medium at room temperature.

Five ml of 0·001510*M* manganese^{II} solution were acidified with sufficient 1:1 nitric acid to give an over-all acid concentration of 1·0*M* on dilution to 50 ml in a calibrated flask. The mixture was treated with varying volumes of 5% silver nitrate solution followed by 10 ml of 0·01*M* ammonium hexanitratocerate(IV) solution, then diluted to 50 ml with doubly distilled water. It was immediately transferred to the colorimeter and the dial readings noted at varying intervals of time. In these experiments the molar ratio of manganese^{II} to cerium^{IV} was 1:10.

TABLE IV

5% $AgNO_3$, *ml*	Time, *min*								Remarks
	0·5	1	2	5	10	15	30	60	
	Dial reading of colorimeter								
—	16	26	41	61	84	101	142	169	
0·10	48	69	94	126	157	186	194	194	
0·20	63	94	126	157	186	194	194	194	
0·50	108	137	157	192	194	194	194	194	
1·0	158	187	194	194	194	194	194	194	
2·0	192	194	194	194	194	194	194	194	
5·0	192	194	194	194	194	194	194	194	
7·50	190	190	192	192	192	192	192	192	Brown precipitate* on standing 6 hr.
10	149	149	149	151	151	151	160	168	Brown precipitate* on standing 3 hr.
15	—	—	—	—	—	—	—	—	Brown precipitate* immediately on mixing the solutions

* MnO_2

Table V

Over-all HNO$_3$ *M*	Time, *min* 0·5	1	2	3	4	5	10	Remarks
	Dial reading of colorimeter							
0·25	146	164	176	182	189	192	194	
0·50	174	188	192	194	194	194	194	
1·0	188	194	194	194	194	194	194	
2·0	192	194	194	194	194	194	194	
3·0	159	163	174	184	188	188	188	Development of colour very slow.
4·0	108	126	128	134	138	142	154	No pink colour; on standing a colloidal brown precipitate formed.
5·0	—	—	—	—	—	—	—	On mixing the solutions a brown precipitate formed immediately.

It is evident from Table IV that the reaction is complete in about 1 min when the silver catalyst concentration corresponds to 2·0 ml of 5% silver nitrate solution/50 ml of reaction mixture. When the concentration increases beyond that corresponding to 10 ml, the reaction is definitely retarded. When the catalyst concentration corresponds to 15 ml a brown precipitate is formed immediately the solutions are mixed, leaving a clear yellow supernate.

Influence of nitric acid concentration on silver catalysed reaction

To ascertain the optimum concentration of nitric acid required for this reaction the following experiments were carried out. Five ml of 0·001510*M* manganese^{II} solution were treated with sufficient 1:3 nitric acid to reach different over-all acidities, followed by 2 ml of 5% silver nitrate solution and 10·0 ml of 0·01*M* ammonium hexanitratocerate(IV) solution, then the mixtures diluted to 50 ml in calibrated flasks. The various solutions were measured in the colorimeter at different intervals of time. Allowance was made for the nitric acid introduced through the hexanitratocerate(IV) solution.

In view of the observations in Table V it was decided to maintain the concentration of nitric acid between 0·5 and 2·0*M* in subsequent experiments. If the concentration exceeds 2·0*M*, the reaction may be retarded and manganese dioxide may be precipitated.

Influence of cerium^{IV} concentration on silver catalysed reaction

Five ml of 0·001510*M* manganese^{II} solution were acidified with sufficient 1:1 nitric acid to give an over-all acidity of 1·0*M* when diluted to 50 ml in a calibrated flask, then 2 ml of 5% silver nitrate

Table VI

Manganese^{II}:cerium^{IV}	Time, *min* 1	2
	Dial reading of colorimeter	
1:5	140	—[a]
1:10	194	194
1:15	193	194
1:20	194	193

[a] Because added hexanitratocerate(IV) solution is in insufficient excess, a colloidal brown precipitate of manganese dioxide was obtained.

solution and sufficient 0·02M ammonium hexanitratocerate(IV) solution to give the desired molar ratio of reactants added. The final volume was made to 50 ml with doubly distilled water, and the developed color measured in the colorimeter.

From the observations in Table VI it is evident that, under the conditions employed, the reaction is complete in 1 min when the ratio of manganese^{II}:cerium^{IV} is 1:10.

Stoichiometry of reaction

In all procedures previously prescribed for the colorimetric determination of manganese^{II} based on oxidation with lead dioxide, sodium bismuthate, potassium persulphate or potassium periodate, it appears to be tacitly assumed that the product is permanganic acid, without any precise data regarding the stoichiometry of the reaction being provided. In the present case proof is provided as follows. Five ml of 0·001510M manganese^{II} solution were oxidised with excess ammonium hexanitratocerate(IV) under the conditions prescribed in the recommended procedure, then diluted to 50 ml. The solution contains nitric acid at 1·0M concentration. The developed colour of the solution was measured in the colorimeter against a blank of cerium^{IV} solution of equivalent concentration, the dial reading of the instrument being 194. A carefully standardised solution of analytical reagent grade potassium permanganate (B.D.H. Ltd., England) was suitably diluted to give a 0·001510M solution of the salt in 1·0M nitric acid. This solution gave a dial reading of 193 in the colorimeter. Furthermore, the absorption spectrum of a similarly prepared experimental solution (containing 0·0002M manganese^{II}) and that of 0·0002M permanganate were determined in 1·0M nitric acid using a Hilger Uvispek spectrophotometer and 1-cm cells in the region 480–760 mμ. The absorption of the experimental solution was measured against a blank of cerium^{IV} solution of equivalent concentration. The two absorption curves very nearly overlap (Fig. 1). The molecular extinction coefficient of the experimental solution is $2{\cdot}30 \times 10^3$ and that of the potassium permanganate $2{\cdot}275 \times 10^3$, an agreement within 1·1%, which must be considered sufficiently good considering the extreme dilution at which the absorption measurements are made.

The data presented is sufficient to show that:

(1) The product of the oxidation of manganese^{II} by ammonium hexanitratocerate(IV) in a nitric acid medium is permanganic acid.

(2) The manganese^{II} is stoichiometrically converted into permanganic acid.

Stability of permanganic acid formed

The constancy of the optical absorption of the experimental solution over a period of at least 24 hr shows that the permanganic acid is very stable. Hence the new method can be considered well suited to routine work under ordinary laboratory conditions.

Limits of applicability

Working with solutions of different concentrations of manganese^{II} it has been observed (Fig. 2) that Beer's Law is applicable for experimental solutions containing 0·0332–1·9932 mg/100 ml.

Recommended procedure

A volume of 5–10 ml of test solution, containing about 0·033 to 2 mg of manganese^{II}/100 ml, is treated with sufficient 1:1 analytical reagent grade nitric acid to give an over-all acid concentration of 0·5–2·0M on dilution to 50 ml, followed by the addition of 2 ml of 5% silver nitrate solution and an approximately ten-fold molar excess of hexanitratocerate(IV) solution. The total volume is then made to 50 ml in a calibrated flask. After allowing to stand for 2 min, the developed colour is measured in a Klett-Summerson photoelectric colorimeter, using a green filter transmitting in the wavelength region 525–540 mμ, against a blank solution containing an equivalent amount of cerium^{IV} solution to that used in the test sample.

Typical results of such determinations are presented in Table VII. The amount of manganese^{II} present in each sample is deduced from a calibration curve (Fig. 2), or alternatively the manganese content can be deduced by comparing the colour of the test solution against that of a standard permanganate solution of about the same strength in 1·0M nitric acid.

INTERFERENCES

Nitrate (as sodium or ammonium salt) does not interfere even when present up to 720 mg/50 ml. Similarly, perchlorate and borate (as their sodium salts) do not interfere even at a concentration of 150 mg/50 ml. Traces of chloride, bromide and iodide inhibit the reaction. However, the interference of these ions can be eliminated by precipitating them with silver nitrate and filtration before the oxidation with cerium^{IV} solution. Our results show that the interference of up to at least 21·6 mg

Table VII

Manganese^{II} taken, *mg*	Manganese^{II} found, *mg*
0·04957	0·04977
0·07128	0·07099
0·09914	0·09896
0·1496	0·1510
0·2478	0·2501
0·3892	0·3932
0·4698	0·4704
0·9912	0·9936

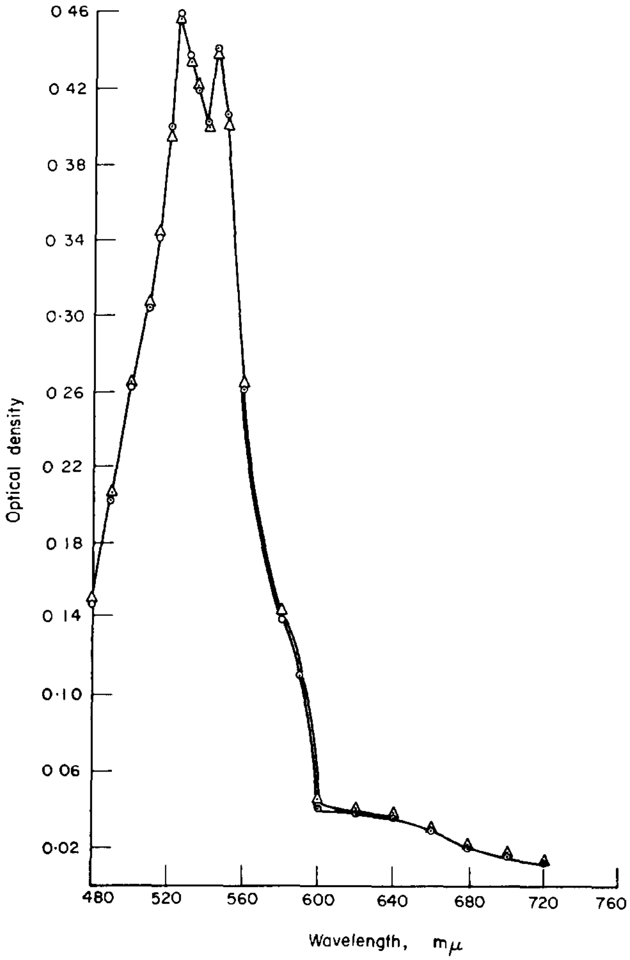

Fig. 1.—Absorption spectra of manganese^{VII} in 1·0*M* nitric acid:
△—△ 0·0002*M* manganese^{VII} from potassium permanganate,
○—○ 0·0002*M* manganese^{VII} after oxidation of manganese^{II} with hexanitratocerate(IV).

of chloride ion/50 ml can be eliminated in this way. Similar experiments have shown that the interference of up to at least 16 mg of bromide and 25·4 mg of iodide can be eliminated satisfactorily. Sulphate ion does not interfere when present below 2 mg/50 ml. The interference of larger amounts can be eliminated by initially treating the hot test solution with barium nitrate and filtering off the precipitated barium sulphate. In this way the interference of sulphate even up to a concentration of 38·4 mg/50 ml can be overcome.

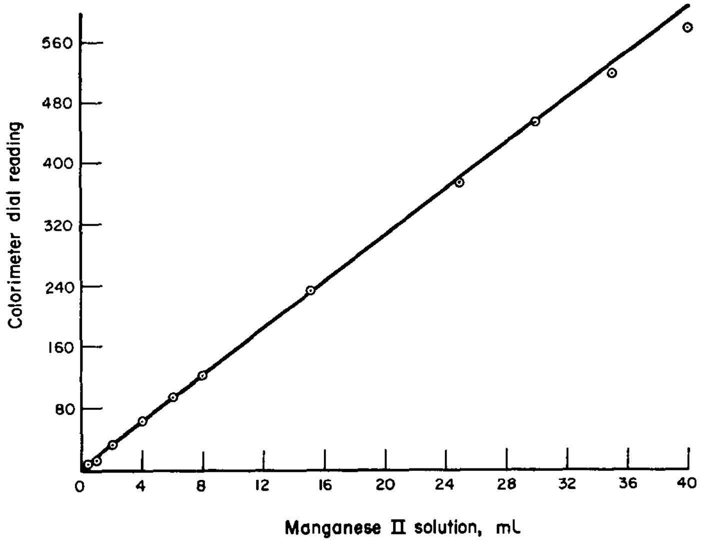

FIG. 2.—Beer's law curve for determination of manganese^{II} with hexanitratocerate(IV) ($6·04 \times 10^{-4}M$ manganese^{II} sulphate solution).

Previously published colorimetric procedures for manganese also suffer interference from chloride. In the bismuthate method the sample is usually evaporated with nitric and sulphuric acids to remove chlorides. In the persulphate method chloride is removed by adding an excess of silver nitrate. Concerning the interference of chloride in the periodate method, the statement of Willard, as quoted by Yoe,[21] is interesting: "It has been stated in various references to this method that the presence of chloride would not interfere. This is true only to a limited extent and only when the operator has taken care to add sufficient periodate to oxidise all the chloride. It is preferable to remove chloride by evaporation with nitric or sulphuric acid." Thomson and Wilson,[22] who applied the periodate method to the determination of manganese in sea water, removed the chloride by treating the evaporation residue with concentrated sulphuric acid, heating to expel the acid and fuming the salts.

The interference of sulphate constitutes a drawback for the new method as compared with the persulphate and periodate procedures. According to Yoe[23] the bismuthate method is satisfactory only when most of the sulphuric acid has been driven off. He states that this is necessary for the reason that the shade of the permanganate is not the same in sulphuric and nitric solutions.

Nickel^{II}, iron^{III}, copper^{II}, calcium^{II}, barium^{II} and molybdenum^{VI} do not interfere even when present up to 40 mg/50 ml. Cobalt^{II}, when compensated for its own colour, does not interfere even up to 100 mg/50 ml. Tungsten^{VI} interferes because of precipitation of tungstic acid in the mineral acid medium. The interference from chromium^{III} has been mentioned above (chromium^{III} also interferes in the periodate and persulphate methods).

Application of New Method to Determination of Manganese in Steel

About 1 g of silico-manganese spring steel (supplied by Messrs Globe Steels, Bombay, India) was treated with 60 ml of 1:1 nitric acid in a 600-ml Pyrex beaker, then heated on a hot-plate for 40–50 min, by which time all volatile and carbonaceous matter was completely decomposed. The resulting yellow solution contained a spongy brown mass (colloidal silicic acid with adsorbed iron^{III}) in suspension which was filtered off, after dilution to about 200 ml, through a Whatman No. 42 filter paper, the filtrate being collected in a 500-ml calibrated flask. The residue on the filter paper, after being washed twice with distilled water, was transferred along with the filter paper to a silica crucible and incinerated to a brown mass. After cooling to room temperature, it was leached with a few drops of 1:1 nitric acid and a few drops of hydrofluoric acid, and the extract transferred to a platinum dish and evaporated to dryness. The resulting mass, after twice evaporating with a mixture of 2 ml of 1:1 nitric acid and 2 ml of hydrofluoric acid, readily dissolved in dilute nitric acid. The solution obtained was transferred to the calibrated flask containing the main bulk of the solution and diluted to the mark. Three different aliquots of this solution (5, 10 and 15 ml) treated according to the new procedure gave the manganese present in the sample as 1·128, 1·127 and 1·130%, respectively, as against a value of 1·150% by the potentiometric procedure of Lingane and Karplus.[19] The agreement between the two methods is considered satisfactory.

Acknowledgement—One of us (P. V. K. R.) desires to thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Es wurde beobachtet, daß Mangan(II) durch einen schwachen Überschuß von Ammoniumhexanitratocerat(IV) in 0·5–2m HNO_3 bei Zimmertemperatur zu Permangansäure oxydiert wird. Die Reaktion wird durch Silbernitrat merklich katalysiert, sodaß die quantitative Oxydation von Mangan(II) in einer Minute beendet ist. Es wurde eine Arbeitsvorschrift entwickelt, die die katalysierte Reaktion zur kolorimetrischen Bestimmung von Mangan zwischen 0·33 und 19·93 mg/l zu verwenden gestattet. Die neue Methode hat vor den derzeit verfügbaren den Vorteil, daß die Oxydation von Mangan(II) bei Zimmertemperatur stöchiometrisch zu Ende geht. Unter den vorgeschriebenen Bedingungen ist die gebildete Permangansäure mindestens 24 Stunden beständig. Die Störung durch Sulfat und Halogenide (Chlorid, Bromid und Jodid) kann durch Behandlung der Probelösung mit Bariumnitrat beziehungsweise Sibbernitrat vor der Oxydation mit Cer(IV)-Lösung eliminiert werden. Die Anwendung der Methode auf die Manganbestimmung in Stahl wird erörtert.

Résumé—On a observé que le manganèse(II) est oxydé en acide permanganique par traitement avec un léger excès d'hexanitratocérate(IV) d'ammonium en milieu acide nitrique 0,5 à 2M à température ambiante. La réaction est nettement catalysée par le nitrate d'argent, de sorte que l'oxydation quantitative du manganèse(II) est complète en une minute. On a établi les conditions d'emploi de la réaction catalysée pour le dosage colorimétrique du manganèse entre 0·33 et 19·93 mg par litre. Par rapport aux méthodes couramment disponsibles, cette méthode est avantageuse par le fait que l'oxydation du manganèse(II) est effectuée à température ambiante, de façon stoechiométrique. Dans les conditions prescrites, l'acide permanganique formé est stable 24 hau moirs. L'interférence des sulfates et des halogénures (chlorure, bromure et iodure) peut être éliminée en traitant la solution essai au nitrate de baryum ou au nitrate d'argent, respectivement, avant oxydation par la solution de cérium(IV). On considère aussi l'application de la méthode au dosage du manganèse dans l'acier.

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POLAROGRAPHIC DETERMINATION OF DISSOLVED OXYGEN IN PETROL

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Summary—A method is described for the determination of dissolved oxygen in petrol using a cathode ray polarograph. Oxygen produces two waves, with reduction potentials at −0·67 V and −1·25 V against a mercury pool anode, when an ethanolic solution of lithium chloride is used as supporting electrolyte. Calibrations are carried out using water of known oxygen content for the preparation of standards and the wave at −0·67 V is preferred for quantitative measurement.

INTRODUCTION

THE determination of oxygen in hydrocarbons has been carried out in these laboratories by a chemical procedure based upon that of McArthur,[1] who developed an analytical method for determination of the oxygen content of various plant gases. As applied to hydrocarbons, this method depends upon the removal of oxygen in a stream of oxygen-free nitrogen and its absorption into a 0·01*N* solution of chromium^{II} chloride. The excess chromium^{II} chloride is subsequently determined by titration with cerium^{IV} sulphate using ferroïn as indicator.

Polarography has been used for the determination of oxygen in a number of materials and it appeared an attractive alternative, having the virtues of speed and specificity.

It is well established that dissolved oxygen is reduced at the dropping mercury electrode to produce two waves.[2] The first wave results from reduction to hydrogen peroxide:

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \text{ (acid medium)}$$

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \text{ (neutral or alkaline medium).}$$

The second wave corresponds to the reduction of the hydrogen peroxide either to water or hydroxyl ion, depending on the pH:

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \text{ (acid medium)}$$

$$H_2O_2 + 2e \rightarrow 2OH^- \text{ (alkaline medium).}$$

The diffusion currents are normally well-defined and show a linear dependence on oxygen concentration. However, three main difficulties are encountered in the application of polarography to the determination in petrol: the limited solubility of petrol in aqueous or semi-aqueous electrolyte systems, the exclusion of atmospheric oxygen in handling samples and the accurate calibration of the instrument. The first difficulty was resolved by adopting a supporting electrolyte of lithium chloride in absolute alcohol and the second by the design of a special cell. Two ways of calibrating the polarograph were investigated: by using water of known dissolved oxygen content directly as a calibration standard, and by using air-saturated alcoholic electrolyte as a secondary standard, the dissolved oxygen content being determined polarographically using water as a primary standard.

EXPERIMENTAL

A 0.1*M* ethanolic solution of lithium chloride proved a suitable supporting electrolyte and gave reduction waves from dissolved oxygen at −0·67 V and −1·25 V.

In early experiments calibrations were achieved by determining the dissolved oxygen content of the supporting electrolyte and using this as a secondary standard. However, the calibration procedure given below was preferred because, under the conditions given, petrol, electrolyte and water formed a completely homogeneous system.

Apparatus

Polarograph. A Southern Analytical Differential Cathode Ray Polarograph was used, but any conventional polarograph of adequate sensitivity would be suitable.

Sampling tube. A sampling tube connected to the polarographic cell is shown in Fig. 1. It comprises a tube of about 5-ml capacity with two 3-way taps C and D, but so arranged that the sample is delivered *via* tap C to the polarographic cell. The volume of the sample tube is determined by filling it with water and weighing.

Polarographic cell. This is also illustrated in Fig. 1. A specially designed cell is so arranged that the dropping electrode, sample inlet tube and stirrer emerge through a tight-fitting bung into the cell. It contains two taps A and B, A being a 3-way tap, the inlet of which is connected to an argon supply and arranged so that the electrolyte can be degassed. Tap A can also be fitted to tap D of the sample tube and argon used to gently transfer the petrol through taps C and B into the cell, the latter being connected by means of polyvinylchloride tubing. A side arm is also provided for the anode connection, thus preventing any fouling by the stirrer.

Reagents

0.1*M* *Lithium chloride.* Prepare a 0·1*M* ethanolic solution of lithium chloride by dissolving 4·24 g of lithium chloride in absolute alcohol and diluting to 1 litre with this solvent.

Air-saturated water of known oxygen content. For most purposes a published value can be assumed for the oxygen content,[3] but for more accurate work the dissolved oxygen should be determined by the Winkler method.[4] Air-saturated water may be prepared by shaking a partially filled flask of water for several minutes, recording the temperature at which this is done.

Argon (oxygen-free). High quality nitrogen may be used as an alternative.

Procedure

Calibration of polarograph. Add 35 ml of 0.1*M* lithium chloride and 5 ml of petrol to the polarographic cell, which contains a mercury pool as anode. Fit the bung to the cell, close tap B and degas the solution by turning tap A and bubbling argon through the electrolyte for 5–10 min. Close tap A. Set the start potential at −0·2 V and measure the wave height of any remaining oxygen at −0·67 V (this should be very small; if not, continue degassing). Record this reading. Introduce 5 ml of air-saturated distilled water at a known temperature by means of a microburette through tap B and stir rapidly by switching on the electric motor after closing tap B. When a homogeneous solution is obtained, with start potential at −0·2 V, measure the height of the oxygen wave at −0·67 V. Record this reading and empty the cell.

Now take 35 ml of 0·1*M* lithium chloride, 5 ml of petrol and 1 ml of water into the polarographic cell and degas with argon *via* tap A for 5–10 min. Close tap A and measure the wave height of any residual oxygen. Introduce 4 ml of air-saturated water by means of a microburette through tap B, stir and record the wave height of the resulting polarogram.

Repeat this procedure with 35 ml of 0·1*M* lithium chloride/5 ml of petrol/2 ml of water, 35 ml of 0.1*M* lithium chloride/5 ml of petrol/3 ml of water and 35 ml of 0.1*M* lithium chloride/5 ml of petrol/4 ml of water, degas, then add 3, 2 and 1 ml of water, respectively. Convert ml of water to mg of oxygen from the tables relating temperature of water to dissolved oxygen content[3] and construct a graph relating peak height to concentration of oxygen.

Determination of dissolved oxygen in petrol. Connect the sample tube to sample point with polyvinylchloride tubing (Notes 1 and 2) and purge well with petrol. Close taps C and D so that the tube is completely filled with petrol.

Add 35 ml of 0·1*M* lithium chloride solution to the polarographic cell and 5 ml of water. Connect the rubber bung to the cell and close tap B. Degas the system by bubbling argon *via* tap A into the solution for 5–10 min. Close tap A and with start potential at −0·2 V record the polarogram of the solution. If a wave appears, continue degassing, then repeat the voltage sweep until no oxygen wave or only a small 'blank' is recorded.

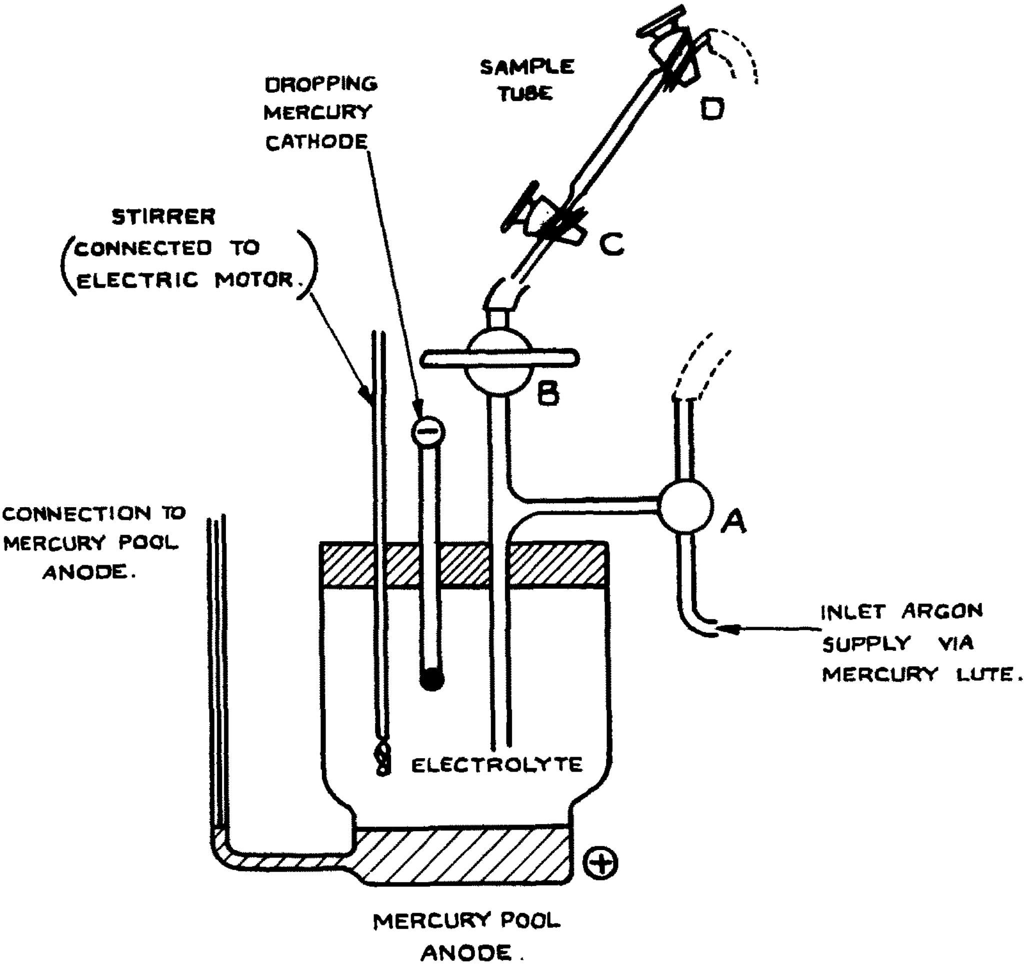

Fig. 1

Connect the sample tube to the cell with polyvinylchloride tubing between taps B and C and between taps A and D as shown in Fig. 1. Turn tap A so that argon purges through tap D for about 1 min, then close tap D and open taps B and C and purge with argon for the same period. Close taps B and C. Close tap A to the cell and turn it to the polyvinylchloride connection between A and D, opening taps D and C in that order and then tap B in such a manner that the sample is very slowly added to the cell. Close tap B after the addition of sample.

Record the polarogram from a start potential of −0·2 V at a sensitivity to give a maximum wave height. Measure the wave height of the oxygen wave and read the mg of oxygen to which this is equivalent from the calibration graph.

Notes

1. Avoid the use of rubber tubing and silicone tap grease because this interferes with the polarographic determination.
2. The amount of polyvinylchloride tubing should be kept to a minimum because it is porous to oxygen.

Calculation

Let a be the mg of oxygen from the graph and v be the volume of sample. Hence

$$(\text{ppm w/v}) = \frac{a \times 10^3}{\text{v}}.$$

RESULTS AND DISCUSSION

In all experiments the total volume and electrolyte/petrol/water ratios were maintained the same, thus providing identical backgrounds for the evaluation of the oxygen wave heights. The quantitative nature of the two oxygen waves at −0·67 V and −1·25 V was demonstrated by polarographing varying amounts of a sample of air-saturated petrol in a water and alcoholic solution of 0·1*M* lithium chloride, but maintaining the total volume and ratio of water/petrol and electrolyte the same. The linear variation of peak height with concentration is shown in Table I.

TABLE I.—MEASUREMENT OF OXYGEN WAVE AT −0·67 V AND −1·25 V

Air-saturated petrol, *ml*	Peak height at −0·67 V converted to the same scale factor	Peak height at −1·25 V converted to the same scale factor
5	186	156
3	112	96
1	35	33

It was found preferable, however, to use the oxygen wave at −0·67 V because polarographic determination in this electrolyte/petrol media caused serious streaming of the dropping mercury electrode at the higher potential.

An important feature of the polarographic method is the fact that by degassing the sample cell with argon or nitrogen, all of the dissolved oxygen is completely removed. Thus, any doubts that it is the oxygen wave being measured can be confirmed by the simple technique of degassing, when this wave will disappear. Using this technique, the calibration was easily checked by preparing standard solutions of oxygen from air-saturated water and degassed petrol and the recoveries obtained are shown in Table II.

TABLE II.—RECOVERIES OF OXYGEN ON STANDARD SOLUTIONS

Oxygen added, *ppm*	Oxygen found, *ppm*
44	43
26	25
26	26
9	10
9	7

The determination on samples taken in duplicate shows the polarographic method to be highly reproducible, a number of petrol samples being analysed which were shown to have dissolved oxygen contents between <1 ppm and 30 ppm. The fact that figures of <1 ppm could be recorded also confirmed that the special sampling and cell arrangement precluded absorption from atmospheric oxygen. The results on duplicate samples are given in Table III.

TABLE III.—DUPLICATE DETERMINATIONS OF DISSOLVED OXYGEN (ppm) IN SAMPLES OF PETROL

Detm.	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
1	0·8	1·3	1·6	10	14	21	23	30
2	0·8	1·4	1·8	11	16	21	25	33

Finally, by the analysis of identical samples of petrol, a comparison of the polarographic and chemical[1] methods was made. In the latter the petrol was degassed in a stream of oxygen-free nitrogen and the oxygen absorbed in an acid solution of 0·01*N* chromium^{II} chloride. The change in chromium^{II} ion concentration was then related to the amount of oxygen which the sample contained. The excess chromium^{II} ion was determined by adding the solution under test to iron^{III} alum solution and the equivalent iron^{II} ion produced titrated with a standard solution of cerium^{IV} sulphate using ferroïn as indicator. Comparison of the two techniques is shown by the results in Table IV.

TABLE IV.—COMPARISON OF RESULTS FOR DISSOLVED OXYGEN BY POLAROGRAPHIC AND CHEMICAL TECHNIQUES

By polarography, *ppm*	By chemical method, *ppm*
0·8	<1
4·5	4·0
3	2·5
6	9
15	13
10	7
15	10
36	32

These results show reasonable agreement, but the speed with which determinations can be completed by polarography compared with the chemical method and the high reproducibility on duplicate samples makes this the more attractive method for the determination of dissolved oxygen in petrol.

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Zusammenfassung—Eine Methode zur Bestimmung von gelöstem Saurestoff in Petroleum mit Hilfe eines Kathodenstrahlpolarographen wird beschrieben. Sauerstoff gibt zwei Stufen mit Reduktionspotentialen bei −0,67 V und −1,25 V gegen das Bodenquecksilber als Anode, wenn als Trägerelekrolyte eine äthanolische Lithiumchloridlösung benutz wird. Geeicht wird mit Wasser bekannten Sauerstoffgehalts zur Herstellung von Standardlösungen; die Stufe bei −0,67 V wird zur quantitativen Messung vorgezogen.

Resume—On décrit une méthode de dosage de l'oxygène dissous dans l'essence, au moyen d'un polarographe oscillographique. L'oxygène produit deux vagurs, avec des potentiels de réduction à −0,67 V et −1,25 V, par rapport à une anode à masse de mercure, lorsque l'électrolyte support est une solution éthanolique de chlorure de lithium. Les étalonnages sont effectués en utilisant de l'eau à teneur en oxygène connue pour la préparation des étalons et, pour les mesures quantitatives, on préfère la vague à −0,67 V.

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SHORT COMMUNICATIONS

New ideas on the reaction mechanism of determinations based on decolorisation

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PHOTOMETRIC determinations of fluoride are mostly based on decolorisation, *i.e.*, decrease in colour intensity of a metal-dye (MD) chelate and increase in that of the free dye. *All* decolorisation determinations of fluoride have, therefore, been interpreted as being indirect methods, based on a substitution mechanism, which can be formulated as

$$M = D^{(m-d)+} + nF^- + hH^+ + \rightarrow MF_n^{(m-n)+} + H_hD^{(d-h)-} \tag{1}$$

where M^{m+} is a metal ion, D^{d-} and $H_hD^{(d-h)-}$ are different protonation forms of a dye, $=$ represents the chelate ring responsible for the colour of the metal-dye chelate, and $h \lesseqgtr 0$.

Probably the first direct colour (colorisation) reaction of fluoride was described by Feigl and Rajmann,[1,2] but today this reaction is forgotten because of its small practical use. A direct determination of fluoride which has received wide attention, is that of Belcher and coworkers:[3,4] a yellow solution of alizarin complexan gives rise to a red chelate with cerium^{III}, and this in turns yields a blue ternary complex with fluoride. When the fluoride concentration increases, the solution becomes yellow because of the rupture of all of the MD bonds according to equation (1). Belcher and coworkers' interpretation of the blue colour may be generalised as follows. The strongly electronegative fluoride ion, after reacting with a metal-dye chelate derived from the dye DOH^{d-} (which even after reacting with the metal still has a free hydroxyl group)

$$M{=}DOH^{(m-d)+} + nF^- \rightarrow F_nM{=}DOH^{(m-d-n)+} \tag{2}$$

labilises the hydrogen in the free hydroxyl group of the dye:

$$F_nM{=}DOH^{(m-d-n)+} \rightarrow F_nM{=}DO^{(m-d-n-1)+} + H^+ \tag{3}$$

This reaction is accompanied by a change of colour, which clearly indicates the formation of a ternary complex.

For reaction (3) to occur, at least two conditions must be fulfilled: (i) The dye, after having reacted with the metal, must have at least one hydroxyl (phenolic) group conjugate with the resonance system of the dye. (ii) The pH at which reaction (2) takes place must be such that (a) the dissociation of the free hydroxyl group does not take place spontaneously, and (b) the dissociation of the free hydroxyl group which is labilised by the reaction between the metal-dye chelate and fluoride must not be supressed. Alizarin complexan forms coloured binary chelates with a number of metals. Binary complexes fulfilling these conditions, which are easily identified by colour changes, are formed with cerium^{III}, lanthanum and praseodymium. Ternary complexes with other metals probably formed at a pH other than that required by condition (ii), are not easily identified.

Dyes which have one or two dicarboxymethylaminomethyl groups but no free hydroxyl group, as does alizarin complexan, can react analogously to reaction (2) in the following manner

$$M{=}D^{(m-d)+} + nF^- \rightarrow F_nM{=}D^{(m-d-n)+} \tag{2'}$$

Such dyes as Semixylenol Orange and Xylenol Orange (SXO, XO) have no superfluous hydroxyl group and therefore reaction (3), with the accompanying colour change indicating the formation of a ternary complex, cannot take place.

By generalisation of the interpretation of Belcher and coworkers, the existence of FDM complexes with the same colour as the binary metal chelate may be assumed. From the work of Přibil and Kopanica[5] ternary complexes having the same colour as the free dye is possible. They found that slight acidification caused the violet complex of copper^{II} with Xylenol Orange to turn yellow. Because copper^{II} ions could not be detected (polarographically) in this solution, the colour change could not be explained in terms of the replacement of copper^{II} in the copper-Xylenol Orange chelate by hydrogen ion. Even in this more acidic solution copper^{II} must still be bound by the dicarboxymethylaminomethyl group of Xylenol Orange. The existence of a "decolorised" binary complex that originated in accordance with the reaction

$$M{=}D^{(m-d)+} + H^{+} \rightarrow M{-}HD^{(m-d+1)+} \qquad (4)$$

has to be anticipated, by analogy with copper-Xylenol Orange. Of course, one cannot easily prove (polarographically) that zirconium has not been replaced by hydrogen ion.

The present author has shown that six coloured MD chelates which he studied, are decolorised by fluoride (and sulphate) only by a higher acidity than that pH at which these chelates mostly originate. This means that fluoride "decolorises" the system MD until the conditions are reached when the chelate is decolorised under the influence of hydrogen ions.

Fluoride that has reacted with a binary chelate in accordance with reaction (2) or (2′), labilises, of course, not only the hydrogen bound in the "remote" phenolic group but also, and preferentially, that in the "nearer" bonds between M and D. In the case when fluoride reacts with zirconium-Xylenol Orange under such acidity conditions that reaction (4) has already partially taken place, labilisation of the bond between the metal and the functional group of the resonance system of the dye (which is much weaker than the bond between the metal and the strongly complexing dicarboxymethylaminomethyl group) makes possible the reaction

$$F_nM{=}D^{(m-d-n)+} + H^{+} \rightarrow F_nM{-}HD^{(m-d-n+1)+} \qquad (4')$$

by which (already when n = 1) the "decolorised" ternary complex originates more easily than the analogous "decolorised" binary system in accordance with reaction (4). If the concentration of fluoride increases considerably, so many fluoride ions react with the metal that all of the metal-dye bonds are broken, *i.e.*, reaction (4′) passes over to reaction (1). Reaction (1), which corresponds to the existing ideas about the mechanism of decolorisation determinations of fluoride, appears as one limiting case of reactions that are probably best considered from the new point of view.

All that has been said about decolorisation methods for fluoride also applies analogously to decolorisation determinations of (or interferences from) sulphate and other anions. As long as individual decolorisation determinations are not conclusively proved experimentally to be methods with an indirect mechanism of the type of reaction (1), the possibility that the cause of decolorisation is really colorisation of a ternary complex of the same basic colour as the free dye cannot be excluded.

The only experimental data quoted here in support of the new conception of decolorisation reaction mechanisms is as follows. After having added a sufficient quantity of fluoride to the red solution of zirconium-Xylenol Orange, one obtains a yellow solution whose spectrum agrees qualitatively with that of a solution of the same amount of dye, though quantitatively it is less intense. Only after the addition of even higher amounts of fluoride do the spectra of the two solutions become identical from the quantitative point of view. It is, therefore, necessary to assume that before the limiting reaction (1)—connected with the identification of both spectra—occurs, a ternary complex is present in accordance with reaction (4′), and its colour intensity is (always slightly) lower than that of the free dye. If fluoride is added to a solution of zirconium-Xylenol Orange (or better if Semixylenol Orange is used), a polarographic curve is obtained which is intermediate between the curve of the free dye and the curve of the binary chelate (*i.e.*, after the addition of fluoride the curve with $\pi_{1/2}$ of the free dye does not appear).

The interference from sulphate, *etc.*, in the determination of fluoride with zirconium-Xylenol Orange in hydrochloric acid solution is less than in perchloric acid solution. The "protective" influence of chloride and other facts may best be explained by means of "undecolorised" ternary complexes of the type ClZrXO. By "decolorising" these complexes a quaternary complex of the type F(Cl)ZrXO presumably originates.

Other aspects of the author's ideas have already been reported,[6] and experimental data will be published elsewhere.[7]

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Summary—The existence of fluoride-metal-dye (FDM) ternary complexes which have a different colour from that of the MD chelate and of the free dye, as well as the existence of MD binary chelates with the same colour as the free dye, is known. By analogy, the existence of FDM ternary complexes with the same colour as MD or as D

may be assumed. Such ternary complexes may be formed in some determinations based on "decolorisation", so that these determinations should not generally be considered as indirect methods.

Zusammenfassung—Ternäre Fluorid-Metall-Farbstoff-(FMD)-Komplex mit von deer des Metall-Farbstoff-(MD)-Chelats und des freien Farbstoffs verschiedener Farbe sind bekannt, desgleichen binäre Chelate MD mit derselben Farbe wie der freie Farbstoff. Analog kan die Existenz von ternären FDM-Komplexen mit derselben Farbe wie MD oder D angenommen werden. Solche ternären Komplexe Können bei einigen auf "Entfärbung" beruhenden Bestimmungen gebildet werden; daher sind diese Bestimmungen nicht allgemein als indirekte Methoden zu betrachten.

Résumé—On connaît l'existence de complexes ternaires fluorure-métal-colorant (FDM) dont la couleur diffère de celle du chélate métal-colorant (MD) et de delle du colorant libre (D), ainsi que l'existence de chélates binaires métal-colorant (MD) de même couleur que le colorant libre. Par analogie, on peut supposer l'existence de complexes ternaires FDM de même couleur que MD ou D. De tels complexes ternaires peurvent se former lors de quelques dosages basés sur la "décoloration", de sorte que ses dosages ne devraient pas en général être considéres comme des méthodes indirectes.

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The determination of chlorosuccinic acid in aqueous solutions

(*Received* 27 *July* 1963. *Accepted* 10 *March* 1964)

INTRODUCTION

THE electrochemical reduction of dichloromaleic acid in buffered media has been shown to yield both chlorosuccinic and succinic acids.[1] Furthermore, the relative amounts of these products depend on the pH at which the reduction is accomplished. It was therefore necessary to develop a method for the determination of small amounts of chlorosuccinic acid ($10^{-3} - 10^{-2}M$) in the presence of succinic citric and phosphoric acids (the two last occurring as components of the buffer used in the reduction). A simple procedure has been developed which involves the dehydrohalogenation of chlorosuccinic acid followed by a polarographic determination of the fumaric acid formed.

EXPERIMENTAL

Reagents

Fumaric acid: Matheson, Coleman and Bell, technical grade (99+ %) fumaric acid was recrystallised several times from water.

Sodium hydroxide: Fisher Scientific Co., aqueous 50%, by weight.

Hydrochloric acid: Fisher Scientific Co., concentrated, reagent-grade.

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Zusammenfassung—Ternäre Fluorid-Metall-Farbstoff-(FMD)-Komplex mit von deer des Metall-Farbstoff-(MD)-Chelats und des freien Farbstoffs verschiedener Farbe sind bekannt, desgleichen binäre Chelate MD mit derselben Farbe wie der freie Farbstoff. Analog kan die Existenz von ternären FDM-Komplexen mit derselben Farbe wie MD oder D angenommen werden. Solche ternären Komplexe Können bei einigen auf "Entfärbung" beruhenden Bestimmungen gebildet werden; daher sind diese Bestimmungen nicht allgemein als indirekte Methoden zu betrachten.

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Hydrochloric acid: Fisher Scientific Co., concentrated, reagent-grade.

Chlorosuccinic acid: Delta Chemical Works, Inc., purified by recrystallisation from ethyl acetate and light petroleum ether and vacuum sublimation: m.p. found 146–148°, reported 146–148°.[2]

Apparatus

Polarograph, constant temperature bath, H-cell with saturated calomel electrode as reference, purified nitrogen.

Procedure

Dehydrohalogenation: The following procedure was used to analyse solutions containing $10^{-3} - 10^{-2}M$ chlorosuccinic acid. An aliquot (5–25 ml) of the solution was pipetted into a 100-ml volumetric flask, 5 ml of 50% w/w sodium hydroxide were then added, and the solution was allowed to stand for 60 min. After the addition of 10–15 ml of distilled water and 10 ml of hydrochloric acid, the solution was cooled and was diluted to the mark with distilled water.

Polarographic analysis: After removal of oxygen by passing nitrogen through the solution for 10 min, a portion of the above solution was transferred to the H-cell and polarographed. The limiting current at —0·85v *vs*. SCE was recorded and corrected for the residual current of the supporting electrolyte. A stock solution of $5\text{–}8 \times 10^{-4}M$ fumaric acid in the same supporting electrolyte was used to obtain the current-concentration ratio, i_d/c. The concentration of chlorosuccinic acid was then calculated in the following manner.

$$\frac{i_d}{K} \times \frac{100}{A} = \text{molarity of chlorosuccinic acid in the original solution}$$

i_d = corrected limiting current at —0·85v *vs*. SCE,

K = current-concentration ratio for fumaric acid,

A = aliquot of sample which was dehydrohalogenated.

RESULTS AND DISCUSSION

Effect of pH and ionic strength

The variation in current-concentration ratio with pH and ionic strength was checked to determine how closely the procedure should be standardised. It was found that the constant did not change significantly in the pH range 0·45–1·5. However, a two-fold variation in ionic strength caused deviations of 6–7% (relative), the ratio increasing with decreasing ionic strength. Thus, if a standard-addition method was used to determine the fumaric acid, a negative bias was introduced, the magnitude of which depended on the change in ionic strength which occurred upon addition of the aliquot of fumaric acid. For example, if 25 ml of the final solution were analysed and a 2-ml aliquot of fumaric acid stock solution (in water) was added to the cell, the results were consistently low by approximately 1% (relative). For highly accurate work this error was eliminated by standardising the procedure so that the ionic strength of the final solution was always the same, and the ratio was determined in this electrolyte. The accuracy and precision of the method were evaluated by analysing solutions of pure chlorosuccinic acid. The 95% confidence limits of any single determination were found to be ±3·4% (relative). The average of 10 determinations was within 0·2% of the true value.

Interferences

Although no interferences were noted in this research, a number of possible complications can be expected. Polarographically reducible material (inorganic and organic) in the original solution, which is not affected by base, need not cause any significant error even if reducible at the same potential as fumaric acid. The difference in the limiting current before and after dehydrohalogenation can be used to determine the chlorosuccinic acid. The magnitude of this difference will determine the reliability of the determination.

Material sensitive to base may be divided into compounds which are originally reducible and are transformed into other compounds on treatment with base, and compounds which are originally inactive but are transformed to active material under basic conditions. Both chloromaleic and chlorofumaric acids fall in the first category.[1] Chlorofumaric acid may be determined by polarographing at pH 9·5, where chloromaleic acid interference is minimised. Chloromaleic acid is determined at pH 7·2, where the reduction of chlorofumaric is more negative than the supporting electrolyte discharge. Both of these acids are dehydrohalogenated to acetylene dicarboxylic acid, which does not interfere if the pH is much above 3. The final solution is adjusted to pH 5·1 for the analysis of the fumaric acid, and the limiting current is recorded at —1·30v *vs*. SCE. Dichlorosuccinic acid in not reducible; it is, however, dehydrohalogenated to chlorofumaric acid, and thence to acetylene dicarboxylic acid. Again the pH of the final solution is adjusted to 5·1 for polarography of the fumaric acid. (Small amounts of chlorofumaric acid which may still be present will not interfere at this pH.)

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Summary—Chlorosuccinic acid is determined by dehydrohalogenation and polarographic determination of the fumaric acid formed.

Zusammenfassung—Chlorbernsteinsäure wird bestimmt durch Abspaltung von Chlorwasserstoff und polarographische Bestimmung der gebildeten Fumarsäure.

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A Method of estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions, also containing similar amounts of plutonium^{IV}, was required for some investigations concerning redox reactions between hydrogen peroxide and plutonium ions. Such solutions are unstable because of (a) the redox reaction of hydrogen peroxide with plutonium^{IV}, and (b) the slow catalytic decomposition of hydrogen peroxide. They are, therefore, not of unique composition but time dependent. Nevertheless, it is possible to evaluate such mixtures because hydrogen peroxide is quantitatively destroyed as soon as an excess of potassium dichromate or of iron^{II} sulphate is added. For this purpose Newton and Baker's method,[1] applicable to milligram quantities in a sulphuric acid medium, has been suitably modified.

In the modified method, two aliquots of the mixture are taken separately in 1·5–2·0 ml of approximately 2·5*M* sulphuric acid. To one portion a sufficient excess of standard 0·005*N* potassium dichromate solution is added by a micropipette to oxidise both the hydrogen peroxide and plutonium^{III}, followed by addition of a known quantity of standard 0·005*N* iron^{II} sulphate solution, also in excess. The solution is titrated against standard 0·005*N* cerium^{IV} sulphate solution delivered from an Agla micrometer syringe burette, using ferroïn as internal indicator (20 μl of approximately 1·2 mM ferroïn). This titration gives a measure of the sum of plutonium^{III} and hydrogen peroxide. To the second aliquot the same quantities of dichromate and iron^{II} solutions are added, but in the reverse order, and the titration is completed as before. This gives a measure of the difference between the plutonium^{III} and hydrogen peroxide. From these measurements the concentrations of plutonium^{III} and hydrogen peroxide can easily be calculated. During a titration the solution is stirred either by a stream of nitrogen bubbles or by a suitable magnetic stirrer. The nitrogen stream did not produce any significant difference, indicating that the method is independent of the presence of dissolved air.

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In the modified method, two aliquots of the mixture are taken separately in 1·5–2·0 ml of approximately 2·5M sulphuric acid. To one portion a sufficient excess of standard 0·005N potassium dichromate solution is added by a micropipette to oxidise both the hydrogen peroxide and plutonium^{III}, followed by addition of a known quantity of standard 0·005N iron^{II} sulphate solution, also in excess. The solution is titrated against standard 0·005N cerium^{IV} sulphate solution delivered from an Agla micrometer syringe burette, using ferroïn as internal indicator (20 μl of approximately 1·2 mM ferroïn). This titration gives a measure of the sum of plutonium^{III} and hydrogen peroxide. To the second aliquot the same quantities of dichromate and iron^{II} solutions are added, but in the reverse order, and the titration is completed as before. This gives a measure of the difference between the plutonium^{III} and hydrogen peroxide. From these measurements the concentrations of plutonium^{III} and hydrogen peroxide can easily be calculated. During a titration the solution is stirred either by a stream of nitrogen bubbles or by a suitable magnetic stirrer. The nitrogen stream did not produce any significant difference, indicating that the method is independent of the presence of dissolved air.

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Microestimations carried out by the above method in the presence of a hydrochloric acid content between 0·1 and 0·3 mmole and with known amounts of plutonium^{III} (1·5–5·2 $\times$ 10^{-4} mmole) have yielded results the error range of which lies between +3·0% and −2·0%, the mean error being +1·4%. The errors obtained in experiments with known amounts of hydrogen peroxide (0·80–7·96 $\times$ 10^{-4} mmole) lie between +3·8% and −5·5%, the mean error being −0·6%.

Typical results of estimations with mixtures of hydrogen peroxide, plutonium^{III} and plutonium^{IV}, produced by the addition of known amounts of hydrogen peroxide to known amounts of plutonium^{IV} in 2*M* and 6*M* hydrochloric acid solutions, are shown in Table I. The values in columns 3 and 4 were checked independently by spectrophotometric measurements, showing that the determination of plutonium^{III} by the present method is possible in the presence of both plutonium^{IV} and hydrogen peroxide. The data in columns 6 and 7 seem to show clearly that the equivalent of hydrogen peroxide consumed in each experiment was very close to that of plutonium^{III} formed, as expected, and thereby afford an indirect check on the estimation of hydrogen peroxide. The data in the table show a very slow rate of catalytic decomposition as compared to the reaction rate between hydrogen peroxide and plutonium^{IV}. Concentrations of plutonium^{IV} in up to about a twenty-fold excess over plutonium^{III} can be tolerated. Blank experiments confirming the stability of plutonium^{IV} through the method have been carried out.

TABLE I

HCl, *M*	Time, *min*	Pu^{III} (by present method), *mequiv* $\times$ 10^6	Pu^{IV} remaining (by difference from total Pu taken), *mequiv* $\times$ 10^6	H_2O_2 remaining (by present method), *mequiv* $\times$ 10^6	Pu^{III} produced (calculated by difference from data of column 3), *mequiv* $\times$ 10^6	H_2O_2 consumed (calculated by difference from data of column 5), *mequiv* $\times$ 10^6
2	0	Nil	(500·0^{a})	(375·0^{b})	—	—
	10	169·8	330·2	203·8	169·8	171·2
	62	351·7	148·3	19·0	181·9	184·8
	166	366·9	133·1	1·0	15·2	18·0
6	0	Nil	(500·0^{a})	(450·0^{b})	—	—
	10	251·4	248·6	195·4	251·4	254·6
	0	38·5	(461·5^{a})	(50·0^{b})	—	—
	35	67·5	432·5	20·0	29·0	30·0

^{a} Known amount of Pu^{IV} taken initially. ^{b} Known amount of H_2O_2 taken initially.

In the method described above, dichromate and cerium^{IV} sulphate are used as oxidising agents, while potassium permanganate and dichromate, respectively, were recommended by Newton and Baker. It has been observed in the present work that the use of excess potassium permanganate or cerium^{IV} sulphate as the initial oxidising agent is unsuitable because of the presence of chloride ions, the error being as high as +80% with permanganate and +20% with cerium^{IV} sulphate. While finishing the titration potentiometrically with dichromate, as in the method of Newton and Baker, it has been found that the change in potential towards the end-point is not sharp under our experimental conditions. Further, the use of an internal indicator, *e.g.*, ferroïn is more convenient, provided a stronger oxidising agent, *viz.*, potassium permanganate or cerium^{IV} sulphate is used, which when employed for completing the titration does not seem to introduce significant error, even up to a hydrochloric acid content of 0·5 mmole. The effect of larger amounts of hydrochloric has not, however, been investigated. The method, as described, is applicable to as low as about 2 $\times$ $10^{-5}M$ plutonium^{III} and 8 $\times$ $10^{-6}M$ hydrogen peroxide in 0·3*M* hydrochloric acid. At higher hydrochloric acid concentrations the sensitivity may decrease.

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Summary—A method has been developed for the estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions containing plutonium^{IV}. The sum of plutonium^{III} and hydrogen peroxide is obtained by successive addition, in excess, of known quantities of potassium dichromate and iron^{II} sulphate to one aliquot of the mixture, then titrating with cerium^{IV} sulphate using ferroïn as indicator. Their difference is obtained by adding the same quantities of the first two reagents in reverse order to another aliquot, then completing the titration as before.

Mikrotitration von Plutonium(III) und Wasserstoffperoxyd neben Plutonium(IV) in salzsauren Lösungen.
Zusammenfassung—Eine Methode zur Bestimmung einiger Zehntel Mikrogramm Plutonium(III) und Wasserstoffperoxyd in Plutonium(IV) enthaltenden salzsauren Lösungen wurde entwickelt. Die Summe von Plutonium(III) und Wasserstoffperoxyd erhält man durch aufeinanderfolgende Zugabe bekannter überschüssiger Menger Kaliumdichromat und Eisen(II)-sulfat zu einem aliquoten Teil der Lösung und nachfolgende Titration mit Cer(IV)-sulfat und Ferroin als Indikator. Die Differenz erhält man durch Zugabe derselben Mengen der beiden ersten Reagentien in umgekehrter Reihenfolge zu einem andern aliquoten Teil der Lösung und Abachluß der Titration wie vorher.

Résumé—On a élaboré une méthode de dosage de quelques dizaines de microgrammes de plutonium (III) et d'eau oxygénée dans des solutions chlorhydriques contenant du plutonium (IV). La somme du plutonium(III)et de l'eau oxygénée est obtenue par addition successive, en excès, de quantités connues de bichromate de potassium et de sulfate de fer (II) à une partie aliquote du mélange, puis titrage au moyen de sulfate de cérium (IV) en présence de ferroïne comme indicateur. Leur différence est obtenue en ajoutant, à une autre partie aliquote, les mêmes quantités des deux premiers réactifs, dans l'ordre inverse, puis en terminant le dosage comme précédemment.

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The response of cation-sensitive glass electrodes to alkali metal ions in partially aquated media

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In 1957, Eisenman[1] reported on the properties of cation-sensitive glass electrodes which developed potentials proportional to the logarithm of the univalent cation activity. Improved electrodes of this type are now commercially available.

A Beckman Model 76 Expanded Scale pH Meter equipped with a 39137 cation-sensitive glass electrode and a fibre-junction saturated calomel electrode (constrained diffusion junction type) was used to measure the response of the glass electrode to $10^{-1} - 10^{-3}M$ alkali metal chlorides in mixtures of water and ethanol, ethylene glycol, acetone, and *N,N*-dimethylformamide (DMF),[2] respectively. These represent the amphiprotic (alcohols), aprotic (ketones) and protophilic (DMF) solvent types.[3] Protogenic (acids) solvents were not used owing to the response of the cation electrode to the hydrogen ion below pH = 5. Electrodes are preconditioned in the appropriate solvent, containing $0{\cdot}1M$ KCl, for approximately 18–24 hr before use, washed with solvent after each measurement, and stored in the conditioning solution between measurements. Stable, reproducible responses to alkali metal ions in 0–90 volume-% of organic solvent were obtained. The slopes of plots of mv *vs.* $-\log [M^+]$ at 25·0 ± 0·5° are summarised in Table I. Deviations from the predicted[4] Nernst slope of 55·0 mv at high concentrations of ethanol and acetone can be attributed to ion association and ion pairing.[3,5,6] The selectivity order of the cation electrode response in all solvents is found to be $K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$, as would be predicted from theoretical considerations.[7]

Summary—A method has been developed for the estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions containing plutonium^{IV}. The sum of plutonium^{III} and hydrogen peroxide is obtained by successive addition, in excess, of known quantities of potassium dichromate and iron^{II} sulphate to one aliquot of the mixture, then titrating with cerium^{IV} sulphate using ferroïn as indicator. Their difference is obtained by adding the same quantities of the first two reagents in reverse order to another aliquot, then completing the titration as before.

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(*Received* 18 *January* 1964. *Accepted* 29 *February* 1964)

In 1957, Eisenman[1] reported on the properties of cation-sensitive glass electrodes which developed potentials proportional to the logarithm of the univalent cation activity. Improved electrodes of this type are now commercially available.

A Beckman Model 76 Expanded Scale pH Meter equipped with a 39137 cation-sensitive glass electrode and a fibre-junction saturated calomel electrode (constrained diffusion junction type) was used to measure the response of the glass electrode to $10^{-1} - 10^{-3}M$ alkali metal chlorides in mixtures of water and ethanol, ethylene glycol, acetone, and *N,N*-dimethylformamide (DMF),[2] respectively. These represent the amphiprotic (alcohols), aprotic (ketones) and protophilic (DMF) solvent types.[3] Protogenic (acids) solvents were not used owing to the response of the cation electrode to the hydrogen ion below pH = 5. Electrodes are preconditioned in the appropriate solvent, containing 0·1*M* KCl, for approximately 18–24 hr before use, washed with solvent after each measurement, and stored in the conditioning solution between measurements. Stable, reproducible responses to alkali metal ions in 0–90 volume-% of organic solvent were obtained. The slopes of plots of mv *vs.* $-\log [M^+]$ at 25·0 ± 0·5° are summarised in Table I. Deviations from the predicted[4] Nernst slope of 55·0 mv at high concentrations of ethanol and acetone can be attributed to ion association and ion pairing.[3,5,6] The selectivity order of the cation electrode response in all solvents is found to be $K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$, as would be predicted from theoretical considerations.[7]

TABLE I.—RESPONSE OF CATION-SENSITIVE GLASS ELECTRODES TO ALKALI METAL IONS IN MIXED SOLVENTS. SLOPES OF PLOTS OF mv *vs.* — log [M^+].

	10	30	50	70	90 *volume-%*
Ethanol					
KCl	56·0	55·0	55·0	56·0	53·0
KCl*	56·0	55·0	55·0	56·0	53·0
RbCl	56·0	55·0	55·5	56·0	53·0
NaCl	55·5	53·0	55·0	54·0	52·0
Acetone					
KCl	57·0	54·5	55·0	53·0	44·0
KCl†	57·0	54·5	55·0	53·0	44·0
RbCl	55·0	55·0	55·5	50·0	44·0
NaCl	55·0	54·0	54·5	49·0	43·7
Ethylene glycol					
KCl	56·0	57·0	57·0	56·0	56·0
RbCl	57·5	56·0	56·0	55·8	55·7
NaCl	56·0	56·0	55·0	55·0	55·0
					volume %
	8·3	25·0	41·7	58·3	75
DMF					
KCl	52·5	53·3	54·0	51·0	50·0
RbCl	53·5	50·0	55·7	50·0	48·0
NaCl	51·0	51·0	55·0	51·0	52·5

* *vs.* ESCE † *vs.* ASCE

Increasing fractions of organic constituent in the solvent mixture yielded increasing cell e.m.f.'s for any given concentration of solute. This effect may be attributed to changes in the liquid-junction potential at the reference electrode rather than to a change in the response of the cation-sensitive electrode This view is supported by the work of Zielen,[8] Uitert[9] and Bates[5] on e.m.f. measurements in solutions of strong acids, salts, and buffers in aqueous and partially aqueous media. For experimental confirmation of this hypothesis, the following cells were constructed:

Cation glass electrode ‖y*M*KCl, X% ethanol, (100 − X)% H_2O

|KCl (satd.), 100% ethanol, Hg_2Cl_2 (satd.); Hg (I)

Cation glass electrode ‖y*M*KCl, X% ethanol, (100 − X)% H_2O

|KCl (satd., aq.), Hg_2Cl_2 (satd., aq.); Hg (II)

Hg; Hg_2Cl_2 (satd.), 100% ethanol, KCl (satd.)

|KCl (satd.), Hg_2Cl_2 (satd.), X% ethanol, (100 − X)% H_2O

|KCl (satd., aq), Hg_2Cl_2 (satd., aq.); Hg (III)

The reference electrode for cell (I), an ethanolic saturated calomel electrode (ESCE) was constructed in a typical "H" cell with a sintered-glass frit providing a constricted diffusion junction. The electrolyte solution was saturated with KCl and Hg_2Cl_2 in absolute ethanol. Preparation of the ESCE is as follows: a dry mixture of Hg_2Cl_2, KCl and Hg is intimately ground together and then placed into the prepared cell. A layer of KCl crystals is deposited on the mixture, and the cell is filled with the electrolyte solution. Contact with the mercury pool is made by means of a platinum wire sealed in soft glass. The cell is then sealed to prevent evaporation of the ethanol. The ESCE was found to be stable and gave reproducible responses in cell (III), where X = 100%, of +36·0 ± 0·5 mv after 8·67 days. An acetone-saturated calomel electrode (ASCE) was constructed in a similar manner, and gave reproducible e.m.f readings of +30·9 ± 0·5 mv after 3·5 days of aging.

If Ecell (II) − Ecell (I) = Ecell (III), the change in e.m.f. noted upon replacement of water by organic constituents in the solvent mixture cannot have arisen at the glass electrode, but must result

TABLE II.—POTENTIAL MEASUREMENTS WITH NON-AQUEOUS REFERENCE ELECTRODES

	Glass *vs.* SCE, *mV*	Glass *vs.* ESCE, *mV*	Column 1 − 2, *mV*	Δ, *mV*
Ethanol				
10 volume-%			+40·0*	
0·1*M* KCl	+145	+105	+40·0	0
0·05	128	90	38·0	+2·0
0·025	110	72	38·0	+2·0
0·01	88	52	36·0	+4·0
30 volume-%			+39·5*	
0·1	163	124	39·0	+0·5
0·05	148	107	41·0	−1·5
0·025	130	91	39·0	+0·5
0·01	109	70	39·0	+0·5
50 volume-%			+38·0*	
0·1	185	148	37·0	+1·0
0·05	169	132	37·0	+1·0
0·025	150	117	33·0	+5·0
0·01	130	93	37·0	+1·0
70 volume-%			+37·0*	
0·1	209	173	36·0	+1·0
0·05	190	152	38·0	−1·0
0·025	175	141	34·0	+3·0
0·01	153	117	36·0	+1·0
90 volume-%			+36·5*	
0·1	273	239	34·0	+2·5
0·05	256	223	33·0	+3·5
0·025	240	205	35·0	+1·5
0·01	220	186	34·0	+2·5
Acetone		Glass *vs.* ASCE		
10 volume-%			+24·0†	
0·1	160	138	22.0	+2·0
0·05	142	120	22·0	+2·0
0·025	125	101	24·0	0
0·01	103	81	22·0	+2·0
30 volume-%			+27·0†	
0·1	173	148	25·0	+2·0
0·05	157	130	27·0	0
0·025	140	112	28·0	−1·0
0·01	119	94	25·0	+2·0
50 volume-%			+27·3†	
0·1	194	166	28·0	−0·7
0·05	178	153	25·0	+2.3
0·025	160	133	27·0	+0·3
0·01	139	111	28·0	−0·7
70 volume-%			+28·0†	
0·1	223	196	27·0	+1·0
0·05	209	181	28·0	0
0·025	190	163	27·0	+1·0
0·01	170	140	30·0	−2·0
90 volume-%			+31·0†	
0·1	281	250	31·0	0
0·05	269	239	30·0	+1·0
0·025	254	224	30·0	+1·0
0·01	237	207	30·0	+1·0

* SCE *vs.* ESCE, cell(III) † SCE *vs.* ASCE, cell (III)

from effects involving the reference electrode. The confirmatory experimental results using the appropriate non-aqueous reference electrodes are summarised in Table II for both the ethanol–water and acetone–water mixtures. Table II is constructed in the following manner. Subtraction of column 2 from column 1 gives the values in column 1–2. This is equivalent to Ecell (II) − Ecell (I) = Ecell (III) (calculated). The numbers marked with asterisks and quotation marks in column 1–2 are the values of Ecell (III) obtained by direct experimental measurements. Column Δ is obtained by subtracting Ecell (III) calculated values from Ecell (III) experimental values to find apparent differences; according to our theory, Ecell (III) calculated should equal Ecell (III) experimental. The values of column Δ fall well within the range of experimental error using the high-resistance glass electrodes, and confirm our prediction. The average deviations of Δmv are +1·05 and +0·66 mv for the ethanol–water and acetone–water systems, respectively. The average deviation of the mean of Δmv is +0·24 mv for the ethanol–water mixtures and +0·15 mv for the acetone–water mixtures. Furthermore, using a knowledge of degenerate activity coefficients for single ions, Gutbezahl and Grunwald[10] have calculated liquid-junction potentials (E_L) for the hydrogen electrode *vs.* SCE (aqueous) of various acids in ethanol–water solvents, and have obtained E_L's that are dependent only on solvent compositions. These results agree well with ours for systems containing up to 87 weight-% of ethanol. Thus, the effects caused by changes in activity coefficients of salt solutions with changes in solvent composition (replacement of water with organic solvent) are small compared to the change in liquid-junction potential and may be neglected.

We conclude, therefore, that the response of the cation-sensitive glass electrode is essentially solvent-independent, but depends on the nature and concentration of the solute. The results also suggest that such electrodes might be useful as reference electrodes in solvent mixtures containing substantial concentrations of alkali metal cations.

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Summary—The response of cation-sensitive glass electrodes to alkali metal ions in ethanol–water and acetone–water mixtures has been evaluated. The increase in measured potential when water is replaced with organic solvent is proved result from to the changing liquid-junction potential of the reference electrode. The response of the glass electrode is essentially solvent-independent for a given concentration and type of solute.

Zusammenfassung—Das Ansprechen der Kationenempfindliche Glaselektroden auf Alkalimetallionen in Äthanol–Wasser- und Aceton–Wasser-Gemischen wurde gemessen. Es wird gezeigt, daß das Ansteigen des gemessenen Potentials bei Ersatz von Wasser durch organisches Lösungsmitte auf der Änderung des Diffusionspotentials in der Brücke zur Referenzelektrode beruht. Die Empfindlichkeit Glaselektrode ist bei gegebener Konzentration und Art des gelösten Stoffes im wesentlichen vom Lösungsmittel unabhängig.

Résumé—On a évalué la résponse de ces électrodes aux ions métalliques alcalins dans des mélanges éthanol–eau et acétone–eau. On a démontré que l'accroissement du potentiel mesuré que l'on observe lorsqu'on remplace l'eau par un solvant organique, est dû à la variation de potentiel du liquide de jonction de l'électrode de référence. La réponse de l'électrode de verre est essentiellement indépendante du solvant, pour une concentration et un type de soluté donnés.

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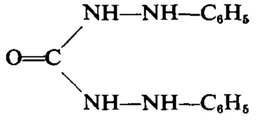
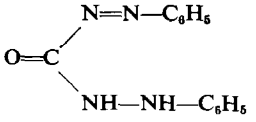
Separation of commercial diphenylcarbazone into its components

(*Received* 11 *February* 1964. *Accepted* 25 *March* 1964)

KRUMHOLZ and Krumholz verified in 1937 that "diphenylcarbazone" (1,5-diphenylcarbohydrazone), m.p. 157°, was probably an intermolecular compound of diphenylcarbazide (I) and pure diphenylcarbazone, m.p. 127° (II), which they succeeded in separating by batch extraction of alkaline solutions of the product with ethyl ether.[1] Diphenylcarbazone, being acidic, remains in solution in its anionic form, whereas diphenylcarbazide, which is not acidic, is carried into the organic solvent.



(I)



(II)

However, the commercial AnalaR grade product available nowadays is still the substance melting at 157° and catalogues do not list the existence of a different form.

In an attempt to confirm Krumholz's results we have found that commercial diphenylcarbazone could be separated into its components by thin-layer chromatography. The support used was a layer of Merck Silica-gel GF_{254}, and the eluent was a mixture of chloroform (75%) and acetone (25%). In recently-coated plates, pure diphenylcarbazone showed up as a red spot ($R_f \simeq 0{\cdot}75$) and diphenylcarbazide as a purple one ($R_f \simeq 0{\cdot}20$) after spraying with a dilute acid solution of potassium chromate. The time of elution was 15–20 min. This confirms the findings of the previous workers, but this method is not very suitable for preparing substantial amounts of the reagent. We have therefore adapted Krumholz's procedure to a continuous liquid-liquid extraction technique which gave excellent results.

An extractor similar to that used by Ashley and Murray for the extraction of $FeCl_3$ with ether[2] appeared to be best suited for the purpose and the procedure was as follows. One g of commercial diphenylcarbazone (m.p. 157°) was dissolved in 100 ml of 5% NaOH containing a few mg of KCN. The solution was transferred to the extractor, and the necessary volume of ethyl ether was added to fill the extractor up to the level of its horizontal arm. The Erlenmeyer flask containing about 100 ml of ethyl ether was connected, and the solvent was refluxed for about 36 hr.

Diphenylcarbazide was carried into the Erlenmeyer flask, where it crystallised in long colourless needles, m.p. 172–3°. The basic aqueous solution was then taken out of the extractor, filtered through a sintered-glass filter-funnel, and acidified with dilute H_2SO_4. A precipitate formed, and the suspension was allowed to settle for 1 hr when the solid was collected and dissolved in the minimum amount of hot ethanol. Twice its volume of de-ionised water was added with stirring, and the solution was allowed to crystallise. Deep orange crystals of pure diphenylcarbazone were obtained in small needles, m.p. 126–7° (rapid heating). The yield for the first crystallisation was 120 mg (~24%).

Pure diphenylcarbazone is easily soluble in ethanol, chloroform and methylene dichloride up to concentrations of the order of $10^{-3}M$; it is also soluble, but not so easily, in ether, benzene and carbon tetrachloride, among the more usual solvents.

For solutions in carbon tetrachloride, the following absorption maxima and respective molar extinction coefficients were observed:

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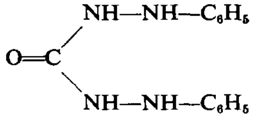
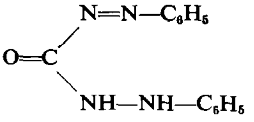


(I)



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For solutions in carbon tetrachloride, the following absorption maxima and respective molar extinction coefficients were observed:

λ_{max}	ε_{max}
290 mμ	12,750
466 mμ	3,300
563 mμ	800

The samples we obtained using Krumholz's technique were more reddish in colour and had lower values of ε_{max} than those prepared by the method now described. Balt and van Dalen,[3] who recently started a systematic study of the metal complexes of diphenylcarbazone, and purified their reagent according to the previous authors, reported values for ε_{max} close to ours but not quite so high.

Spectra, and more detailed observations, will be published elsewhere.[4]

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Summary—Confirming results of previous workers, it is shown that commercial AnalaR diphenylcarbazone can be separated into its components (diphenylcarbazide and pure diphenylcarbazone) by thin-layer chromatography or continuous liquid-liquid extraction, the latter method being preferred for preparative purposes. Some physical properties of pure diphenylcarbazone are reported.

Zusammenfassung—In Übereinstimmung mit Ergebnissen früherer Forscher wird gezeigt, daß handelsübliches analysenreines Diphenylcarbazon durch Dünnschichtchromatographie oder kontinuierliche flüssig-flüssig-Extraktion in seine Komponenten Diphenylcarbazid und reines Diphenylcarbazon aufgetrennt werden kann. Die zweite Methode ist für präparative Zwecke vorzuziehen. Einige physikalische Eigenschaften des reinen Diphenylcarbazons werden angegeben.

Résumé—On confirme des résultats d'autres chercheurs en montrant que la diphénylcarbazone p.a. commerciale peut être séparée dans ses components (diphénylcarbazide et diphénylcarbazone pure) par chromatographie sur couche mince et par extraction liquide-liquide continuelle, cette dernière méthode étant préférée pour sa préparation. On indique quelques propriétés physiques de la diphénylcarbazone purifiée.

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LETTER TO THE EDITOR

The determination of phosphate in the presence of calcium by the molybdovanadate method

SIR,

THE method of Bridger *et al.*,[1] incorporating the methods of Maksimova *et al.*[2] and Misson,[3] *i.e.*, the molybdovanadate colorimetric method for the determination of phosphorus, has been applied to the determination of orthophosphate in the presence of calcium.

It has been found that grossly unreliable results are obtained when the phosphate (P_2O_5):calcium (Ca) ratio exceeds 1:10,000. Temperature effects are quite noticeable, in that if the determination is carried out at temperatures in excess of 22° the results are erratic, being approximately double the expected level. The most reliable temperature for carrying out the determination is below 14°, but even at this temperature poor results are obtained if the phosphate:calcium ratio is greater than 1:20,000. The position is not improved if the extraction finish, as described by Elwell *et al.*,[4] and by Booth *et al.*,[5] is used.

The quinoline molybdophosphate method of Wilson[6] gives satisfactory results down to a phosphate:calcium ratio of 1:50,000. The "molybdenum blue" method of Berenblum *et al.*,[7] gives satisfactory results down to a phosphate:calcium ratio of 1:200,000, provided that the determination is carried out in the temperature range 18°–24°.

Acknowledgements—The writer thanks the Directors of John & E. Sturge Limited, for permission to publish this letter.

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9 *April* 1964

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NACHWEIS UND QUANTITATIVE BESTIMMUNG VON CHLORIERTEN CYCLOPENTADIENDERIVATEN DURCH GASCHROMATOGRAPHIE UND UV-SPEKTROPHOTOMETRIE

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(*Eingegange am* 24 *November* 1963. *Angenommen am* 10 *März* 1964)

Zusammenfassung—Zur qualitativen und quantitativen Bestimmung von Hexachlorcyclopentadien in Gegenwart von chlorierten Cyclopentadienderivaten wurde eine gaschromatographische und eine UV-spektrophotometrische Methode ausgearbeitet.

HEXACHLOROCYCLOPENTADIEN ist einer der Grundstoffe der Pflanzenschutzmittel vom Cyclodien-typ. Bei seiner Erzeugung durch Chlorieren von Cyclopentadien sind in dem anfallenden Produkt ausser Hexachlorocyclopentadien auch Oktachlorcyclopenten und andere Cyclopentadienderivate von verschiedenem Chlorierungsgrad anwesend.

Zur Ermittlung der optimalen Bedingungen der Chlorierung ist es erforderlich, den Hexachlorcyclopentadiengehalt des Reaktionsproduktes zu bestimmen. Zur Lösung dieser Aufgabe hielten wir unter den analytischen Bestimmungsmethoden die Gaschromatographie und die UV-Spektrophotometrie für geeignet.

In der Untersuchung der Proben bereitete der Umstand, dass das Hexachlorcyclopentadien in einem Gemisch bestimmt werden musste, das durchschnittlich 10 bis 12 chlorierte Cyclopentadienderivate von unbekannter Zusammensetzung und von stark unterschiedlichem Siedepunkt enthielt, grosse Schwierigkeiten. In Proben, die Komponenten mit höherem Chlorierungsgrad als das Hexachlorocyclopentadien enthalten, lässt sich das Hexachlorcyclopentadien mit dem Gaschromatographen qualitativ und quantitativ gut bestimmen. Die Untersuchungen zeigten, dass sich das Hexachlorocyclopentadien in Gemischen, die Verbindungen mit niedrigerem Chlorierungsgrad als die des Hexachlorcyclopentadiens enthalten, mit der gaschromatographischen Methode wegen der Anwesenheit einer Störkomponente mit nahezu gleicher Retentionszeit nicht bestimmen lässt.

Zur Untersuchung von Proben solcher Zusammensetzung wurde mit Erfolg die UV-Spektrophotometrie verwendet.

Untersuchungen mit der gaschromatographischen Methode

Die Untersuchungen wurden mit dem Gaschromatographen Fractovap B der Firma Carlo Erba durchgeführt. Die Thermostatkammer des Gerätes ist zwischen 0 und 230°C auf eine beliebige Temperatur einstellbar. Die Temperatur wird mit einem elektronischen Temperaturregler stabilisiert. Als Messgeber dient eiene Wärmeleitfähigkeitszelle. Die Strömungsgeschwindigkeit des Trägergases wird mit einem Rotameter gemessen. Zur Registrierung der Messergebnisse dient ein potentiometrisches Linienschreibgerät. Die Flächen unter den chromatographischen Spitzen werden mit einem elektronischen Integrator gemessen.

Als Standard wurden durch Destillation gereinigte Hexachlorcyclopentadien und mit Alkohol mehrmals umkristallisiertes Oktachlorcyclopenten verwendet.

Als Trennflüssigkeit diente Apiezon N Vakuumhahnfett und als Trägermittel Thermolytziegelpulver bzw. Polyäthylenpulver von 0,3 bis 0,4 mm Korngrösse. Vor dem Imprägnieren wurde das Thermolytziegelpulver bei 160°C aktiviert. Die Menge der Trennflüssigkeit betrug im Falle von Thermolytziegelpulver 10% und von Polyäthylenpulver 1%. Das Apiezonfett wurde als Lösung in Äther mit dem Trägermittel vermischt. Das Lösungsmittel wurde auf einem Wasserbad verdampft.

Bei der Bestimmung des Hexachlorcyclopentadiens aus einem Gemisch, das kein Oktachlorcyclopenten enthielt, betrug die Höhe der chromatographischen Säule 1 m und ihr Durchmesser 6 mm. Als Füllstoff wurde mit 10% Apiezon N benetztes Thermolytziegelpulver verwendet. Die Temperatur der Thermostatkammer wurde zu 165°C und die des Verdampferraumes zu 230°C ausgeregelt. Die Strömungsgeschwindigkeit des Wasserstoff-Trägergases betrug 2 l/h (Abb. 1).

Bei der Ausarbeitung der quantitativen Bestimmungsmethode bestätigten wir mit der inneren Standardmethode mit Hilfe von Proben von bekanntem Hexachlorcyclopentadiengehalt die Lineariät des Zusammenhanges zwischen der Konzentration und der Grösse der Fläche unterhalb der Spitze. Als innerer Standard wurde Cyclohexan verwendet. Die Cyclohexankonzentration betrug in jedem Fall 20 Gew. %. Die Konzentration des Hexachlorcyclopentadiens wurde zwischen 10% und 60% geändert. Als dritte Komponente wurde chloriertes Gemisch verwendet, das kein Hexachlorcyclopentadien enthielt. Die Ergebnisse wurden auf Grund der unterhalb der Spitzen ausgemessenen Flächen und der Höhen der Spitzen ausgewertet. Aus den Chromatogrammen wurden die Quotienten

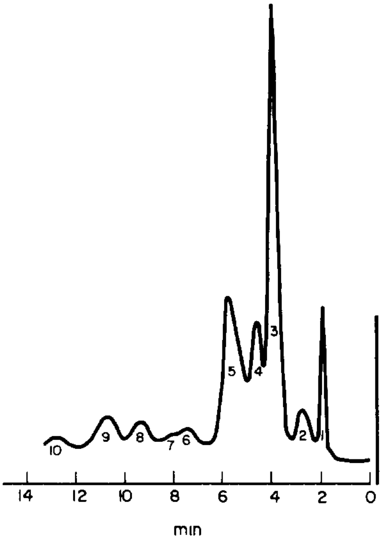

ABB. 1.—1,2,4-9: chlorierte Cyclopentadien.
3: Hexachlorcyclopentadien.
10: Oktachlorcyclopenten.

$$\frac{\text{Fläche unter der Hexachlorcyclopentadien-Spitze}}{\text{Fläche unter der Spitze des inneren Standards}} = \frac{H_T}{St_T} \text{ und}$$

$$\frac{\text{Höhe der Spitze des Hexachlorcyclopentadiens}}{\text{Höhe der Spitze des internen Standards}} = \frac{H_M}{St_M}$$

bestimmt. Die auf diese Weise erhaltenen Werte, als Funktion der Hexachlorcyclopentadien-Konzentration dargestellt, ergaben mit beiden Berechnungsmethoden Geraden.

Aus dem vorliegenden Chromatogramm wurde auch die auf die Summe der Flächen unterhalb der Spitzen bezogene prozentuelle Konzentration des Hexachlorcyclopentadiens, bestimmt. Die auf diese Weise erhaltenen quantitativen Ergebnisse stimmten mit der Einwaage ausreichend überein. Zu den weiteren Untersuchungen wurde die letztere einfachere Berechnungsmethode verwendet.

Bei Proben, die Oktachlorcyclopenten enthielten, konnte die Bestimmung des Hexachlorcyclopentadien aus der Gesamtfläche unter den oben angeführten Chromatographierungsbedingungen nicht angewendet werden; wir beobachteten nämlich, dass auf dem Chromatogramm nur ein Teil des Oktachlorcyclopenten, etwa 40 bis 50%, erschien. Es wurde vermutet, dass der negative Fehler auf die Zersetzung infolge der Temperatur sowie der katalytischen Wirkung des Kolonnenfüllstoffes zurückzuführen ist. Diese Annahme wird auch durch Beckman[1] unterstützt. Die Erhöhung der Temperatur der Thermostatkammer erschien daher nicht als zweckmässig.

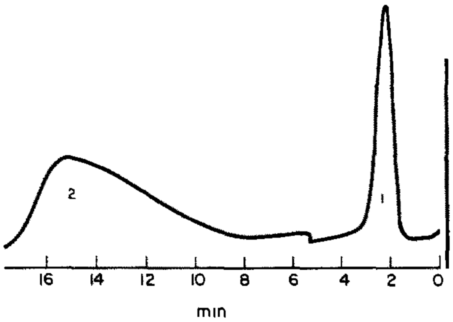

Abb. 2.—1: Hexachlorcyclopentadien.
2: Oktachlorcyclopenten.

Um auch die Bestimmung des Oktachlorcyclopentens quantitativ zu gestalten und zugleich bei der Bestimmung des Hexachlorcyclopentadiens die Anwendung der schwerfälligen internen Standardmethode zu vermeiden, wurde eine Säule von 0,25 m Länge und 4 mm Durchmesser, die mit 1% Apiezonfett benetztem polyäthylenpulver gefüllt wurde, verwendet. Die Temperatur der Thermostatkammer wurde zu 100°C, die des Verdampferraumes zu 230°C ausgeregelt. Die Strömungsgeschwindigkeit des Wasserstoffträgergases betrug 41/h (Abb. 2).

Unter diesen Umständen liess sich in entsprechender Konzentration auch das Oktachlorcyclopenten ohne Zersetzung quantitativ bestimmen; somit kann das Hexachlorcyclopentadien auch in der Gegenwart der hochsiedenden Komponente mit der einfachen und schnellen, auf die Gesamtfläche bezogenen Methode berechnet werden.

Untersuchungen mit der UV-spektrophotometrischen Methode

Die spektrophotometrischen Bestimmungen wurden mit einem Spektrophotometer Unicam Sp-700 vorgenommen. Der Messbereich des Gerätes erstreckt sich vom Ultra-violett-Gebeit bis zum nahen Infrarot-Gebiet 3·6 μ. Das Gerät registriert automatisch die auf die Referenzsubstanz bezogene Lichtabsorption der Probe.

Bei der Untersuchung der Spektren des Hexachlorcyclopentadiens und Oktachlorcyclopentens konnte festgestellt werden, dass die Absorptionsmaxima mit den in der Literatur angegebenen Werten übereinstimmen.[2,3]

Im untersuchten Ultraviolett-Gebiet weist das Specktum der Lösung des Hexachlorcyclopentadiens in Tetrachlorkohlenstoff bei 259 mμ and 318 mμ liegende zwei Absorptionsmaxima auf. Das Oktachlorcyclopenten und die übrigen chlorierten Cyclopentadienderivate ergeben nur ein Absorptionsmaximum bei 259 mμ (Abb. 3). Dadurch kann das Hexachlorcyclopentadien mit Hilfe des Absorptionsmaximums

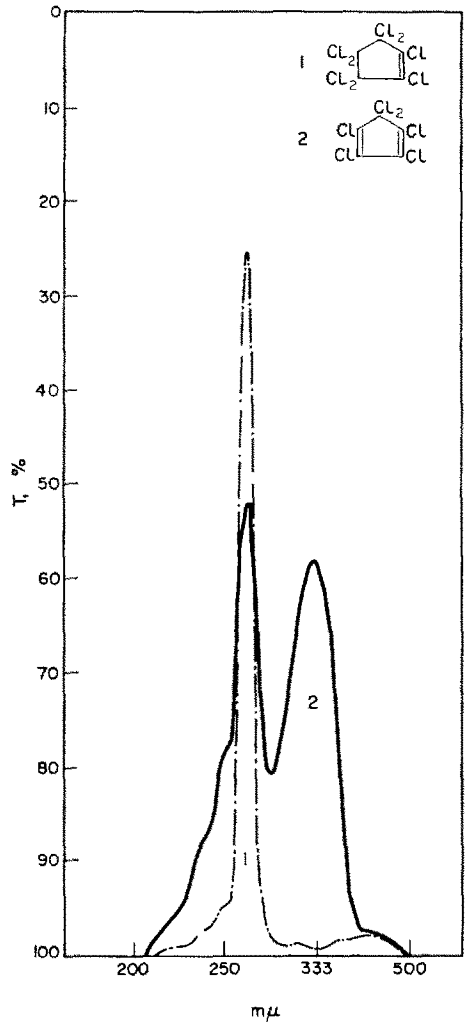

Abb. 3.—Absorptionsspektren von Hexachlorcyclopentadien und Oktachlorcyclopenten in Tetrachlorkohlenstoff als Lösungsmittel.

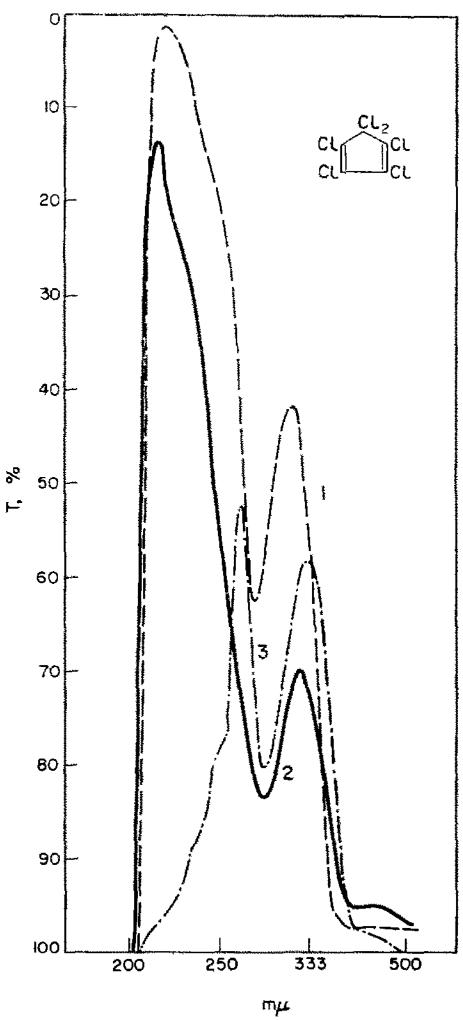

Abb. 4.—Absorptionsspektrum von Hexachlorcyclopentadien in verschiedenen Lösungsmitteln.

1: n-Hexan.
2: Äthanol.
3: Tetrachlorkohlenstoff.

bei 318 mμ auch in Gemischen, bei denen die gaschromatographische Methode nicht anwendbar ist, bestimmt werden.

Bei der Ausarbeitung der quantitativen Bestimmungsmethode wurden die Transmissionen von Hexachlorcyclopentadien-Lösungen verschiedener Konzentration bestimmt. Die geeignete Konzentration zur quantitativen Bestimmung ergab sich zu 10^{-4} mol/l. Die Messungen wurden in einer Quarzküvette von 1 cm n-Hexan, Äthanol bzw. Tetrachlorkohlenstoff als Lösungsmittel durchgeführt. Die in den verschiedenen Lösungsmitteln gemessenen Absorptionsmaxima zeigen einige mμ Abweichung (Tab. 1, Abb. 4).

TABELLE 1.—ABSORPTIONSMAXIMA IN VERSCHIEDENEN LÖSUNGSMITTELN

Verbindung	Lösungsmittel	max.,	$m\mu$
Hexachlorcyclopentadien	n-Hexan	230	310
	Äthanol	209	318
	Tetrachlorkohlenstoff	259	318
Oktachlorcyclopenten	n-Hexan	210	—
	Äthanol	230	—
	Tetrachlorkohlenstoff	259	—

Der Vergleich der mit Gaschromatographie bzw. mit UV.-Spektrophotometrie erhaltenen Ergebnisse der Hexachlorcyclopentadien Bestimmung zeigt, dass die Abweichung zwischen den beiden Methoden 1,0 abs. % nicht übertrifft (Tab. 2).

TABELLE 2.—ABWEICHUNGEN IN DER BESTIMMUNG DES HEXACHLORCYCLOPENTADIENGEHALTS

Nr.	Hexachlorcyclopentadien, Gehalt in Prozenten		Abweichung, %
	gaschromatographisch bestimmt	spektrophotometrisch bestimmt	
1	19,5	18,5	1,0
2	18,5	17,7	0,7
3	27,0	26,7	0,3
4	32,6	33,0	0,4
5	66,5	65,8	0,7

GANG DER ANALYSE

Bestimmung von Hexachlorcyclopentadien

Von der Probe werden unter den bereits beschriebenen gaschromatographischen Bedingungen mit einer Injektionsspritze 10 μl eingemessen. Aus dem Chromatogramm lässt sich die Art der Cyclopentadienderivate der Probe feststellen. Ist keine Komponente zugegen, die die gaschromatographische Bestimmung des Hexachlorcyclopentadiens stören würde, so wird das Chromatogramm mit der Berechnungsmethode der Flächensumme ausgewertet. Falls die Bestimmung in Gegenwart von Cyclopentadienderivaten niedrigeren Chlorierunggrades ausgeführt werden soll, wird das folgende Verfahren angewandt.

In einem Normalkolben wird aus der Analysenprobe auf einer analytischen Waage so viel eingewogen, dass die Konzentration der Lösung 10^{-4} Mol/Liter betrage, nachher wird der Kolben mit Tetrachlorkohlenstoff bis zur Marke aufgefüllt. Die Transmission wird in einer Quartzküvette von 1 cm gegen Tetrachlorkohlenstoff bei 318 mμ gemessen. Die Konzentration wird unter gleichen Bedingungen mit Hilfe einer unter gleichen Bedingungen mit reinem Hexachlorcyclopentadien aufgenommen Kalibrierungskurve bestimmt.

Bestimmung von Oktachlorcyclopentan

Zur gaschromatographischen Bestimmung werden 20 μl der Probe ausgemessen; bei hohem Oktachlorcyclopentengehalt ist die Probe fest, in diesen Falle wird die Probe in wenig Tetrachlorkohlenstoff gelöst. Die Auswertung erfolgt mit der Berechnungsmethode der Flächensumme.

Zur spektrophotometrischen Bestimmung wird aus der Analysenprobe dem zu erwartenden Oktachlorcyclopentengehalt entsprechend in einen Normalkolben so viel ausgemessen, dass die Konzentration der Lösung 10^{-4} Mol/Lit. betrage.

Der Kolben wird mit Tetrachlorkohlenstoff bis zur Marke aufgefüllt. Die Transmission wird in einer Quarzküvette von 1 cm gegen Tetrachlorkohlenstoff bei 259 mμ gemessen. Die Konzentration wird mit Hilfe einer Kalibrationskurve, die mit einem Oktachlorcyclopentadienstandard aufgenommen wurde, bestimmt.

Summary—A gas-chromatographic and ultraviolet-spectrophotometric method has been developed for the detection and quantitative determination of hexachlorocyclopentadiene in the presence of chlorinated derivatives of cyclopentadiene.

Résumé—On a élaboré une méthode de chromatographie en phase vapeur et de spectrophotométrie ultraviolette pour la détection et le dosage de l'hexachlorocyclopentadiène en présence de dérivés chlorés du cyclopentadiène.

SCHRIFTTUM

[1] H. F. Beckman und A. Bevenue, *J. Chromatog.*, 1963, **10**, 231.
[2] E. T. McBee, J. D. Idol und C. W. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 4375.
[3] J. D. Idol, V. W. Roberts und E. T. McBee, *J. Organic Chem.*, 1955, **20**, 1743.

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RAPID DETERMINATION OF BORON IN IRON AND STEEL BY PYROHYDROLYSIS AND CONSTANT-CURRENT COULOMETRY*

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Summary—An accurate and simple method for the determination of boron in steel is proposed. A pyrohydrolytic method for separating boron has been applied to boron steel. The sample, heated in a furnace, is decomposed by water vapour, and boron in the sample is collected in a dilute sodium hydroxide solution, together with the water vapour, within 20–40 min. The boron content in the receiver is determined by constant-current coulometry using mannitol. Accurate results have been obtained within 30–50 min for several boron steels containing 0.0002–0.01% of boron.

IN spite of its very low content in steels, boron has a marked effect upon the hardening of steel. Therefore the determination of the element is very important. A methylborate separation and colorimetric determination[1–5] have been commonly applied for iron samples. These methods, however, require the treatment of acid-insoluble boron compounds, and are very complicated and time-consuming; moreover, the results obtained are not satisfactory unless the analyst is fairly skilled.

A pyrohydrolytic procedure,[6–9] as a separation method for boron or halide ions, has been adopted for the determination of these elements in those ceramic or atomic reactor samples which contain relatively large amounts of boron. This procedure has not yet, however, been applied to small amounts of boron, especially in steel samples.

According to the literature[10] and the authors' recent investigations,[11,12] 1–500 μg of boron can be determined by constant-current coulometry using mannitol, and very reliable results have been obtained. For determining microamounts of boron in steels, this coulometric method has now been combined with the pyrohydrolytic procedure already mentioned, and a more rapid and more accurate method has resulted.

EXPERIMENTAL

Apparatus for pyrohydrolysis

A schematic diagram of the apparatus for pyrohydrolysis of the sample is shown in Fig. 1. The furnace commercially available for the determination of sulphur in steel is satisfactory for this purpose, and a large combustion boat (1 cm deep, 1 cm wide and 8 cm long) is used, after pretreatment by the following procedure. It is washed by scrubbing with tap water, and is treated with 6*M* hydrochloric acid; after washing with distilled water until free from chloride, it is dried, and heated in the furnace in the same conditions as those used for the sample treatment. By this means the blank value for the boat is reduced to less than 1 μg. Steam, which is passed over the sample, is controlled by the adjustment of the voltage of the heating mantle. A 1-litre quartz flask, containing 2–3 g of sodium hydroxide in 1 litre of water, is used for steam generation. Other detailed dimensions are shown in Fig. 1.

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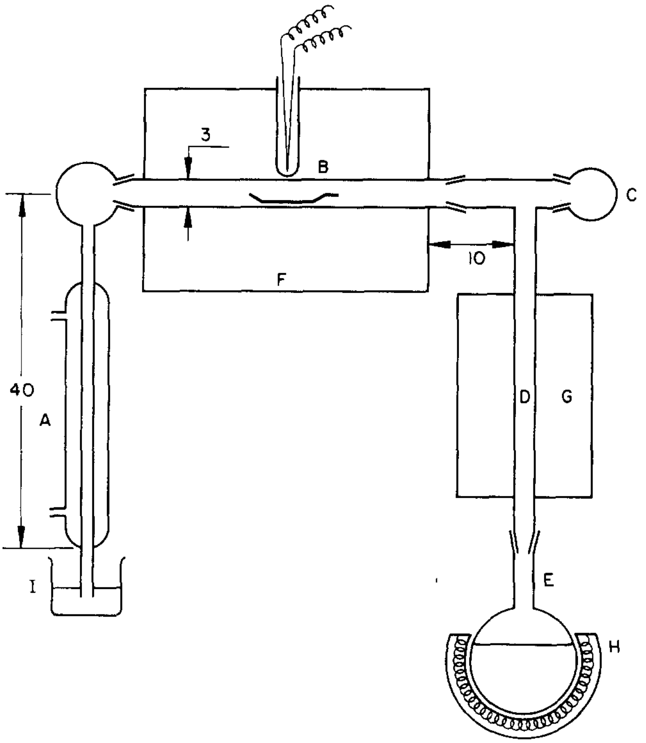

FIG. 1.—Apparatus for pyrohydrolysis

A: Quartz jacket condenser	E: Quartz round-bottomed flask (1 litre)
B: Quartz reaction tube	F: Reaction furnace
C: Sample inlet	G: Preheater furnace
D: Quartz T-connector tube	H: Heating mantle
	I: Quartz or Polyethylene beaker

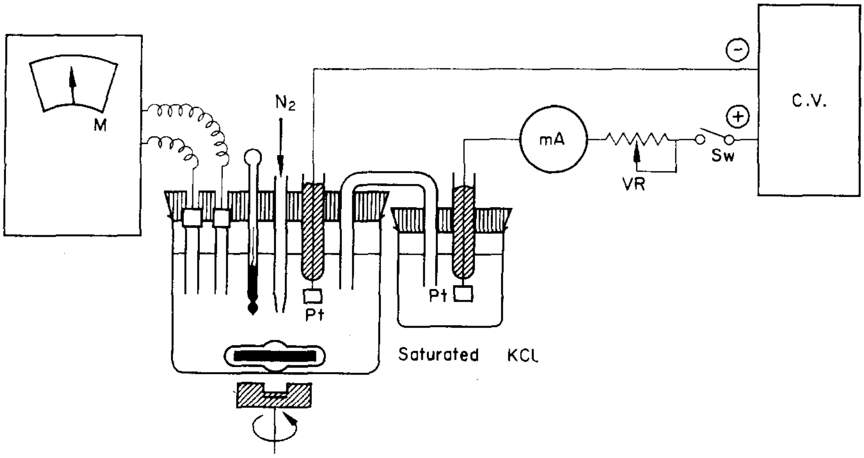

FIG. 2.—Apparatus for coulometric titration

Pt: Pt-electrode (1 × 1 cm)	C.V: D.C. Constant voltage source (250 v, 150 mA)
mA: Milliammeter (1 mA or 10 mA)	Sw: Switch
VR: 25 K – 500 K Variable resistor	M: pH meter with glass electrode

Apparatus for constant-current coulometry

The coulometric titration apparatus for determining boron is shown in Fig. 2. The electrolysis cell is made from a quartz or polyethylene beaker, and the tubes for introducing nitrogen and those for salt bridge are made of polyethylene. The rotating part of the stirrer is also covered with polyethylene. Constant current is applied using an electronic constant-voltage supply and a variable resistor of high resistance.

The accuracy and the lower limit of the results obtainable by this apparatus depend largely on the accuracy of the pH meter. A pH meter, Model P, with glass electrode, made by the Hitachi-Horiba Instrument Co. is fairly satisfactory.

Reagents

"Analytical Grade" reagents and redistilled water are used. The purity of the mannitol is most important in this method. Even trace amounts of acidic materials in this reagent harms the results; the reagent with the least blank value should be chosen from several lots. The complete washing of the nitrogen introduced into the cell is also important. In order to remove alkaline materials introduced by the washing with solid sodium hydroxide it was necessary to wash at least 4 times with water.

Pyrohydrolytic separation of boron from steel

Only one example has been found in the literature[8] of the pyrohydrolytic separation of boron in steel containing a relatively large amount of boron, but the details are not given. For the determination of a small amount of boron in ordinary boron steel, no method has been described.

To obtain the optimum conditions for the separation of microamounts of boron in steel, the following method was used.

Procedure: The sample, weighed into the boat, was placed in the furnace which was above 1100°; preheated water vapour (about 900°) was then passed for 20–90 min. The rate of the flow of the steam was adjusted by controlling the voltage of the heating mantle (Fig. 1, H). The steam, containing the boron from the sample, was condensed and collected in the quartz or polyethylene beaker containing dilute sodium hydroxide solution. After passage of the steam, the distillate was evaporated, if necessary, to about 100 ml, and the boron content was determined by constant-current coulometry, as described later.

The rate and efficiency of boron recovery in the distillate is dependent on such factors as the temperature of the reaction tube, the rate of flow of the steam, the time of pyrohydrolysis, and the amount of the sample.

Rate of flow of steam

With increase in the rate of flow of the steam, the volume of the distillate becomes very large, and therefore a large amount of mannitol must be added to the electrolyte. This causes a high blank value because of the acidic matter in the reagent. If the rate is too slow, the boron compound may be condensed at the exit of the reaction tube.

TABLE I.—EFFECT OF THE RATE OF PASSAGE OF STEAM

Rate of steam, *ml/min*	Recovery of boron, %
5	98·5
4	99·4
3	100·0
2	102·2

The rate of the flow of the steam was changed from 2 to 5 ml per min (as liquid) and the other conditions were kept constant as follows: sample 1·5 g, furnace temperature 1350°, and time of pyrohydrolysis 30 min.

The results in Table I demonstrate that the rate of flow of steam had not much effect on the results within this range. Because of the considerations mentioned, however, a rate in the range 2–3 ml/min (as liquid) is preferred.

Time of pyrohydrolysis and temperature

Because the vapour pressure of boric oxide increases at high temperature, the time of pyrohydrolysis may be shortened if the furnace temperature is raised. The relation between the temperature of the furnace and the time of pyrohydrolysis is shown in Fig. 3. To obtain these results, the following conditions were kept constant: sample (NBS standard sample No. 151) 1·5 g, rate of flow of steam 2–4 ml/min. When the temperature of the furnace was kept at 1400°, the boron in the sample could be completely recovered within 20 min, and when it was kept at 1150°, 90 min pyrohydrolysis were needed to recover the element completely.

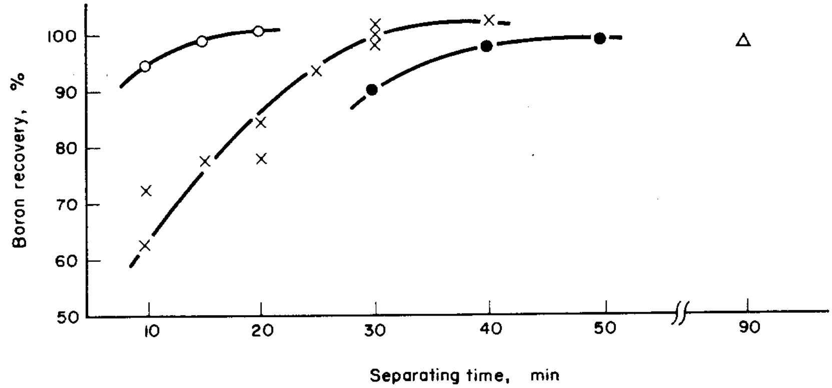

FIG. 3.—Recovery of boron as function of separating time and separating temperature;
—○— 1400°;
—×— 1350°;
—●— 1250°;
△ 1150°.

Although the time of pyrohydrolysis may change according to the amount of sample and the size of the chips, the time necessary for separation of boron from steel samples is greatly shortened if the temperature of the furnace is kept above 1300°. Moreover, evaporation of the distillate, occasionally required in colorimetric procedures, is now not necessary if the time limits described are adhered to.

Recommended procedure for pyrohydrolysis

Weigh the relatively finely divided sample (0·5–3 g) into the boat, treated as described above, and carefully charge it into the furnace, which is kept above 1350°. Connect up the apparatus as shown in Fig. 1. Use about 15 ml of water containing 3–5 drops of 0·5*M* sodium hydroxide solution to collect the distillate. Introduce the steam, preheated to about 900°, at the rate of 2–3 ml per min (as liquid), and maintain this rate for 20–40 min, according to the temperature and the size of the sample. After this time interval, remove the reservoir, and transfer the distillate to the electrolysis cell. Add about 3 g of sodium bromide and dissolve it. Adjust the volume of the solution to about 100 ml. Determine the content of boron in this solution by the constant-current coulometric method described later.

Determination of boron by constant-current coulometry

Many experiments appear in the literature[10–14] for the acidimetric determination of boron using mannitol. In these, however, the pH value when the mannitol is added and that at the end-point do not coincide. In addition, the determination has been of a relatively large amount of boron, and a titration curve for less than 1 mg of boron has not yet been described. According to the present authors' experiments, pH values and the concentration of mannitol at this level do not coincide with those in the literature.

The minimum concentration of mannitol in the electrolyte to determine such a microamount of boron was investigated, and the results obtained are illustrated in Fig. 4. These results show that it is necessary to add more than 6·0 g of mannitol to 100–120 ml of the electrolyte.

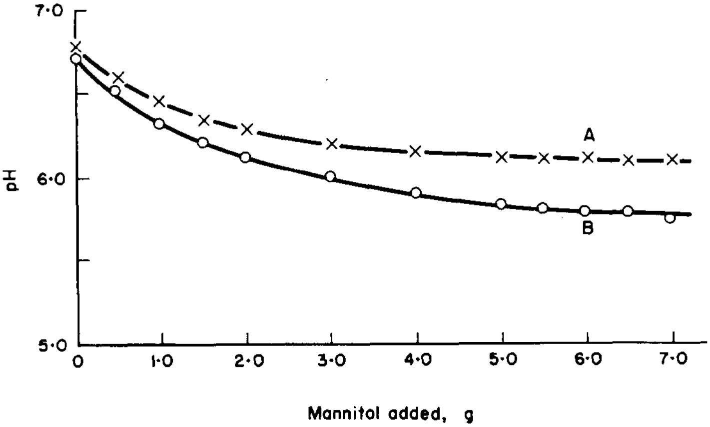

FIG. 4.—Decrease of pH of the electrolyte containing boric acid by the addition of mannitol:

A: 50 μg of boron, B: 100 μg of boron.

One hundred ml of 0·5*M* sodium bromide solution and a definite amount of sodium borate sample solution were placed in the quartz or polyethylene beaker, and it was assembled for the coulometric titration of boron as shown in Fig. 2. Nitrogen was passed through the solution to remove atmospheric carbon dioxide, and the solution was acidified with dilute hydrochloric acid (pH about 2). The solution was then neutralised to a definite pH value (pH 5·5, 6·5, or 7·5) with dilute sodium hydroxide solution, using electrical control. After addition of 6·00 g of mannitol, and a coulometric titration, using constant current, was carried out.

The results of these experiments are shown in Figs. 5–7.

When the boron content is more than 10 mg, the pH-change is sufficient for the use of an indicator such as phenolphthalein (Fig. 5, curve I; Fig. 6, curve I; Fig. 7, curve I). When the boron content is decreased to about 1·0 mg, or less, the concentration of alkaline standard solution or the current of electrolysis should be decreased, and the pH value after the end-point does not increase sufficiently for the use of phenolphthalein (Fig. 5, curves II, III; Fig. 6, curve II; and Fig. 7, curves II, III). When the boron content is decreased to 0·1 mg or less, the pH change near the end-point decreases, and therefore the pH value at the end-point should be lowered. In this case it is very difficult to obtain a clear end-point (Fig. 5, curve IV).

In any event, mannitol must be added at pH 6·5, because otherwise the results obtained are too high or too low (Figs. 5, 6 and 7).

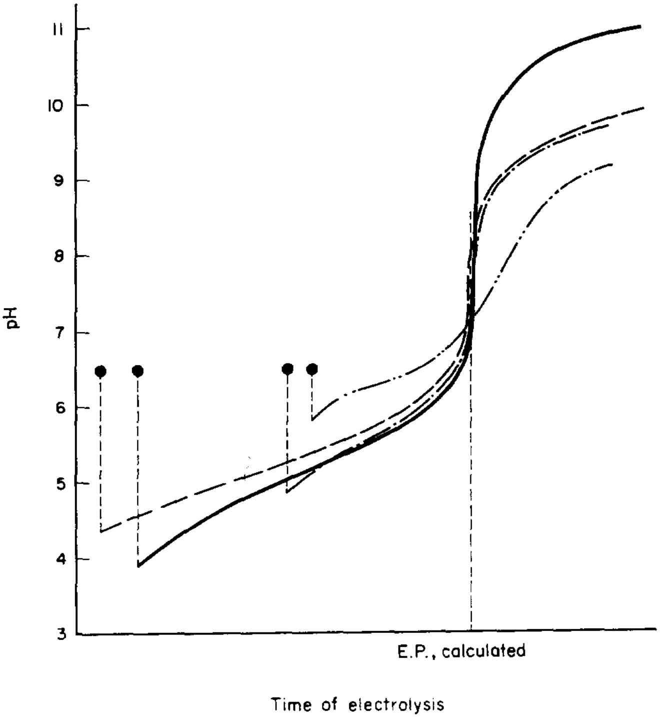

FIG. 5.—Coulometric titration curves (mannitol added at pH 6·5):

Curve I ——— 10·8 mg of boron, 216 mA, Curve III —.—. 0·50 mg of boron, 19 mA;
Curve II ——— 1·08 mg of boron, 19 mA; Curve IV —.—. 0·10 mg of boron, 4·5 mA;

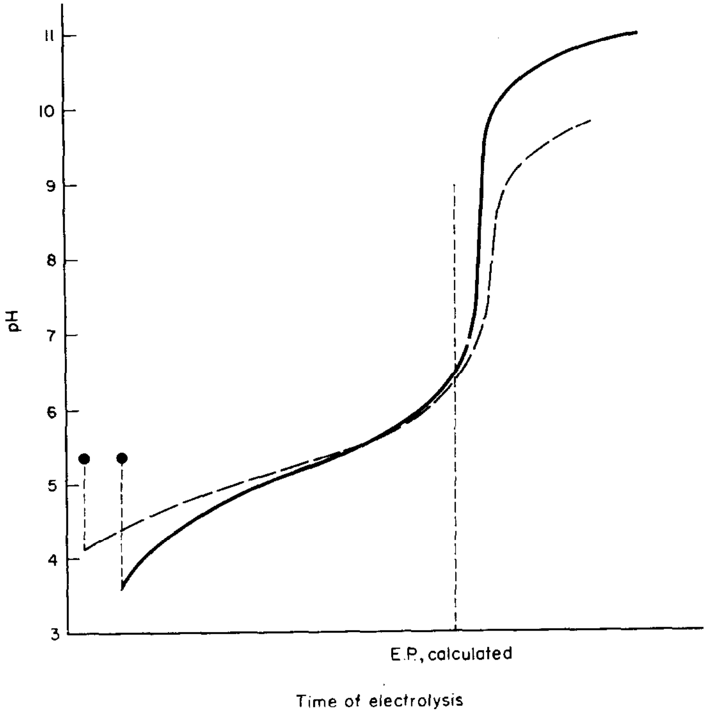

FIG. 6.—Coulometric titration curves (mannitol added at pH 5·5);

Curve I ——— 10·8 mg of boron, 216 mA; Curve II ——— 1·08 mg of boron, 19 mA.

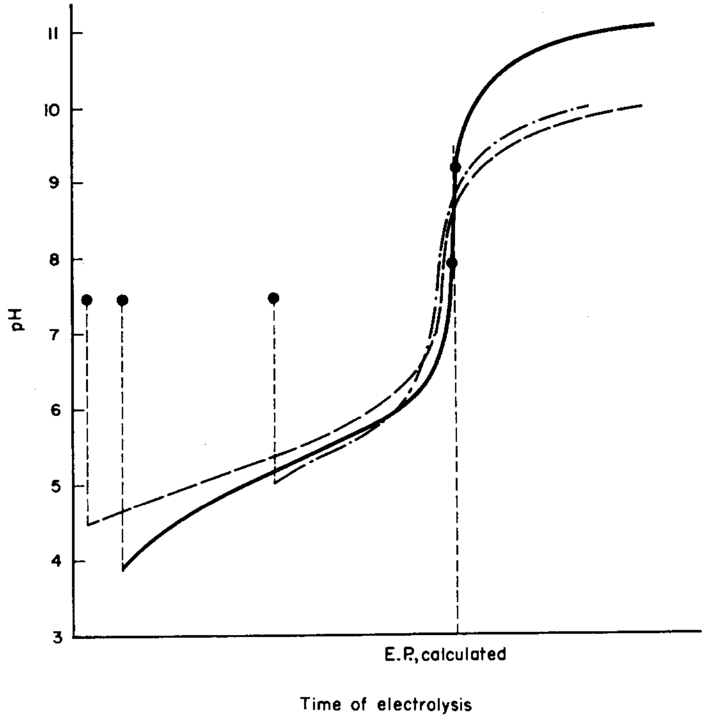

FIG. 7.—Coulometric titration curves (mannitol added at pH 7·5);
Curve I ——— 10·8 mg of boron, 216 mA;
Curve II ——— 1·08 mg of boron, 19 mA;
Curve III —.—. 0·50 mg of boron, 19 mA.

TABLE II.—EFFECT OF pH OF THE ELECTROLYTE BEFORE ADDITION OF MANNITOL AND AT THE END-POINT

pH at the end-point	Boron taken, μg	Boron found, μg	Difference	
			μg	%
5·91	50·3	44·0	−6·3	−12·5
6·31	50·3	45·8	−4·5	−8·9
6·50	50·3	50·5	+0·2	+0·4
6·80	50·3	50·2	−0·1	−0·2
6·97	50·3	48·1	−2·2	−4·4
6·05	10·1	7·5	−2·6	−25·8
6·31	10·1	8·3	−1·8	−17·8
6·50	10·1	9·2	−0·9	−8·9
6·80	10·1	9·9	−0·2	−2·0
7·00	10·1	9·7	−0·4	−4·0

For the titration of relatively high boron concentrations, the pH at the end-point is not so important because of the large pH change, and therefore pH 7, 7·5 or 8 can be chosen. For extremely low boron concentrations, however, the pH value at the end-point is very important; in this case pH 7 (or less) is advisable. For example, pH 7 is preferable for 0·1 mg or boron.

As a result of these experiments the procedure described below is recommended for the determination of the small amounts of boron occurring in ordinary boron steel. With this procedure, the pH of the electrolyte before the addition of mannitol and that at the end-point of the electrolysis coincide with each other, and this has an influence on the results. The element was determined at various pH values of the electrolyte, and the results were shown in Table II. The most satisfactory results were obtained between pH 6·5 and 6·8 for 10–50 μg of boron in the electrolyte. This pH range was nearly equal to the value mentioned elsewhere.[11]

Recommended procedure for constant-current coulometry

Acidify the sample solution in the electrolytic cell containing sodium borate with 0·5*M* hydrochloric acid till the pH is about 2, and adjust the volume to about 100 ml. Add sodium bromide until its concentration in the solution reaches about 0·5*M*. Introduce nitrogen (free from carbon dioxide), adjust the pH value to about 6·2 by adding 0·5*M* and 0·01*M* sodium hydroxide solution. Stop the nitrogen flow, and neutralise the solution with the electrolytically generated hydroxyl ion until the pH increases to 6·6–6·8. During this period adjust the electrolysis current to a convenient value. Add 6·00 g of mannitol to the solution, and pass nitrogen (free from carbon dioxide) for several min.

Table III.—Determination of boron in NBS and BCS standard samples

NBS and BCS standard sample no.	Certified value of boron, %	Wt. of sample taken, *g*	Boron found, %
NBS no. 151	0·0027	1·490	0·0026
		1·545	0·0027
		1·553	0·0025
		1·474	0·0028
		1·533	0·0029
BCS no. 271	0·013	0·518	0·0132
		0·565	0·0123
		0·559	0·0126
BCS no. 274	0·0080	0·525	0·0081
		0·526	0·0081
		0·598	0·0081
BCS no. 275	0·0010	1·321	0·0009
		1·344	0·0011
BCS no. 276	0·0045	1·005	0·0044
		1·104	0·0043
		1·063	0·0041

Table IV.—Determination of boron in boron steels

Sample	Boron content, %	Wt. of sample taken, *g*	Boron found, %
A	0·0027 (colorimetric method)	1·563	0·0026
		1·652	0·0028
		1·539	0·0031
		1·487	0·0027
		2·141	0·0026
		3·094	0·0028
B	*ca.* 0·003	1·506	0·0034
		1·481	0·0036
		1·554	0·0035
		1·441	0·0036
C	*ca.* 0·003	1·221	0·0035
		1·402	0·0035
		1·401	0·0037
		1·559	0·0036

Begin the electrolysis with constant current, and at the same time start a stop-watch. Continue the electrolysis until the pH value of the electrolyte returns to the initial value, and stop the stop-watch immediately. Because the pH value shown by the pH meter is often influenced by the electrolytic current flowing through the cell, the electrolysis should be repeated at brief intervals near the end-point, including the time increment for each interval of electrolysis. At the true end-point, the pH value shown by the pH meter should coincide with the initial value when the electrolytic current has been stopped. From the value of the current and the total time of electrolysis, the amount of boron may be calculated by Faraday's equation.

Analyses of standard boron steels and commercial boron steels

Using the recommended procedure, several standard samples obtained from B.C.S. and N.B.S. were analysed, as well as some other boron steels commercially available. The results of these experiments are summarised in Tables III and IV.

According to the results in Table III, the maximum error of 16 experiments on 5 samples was 10%, and the mean values for each of these samples almost coincided with their certified values. The results for the other samples also show the good reproducibility of this method.

Zusammenfassung—Eine genaue und einfache Methode zur Bestimmung von Bor in Stahl wurde vorgeschalgen. Bor wurde durch Pyrohydrolyse abgetrennt: Die im Ofen erhitzte Probe wird durch Wasserdampf zersetzt und das Bor mit dem Wasserdampf in verdünnter Natronlauge aufgefangen. Der Borgehalt der Lösung wird dann nach Mannitzusatz durch Coulometrie bei konstanter Stromstärke bestimmt. Für verschiedene Borstähle mit Borgehalten von 0,0002 bis 0,01% ließen sich genaue Ergebnisse in 30 bis 50 Minuten erzielen.

Résumé—On propose une méthode simple et précise de dosage du bore dans l'acier. On applique la méthode pyrohydrolytique de séparation du bore à l'acier au bore. L'échantillon chauffé dans le four est décomposé à la vapeur d'eau, et le bore de l'échantillon est recueilli dans la solution diluée de soude, avec la vapeur d'eau, pendant 20 à 40 mn. La teneur en bore du condensat est déterminée par coulométrie à courant constant, avec emploi de mannitol. On a obtenu des résultats exacts pour différents aciers au bore renfermant 0,0002 à 0,01% de bore ne 30–50 mn.

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THE USE OF A HIGH-FREQUENCY TESLA DISCHARGE TUBE FOR THE DETERMINATION OF NITROGEN AND OXYGEN IN HELIUM

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Summary—A study has been made of the variation in light intensity, within the wavelength range 300–700 mμ, of a high-frequency (Tesla) discharge in helium and in mixtures of this gas with nitrogen and oxygen. The increase in intensity in the presence of nitrogen and the decrease in intensity in the presence of oxygen have been related to the amounts present, and applied to the determination of up to 1% of nitrogen and up to 0·7% of oxygen (v/v). The interfering effect of nitrogen on the latter determination has been studied. The precision of the determinations and the recovery on synthetic mixtures are satisfactory.

INTRODUCTION

THE theory and practice of the high-frequency excitation of gaseous mixtures, used as an analytical tool, have been reviewed by McGrath, Magee, Pickering and Wilson.[1]

The possible applications of a Tesla discharge tube for the analysis of gaseous mixtures have been mentioned by Stemberg and Poulson,[2] and preliminary experimental work confirmed that the light intensity of such a discharge varies considerably with the impurity content. An analytical technique based on this phenomenon would have the advantages of not requiring expensive equipment and of being simple and potentially versatile. It was decided, therefore, to study the changes in the light intensity of a discharge tube containing helium on the introduction of nitrogen or oxygen, using a selenium photocell mounted on the side of the tube as a light detector. It was realised, however, that an analytical method based on such a study must be largely empirical, and that the effect of possible interfering factors, particularly pressure variations, would require careful investigation.

DISCUSSION

The important fundamental processes involved in a high-frequency discharge can be expressed as follows:

$$R + C^* \rightarrow R^+ + 2e \qquad \text{ionisation by electron impact} \qquad (1)$$

$$R + C^* \rightarrow R^* + C \qquad \text{excitation by electron impact} \qquad (2)$$

$$R^* \rightarrow R + h\nu \qquad \text{light emission} \qquad (3)$$

where R is a gas molecule or atom,
R^* is an excited molecule or atom,
R^+ is an ion,
and C^* is an electron with a high kinetic energy.

Processes (1) and (2) are often referred to as collisional processes of the first kind.[3]

Excitation and ionisation can also be effected by the impact of fast moving atoms or molecules, and by light quanta. The excitation or ionisation of a molecule or atom by an excited atom or ion is referred to as a collisional process of the second kind. The ionisation of a gas by metastable helium atoms is particularly important and is referred to as the Penning effect:

$$\mathrm{He}^* + \mathrm{R} \rightarrow \mathrm{He} + \mathrm{R}^+ + e \tag{4}$$

The energy of a metastable helium atom is about 20 *e*v, sufficient to ionise the permanent gases, most of which have an ionisation potential of about 15 *e*v. In absolutely pure helium the effective collisional process is of the first kind [processes (1) and (2)], but in the presence of traces of impurity, process (4) becomes effective, and is made use of in the present paper for the determination of nitrogen.

The principal loss of ions in a discharge is through the recombination of positive and negative ions. This is 10^5–10^8 times as probable as the recombination of a positive ion with an electron. Oxygen, the halogens and compounds of either are able to capture free electrons to form negative ions, which then combine with positive ions to decrease the number of ions present.

$$\mathrm{R}^+ + \mathrm{O_2}^- \rightarrow \mathrm{R} + \mathrm{O_2} \tag{5}$$

This recombination effect means that the presence of oxygen, in particular, can seriously interfere with the spectral examination of a gas, but it has been made use of in the present paper as a method for the determination of oxygen and by Lovelock and Lipsky[4] in the Electron-Capture Ionisation Detector.

A further process involves non-elastic collision between fast electrons and gas molecules, whereby electrons lose energy and the processes (1) to (4) are partially suppressed:

$$\mathrm{C}^* + \mathrm{R} \rightarrow \mathrm{C} + \text{energised R} \tag{6}$$

Collisions between electrons and an inert gas molecule are elastic, and the suppressing effect of the introduction of a foreign gas into an inert gas discharge is made use of by Ellis and Forrest[5] as the basis of a gas chromatographic ionisation detector. Reaction (6) is very important in high-frequency spectra work, and may outweigh the Penning Effect (4) at high impurity concentrations.

EXPERIMENTAL

Apparatus

High-frequency generator

A mains-operated Ferranti Tesvac was used, having an output frequency of four megacycles, a maximum output voltage of 30 kv and a power consumption of 30 w.

Discharge tube

High-frequency discharge tubes with internal electrodes are subject to difficulties associated with contamination from the electrode materials and adsorption on the electrode surface. Preliminary work indicated that discharge tubes without internal electrodes gave more reproducible results, and accordingly this type of tube was used in the present work.

The discharge tube (Fig. 1) consisted of a Pyrex capillary tube 1 mm i.d. and 100 mm long, fitted with external electrodes and sealed at one end. The other end was sealed to a bulb of 150-ml capacity fitted with a tap, to permit evacuation and filling. This reservoir was necessary to minimise the effect of "clean up" in the electrical discharge.

Before use, the tube was evacuated, baked at about 400° and conditioned to the sample. The gaseous mixtures were blended and introduced into the discharge tube by the use of conventional high-vacuum gas-transfer techniques.

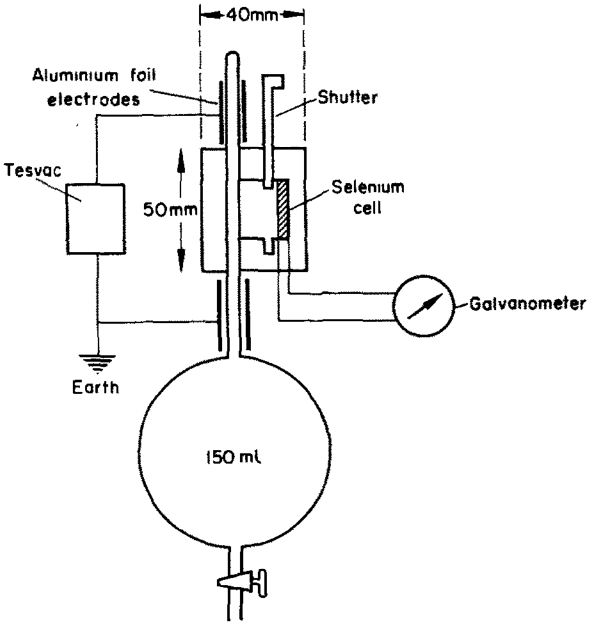

FIG. 1.—Apparatus.

Discharge tube holder and detector assembly

The holder (Fig. 1) was fabricated from Tufnol and kept the discharge tube at a fixed distance from the light detector whilst excluding extraneous light. A fixed aperture, with a shutter, allowed light from the tube to fall upon the detector, a selenium photocell (Hilger No. 633). Leads were taken from the photocell to a Pye Scalamp galvanometer (Cat. No. 7901/S) which provided a means of measurement of the light intensity in arbitrary units.

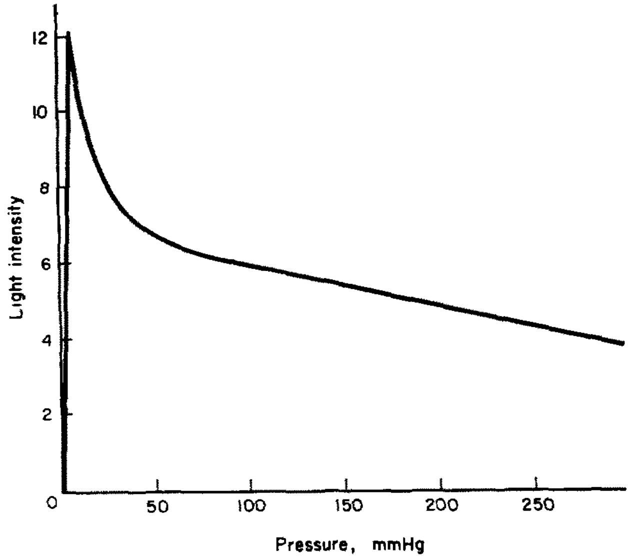

FIG. 2.—Variation of light intensity from helium with pressure.

Sampling pressure

Helium was introduced into the discharge tube, and the light intensity of the discharge was measured at different pressures. A curve was drawn (Fig. 2) relating the light intensity and the gas pressure. This indicated a maximum light intensity at a pressure of 3 mm of mercury. This condition was difficult to reproduce exactly, and it was decided to sample the helium at the more convenient pressure of 200 mm, where the pressure/light intensity curve is not steep and the intensity is still adequate for accurate measurement.

Effect of prolonged discharge

The discharge tube was filled with helium at 200 mm pressure, and was subjected to a continuous discharge. Readings of the light intensity were taken at intervals. These indicated that the light intensity did not vary with time except during the first minute of the discharge, when the readings were somewhat unsteady. In all succeeding experiments 1 min was allowed to elapse between striking the discharge and measuring the light intensity.

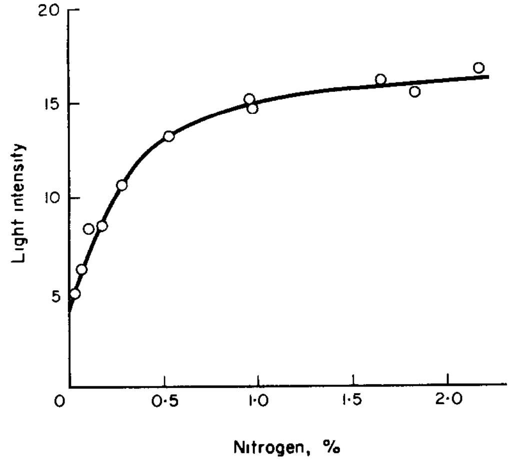

FIG. 3.—Variation of light intensity with nitrogen content, oxygen being absent.

Variation of light intensity with impurities

Mixtures containing up to 2% of nitrogen in helium were made up in a simple gas-blending rig, and were introduced at 200 mm pressure into the discharge tube. The light intensity of each mixture was measured, and a graph was drawn of nitrogen content against light intensity (Fig. 3). This curve showed an increase in light intensity with an increase in nitrogen content up to 2%. In the same way, mixtures containing up to 0·7% of oxygen in helium were prepared, and a graph was obtained (Fig. 4) showing the reduction in light intensity with increase in oxygen content up to 0·7%. It is apparent that the presence of either oxygen or nitrogen will interfere with the determination of the other.

N.B. In these and succeeding experiments the helium used in making up synthetic mixtures was purified by passing through a 5-Å molecular sieve at 77°K before use.

RESULTS AND DISCUSSION

Determination of nitrogen in helium

The light intensities of the discharges in mixtures of helium containing up to 1% of nitrogen were measured at a sampling pressure of 200 mm, and Fig. 3 was used as a calibration curve to calculate the nitrogen content. Table I compares the known nitrogen content with that found using Fig. 3, and indicates that up to 1% the error is about 0·02% of nitrogen.

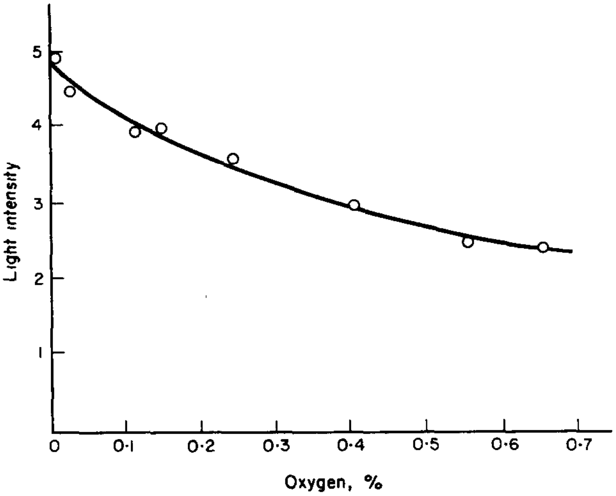

Fig. 4.—Variation of light intensity with oxygen content, nitrogen being absent.

Table I.—The determination of nitrogen in helium

Nitrogen added, %, *v*/*v*	Light intensity (arbitrary units)	Nitrogen recovered, (Fig. 3) %, *v*/*v*	Error
0	5·1		
0·04	6·1	0·04	0·00
0·10	8·4	0·14	+0·04
0·15	8·5	0·13	−0·02
0·27	10·7	0·27	0·00
0·52	13·3	0·52	0·00
0·96	15·2	1·00	+0·04
0·98	15·0	0·94	−0·04

The use of Fig. 3 as a calibration curve for the determination of nitrogen in helium required the prior removal of oxygen to eliminate interference. Commercial helium was therefore passed through a manganous oxide trap to remove any oxygen present and was then introduced into the discharge tube at 200 mm pressure. The light intensity of the discharge was measured under the same conditions as before and Fig. 3 was used as a calibration curve to calculate the nitrogen content of the helium sample. Replicate results were obtained for a sample of helium containing 0·10% of nitrogen (determined mass spectrometrically), and are recorded in Table II.

Determination of oxygen in helium

The interfering effect of nitrogen on the determination of oxygen in helium cannot be easily eliminated, because the removal of the nitrogen from the sample is difficult. It was decided to investigate this interference in more detail. Mixtures of helium and nitrogen were prepared containing up to 40% of nitrogen, and the light intensity of each was measured. Initially, the discharge colour was pink and the light intensity rose sharply with increasing nitrogen content; it remained sensibly constant between 2% and 5% of nitrogen; and it then fell rapidly throughout the rest of the range considered, where the colour of the discharge was deep purple.

TABLE II.—THE DETERMINATION OF NITROGEN IN HELIUM

Light intensity (arbitrary units)	Nitrogen found, %, *v/v* (Fig. 3)
8·8	0·15
8·4	0·14
6·5	0·06
6·3	0·05
7·2	0·09
8·0	0·12
7·8	0·11
7·7	0·10
Mean result	0·10%
Standard deviation	0·03

A series of mixtures containing up to 0·5% oxygen in helium were made up and various amounts of nitrogen were added to each. The light intensity of each mixture was measured, and Table III and Fig. 5 show the relationship between oxygen content and light intensity despite the variation in nitrogen content from 1·6% to 5·3%. Two results, for concentrations of 0·1% and 15·0% nitrogen respectively, are included in the Table to show the necessity for control of the nitrogen content.

TABLE III.—THE DETERMINATION OF OXYGEN IN HELIUM CONTAINING NITROGEN

Nitrogen added, %, *v/v*	Oxygen added, %, *v/v*	Light Intensity (arbitrary units)	Oxygen recovered, %, *v/v* (Fig. 5)	Error, %
3·0	0·00	16·0		
2·0	0·02	14·8	0·04	+0·02
3·1	0·11	13·8	0·11	0·00
2·3	0·20	12·6	0·21	+0·01
3·9	0·24	12·5	0·22	−0·02
2·1	0·30	11·6	0·30	0·00
1·6	0·34	11·4	0·32	−0·02
5·3	0·42	10·6	0·41	−0·01
1·9	0·51	9·2	0·57	+0·06
1·7	0·66	9·0	0·60	−0·06
0·1*	0·02	8·4	>0·7	
15·0*	0·12	8·5	>0·7	

* Effect of nitrogen content outside the set limits.

Fig. 5 can be used as a calibration curve for the determination of up to 0·7% of oxygen in helium. An analytical method based on this curve would first require the determination of the nitrogen and then its adjustment to between 2% and 5% by the addition of the calculated amount of pure nitrogen. Table III gives the oxygen content as determined from Fig. 5 using the observed light intensity values, and compares them with the actual oxygen figures. It can be seen that the average error is about 0·02% of oxygen.

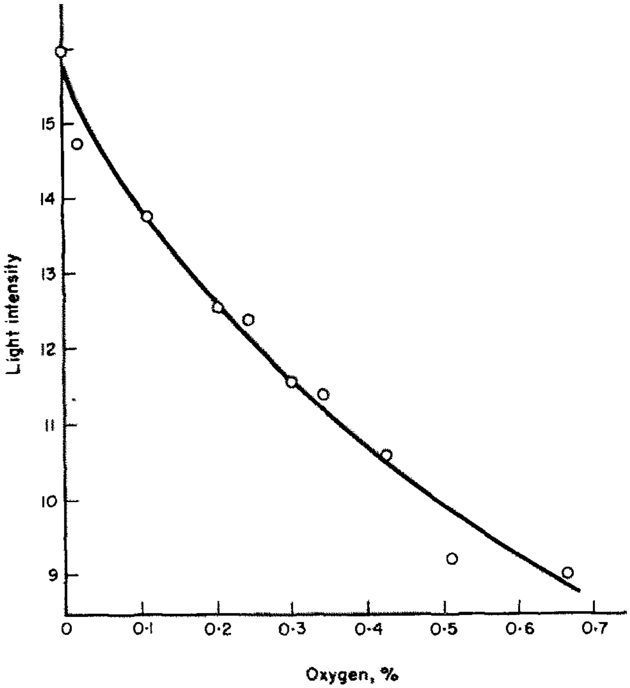

FIG. 5.—Variation of light intensity with oxygen content, nitrogen being present.

CONCLUSIONS

A selenium photocell connected directly to a galvanometer is sufficiently sensitive for the satisfactory measurement of the light intensity from a Tesla discharge tube containing helium. The light intensity from such a discharge increases on the addition of small amounts of nitrogen, and if oxygen is removed, *e.g.*, by a manganous oxide trap, it is possible to use this property to measure the nitrogen content of helium over the range 0–1 % by volume. The light intensity decreases on the addition of oxygen, and this property can be used to measure the oxygen content of helium over the range 0–0·7% by volume, provided that no nitrogen is present or that the nitrogen content can be adjusted to between 2 and 5%. The probable error involved in the determination of nitrogen or oxygen by these techniques is about ±0·03%.

The method is a rather restricted one, and liable to extreme error if indiscriminately applied to the analysis of gas mixtures in general. It is also very sensitive to physical parameters such as pressure.

Zusammenfassung—Die Änderung der Lichtintensität zwischen 300 und 700 mμ einer Hochfrequenz-(Tesla-)entladung in Helium und Gemischen von Helium mit Stickstoff und Sauerstoff wurde untersucht. Der Intensitätszuwachs in Gegenwart von Stickstoff und die Abnahme mit Sauerstoff wurde zu den anwesenden Mengen in Beziehung gesetzt und für die Bestimmung von bis zu 1% Stickstoff und 0,7% Sauerstoff (V/V) verwendet. Die Störung von Stickstoff bei der Sauerstoffbestimmung wurde ebenfalls untersucht. Die Genauigkeit der Bestimmung und die Ergebnisse an selbst hergestellten Mischungen sind zufriedenstellend.

Résumé—Dans le domaine de longueurs d'onde compris entre 300 et 700 mμ, on a étudié la variation de l'intensité de lumière d'une décharge haute fréquence (Tesla) dans l'hélium et dans des mélanges de ce gaz avec l'azote et l'oxygène. L'accroissement de l'intensité en présence d'azote, et son décroissement en présence d'oxygène ont été reliés aux quantités présentes, et appliqués aux dosages de l'azote jusqu'à 1% et de l'oxygène jusqu'à 0,7% (v/v). On a étudié l'effet perturbateur de l'azote sur le dernier dosage. La précision du dosage et la récupération, pour des mélanges synthétiques, sont satisfaisantes.

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THE USE OF TESLA-LUMINESCENCE SPECTRA FOR THE DETERMINATION OF NITROGEN IN HELIUM

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Summary—The Tesla-luminescence spectra of helium containing up to 2% of nitrogen have been examined using a commercial flame photometer. The intensity of lines attributable to nitrogen have been measured relative to those of several internal-standard lines. The ratios of the intensities of these lines can be used to measure the nitrogen content over the range 0–2% with a coefficient of variation of about 3%.

INTRODUCTION

The analysis of helium for impurities is usually effected either mass spectrometrically or gas chromatographically. As an alternative or complementary method it was decided to investigate the use of luminescence spectra techniques.

There are few references in the literature to work on the analytical applications of Tesla-luminescence spectra. Chakrabarti, Magee and Wilson[1] have determined carbon dioxide in argon by high-frequency excitation, and Bochkova, Razumovskaza and Frish[2] have used the technique for the analysis of inert gases for purity. General information, and references to earlier work, are to be found in Twyman.[3]

When an enclosed gas is subjected to a high-frequency a.c. field, any free electrons present will acquire sufficient energy to excite and ionise molecules and atoms. If the field is strong enough, the rate of production of ions and electrons becomes greater than their loss (by recombination, *etc.*), and the process becomes cumulative, leading to a breakdown in the insulating properties of the gas and the production of a luminous discharge. The spectrum so obtained is characteristic of the gas present, and consists usually of both atomic and molecular band spectra.

A high-frequency discharge differs from a static d.c. discharge in that internal electrodes are not required; the high-frequency field can be applied from a remote conductor. This means that no secondary processes are required to replace electrons lost to the anode, and that lower field strengths are required than with static fields. Also, the absence of internal electrodes means that the spectra are free from lines arising from metallic conductors. The physical dimensions of the containing vessel, the pressure of the gas, and the applied field all have a marked effect on the character of the discharge, and it is essential to adhere rigidly to standardised experimental conditions in order to obtain reproducible results. The lack of reproducibility of light emission from a high-frequency discharge has been recorded in the literature,[3] and in general it is considered advisable to adopt an internal standardisation technique for quantitative analysis.

The processes of ionisation and excitation are usually achieved by a flame (as in flame photometry), or by an arc or spark (as in emission spectrography). These methods can be used for gases, but a more common technique involves the use of a discharge tube to which is applied a d.c. potential. Also, work has been carried out with high-frequency discharges in which a Tesla coil has been used as one type of source. Tesla-luminescence spectra, in common with other visible spectra, can be recorded either photographically or photoelectrically, and a conventional spectrograph or flame photometer can be used.

The present report deals with the application of luminescence spectra to the determination of nitrogen in helium, using a helium line as an internal standard. The method could also be applied to the determination of oxygen and argon in helium.

EXPERIMENTAL

Apparatus

High-frequency generator: A mains-operated Ferranti Tesvac was used, having an output frequency of 4 megacycles, a maximum output voltage of 30 kv, and a power consumption of 30 w.

Discharge tube (*Fig.* 1)*:* This consisted of a Pyrex capillary, 1 mm i.d. and 10 cm long, fitted with external electrodes and sealed at one end. The other end was sealed to a bulb of 150-ml capacity, fitted with a tap to permit evacuation and filling. This reservoir was necessary to minimise the effect of "clean up" in the electrical discharge.

Examination of spectra: A Unicam SP. 900 Flame Photometer was used to detect and examine the spectra. The discharge tube was held in a simple holder which replaced the flame unit and kept the tube at a fixed position relative to the aperture of the instrument, and which excluded extraneous light. The spectra were recorded continuously by a Bristol Pen Recorder.

RESULTS AND DISCUSSION

Sampling pressure

The total light intensity of the helium discharge from 300 to 700 mμ was measured at different pressures by means of a simple selenium photocell mounted on the side of the discharge tube. In this series of experiments, the gas was admitted into a discharge tube and the total light output measured at several different pressures. A curve was drawn (Fig. 2) relating the total light intensity to the sampling pressure; this indicated maximum light intensity for helium at a pressure of 3 mm of mercury.

Examination of spectra

Attempts to use the Hilger "Uvispek" for the examination of spectra were not entirely successful; it was difficult to screen the instrument completely from the high-frequency source. The disadvantage of using a Hilger Medium Quartz Spectrograph for this work lies principally in the time required for exposure and treatment of plates. The Unicam S.P. 900 Flame Photometer is a direct-reading instrument, easily screened from the high-frequency source, and was used for the remainder of this work. The wavelength drum of the Photometer was calibrated against standard lines from a mercury vapour discharge tube.

The gases were introduced into the sample discharge tube by the use of conventional high-vacuum gas transfer techniques. Before use, each discharge tube was conditioned by baking it under vacuum and flushing it out several times with a sample of the gas being studied.

The discharge tube was sparked continuously throughout each scan, which covered the wavelength range 300–700 mμ. The following instrument settings were used: slit width, 0·02 mm; gain, 4·0; electrical band width, 3.

The spectra of many pure inorganic gases were studied, each gas being sampled at that pressure which gave the maximum light intensity. The spectra of nitrogen and helium are discussed below.

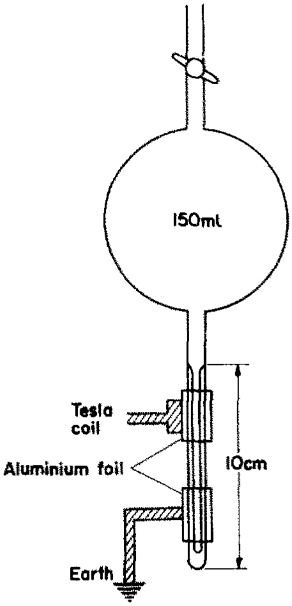

FIG. 1.—Discharge tube without electrodes.

Spectrum of nitrogen

The sample was taken at a pressure of 10 mm of mercury from a cylinder of high-purity nitrogen, and was used without further purification. The spectrum it afforded (Fig. 3) was found to be very intense, consisting of 11 main peaks. Of these, the two principal characteristic peaks were at 337 mμ and 358 mμ.

Helium

A sample of helium was taken from a cylinder at a pressure of 3 mm of mercury, and gave a spectrum (Fig. 4a) containing strong oxygen and nitrogen lines. When

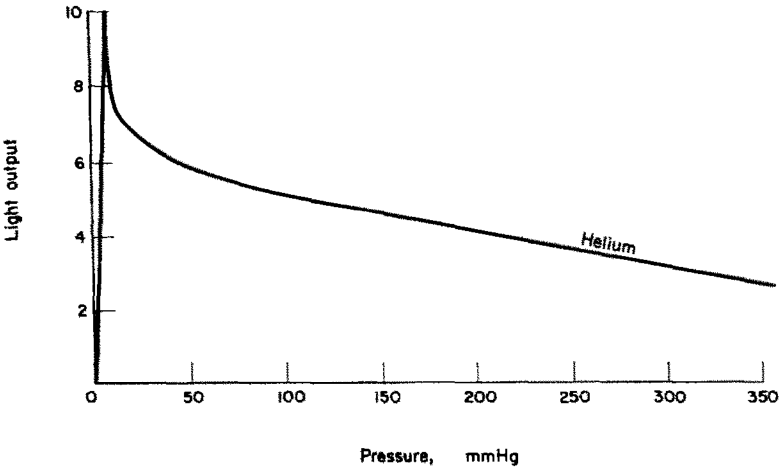

FIG. 2.—Variation of light output with pressure.

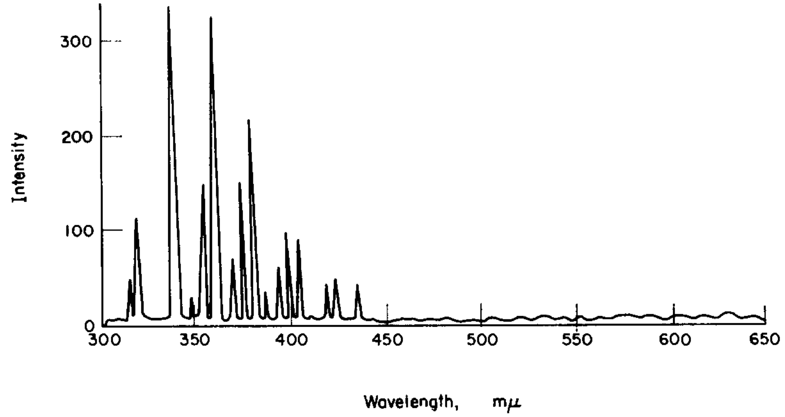

FIG. 3.—Spectrum of nitrogen.

gettered with titanium sponge at 400° for 1 hr, the resulting purified helium gave a spectrum (Fig. 4b) free from oxygen and nitrogen peaks. The spectrum consisted of nine major peaks, the three most intense being at 389 mμ, 502 mμ and 588 mμ.

A sample of helium was also taken at a pressure of 250 mm of mercury and the spectrum was recorded. The oxygen and nitrogen impurity peaks were found to be more intense relative to the helium peaks than when sampled at a pressure of 3 mm. The ratio of the peak heights are obviously dependent upon pressure, which must be standardised. For quantitative analytical work it would appear advantageous to sample the gas at the relatively high pressure of 250 mm, because this pressure would be more reproducible and less critical than the pressure of 3 mm.

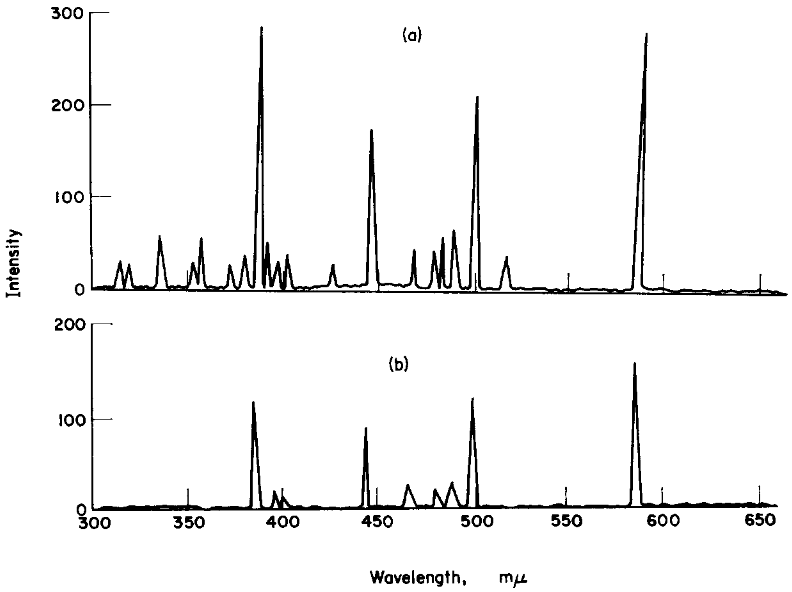

FIG. 4.—Spectrum of helium:
(*a*) Top: impure;
(*b*) Bottom: pure.

Spectra of helium-nitrogen mixtures

Mixtures containing 0–2% of nitrogen in helium were made up in a gas blending rig, small amounts of oxygen being present as an impurity (<0·04% determined mass spectrometrically). A sample was taken of each mixture at a pressure of 250 mm of mercury, and the high-frequency spectra were examined. A typical spectrum consisted of the main lines shown in Table I, identified by reference to the previously-determined spectra of the pure gases.

TABLE I.—SPECTRA OF MIXTURE OF HELIUM AND NITROGEN

Wavelength of main lines, $m\mu$	Element
558	Helium
502	Helium
469	Helium
389	Helium
358	Nitrogen
337	Nitrogen
391	Not identified

Selection of a reference line as internal standard

The helium line at 502 mμ proved to be the most satisfactory for use as an internal standard. The other three main helium lines were unsuitable for the following reasons:

(*a*) At the higher nitrogen levels (>0·05%) the 389-mμ peak existed as a shoulder on the larger peak at 391 mμ.

(*b*) The presence of numerous small peaks very close to the one at 469 mμ made accurate measurement difficult.

(*c*) The line at 588 mμ became very weak on increasing the nitrogen concentration above 0·5%.

Variation of line intensities with nitrogen content

The spectra of the mixtures of helium and nitrogen were examined and the line intensities were measured. Table II gives the intensities of the more important lines for each mixture, in arbitrary units. The intensities of the nitrogen lines at 358 mμ (I_{358}) and 337 mμ (I_{337}) were virtually identical for each mixture, hence results quoted for the line at 358 mμ will also apply to that at 337 mμ.

TABLE II.—VARIATION OF LINE INTENSITIES AND EMISSION RATIOS WITH NITROGEN CONTENT

Oxygen,* %	Nitrogen,† %	I_{358} (N_2)	I_{502} (He)	I_{358}/I_{502}
0·01	0·04	35	13	2·70
0·02	0·06	63	16	3·95
0·03	0·27	182	15·5	11·7
0·02	0·52	225	13	17·3
0·01	0·96	238	10	23·8
0·04	1·65	166	5·0	33·2
0·02	2·17	221	6·0	36·8

* Measured mass spectrometrically.

† Made up in gas blending rig and checked mass spectrometrically.

The curve showing the variation of the intensity of the nitrogen line at 358 mμ with nitrogen content (Fig. 5) is valueless as a calibration curve and illustrates the necessity for the use of an internal standard. The variation of the intensity of the helium line at 502 mμ is also shown graphically (Fig. 5).

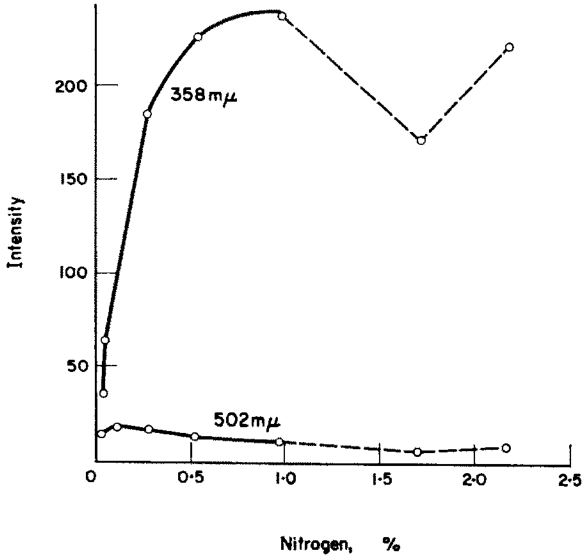

FIG. 5.—Variation of line intensities with nitrogen content.

Variation of emission ratio with nitrogen content

The emission ratio I_{358}/I_{502} for each mixture is shown in Table II. The smooth curve (Fig. 6) obtained for the variation of the ratio with nitrogen content is suitable for use as a calibration curve. The upward concavity of the curve may result from self-absorption of emitted energy by unexcited atoms. The curve appears to be parabolic, and a plot of $(I_{358}/I_{502})^2$ against nitrogen content gives a good straight line.

Precision of measurement of emission ratio

The emission ratio I_{358}/I_{502} was measured for several different samples of the mixture containing 0·06% of nitrogen in helium. The results are given in Table III, and show the coefficient of variation to be 3%.

TABLE III.—PRECISION OF MEASUREMENT OF EMISSION RATIO I_{358}/I_{502}

Nitrogen content	0·06%					
Emission ratio (I_{358}/I_{502})	3·95,	4·10,	3·90,	4·05,	4·30,	4·00
Mean ratio	4·05					
Standard deviation	0·13					
Coefficient of variation	3·2%					

Interfering effect of oxygen

The mixtures of nitrogen in helium used in these experiments contain small amounts of oxygen varying from 0% to 0·04%. Variations of oxygen content at

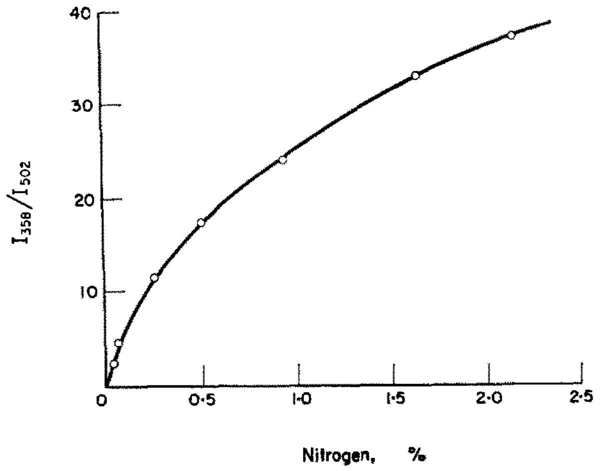

FIG. 6.—Variation of emission ratio with nitrogen content.

this level, whilst affecting the individual line intensities (see result for mixture containing 0·04% of oxygen), do not appear to affect the emission ratio (Fig. 6). However, at concentrations of oxygen in excess of 0·04% the results were somewhat unpredictable (Table IV) and it is considered advisable to reduce the oxygen content to as low a value as possible, *e.g.*, by means of a manganous oxide trap.

TABLE IV.—EFFECT OF OXYGEN

Nitrogen, %	Oxygen, %	I_{358}	I_{502}	I_{358}/I_{502}
0·06	0·02	63	16	4·0
0·06	0·10	53	14·3	3·7
0·06	0·24	39	10·9	3·6
0·06	0·65	31	6·3	4·9

Suggested analytical procedure

The calibration curve (Fig. 6) is sufficiently accurate within the range 0–2% of nitrogen to be used as the basis of an analytical method. The general procedure for such a method is outlined below.

(1) Remove oxygen from the sample, *e.g.*, by a manganous oxide trap.

(2) Sample the impure helium at a pressure of 250 mm of mercury in the discharge tube described.

(3) Excite spectrum by a Ferranti "Tesvac".

(4) Detect and measure the helium line at 502 mμ and the nitrogen line at 358 mμ.

(5) Calculate the emission ratio I_{358}/I_{502}, and read off the nitrogen content from the calibration curve.

CONCLUSIONS

(1) The spectra of helium can be excited by a Ferranti "Tesvac", and can be examined qualitatively and quantitatively by a Unicam S.P. 900 Flame Photometer.

(2) The intensity of the nitrogen lines at 358 mμ and 337 mμ, when measured relative to the helium line at 502 mμ as an internal standard, can be used to determine the nitrogen content of helium over the range 0–2%, with a coefficient of variation of 3%.

(3) The presence of oxygen in excess of 0·04% interferes with the determination, and the oxygen content must be reduced below this level.

Zusammenfassung—Die Tesla-Lumineszenzspektren von bis zu 2% Stickstoff enthaltendem Helium wurden mit einem gewöhnlichen Flammenphotometer gemessen. Die Intensität von Stickstofflinien wurde relativ zu der einiger Linien des inneren Standards gemessen. Die Intensitätsverhältnisse dieser Linien können zur Messung des Stickstoffgehalts zwischen 0 und 2% mit einer Streuung von etwa 3% verwendet werden.

Résumé—On a examiné le spectre de luminescence-Tesla de l'hélium contenant jusqu'à 2% d'azote, en utilisant un photomètre de flamme commercial. Les intensités des lignes attribuables à l'azote ont été mesurées par rapport à celles de différentes lignes étalons internes. Les rapports des intensités de ces lignes peuvent être utilisés pour mesurer la teneur en azote dans le domaine 0–2% avec un coefficient de variation d'environ 3%.

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4,5-DIAMINO-6-THIOPYRIMIDINE AS AN ANALYTICAL REAGENT—I

SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM*

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Summary—A number of organic compounds have been screened as reagents for the spectrophotometric determination of small amounts of selenium. 4,5-Diamino-6-thiopyrimidine shows promise for this determination. In ammoniacal solution, even on long standing, this reagent is colourless in the presence of quadrivalent selenium. However, at pH 1·5–2·5 or lower, 4,5-diamino-6-thiopyrimidine forms a yellow colour with quadrivalent selenium, and this has a strong absorption peak at 380 mμ when compared with a reagent blank of the same concentration. Beer's Law holds when the selenium concentration is between 0·1–2·5 μg per ml. The conditions for the quantitative determination of selenium have been investigated. When selenium in solution is in the quadrivalent state, measurement of absorption should be carried out within 30 min of the addition of the reagent. On longer standing, the reagent gives a slight yellow colour with the formation of elemental selenium. The formation of elemental selenium is slow in dilute solutions of selenium.

INTRODUCTION

THE Aerospace Research Laboratories have been actively engaged in the study of light-sensitive crystals of the elements of Groups II and IV. Not only have pure crystals, prepared from one element in each of these groups, been studied, but solid solutions in the form of single crystals prepared from three elements have also been made. These crystals of solid solutions differ in their electrical resistivity, photoconductivity, ultraviolet-excited emission and other phenomena. Crystals prepared for these studies are in the forms of minute platelets, needles and lumps, depending on the static or dynamic method of their preparation.[1] Because their physical properties and especially their photoelectric properties are affected by their chemical composition, reliable chemical methods for their analysis is of the utmost importance in correlating the various phenomena under investigation.

Physical and chemical methods for the determination of single crystals of solid solutions of cadmium sulphide and zinc sulphide have been investigated.[2] Methods for selenium determination in single crystals, of solid solution of cadmium selenide and cadmium sulphide, ranging in weight from 10 μg to 20 mg, are likewise under active investigation.

In the course of examining possible reagents for the spectrophotometric and spectrofluorimetric determination of selenium in semiconductors it has been discovered that 4,5-diamino-6-thiopyrimidine (4,5D6TP) gives a yellow colour in the

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presence of quadrivalent selenium. Both aqueous and alcoholic solutions produce this yellow coloration at the specified pH.

In general, the spectrophotometric determination of selenium is based on two types of reaction:

(1) A reduction of its quadrivalent state to elemental selenium with the formation of a coloured substance.

(2) A reaction between the *o*-diamine fragment of an aromatic compound to form a coloured piazselenol.

In fact, a compound such as 4,5D6TP possesses functional groups capable of reacting with selenium to form a piazselenol. Its reaction can also involve a reduction of quadrivalent selenium to its elemental form. The present work has indicated that this new method is essentially of type (1), although a complex intermediate may have been produced.[3]

Spectrophotometrically, the sensitivity of this compound[4] is more than twice that of prevailing methods such as the spectrophotometric method using 3,3′-diaminobenzidine.[5]* Unlike most piazselenol methods, where the coloured products are extracted into a second solvent,[5–8] spectrophotometric determination by this method can be performed directly on the aqueous solution. After addition of 4,5D6TP and adjustment of the pH to between 1·5 and 2·5, readings can be taken after 30 min standing. The method has been used to analyse synthetic samples containing selenium and various foreign ions. It has also been successfully applied to the determination of selenium in single crystals of a solid solution of cadmium selenide and cadmium sulphide.

Elemental selenium formed from solutions containing quadrivalent selenium and 4,5D6TP has been successfully collected as thin layers, using an apparatus designed for the purpose. These thin layers can be determined by X-ray fluorescence, using a molybdenum target. This procedure has been described in a separate paper.[9]

EXPERIMENTAL

Apparatus

A Beckman spectrophotometer, Model DU, with matched 1-cm Corex cells was used. For pH determination, a Beckman pH meter, Model Zerometic, equipped with general purpose electrodes, was used.

Reagents

Standard selenium solutions: For the preparation of standard selenium solutions, several materials of high purity were employed. Two stock solutions were first prepared using entirely different procedures. In one of these procedures, a weighed amount of pure selenous acid was placed in a 2-litre volumetric flask. The quantity of selenous acid used was sufficient to give a selenium content of 1 mg per ml. The exact content of selenium was determined on an aliquot of the solution in suitable size beakers, both gravimetrically and titrimetrically. For the gravimetric method, a procedure using 4,5D6TP has been adopted as well as the one recommended by Hillebrand, Lundell, Bright and Hoffman.[10] For the titrimetric method the selenous acid was titrated iodimetrically after being treated with an iodide in the presence of nitric acid. The liberated iodine was titrated in the usual manner by sodium thiosulphate. This procedure has been recommended by Willard and Diehl.[11] The selenium contents, as determined by both methods, were in agreement.

A second stock solution was prepared by using high purity elemental selenium. The selenium used was claimed to have a purity of 99·999+%. Emission spectrographic analysis shows only

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* *Note:* It has been reported[19] that 3,3-diaminobenzidene is suggested to have carcinogenic properties, and that it should be handled with care. Aminopyrimidine has also been stated to have growth-inhibiting properties.[20] The present author, therefore, recommends caution in handling 4,5-diamino-6-thiopyrimidine.

trace amounts of impurity. A 500-mg portion of this material was weighed out and treated with 2 ml of fuming nitric acid in a 50-ml covered beaker. After having reacted completely, the solution was evaporated to dryness on a low temperature hot plate, at 48–56°. The selenium was then converted to the quadrivalent state by evaporating twice to dryness with 2 ml of 6*M* hydrochloric acid. The dried selenous acid was transferred, and was diluted to 500 ml in a volumetric flask. The procedure was repeated three times. Diluted standard solutions containing 10 μg per ml were prepared from these stock solutions. They gave the same selenium content by the spectrophotometric method using 4,5D6TP as the reagent.

4,5-*Diamino-6-thiopyrimidine:* Five lots of the reagent purchased at different times over a period of 1 year* were colourless in appearance. (The preparation of the compound has been described in the literature.[14]) Recrystallisation of this material from absolute alcohol did not show any difference from the original material when used for the spectrophotometric determination of selenium. X-ray single crystal rotation photographs[12] as well as X-ray powder patterns appear the same for the recrystallised and the original materials.

Infrared spectra taken with this material are the same as those reported in the literature.[13] This material was found to melt at 256–258°.[14]

Chemicals for cation and anion interferences: To test for interference from foreign ions, analytical reagent chemicals were used without further purification. Solutions were usually made up to contain 3 mg per ml of the ion.

Procedures

Before the determination of selenium in a solution, a calibration curve, absorbance *vs.* concentration, was made. Appropriate quantities of the diluted standard solution, sufficient to give 0·1–2·5 μg/ml of selenium for a total final volume of 20 ml (or other designated volume), were pipetted into glass-stoppered 50-ml flasks. To each of these standard solutions were added 3·0 ml of 0·3*M* HCl and enough distilled water to make a total of 12 ml. With each of the selenium solutions a blank solution was also prepared, using the same quantity of acid and enough water to give a volume of 12 ml. Eight ml of 4,5D6TP (0·02%), freshly prepared from finely divided powder, were added to each solution and to each blank. After 30 min the absorbancy of each solution against its blank solution was taken.

Determination of an unknown solution was carried out in exactly the same manner as for the calibration solutions. For an accurate result by this method two known solutions (with blanks), having the concentration of selenium in one slightly higher and in the other slightly lower than that of the unknown,[16] were also determined.

To determine the amount of selenium in semiconductors containing solid solutions of cadmium selenide and cadmium sulphide, an amount of the semiconductor ranging from 20 μg to 1 mg was weighed out, using a Cahn electro-microbalance, and was placed in a 10-ml covered beaker. To the sample was added 2 drops of fuming nitric acid. After the disappearance of brown fumes, 6 drops of 1:1 (v/v) hydrochloric acid were added, and the mixture was allowed to evaporate to dryness on a low temperature hot plate (about 50–60°). To ensure complete conversion of all the selenium to the quadrivalent state, the mixture was evaporated again with a few drops of hydrochloric acid. The remainder of the procedure was the same as that for the preparation of standard solution.

RESULTS AND DISCUSSION

Characteristics of absorbance spectra

Two absorbance curves, A and B, are shown in Fig. 1. A_1 is the curve for quadrivalent selenium treated with 4,5D6TP, and B_1 is the curve for 4,5D6TP alone, the pH for both being 1·5. A_2 and B_2 are enlarged portions of curves A_1 and B_1. These curves were taken with water as reference. A comparison of selenium solutions treated with 4,5D6TP and a reagent blank of the same concentration, with a maximum absorbance at 380 mμ, is shown in Fig. 2. The molar absorptivity at this wavelength, based on a number of observations, was 19,200. Curve A and curve B in Fig. 2 contain, respectively, 1·5 μg and 2·5 μg selenium per ml. Although the maximum appears at 380 mμ, appreciable absorbance of the blank solution is noted at this wavelength. An inspection of curves A_1 and A_2 and of curves B_1 and B_2 in Fig. 1

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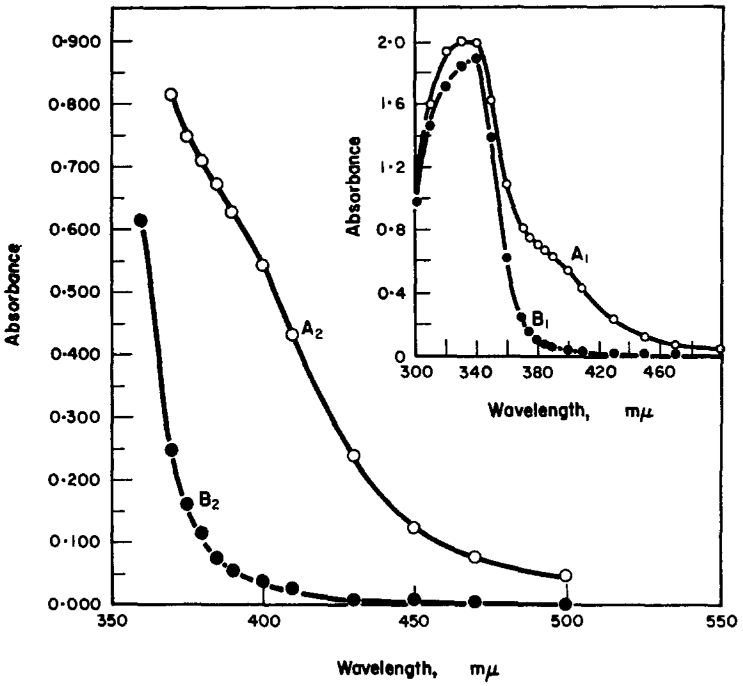

FIG. 1.—Absorbance spectra in aqueous solution:
A_1 and A_2: 2·5 μg of Se per ml; pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.
B_1 and B_2: Blank; pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

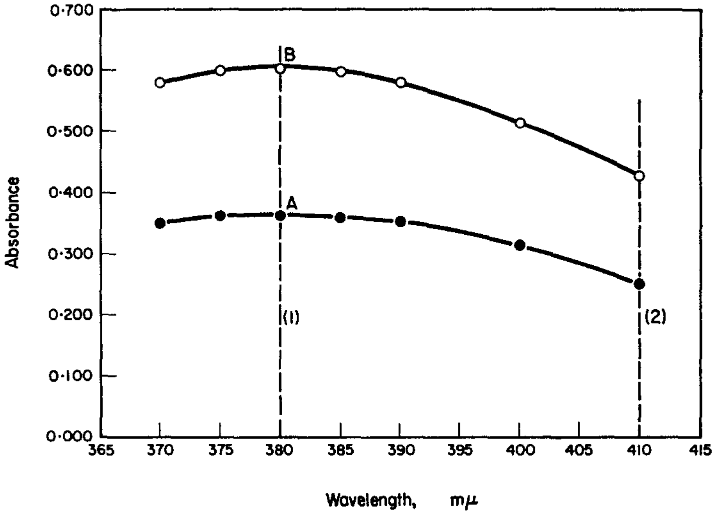

FIG. 2.—Absorbance spectra of two typical selenium solutions *vs*. reagent blanks. Dotted line (1) indicates maximum absorbance and dotted line (2) indicates maximum ratio (selenium solution absorbance: blank absorbance) as compared with water:
A: 1·5 μg of Se per ml.
B: 2·5 μg of Se per ml.
Blanks and solutions: pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

TABLE I.—EFFECT OF ACIDITY ON ABSORBANCE*

HCl in final solution, *M*	Absorbance	
	380 mμ	410 mμ
None (distilled water)	0·015	0·007
0·009	0·370	0·260
0·045	0·363	0·256
3·0	0·260	0·176

* 10 ml of final solution contains 15 μg of selenium and 4 ml of 0·02% 4,5D6TP.

reveals that at 410 mμ the absorbance for the blank has been reduced two and one-half times as compared with the absorbance for the selenium solution. In one set of results the ratio of absorbance for selenium solution treated with 4,5D6TP to that of the reagent blank of the same concentration was 6·35 at 380 mμ as compared with 15·45 at 410 mμ. It is therefore recommended that two readings, one at 380 mμ and another at 410 mμ be taken for analysis by this method. Fig. 3 shows two calibration curves used for the quantitative analysis of selenium.

Effect of pH

The colour intensity of quadrivalent selenium treated with 4,5D6TP is dependent on the acidity of the solution. The solution is colourless in ammoniacal solution. The optimum pH is between 1·5 and 2·5. Table I shows the absorbance at different acidities, measured at 380 mμ and at 410 mμ. The solutions under investigation were neutral, and appropriate quantities of hydrochloric acid were added to give a pH of 1·5–2·5. For semiconductors containing solid solutions of cadmium selenide and cadmium sulphide, oxidation of the selenide and sulphide was carried out with concentrated nitric acid, *aqua regia* or fuming nitric acid, and the solutions were

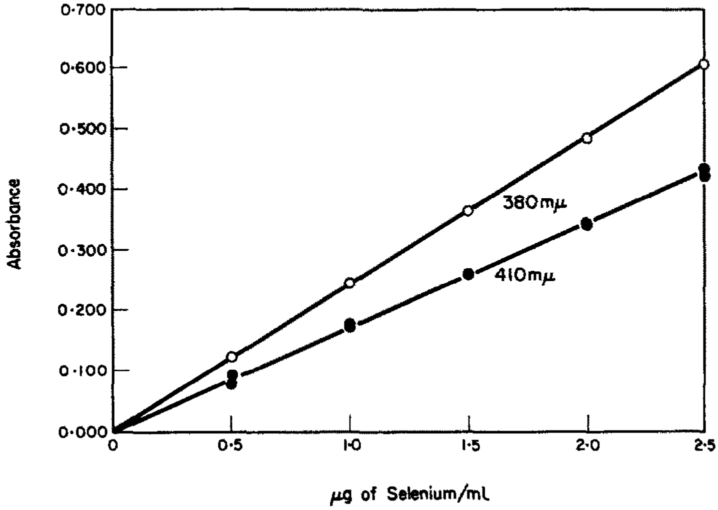

FIG. 3.—Absorbance *vs.* selenium concentration. pH 1·5; 4,5D6TP (0·02%), 0·4 ml per ml of final solution.

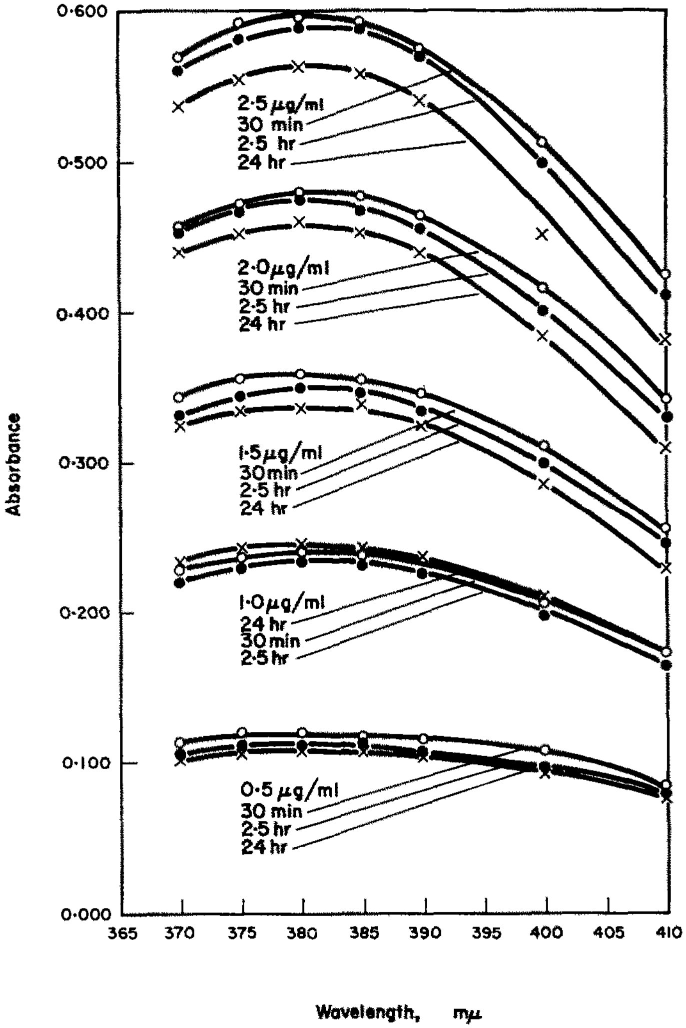

FIG. 4.—Effect of time on the absorbance between 370 mμ and 410 mμ. Solution and blank: pH 1·5; 4,5DF6TP (0·02%), 0·4 ml per ml of final solution.

subsequently treated with hydrochloric acid to convert to quadrivalent selenium. Any excess acid was removed by evaporating at slightly elevated temperature to dryness. It is essential that the pH of the solution be adjusted before making absorbance measurement. Besides hydrochloric acid, formic acid has been used successfully.

Effect of standing time

The absorbance of solutions containing 0·5–2·5 μg/ml of selenium changes but slightly between 30 min and 1·5 hr. On longer standing, especially for solutions with higher concentrations of selenium, the absorbances of the solutions decrease appreciably. For example, on 24 hr standing, solutions containing 2·5 μg/ml decreased by 6–10%. Fig. 4 shows the effect of standing time on the absorbance between 370 mμ and 410 mμ. The change in absorbance probably arises from two factors.

One of these is the air oxidation of 4,5D6TP at pH 1·5–2·5. Blanks to investigate the extent of this oxidation were allowed to stand from a few hours to 14 days. At the end of 9 days standing, the absorbance at 380 mμ was eleven-fold compared with blanks freshly prepared. At the end of 14 days the absorbance was similar to that after 9 days. When these results were plotted against the corresponding wavelengths, the shape of the curves were much the same as for those obtained using selenous acid to react with the reagent. A search of the recent literature has revealed that most reagents available for the spectrophotometric determination of selenium are subject to air oxidation to some degree[5–7,16,17] and the same has been found in this laboratory for the determination of selenium using 3,3′-diaminobenzidine as reagent, the reagent turning red after a few hours at room temperature.[5] Lott *et al.*[7] have pointed out that the air oxidation of 2,3-diaminonaphthalene is pronounced, especially when heated.

The second factor causing the change in absorbance on standing is the formation and coagulation of selenium. It can be seen on the bottom of the container, especially in solutions with 1 μg/ml or more of selenium. However, this factor is not pronounced compared with air oxidation. In a recent paper[18] the same conclusion has been reached.

The reproducibility, in terms of % standard deviation, is shown in Table II. Twenty-four observations were made using standard selenium solution, and from these the % standard deviation was calculated. Absorbance readings taken after 30 min and after 2·5 hr standing differed by a few tenths to 3%.

TABLE II.—REPRODUCIBILITY OF THE PROPOSED METHOD ON STANDARD SELENIUM SOLUTIONS (30·0 μg OF SELENIUM IN 20 ml OF FINAL SOLUTION)

Se found,* μg	Deviation, %	(Deviation)², %	Se found,* μg	Deviation, %	(Deviation)², %
30·1	+0·33	0·1089	30·2	+0·66	0·4356
29·9	−0·33	0·1089	29·6	−1·35	1·8225
29·9	−0·33	0·1089	30·2	+0·66	0·4356
30·0	±0·00	0·0000	30·2	+0·66	0·4356
29·8	−0·67	0·4489	29·6	−1·35	1·8225
30·2	+0·66	0·4356	30·4	+1·32	1·7424
29·9	−0·33	0·1089	30·4	+1·32	1·7424
30·2	+0·66	0·4356	30·2	+0·66	0·4356
30·2	+0·66	0·4356	30·2	+0·66	0·4356
29·8	−0·67	0·4489	30·0	±0·00	0·0000
29·7	−1·01	1·0201	30·2	+0·66	0·4356
30·5	+1·64	2·6896	29·6	−1·35	1·8225

% standard deviation = 0·88.

* Selenium found in the first column was based on absorbance measurements taken at 380 mμ; in the fourth column 410 mμ.

Effect of reagent concentration on absorbance

Fig. 5 shows that in a series of solutions containing 1·5 μg/ml of selenium the absorbance increases as the reagent is increased, up to a certain concentration. Beyond the threshold concentration the absorbance remains constant.

Effect of diverse ions

Various ions were purposely added to the solutions to ascertain their effect on the determination of selenium by this method. Table III shows some of the ions used for

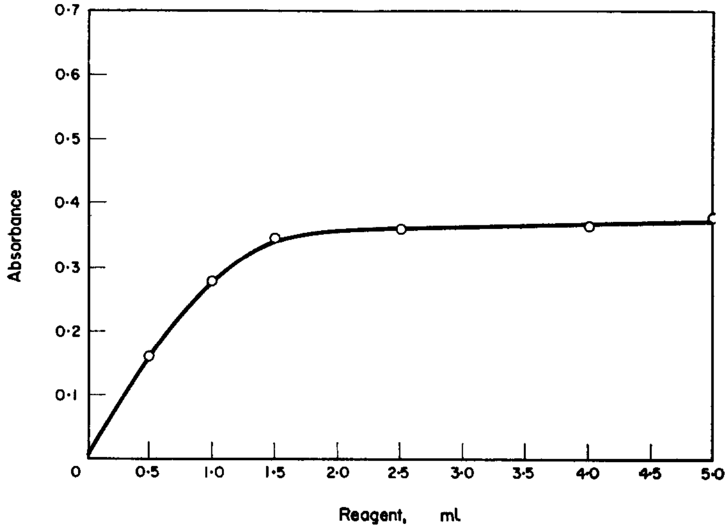

FIG. 5.—Absorbance of selenium solution containing varying amounts of 4,5D6TP. Abscissa shows ml of 0·02% reagent in 10 ml of selenium solutions and blanks. (pH 1·5; selenium 1·5 μg per ml; wavelength 380 mμ.)

this investigation. In general, the ions listed have a negligible effect on the determination of selenium by this method. These diverse ions in solutions were such that their concentration was 500-fold that of the selenium present. In Table IV is listed a number of ions commonly known to interfere with the spectrophotometric determination of selenium. Ions such as Fe^{3+}, Fe^{2+}, $S_2O_3^{2-}$, SO_3^{2-}, BrO_3^- and Cu^{2+} must be removed, or the solution must be treated with reagents for the formation of

TABLE III.—EFFECT OF DIVERSE IONS ON THE DETERMINATION OF SELENIUM[a] 20 ml OF FINAL SOLUTION CONTAINS (30 μg OF SELENIUM^{IV})

Ion	Se^{IV}[b] found, μg	Error, %
Cd^{2+}	30·4	+1·3
Zn^{2+}	30·2	+0·7
Al^{3+}	30·8	+2·6
Mg^{2+}	30·2	+0·7
Ba^{2+}	30·0	±0·0
Sr^{2+}	30·7	+2·3
Li^+	28·9	−0·6
Na^+	29·9	−0·3
K^+	30·5	+1·7
NH_4^+	30·0	±0·0
Cl^-	30·6	+2·0
F^-	28·7	−0·4
Br^-	29·8	−0·7
NO_3^-	28·9	−0·4
SO_4^{2-}	29·8	−0·7

[a] Diverse ions in solution, 15,000 μg; ratio of diverse ion to selenium 500; pH 1·5; each ml of final solution contains 0·4 ml of 0·02% 4,5D6TP.

[b] Average results from absorbance values taken at 380 mμ and 410 mμ.

TABLE IV.—DIVERSE IONS WHICH NORMALLY INTERFERE WITH THE SELENIUM DETERMINATION

Solution contains 1·5 μg/ml of Se, pH 1·5, 500 μg of diverse ion per μg of Se, 0·4 ml of 0·02% 4,5D6TP

Diverse ion	Appearance after adding 4,5D6TP	Absorbance	
		380 mμ	410 mμ
None	Yellow colour	0·360	0·256
Fe^{3+}	Yellow colour	Grossly interferes	
MoO_4^{2-}	Very cloudy on standing, with green colour	Grossly interferes	
Fe^{2+}	Yellow colour	0·500	0·343
$S_2O_3^{2-}$	Colourless with formation of precipitate	0·295	0·300
SO_3^{2-}	Trace of yellow colour	0·011	0·014
BrO_3^-	Yellow colour	0·621	0·302
Cu^{2+}	Yellowish green	0·205	0·150
ClO_3^-	Yellow colour	0·382	0·275
$C_2O_4^{2-}$	Yellow colour	0·358	0·255
ClO_4^-	Yellow colour	0·363	0·256
I^-	Yellow colour	0·366	0·264

complex ions before selenium is determined. Copper^{II} and iron^{III} can conveniently be removed by liquid-liquid extraction with chloroform, as the cupferrates. Ions such as $C_2O_4^{2-}$,ClO_4^- and I^- do not affect the quantititative determination by the present method. The presence of ClO_3^- gives a somewhat higher result, as shown in Table IV. In a recent paper[18] these ions are listed as interfering with the determination of selenium.

Determination of selenium in semiconductors

A number of solid solutions of cadmium selenide and cadmium sulphide were prepared by the vaporization method at temperatures above 1200°. These samples were analysed for their selenium content by titrimetric and gravimetric methods, as described above. A few tenths of a mg or less of these samples were weighed out and

TABLE V.—SPECTROPHOTOMETRIC DETERMINATION OF SELENIUM IN SOLID SOLUTIONS OF CADMIUM SELENIDE AND CADMIUM SULPHIDE BY 4,5-DIAMINO-6-THIOPYRIMIDINE: AQUEOUS SOLUTIONS FROM SEMICONDUCTORS

	% by weight of selenium in semiconductors	Selenium, *ppm*		
		Present	Found	Average
(A)	19·85	0·98	0·89	0·96
			1·02	
(B)	50·00	2·22	2·14	
			2·27	
			2·18	2·20
(C)	60·99	(1) 8·91	8·35	8·35
		(2) 7·18	7·17	7·17
(D)	69·77	3·18	3·00	
			3·00	3·00
(E)	79·36	2·48	2·23	
			2·16	2·20

the selenium was converted to its quadrivalent state. The selenium, in parts per million, is shown in Table IV. Appropriate quantities of these solutions were pipetted out, and the selenium determined spectrophotometrically using 4,5D6TP. The results are shown in Table IV. This method is applicable to samples in the form of small needles weighing 20–30 μg or more. An individual needle can be taken for analysis.

CONCLUSIONS

1. 4,5-Diamino-6-thiopyrimidine has been found to give a colour reaction with selenium in its quadrivalent state. Spectrophotometric determination of this element in solution can be carried out at the maximum peak of 380 mμ, using a reagent blank of the same concentration and prepared at the same time. The determination can also be made at 410 mμ, where the blank absorbance is comparatively low.

2. Because elemental selenium makes its appearance on standing, the reading of the absorbance should preferably be taken within 30 min of the addition of the reagent. However, the trace of elemental selenium does not greatly affect the result, especially in the early stage of its formation. This was confirmed by other investigators on reactions in which elemental selenium is one of the end-products. For accurate determinations, two known solutions with concentrations one slightly above and one slightly below that of the unknown should be used as controls.

3. The slow formation of elemental selenium has the added advantage of supplementing the spectrophotometric determination of this element. It further confirms the results from absorbance for determination of this element. Elemental selenium so formed can be collected in a thin layer and this layer can be determined by an X-ray fluorescence method involving no matrix effect, the procedure of which has been published in a separate paper.

4. Preliminary experiments have been carried out on the Tyndall effect and light scattering phenomena of this reaction. Both X-ray single crystal rotation photographs and X-ray powder patterns have been taken for the reagent and the treated material. Nuclear magnetic resonance spectra have also been taken during the course of the reaction for 4,5D6TP, as well as for other substances, such as *o*-phenylenediamine and 2,3-diaminonaphthalene, with and without selenium. These spectra are being studied along with infrared and ultraviolet spectra. Elemental microanalysis on the treated material are currently being made, and these results will be correlated with other results available.

Zusammenfassung—Eine Anzahl von organischen Verbindungen wurden auf ihre Eignung zur spektralphotometrischen Bestimmung von kleinen Selenmengen geprüft. 4,5-Diamino-6-thiopyrimidin verspricht dabei gute Ergebnisse. In ammoniakalischer Lösung bleibt das Reagens in Gegenwart vierwertigen Selens auch bei langem Stehen farblos. Bei pH 1,5 bis 2,5 oder niedriger bildet sich dagegen eine gelbe Lösung mit starkem Absorptionsmaximum bei 380 mμ, verglichen mit der gleichkonzentrierten Reagenslosung. Das Beersche Gesetz gilt bei Selenkonzentrationen zwischen 0,1 und 2,5 Mikrogramm pro Milliliter. Die Bedingungen für die quantitative Bestimmung von Selen wurden geprüft. Wenn Selen in der Lösung vierwertig vorliegt, sollte die Absorptionsmessung innerhalb 30 Minuten nach Zugabe des Reagens ausgeführt werden. Bei längerem Stehen gibt das Reagens eine schwach gelbe Farbe unter Bildung von elementarem Selen. In verdünnten Lösungen geht die Bildung von elementarem Selen langsam.

Résumé—Un certain nombre de composés organiques ont été examinés pour le dosage spectrophotométrique de petites quantités de sélénium. La 4,5-diamino-6-thiopyrimidine s'est révélée prometteuse pour ce dosage. En solution ammoniacale, meme après un long repos, ce réactif est incolore en présence de sélénium tétravalent. Toutefois, à pH 1,5 à 2,5, ou inférieur, la 4,5-diamino-6-thiopyrimidine développe une coloration jaune avec le sélénium tétravalent est présente un fort pic d'absorption à 380 mμ, lorsqu'on effectue la comparaison par rapport à un témoin de réactif à la meme concentration. La loi de BEER est respectée lorsque la concentration en sélénium est comprise entre 0,1 et 2,5 microgrammes par millilitre. On a étudié les conditions de dosage du sélénium. Lorsque le sélénium en solution est à l'état tétravalent, la mesure de l'absorption doit etre effectuée au plus tard trente minutes après l'addition du réactif. Par un repos plus long, le réactif présente une légère coloration jaune avec formation de sélenium élémentaire. La formation de sélénium élémentaire est lente en solutions diluées de sélénium.

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

TITRIMETRIC DETERMINATION OF URANIUM^{IV} ALONE AND IN MIXTURE WITH IRON^{II}, MANGANESE^{II}, CERIUM^{III} OR VANADIUM^{IV}

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Summary—The potentiometric titration of uranium^{IV} is possible at room temperature with potassium dichromate at all concentrations of phosphoric acid ranging from 3*M* to 12*M*. An inert atmosphere is unnecessary. The potential break at the end-point is about 70–90 mV/0·04 ml of 0·1*N* potassium dichromate in the range 3 to 9*M* of phosphoric acid, 140 mV in 10·5*M* phosphoric acid and 180 mV in 12*M* phosphoric acid. Iron^{II} and uranium^{IV} can be determined in the same solution if the concentration of phosphoric acid is maintained above 11·5*M* at the iron^{II} end-point. Under similar conditions a differential potentiometric titration of uranium^{IV} and vanadium^{IV} is possible. Uranium^{IV} and manganese^{II} can be determined in the same solution if the concentration of phosphoric acid is maintained between 3*M* and 9*M* at the uranium^{IV} end-point, then increased so that it is 12*M* at the manganese^{II} end-point. Under similar conditions the differential potentiometric titration of uranium^{IV} and cerium^{III} is possible. The application of these procedures to uranium-bearing minerals is under investigation.

EWING and Eldridge[1] were apparently the first to have attempted the titration of uranium^{IV} with potassium dichromate using an electrometric end-point. They reduced a solution of uranium^{VI}, heated to 80° in a Jones reductor, and titrated the hot solution in an inert atmosphere with potassium dichromate. The potential (E) *vs.* volume (V) showed two broad inflection points, the first corresponding to the titration of uranium^{III} and the second to the titration of uranium^{IV}. Because the curve corresponding to the second part of the titration does not clearly show the inflection point, Ewing and Eldridge[1] computed the equivalence point of the uranium^{IV} titration from the $\Delta E/\Delta V$ *vs.* V curve. When the concentration of sulphuric acid was varied from 0·36*F* to 3·6*F*, they observed that while the shape of the first part of the curve was not very much affected, the second part was greatly influenced in that the end-point could not be detected when the concentration of sulphuric acid was above 0·36*F*.

Belcher, Gibbons and West[2] investigated the reverse titration of potassium dichromate with a solution of uranium^{IV} chloride and recommended a temperature of 60° for the titration because they believed the reaction to be sluggish at room temperature. Miller and Thomason[3] also found that the electrometric titration of uranium^{IV} is not feasible at room temperature with potassium dichromate. A thermometric titration proved possible, however, and as little as 5 mg of uranium^{IV} could be

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* Part III: see *Talanta*, 1964, **11**, 825.

determined with a relative standard error of ±1.0%. Taking this along with the observation of Rao, Murty and Gopala Rao[4] that the titration of uranium^{IV} is possible at room temperature using N-phenylanthranilic acid as redox indicator, one has to conclude that the reaction between uranium^{IV} and potassium dichromate must be very fast and not slow as believed by previous investigators. The difficulties noted in the electrometric titration must be caused by the inertness of the platinum electrode in titrations involving chromium ions[3] and uranyl ions.[5]

The difficulties encountered in the titration of uranium^{IV} with potassium dichromate using diphenylamine, barium diphenylamine sulphonate or diphenylbenzidine have been discussed by Kolthoff and Lingane.[6] The main difficulty was ascribed to the slowness of the colour development of the indicator at the end-point. They found that the uranium^{VI} salt formed retards the colour change of the diphenylbenzidine indicator, and overcame the difficulty by the addition of an excess of iron^{III} alum solution and titrating the iron^{II} formed with potassium dichromate.

In view of the difficulties experienced in the electrometric titration of uranium^{IV} with potassium dichromate in hydrochloric and sulphuric acid media at room temperature, we have now carried out investigations on the titration in a phosphoric acid medium. It has been observed that uranium^{IV} can be titrated directly with a standard solution of potassium dichromate at room temperature with a potentiometric end-point in a 3-12M phosphoric acid medium. From the previous publications[7,8] from these laboratories it will be obvious that the potentials of the chromium^{VI}/chromium^{III} and uranium^{VI}/uranium^{IV} couples are quite suitable for a chemical reaction to occur at the concentrations of phosphoric acid prescribed.

EXPERIMENTAL

Potentiometric Titration of Uranium^{IV} with Potassium Dichromate in a Phosphoric Acid Medium

Reagents

Uranium^{IV} solution. An approximately 0·1N solution of uranium^{VI} is prepared in 1M sulphuric acid from analytical-reagent grade uranyl acetate supplied by British Drug Houses Ltd., England. This is reduced in a Jones reductor and aerated to give uranium^{IV} solution, which is standardised against potassium dichromate according to the procedure of Kolthoff and Lingane[6] using diphenylamine sulphonic acid as indicator.

Phosphoric acid. "Pro Analysi" grade phosphoric acid (*ca.* 15·5M) supplied by E. Merck, Germany, is employed in this investigation.

Apparatus

The apparatus employed is as described previously.[7]

The potentiometric titration of uranium^{IV} with potassium dichromate is impossible when the concentration of phosphoric acid is less than 3M because under such conditions uranium^{IV} phosphate precipitates. Titration is possible, however, at all concentrations of phosphoric acid from 3M to 12M at the equivalence point. The time required for the attainment of steady potentials is about 1 min in the early stages and 3 min near the equivalence point. The potential break is about 70–90 mV/0·04 ml of 0·1N potassium dichromate solution when the concentration of phosphoric acid is 3–9M, at the equivalence point, and it rises to about 140 mV and 180 mV when the concentration of phosphoric acid is 10·5M and 12M, respectively. Typical results are presented graphically in Fig. 1 for titrations carried out in 3M and 12M phosphoric acid.

Procedure

From 2 to 10 ml of 0·1N uranium^{IV} solution is taken in a 150-ml Pyrex beaker and treated with sufficient phosphoric acid (10–50 ml) and water such that the concentration of phosphoric acid is 3–12M at the equivalence point. The mixture is connected to a saturated calomel electrode through a saturated sodium perchlorate bridge and a saturated sodium nitrate bridge. A bright platinum rod is used as indicator electrode. The mixture is titrated at room temperature with 0·1N potassium

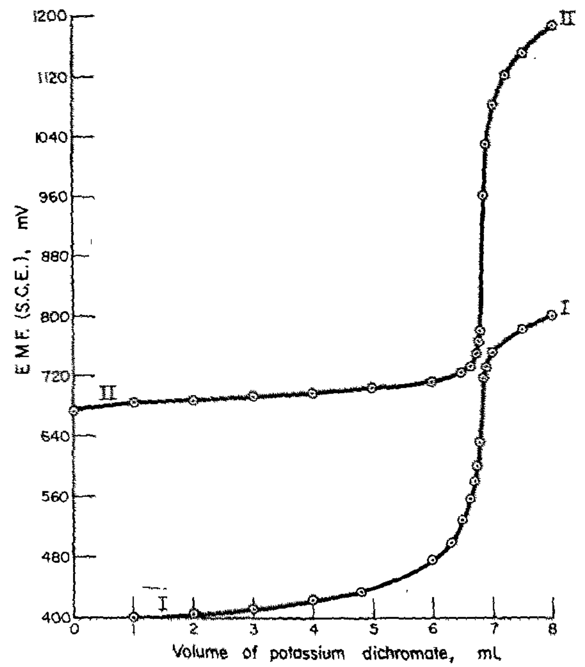

FIG. 1.—Potentiometric titration of uranium^{IV} (81·21 mg) with potassium dichromate in:
I—3*M* H_3PO_4,
II—12*M* H_3PO_4.

dichromate solution while it is stirred electromagnetically. Potentials are initially measured after waiting for 1 min following the addition of each portion of titrant, but after 3 min near the equivalence point.

Some typical results of titrations carried out in 6*M* phosphoric acid are given in Table I. The error is not greater than ±0·27%. Similar results are obtained with media containing phosphoric acid at other concentrations in the range 3 to 12*M*. The method now developed constitutes a significant improvement over the dichromate procedure of Ewing and Eldridge,[1] which requires a temperature of 80° and an inert atmosphere for the potentiometric titration. Even under these conditions, however, the potential break is poor.

TABLE I.—POTENTIOMETRIC TITRATION OF URANIUM^{IV} WITH POTASSIUM DICHROMATE (CONCENTRATION OF PHOSPHORIC ACID AT EQUIVALENCE POINT 6*M*)

Uranium^{IV} taken, *mg*	Uranium^{IV} found, *mg*
26·07	26·06
37·25	37·17
46·46	46·58
60·32	60·22
71·17	71·17
82·11	81·89
91·70	91·85
110·4	110·4

Interferences

Chloride interferes, even at an over-all concentration of 0·1*M*, in the titration of uranium^{IV} with potassium dichromate when the concentration of phosphoric acid is greater than 9*M*. Steady potentials cannot be obtained and there is no break at the equivalence point. At a phosphoric acid concentration of 7·5*M*, however, chloride no longer interferes if the over-all chloride concentration is 0·1*M*, but only if it is 0·25*M*. When the concentration of phosphoric acid is 3–6*M* at the equivalence point, chloride does not interfere even at 0·25*M* concentration. However, the potential break at the inflection point is then reduced from about 90 mV to about 40 mV.

Nitrate and higher valency states of metals such as molybdenum, tungsten, vanadium, iron, *etc.*, which are also reduced in the Jones reductor, interfere. If the phosphoric acid concentration is 3–9*M*, manganese^{II} and cerium^{III} do not interfere. Above a phosphoric acid concentration of 9*M* both uranium^{IV} and manganese^{II} (or cerium^{III}) react with potassium dichromate and the reaction between uranium^{IV} with manganese^{III} or cerium^{IV} under these conditions is slow, requiring 10–30 min for the stabilisation of potentials. The interference of iron^{II} can be eliminated by carrying out the titration in phosphoric acid of concentration greater than 11·5*M*, because for such a mixture two different potential breaks are obtained (see below). Cobalt^{II}, zinc^{II} and nickel^{II} do not interfere, and neither do sulphuric and perchloric acids (in concentrations of about 1*N*).

Differential Potentiometric Titration of Iron^{II} and Uranium^{IV} in Mixture

Ewing and Eldridge[1] stated that when a mixture of uranium^{III}, uranium^{IV} and iron^{II} is titrated with potassium permagnanate at about 80° in an atmosphere of carbon dioxide, three inflections are obtained. The first corresponds to the oxidation of uranium^{III} to uranium^{IV}, the second to the oxidation of uranium^{IV} to uranium^{VI} and the third to the oxidation of iron^{II} to iron^{III}. The inflection corresponding to uranium^{IV} oxidation is not sharp, and with increasing concentration of sulphuric acid it becomes more and more indistinct. Moreover, Ewing and Eldridge did not give sufficient experimental data to ascertain the accuracy of analysis of their mixtures. According to Pappas[9], however, the potentiometric titration of uranium^{IV} with potassium permanganate does not give a sharp break in the potential *vs.* volume curve when iron^{II} is present. The difficulty is said to be overcome by the addition of some acetic acid just before the titration. Hahn and Kelley[10] also experienced difficulty in the potentiometric titration of uranium^{IV} with cerium^{IV} sulphate in the presence of iron^{II}. They proposed the micro titration of uranium^{IV} at room temperature by complexation of iron^{II} with 1,10-phenanthroline. However, the method fails for the analysis of samples containing much more than 1 mg of iron, even if a correspondingly larger amount of 1,10-phenanthroline is added.

Bricker and Sweetser[11] employed a spectrophotometric method for the differential titration of uranium^{IV} and iron^{II} with cerium^{IV} sulphate in an atmosphere of nitrogen. According to these authors, in the simultaneous titration of uranium^{IV} and iron^{II} with cerium^{IV} the rate of reaction near the uranium equivalence point is considerably slower than in the individual titration of uranium^{IV}. They believe that this is because of the slow reaction between uranium^{IV} and iron^{III} formed by the partial oxidation of iron^{II} before all of the uranium^{IV} has been titrated. However, they found that the rate of the uranium^{IV}–iron^{III} reaction can be increased by working at a low acid concentration, *e.g.*, 0·2*N*, although there is the risk of the induced oxidation of uranium^{IV} by atmospheric oxygen in the presence of iron^{II}. Thus, even the spectrophotometric titration procedure prescribed by Bricker and Sweetser[11] is attended with difficulties. Recently, Desai and Murthy[12] preferred to determine uranium^{IV} in the presence of iron^{II} by oxidising uranium^{IV} in the presence of iron^{II}, then titrating the unreacted iron^{III} iodometrically. The latter step requires the use of osmium tetroxide for accelerating the reaction between iron^{III} and hydriodic acid. In addition to the indirect nature of this procedure, it suffers from the disadvantage that it enables the determination of only one component of the mixture, namely uranium^{IV}. Iron^{II} must be obtained by determining the sum of iron^{II} plus uranium^{IV} in another aliquot of test solution and subtracting the uranium^{IV} therefrom.

From the foregoing it is evident that there is no satisfactory method for the direct titrimetric determination of both iron^{II} and uranium^{IV} in the same solution.

We have now observed that when a mixture of iron^{II} and uranium^{IV} is titrated potentiometrically at room temperature with potassium dichromate in a medium containing 11·5–13·5*M* phosphoric acid, in an atmosphere of carbon dioxide, two well-defined breaks are obtained in the potential *vs.* volume curve. The first break corresponds to the oxidation of iron^{II} to iron^{III} and the second to the oxidation of uranium^{IV} to uranium^{VI}. Until near the equivalence point for iron^{II} potentials are stabilised within 1 min, but at the equivalence point one has to wait 10–15 min for the attainment of stable values. The potential break at the equivalence point is about 190 mV/0·04 ml of 0·2*N* potassium dichromate solution. During the titration of uranium^{IV} stable potentials are attained within about 1 min in the early stages and in about 3 min at the equivalence point; the potential break is about 260 mV/0·04 ml of 0·2*N* dichromate. For an accurate determination of iron^{II} all solutions must be deaerated before the addition of phosphoric acid to the mixture containing iron^{II} and uranium^{IV} and rigorous precautions taken to prevent the leakage of atmospheric oxygen into the titration vessel, otherwise the titre for iron^{II} will be low. Unlike that of iron^{II}, the determination of uranium^{IV} is unaffected by the presence of oxygen.

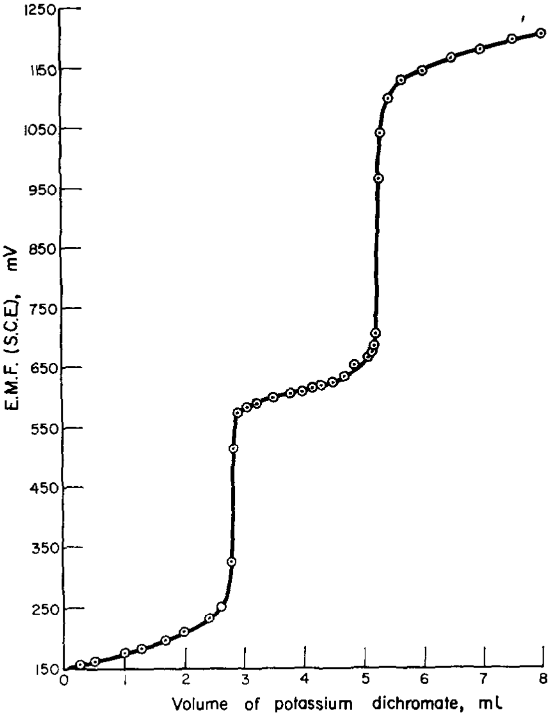

FIG. 2.—Differential potentiometric titration of a mixture of uranium^{IV} (57·59 mg) and iron^{II} (31·71 mg) with 0·2*N* potassium dichromate in a 12*M* phosphoric acid medium.

Procedure

About 10 ml of the solution containing iron^{II} and uranium^{IV} is taken in the titration vessel and the dissolved air expelled by passage of carbon dioxide for about 10 min. Sufficient deaerated phosphoric acid to give a concentration of 11·5*M* at the first equivalence point is added and an atmosphere of carbon dioxide maintained thereafter. The solution is titrated with 0·2*N* potassium dichromate solution using the potentiometric assembly already described, electromagnetic stirring being maintained during the titration.

A typical potentiometric titration curve is given in Fig. 2. Typical results of assays of iron^{II} and uranium^{IV} made by the above procedure are presented in Table II. They show that the error of determination for iron^{II} is not greater than −0·52% and that for uranium^{IV} not greater than ±0·35%. This accuracy and simplicity are not attainable with currently available procedures.

TABLE II.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF IRON^{II} AND URANIUM^{IV} IN MIXTURES

Iron, *mg*[a]		Uranium, *mg*	
Taken	Found	Taken	Found
11·61	11·55	81·17	80·93
24·23	24·12	41·89	41·89
24·34	24·23	66·88	67·11
25·23	25·13	114·2	114·2
31·71	31·60	57·59	57·59
53·37	53·15	51·29	51·17

[a] The iron^{II} solution was prepared from Analar Mohrs salt and standardised against pocassium dichromate.

Differential Potentiometric Titration of Uranium^{IV} and Manganese^{II} in Mixture

When a sulphuric acid solution of uranium^{VI} and manganese^{VII} (or magnanese^{II}) is passed through a Jones reductor, a mixture containing uranium^{IV} and manganese^{II} with a little uranium^{III} is obtained. The uranium^{III} can be converted to uranium^{IV} by aeration for about 5–10 min. When such a solution is titrated with potassium dichromate in a 12*M* phosphoric acid medium two different potential breaks are obtained, the first inflection corresponding to the oxidation of uranium^{IV} and the second to that of manganese^{II}. However, this titration is rather tedious because 20–30 min are required for the establishment of stable potentials after 50% of the uranium^{IV} is oxidised and until the first break is obtained. After the first break the potentials are stabilised in about 1 min after the addition of each portion of potassium dichromate solution. The slow stabilisation of potentials for the uranium^{IV} part of the titration is probably because of the slow reaction between uranium^{IV} and manganese^{III}, formed by the oxidation of manganese^{II} before all uranium^{IV} is oxidised. We have, however, observed that when the concentration of phosphoric acid is maintained at 3–9*M* the potentials are stabilised in about 2–3 min and the break in the potential *vs.* volume curve corresponds to the stoichiometric oxidation of uranium^{IV} to uranium^{VI}. If the concentration of phosphoric acid is then raised to above 12*M* by the addition of further phosphoric acid and the titration continued, a second break is obtained which corresponds to the oxidation of manganese^{II} to manganese^{III}.

Procedure

An aliquot of the mixture of uranium^{IV} and manganese^{II} is taken in a 150-ml Pyrex beaker, treated with 12·5 ml of phosphoric acid, then sufficient water added so that the total volume is 25 ml. The mixture is titrated with 0·2*N* potassium dichromate while it is stirred electromagnetically. After the first break is obtained the titration is continued to some distance, the mixture treated with enough phosphoric acid (35–45 ml) so that the concentration of phosphoric acid is 12*M* at the second equivalence point, then the titration completed for manganese^{II}.

The first break in potential amounts to about 260 mV/0·04 ml of 0·2*N* potassium dichromate when the volume of titration solution is about 30 ml and the second break to about 25 mV/0·04 ml of 0·2*N* dichromate when the volume of titration solution is about 60 ml. A typical potentiometric titration curve is shown in Fig. 3. In view of the small break, the second inflection point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Typical results given in Table III show that the error for uranium^{IV} does not exceed ±0·3% and that for manganese^{II} does not exceed ±0·4%.

Differential Potentiometric Titration of Uranium^{IV} and Cerium^{III} in Mixtures

When a sulphuric acid solution containing uranium^{VI} and cerium^{IV} (or cerium^{III}) is passed through a Jones reductor, a mixture containing uranium^{IV}, cerium^{III} and a little uranium^{III} is obtained. The uranium^{III} can be converted to uranium^{IV} by aeration for about 5–10 min. When such a solution is titrated potentiometrically with potassium dichromate solution in a 12*M* phosphoric acid medium, we have observed two different breaks in the potential *vs.* volume curve. More than 30 min are required for the establishment of stable potentials after 50% of the uranium^{IV} is oxidised, but even with this precaution, the end-point for uranium^{VI} is prematurely obtained. It has, however, been observed that if the concentration of phosphoric acid is 3–9*M*, the potentials are stabilised in about 2–3 min and the break in potential corresponds stoichiometrically to the

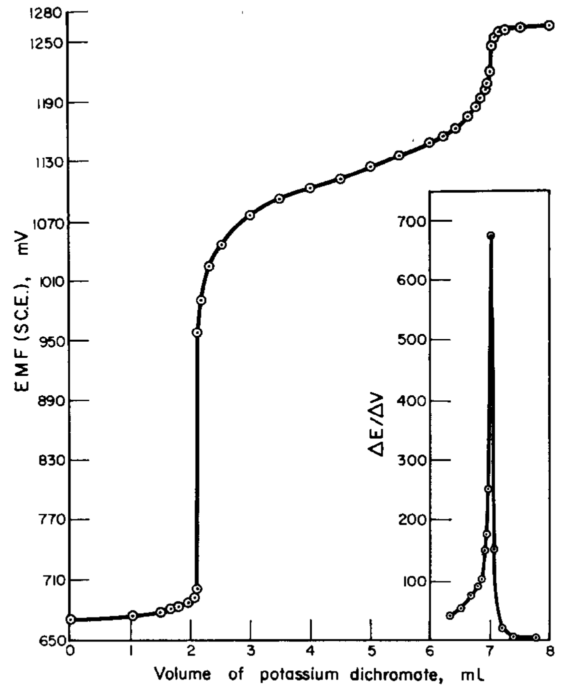

FIG. 3.—Differential potentiometric titration of a mixture of uranium$^{\mathrm{IV}}$ (50·42 mg) and manganese$^{\mathrm{II}}$ (53·95 mg) with 0·2N potassium dichromate in a phosphoric acid medium.

TABLE III.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM$^{\mathrm{IV}}$ AND MANGANESE$^{\mathrm{II}}$ IN MIXTURES

Uranium, *mg*		Manganese, *mg*[a]	
Taken	Found	Taken	Found
41·30	41·30	50·79	59·99
50·42	50·29	53·95	53·81
63·66	63·84	34·08	34·19
80·69	80·93	23·74	23·74
110·4	110·4	27·27	27·27
155·6	155·6	26·71	26·77

[a] For preparation and standardisation of manganese$^{\mathrm{II}}$ solution see G. Gopala Rao and P. Kanta Rao, *Talanta*, 1963, **10**, 1255.

oxidation of uranium$^{\mathrm{IV}}$ to uranium.$^{\mathrm{VI}}$ The concentration of phosphoric acid is then increased to above 12M by the addition of further phosphoric acid and the titration continued until the second break in potential is obtained. This corresponds to the quantitative oxidation of cerium$^{\mathrm{III}}$ to cerium$^{\mathrm{IV}}$.

Procedure

An aliquot of the mixture of uranium$^{\mathrm{IV}}$ and cerium$^{\mathrm{III}}$ is taken in a 50-ml Pyrex beaker, treated with 12·5 ml of syrupy phosphoric acid, then sufficient water added so that the total volume is 25 ml. The mixture is titrated with 0·2N potassium dichromate solution while it is stirred electromagnetically. After the first break is obtained the titration is continued to some distance, the mixture treated with sufficient phosphoric acid (35–45 ml) so that the concentration of phosphoric acid is 12M at the second equivalence point, then the titration completed for cerium$^{\mathrm{III}}$.

The first break in potential amounts to about 260 mV/0·04 ml of 0·2*N* dichromate solution when the volume of titration solution is about 30 ml and the second break to about 50 mV/0·04 ml of 0·2*N* dichromate solution when the volume of titration solution is about 60 ml. A typical potentiometric titration curve is shown in Fig. 4. Because the potential break for the cerium^{III} oxidation is not very large, the second inflection point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Some typical results given in Table IV show that the error of determination for uranium^{IV} is not greater than ±0·33% and that for cerium^{III} not greater than ±0·3%.

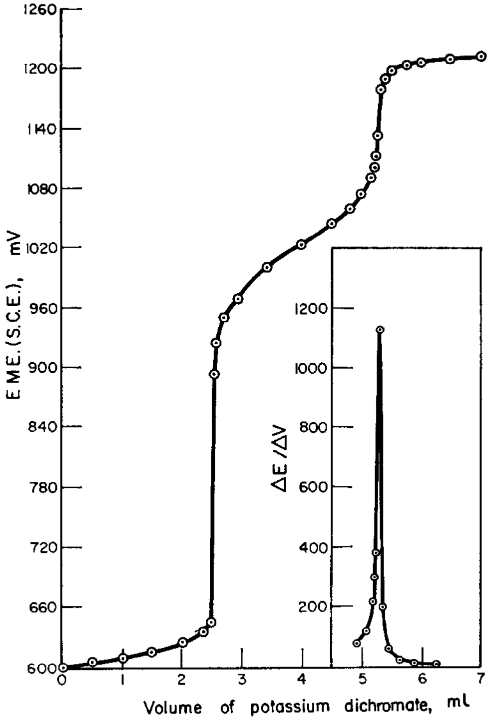

FIG. 4.—Differential potentiometric titration of a mixture of uranium^{IV} (60·32 mg) and cerium^{III} (76·83 mg) with 0·2*N* potassium dichromate in a phosphoric acid medium.

TABLE IV. DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM^{IV} AND CERIUM^{III} IN MIXTURES

Uranium, *mg*		Cerium, *mg*[a]	
Taken	Found	Taken	Found
37·25	37·15	80·48	80·39
51·42	51·59	50·10	49·94
60·32	60·22	76·83	77·05
68·56	68·45	66·80	66·96
72·66	72·83	43·42	43·42
82·11	81·89	80·98	81·23

[a] For preparation and standardisation of Ce^{III} solution see G. Gopala Rao, P. Kanta Rao and S. Bhanojee Rao, *Talanta*, 1964, **11**, 825.

Differential Potentiometric Titration of Uranium^{IV} and Vanadium^{IV} in Mixtures

When a mixture containing uranium^{IV} and vanadium^{IV} is titrated with potassium dichromate solution in a 12*M* phosphoric acid medium two breaks are obtained in the potential *vs.* volume curve. The first break corresponds to the stoichiometric oxidation of uranium^{IV} to uranium^{VI} and the second break to the quantitative oxidation of vanadium^{IV} to vanadium^{V}.

Procedure

An aliquot of the mixture of uranium^{IV} and vanadium^{IV} (5–10 ml) is taken in a 150-ml Pyrex beaker and treated with 40–55 ml of syrupy phosphoric acid. The mixture is titrated with 0·2*N* potassium dichromate solution while it is stirred electromagnetically. The potentials are noted 2–3 min after the addition of each portion of potassium dichromate solution until the first equivalence point, then 1 min after the addition of each portion of potassium dichromate solution until the second break in potential.

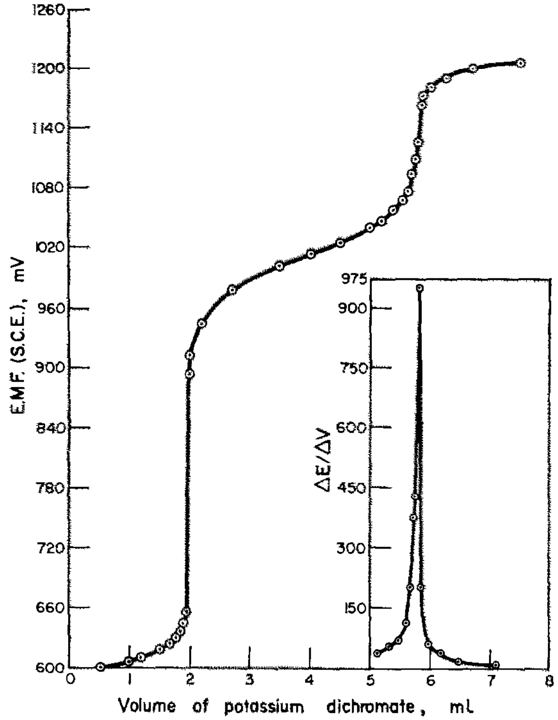

FIG. 5.—Differential potentiometric titration of a mixture of uranium^{IV} (46·46 mg) and vanadium^{IV} (39·07 mg) with 0·2*N* potassium dichromate in a phosphoric acid medium.

TABLE V.—DIFFERENTIAL POTENTIOMETRIC TITRATION OF URANIUM^{IV} AND VANADIUM^{IV} IN MIXTURES

Uranium, *mg*		Vanadium, *mg*[a]	
Taken	Found	Taken	Found
35·28	35·28	45·54	45·64
39·51	39·51	19·36	19·36
46·46	46·58	39·07	39·03
71·17	71·17	30·06	30·06
91·70	91·85	19·54	19·54
109·3	109·2	23·37	23·44

[a] For preparation and standardisation of vanadium^{IV} solution see G. Gopala Rao and P. Kanta Rao, *Talanta*, 1964, **11**, 703.

The potential jump at the first equivalence point is found to be about 260 mV/0·04 ml of titrant and at the second inflection point to about 40 mV/0·04 ml of titrant. A representative potential *vs.* volume curve is shown in Fig. 5. Because the second break in potential is not very great, the end-point is best obtained from the $\Delta E/\Delta V$ *vs.* V curve. Some typical results are given in Table V. They show that the error for uranium^{IV} is not greater than ±0·27% and that for vanadium^{IV} not greater than ±0·3%.

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Zusammenfassung—Die potentiometrische Titration von Uran (IV) mit Kaliumdichromat ist bei Zimmertemperatur bei allen Konzentrationen von Phosphorsäure zwischen 3m und 12m möglich. Schutzgas ist nicht notwendig. Der Potentialsprung am Endpunkt ist für 0,04 ml 0,1 n Kaliumdichromat in 3–9 m Phosphorsäure 70–90 mV, in 10,5 m Phosphorsäure 140 mV und in 12 m Phosphorsäaur 180 mV. Eisen (II) und Uran (IV) können in derselben Lösung bestimmt werden, wenn die Phosphorsäure-konzentration beim Eisen (II)-Endpunkt über 11,5 m gehalten wird. Unter ähnlichen Bedingungen ist die potentiometrische Bestimmung von Uran (IV) und Vanadin (IV) nebeneinander möglich; Uran (IV) und Mangan (II) können in derselben Lösung bestimmt werden, wenn die Phosphorsäure-konzentration beim Uran (IV)-Endpunkt zwischen 3 m und 9 gehalten wird und dann so erhöht wird, daß sie beim Mangan (II)-Endpunkt 12 m ist. Unter ähnlichen Bedingungen kann man Uran (IV) und Cer (III) nebeneinander bestimmen. Die Anwendung dieser Vorschriften auf Uran führende Mineralien wird untersucht.

Résumé—Le dosage potentiométrique de l'uranium (IV) est possible à température ambiante, au moyen de bichromate de potassium, à toutes les concentrations en acide phosphorique comprises entre 3 M et 12 M. Une atmosphère inerte n'est pas nécessaire. Le saut de potentiel au point final est d'environ 70–90 mV/0,04 ml de bichromate de potassium 0,1 N, en acide phosphorique 3 à 9 M, de 140 mV en acide phosphorique 10,5 M et de 180 mV en acide phosphorique 12 M. Le fer (II) et l'uranium (IV) peuvent être dosés dans la même solution si la concentration de l'acide phosphorique est maintenue audessus de 11,5 M au point final du fer (II). Dans les mêmes conditions, un dosage potentiométrique différentiel de l'uranium (IV) et du vanadium (IV) est possible. L'uranium (IV) et le manganèse (II) peuvent être dosés dans la même solution si la concentration en acide en phosphorique est maintenue entre 3 M et 9 M au point final de l'uranium (IV), puis augmentée de facon à atteindre 12 M au point final de manganèse (II). Le dosage potentiométrique différentiel de l'uranium (IV) et du cérium (III) est possible dans les mêmes conditions. L'application de ces techniques aux minerais uranifères est à l'étude.

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TALANTA REVIEW

RECENT DEVELOPMENTS IN THE RING OVEN TECHNIQUE

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Summary—A review of recent developments in the ring oven technique is presented.

IN 1954 the first paper about the ring oven technique was published. This method had originally been developed as a qualitative separation technique for extremely small samples. After a short time, however, it found application in other branches of analytical chemistry, both qualitatively and semiquantitatively. Its use was extended to the analysis of radioactive substances, to electrographic analysis, to the analysis of organic substances, *etc.*

In 1961 a monograph, *Microanalysis by the Ring Oven Technique** (hereafter referred to as *monograph*), surveyed the method and its various applications. Since that time about 60 further publications dealing with this technique have appeared. It is the purpose of the present paper to review these more recent contributions.

THE APPARATUS AND SOME NEWER ACCESSORIES†

The apparatus itself has been little modified in its external appearance; all of its dimensions have proved adequate, so these have remained unchanged. Fig. 1 shows a model of the ring oven in which the variable transformer for regulating the temperature and the actual ring oven are built into a single unit.

West, Llacer and Cimerman[1] described an "auxiliary plate" of aluminium which fits into the bore hole of the ring oven and makes, *quasi*, a ring oven with a smaller bore-hole diameter (14 mm) out of the original ring oven. This makes possible ring to ring separations of substances which are first collected in the 14-mm ring zone, a procedure basically similar to that used by Ballczo in connection with the glass ring oven (see monograph, p. 30). The same authors also designed a "washing ring" which is positioned on the hot ring oven. It serves to purify filter papers for special applications (*e.g.*, selenium in air pollution studies), where commercially available filter paper does not meet the purity requirements. They also suggested a retainer ring with a heat insulated handle (instead of the usual porcelain ring) for keeping the filter paper in place on the hot ring oven.

Reynolds and Monkman[2] also reported an adapter for reducing the bore hole diameter and gave some useful details for constructing the ring oven. For use in air pollution studies, these authors suggest a drilled Teflon plug which is inserted into

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* Herbert Weisz, *Microanalysis by the Ring Oven Technique*. Pergamon Press Ltd., Oxford.

† Ring ovens are produced by National Appliance Company, Portland, Oregon, U.S.A. and ROFA, Reisnerstrasse 41, Vienna 3, Austria.

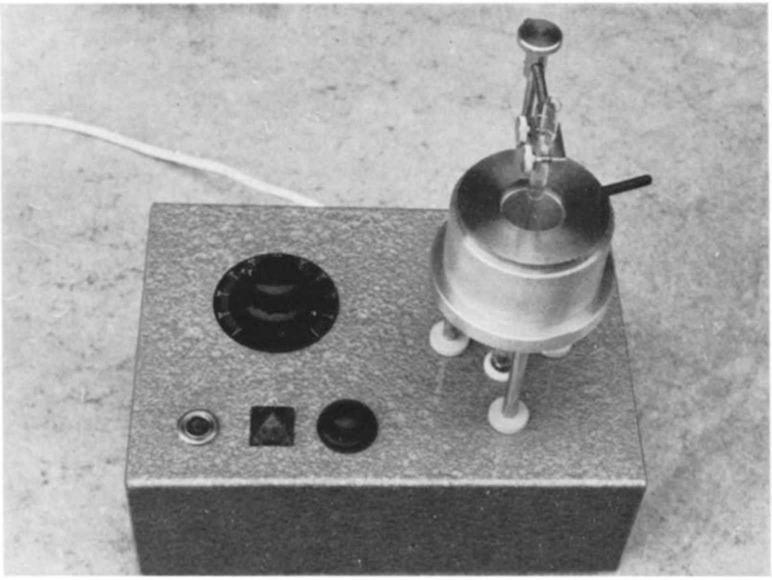

FIG. 1.—Ring oven plus variable transformer as a single unit
(ROFA, Vienna, Austria).

the sampling head of a paper tape sampler. The small spots thus produced may then be washed into the ring zone of the usual 22-mm ring oven.

DISSOLUTION OF SAMPLE

For analysis on the microgram scale where the sample is soluble in acid, it is comparatively simple to transfer the sample drop without loss to the filter paper (*cf.* monograph, p. 34). If a fusion procedure is necessary, however, it is not so convenient to transfer quantitatively the rather greater volume of sample solution to the middle of a filter paper, to carry out spot tests or to perform an analysis with the ring oven method. For this reason, a method[3] has been worked out, in which a small drop of a saturated solution of the decomposition reagent (*e.g.*, sodium peroxide, sodium carbonate, potassium hydrogen sulphate, sodium hydroxide) is placed on a platinum foil (5 × 5 mm square, 0.03 mm thick) and a very tiny amount (several μg, 1 or 2 grains) of the solid sample is added with the aid of a glass needle.

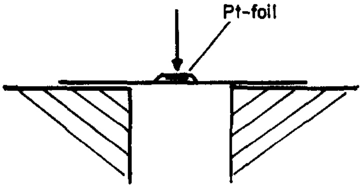

FIG. 2

The foil is then heated over the flame of a micro burner for some sec. After the decomposition, the platinum foil is placed between a filter paper and a little filter paper disk (to provide a capillary surface) and positioned on the ring oven (see Fig. 2). There, the now soluble substances are washed into the ring zone by means of a suitable solvent. In this way, the dissolved substances are concentrated in a sharply outlined ring zone where they can be identified as usual.

QUALITATIVE ANALYSIS OF METAL IONS

In the field of qualitative analysis, several spot reactions have been newly adapted for use with the ring oven method and the total number of such reactions now applicable has been considerably enlarged. Some of them will be mentioned under the present heading: others have been applied to semiquantitative analysis but can certainly be used for identification purposes. Therefore, the reactions mentioned in subsequent sections should also be regarded from the viewpoint of qualitative analysis (*e.g.*, beryllium, antimony, selenium).

Filter paper is commonly used for spot reactions only in those cases where the reaction product is either a coloured insoluble compound or has a pronounced tendency to adsorb on the fibres of the paper. Where the product of an identification reaction does not meet these conditions, it is better to carry out the tests on a spot plate or in a small tube, where the greater depth of the solution permits an easier observation of the colour. The ring oven can, however, be used to concentrate test stains which would otherwise spread badly on filter paper, so that the sensitivity of the test would be greatly diminished. This localisation of spot test colours by use of the ring oven method makes it possible to carry out reactions on filter paper which lead to soluble reaction products. The drop of the sample (for instance titanium: see Fig. 3

is placed in the centre of a filter paper. A drop of reagent (in this case hydrogen peroxide) is placed between the sample spot and the future ring zone. The sample spot is then washed with a suitable solvent (0.05*M* hydrochloric acid) into the ring zone. As the sample migrates, it "picks up" the reagent, reacts with it, and the soluble reaction product is concentrated and thus forms a coloured sector of the ring. In this way the identification limit is remarkably improved (10–100 times). Iron^{III} (with thiocyanate), chromate (with diphenylcarbazide), borate (with turmeric) and titanium (with hydrogen peroxide) can thus be identified on the paper.[4]

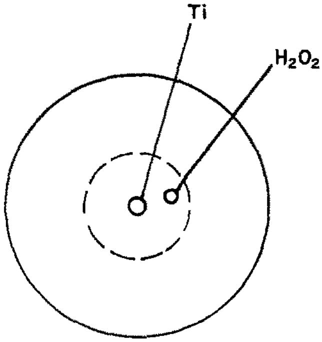

Fig. 3

Antikainen[5] reported the separation and identification of micro-amounts of mixtures of nickel and cobalt on filter paper impregnated with dimethylglyoxime. Nickel is fixed in the centre and the soluble dimethylglyoxime complex of cobalt washed to the ring zone. The inner spot bearing the nickel is punched out and placed on another paper, then the nickel transferred to the ring zone by means of an alcoholic solution of dimethylglyoxime containing bromine water as oxidant. The soluble bright red nickel^{IV} chelate is thus formed.

Matic[6] applied the ring oven technique in combination with preliminary solvent extraction to the routine analysis of technical uranium solutions. Barren solutions from 17 uranium-producing mines were analysed for the presence of 28 elements. Malissa and Ottendorfer[7] described separations of metal ions using the solubility of their diethyldithiocarbamates in pyridine. Aluminium and copper could thus be easily separated.

In connection with toxicological analysis a very sensitive test for thallium^{I} ions has been worked out.[8] A sector of the ring zone containing the thallium is treated with potassium iodide. Thallium^{I} iodide is thus precipitated, but remains invisible because of its low concentration. After the excess of iodide has been removed, the ring zone is treated with silver nitrate. The silver iodide formed by metathesis is exposed to ultraviolet light, then developed in a "physical developer".[9] A very distinct sharp black line indicates thallium (identification limit: 0.01 μg).

Biswas and Dey[10] applied the ring oven method to the separation and identification of some "less familiar" cations (uranium^{VI}, thorium^{IV}, cerium^{III}, cerium^{IV}, titanium,^{IV} zirconium^{IV}, molybdenum^{VI}, tungsten^{VI}, vanadium^{V}, beryllium^{II}, gold^{III}, platinum^{IV} and palladium^{IV}). They did this in a rather unusual way. Instead of using one of the methods for "ring to ring" separations mentioned above or one already cited in the monograph, they used the retainer ring as a heat barrier for the outer ring. They state that "in some cases, the last (outer) ring could not be obtained in a well defined form and was somewhat diffuse". This was to be expected, because the retainer ring only serves the purpose of keeping the filter in place, and certainly does not act as a heat barrier.

Singh and Dey[11] separated and identified metal ions on the ring oven, applying oxalate, tartrate or EDTA as complexing agents. Their separation technique seems nearer to paper chromatography, however, than to true ring oven technique: the various ions form rings at different distances "from the centre to the outer edge".

SEMIQUANTITATIVE DETERMINATION OF METAL IONS

Amongst semiquantitative analytical methods, spot colorimetry occupies a very outstanding place. Therefore it is not surprising that spot colorimetry in conjunction with the ring oven ("ring colorimetry") has found many new applications in the analysis of metal ions, anions and organic substances. Considerations given here are valid not only for the analysis of cations, but also for all the other semiquantitative applications.

This part of the present review could hardly be better introduced than by some statements made by Malissa.[12] "The fact that the capacity of the human eye is commonly underestimated, in conjunction with the modern trend to use precise photometers at a far too early stage in an investigation, has given rise to many unnecessary difficulties. The comparison of colours or shades, as used by Weisz and his coworkers in their contributions to spot colorimetry, brought developments back to the right level" and "It is often overlooked that the eye's capacity for integration and abstraction is something that an instrument does not easily equal."

The question has often been raised whether photometric measurements of the intensity of the rings would make the method still more accurate. Ottendorfer[13] made some density measurements on rings (in this case autoradiographs, but this does not make much difference) and was able to prove that mere visual comparison of the rings (as is usual in ring colorimetry) is at least equal if not superior to instrumental measurements.

In the following, some newer semiquantitative applications of the ring oven technique are described.

Nickel and cobalt. The previously mentioned method for the separation and identification of these two ions on filter paper impregnated with dimethylglyoxime[5] has also been evaluated quantitatively. Nickel can thus be determined in the range 0.1–100 μg, and cobalt from 0.5 to 20 μg.

Thorium. Hainberger and Sanchez[14] determined thorium with aqueous solutions of alizarin S and used this method for the analysis of monazite sand.

Beryllium. West and Mohilner[15] described a detailed study of the determination of beryllium with eriochrome cyanine R in connection with air pollution measurements. As little as 0.05 μg of beryllium can be determined. The average error is $\pm 7\%$. Magnesium, thorium, aluminium and chromium affect this method if present in a one hundred-fold excess.

Another way of determining beryllium[8] utilises the well known fluorescent reaction product of beryllium with morin. EDTA is used to mask any accompanying ions. Comparison of the test rings with a standard scale (stable for several months) is carried out under a quartz lamp. Very small amounts of beryllium (0.005 μg) can thus be determined with an accuracy of better than $\pm 10\%$.

Aluminium. Aluminium has been determined[16] by bathing the rings in methanolic morin solution and fuming them over concentrated hydrochloric acid. The dried cool papers are then compared with a standard scale (prepared in the same way) under an ultraviolet lamp. Incidently, this seems to have been the first example of a "ring-fluorometric" method.

Antimony. A method for the determination of antimony in air pollution measurements is based on the extraction of the tetra-iodo-antimony^{III} complex with a benzene-ethanol mixture (2:1) directly on the ring oven; the colour is then developed by reaction with phosphomolybdic acid (molybdenum blue). The limit of identification was found to be 0.08 μg and the accuracy is within the 5% limit.[17] Only a few ions were found to affect the determination (thallium, selenium, tellurium, tungsten and platinum metals).

Selenium. Selenium can be identified and estimated with 3,3′-diaminobenzidine, the citron yellow piazselenol being formed. The average error for this determination is ±6% in the range 0.1–0.5 μg of selenium; greater amounts of selenium give rings so intensely coloured that visual comparison becomes difficult. Because all tested varieties of filter paper were found to contain selenium, it is necessary to purify them. This is accomplished by treatment with sodium sulphide, which forms soluble seleno-sulphide complexes washable from the paper with distilled water. For this purpose, the "washing ring" mentioned above is used. Interferences were studied; the authors state[18] that the method is readily applicable to air pollution problems.

Universal standard scale

This method of semiquantitative determination (based on the fact that many metal ions can be transformed in one way or another into an equivalent amount of silver sulphide and these silver sulphide rings always compared with the same silver sulphide standard scale, irrespective of the original sample ion) has already been described in the monograph. Application of this method in paper chromatography was suggested and this has now been verified.

A mixture of metal ions is chromatographed on filter paper strips and the various parts of the paper bearing the single spots are cut out. These are ashed and made up to a certain volume (1 ml). From this solution 3 rings are made from suitable drop numbers, and the substances in these rings are transformed into equivalent amounts of silver sulphide, then compared with the silver sulphide standard scale (best derived from a copper solution). The technique has been illustrated by separating and determining mixtures of iron, cobalt and nickel and of lead, copper and cadmium.[19]

In a second approach,[20] this combination of paper chromatography with the universal standard scale has been simplified to avoid the ashing of the filter paper pieces. Varying quantities (1–10 drops) of the solution to be determined are spotted on narrow filter paper strips, then the chromatograms are run. The cut out pieces of the strips (bearing the separated substances) are rolled spirally and placed in a glass tube so that the end of the roll protrudes from the tube and makes contact with the filter paper on the ring oven. The substances are then extracted from the rolled piece of paper to the round filter and there washed into the ring zone. This has to be done with 3 pieces (derived from chromatograms of 3 different numbers of drops of sample solution) of cut out filter paper, thus yielding 3 rings necessary for comparison with the standard scale. The substances contained in the rings are again transformed into equivalent amounts of silver sulphide. It is, of course, essential that the same capillary pipette is used for applying the drops on the chromatogram and for preparing the standard rings. This very simple method, which gives results with an error of only ±5%, has been applied to the analysis of mixtures of copper and lead and of cobalt and zinc. It seems to offer the possibility of separation and determination of small amounts (a few μg) of elements in mixtures of varying composition.

The idea of using a universal standard scale for comparison in ring colorimetry is certainly not limited to the use of silver sulphide. Other compounds offer the same possibility. Ćelap and coworkers[21,22] described the application of a standard scale of copper^{II} hexacyanoferrate(II) for this purpose. Quite a number of metal ions can be precipitated as hexacyanoferrates(II) by bathing the rings in a 2% aqueous solution of potassium hexacyanoferrate(II). After thoroughly rinsing the filter paper, the difficultly soluble precipitates are converted to an equivalent amount of copper^{II} hexacyanoferrate(II) by bathing the rings in a 2% solution of copper^{II} sulphate. The rings thus obtained are then compared with a standard scale of copper hexacyanoferrate(II), prepared from a copper solution of known concentration (0.1 mg of copper/ml). As with the silver sulphide scale, conversion factors for the different ions to be determined need to be calculated. Three sample rings prepared from suitable drop numbers also need to be employed for the comparison, as in all semiquantitative applications of the ring oven method. Uranium, manganese, nickel, cobalt, zinc, cadmium, copper, lead, mercury^{I} and mercury^{II} have been determined. The results obtained deviated on average by ±3%.

ANIONS

In the field of anion analysis, 23 identification reactions were mentioned in the monograph. This number has since been enhanced only slightly. Ballczo and Hodos[23] described the use of barium rhodizonate for the detection of sulphate ions. An inner ring (12-mm diameter) bears barium rhodizonate. The sample drop is spotted at the centre of the paper and washed to this inner ring. Here the sulphate releases an equivalent amount of rhodizonate, which is then washed to the outer ring zone (22-mm diameter) where it can be made visible with barium salt. As little as 0.005 μg of sulphate can thus be detected. It is possible to use this method for semiquantitative estimation. Barney[74] published a method for the detection of submicrogram amounts of fluoride on the ring oven with thorium chloranilate.

Munshi and Dey[24] separated binary and ternary mixtures of some common anions on the ring oven. For ternary mixtures, the "retainer ring" was again used as a heat barrier for the outer ring as already mentioned (*cf.* Biswas and Dey[10]). The same objection as stated there for this type of procedure in the analysis of cations is, of course, still valid in the analysis of mixtures of anions.

Although only very little can be reported of new tests for anions carried out on the ring oven, some systematic separation schemes have been devised for various numbers of anions with this technique.

Musil, Haas and Drabner[25] reported a separation scheme for 8 common anions [bromide, iodide, thiocyanate, sulphate, chromate, phosphate, arsenate and hexacyanoferrate(II)] contained in a single drop. These anions are separated into 3 different rings, where they can be identified by suitable spot test reactions. Arsenate, phosphate and hexacyanoferrate(II) are first fixed in the original spot with zinc acetate, then the other 5 anions are transported to ring I, where they are identified on individual sectors. The precipitated zinc salts are subsequently fumed over hydrochloric acid, after which arsenate and phosphate are washed on a new filter paper into ring II. The remaining zinc hexacyanoferrate(II) is oxidised over bromine vapour, then washed with dilute hydrochloric acid into ring III on a third filter paper.

Another approach to separate anions has been described by Haba and Wilson.[26] Sulphate, chromate, vanadate, hexacyanoferrate(II), hexacyanoferrate(III), hexacyanocobaltate(III), bromide and iodide are first separated into 2 groups by means of barium nitrate. The first 3 anions listed are thus fixed in the centre of the paper, while the others are washed into the ring zone where they can be identified. One of the ions [hexacyanocobaltate(III)] is separated by a "ring to ring" separation in a single sector. The inner spot is punched out, the little disc placed on another filter and the barium salts of chromate and vanadate washed with $0.04M$ hydrochloric acid into the ring zone, whereas barium sulphate remains in the original spot. One μl of sample solution is sufficient for this scheme. The authors also briefly mention the possibility of semiquantitative determinations of the anions by their method.

A systematic scheme for the analysis of common anions on the ring oven has been worked out also by Biswas, Munshi and Dey.[27] Sulphate, sulphite, nitrate, nitrite, fluoride, chloride, bromide, iodide, hexacyanoferrate(II), hexacyanoferrate(III), thiocyanate, phosphate, sulphide, thiosulphate and borate are separated into 5 different rings and identified there. Silver ions are used to fix all of the ions except the first 5 listed here, then successive extractions with $2M$ nitric acid, with nitric acid (1:2), with ammonia solution and with sodium thiosulphate solution bring about the other separations.

Instead of actually separating all the anions into various groups, Mooney[28] employed a number of single tests in a certain sequence of application. By this "exclusion system", 12 anions can be identified (nitrate, borate, silicate, phosphate, sulphate, molybdate, fluoride, cyanide, chromate, bromide, iodide, chloride).

Apart from the semiquantitative determination of sulphate, using its reaction with barium rhodizonate as mentioned above, Huygen[29] described another method for sulphate and sulphite in connection with air pollution measurements. The rings containing the sulphate are bathed in a solution of barium chloride and potassium permanganate, dried and rinsed well with a $1M$ hydrochloric acid solution of oxalic acid. The pink rings (the permanganate is stabilised against reduction by having been included into the crystal lattice of the barium sulphate are compared with the standard scale. Sulphide is determined in the same way after it has been previously oxidised to sulphate with hydrogen peroxide.

The universal standard scale of silver sulphide rings has hitherto only been applied to the determination of metal ions, for instance in combination with paper chromatography (*viz.* above). It is, of course, also possible to determine anions in this way. Most of the anions can be precipitated as difficultly soluble metal salts; these metal salts can be transformed into sulphides and these, in turn, into an equivalent amount of silver sulphide. Obviously, the most direct way is for anions which precipitate with silver ions. A number of anions, such as chloride, bromide, iodide, thiocyanate, arsenate, dichromate and hexacyanoferrate(III), have been determined in this way. The anions are washed into the ring zone and fixed there by bathing them in silver nitrate solution. After rinsing thoroughly, the precipitates are converted into equivalent amounts of silver sulphide by bathing in hydrogen sulphide water. The resulting silver sulphide rings are compared with a standard scale, derived in the same manner from a standard solution of potassium bromide. The results of the comparison are, of course, obtained in "bromide equivalents" and must be multiplied by a suitable conversion factor, which is the quotient of the equivalent weight of the ion to be determined and that of the standard ion (*e.g.*, bromide). The accuracy of this procedure[31] is satisfactory and compares very well with that of ring colorimetry as commonly used.

ORGANIC SUBSTANCES

In the monograph it was mentioned that the ring oven method could prove useful not only in the inorganic field but also in the examination of organic substances. Since then, a number of publications have dealt with the analysis of diverse organic substances.

A sensitive spot test for nitrogen compounds in petroleum fractions and its application to semiquantitative determination seems to have been the first contribution to organic analysis with the ring oven. Tetracyanoethylene (TCNE) yields coloured reaction products with organic nitrogen compounds, such as pyridine, lutidine, pyrrole, indole, *etc.* These colours are stable on heating to 110°, in contrast to the colours produced by the reactions of TCNE with hydrocarbons, which only persist at room temperature. Peurifoy and Nager[32] suggested this method as a quick quality control test for units in which the nitrogen content is an important criterion.

Meisel, Nemeth and Erdey[33] developed a rapid micro method for the detection of several hetero-elements (nitrogen, sulphur, chlorine, bromine, iodine) in organic compounds. The organic substance is fused with metallic potassium and the resulting anions (iodide, bromide, chloride, sulphide, cyanide, thiocyanate) separated by the ring oven method and identified by suitable spot tests. The utility of the procedure has been proved by the analysis of 24 diverse organic substances.

The first published application of the ring oven technique to clinical analysis seems to have been the estimation of microgram amounts of proteins by Farr and Chaney.[34] The authors used a modified ring oven with which the substances are collected in a straight line. For developing the colours, the protein binding of bromophenol blue was employed. The samples investigated were solutions of human blood serum, containing between 0 and 100 ppm of protein. The maximum error is stated to be ±8%. This method has been used for estimation of the protein content of various biological solutions. As little as 10 μg of protein/ml can be evaluated.

Semiquantitative determination of a number of amino acids has been described by Ćelap, Janjić and Ilić.[35] A spot of copper^{II} hydroxide is prepared in the centre of a filter paper and dried. The necessary number of drops of the amino acid solution to be determined is added to this spot and part of the copper^{II} hydroxide is thus dissolved, forming a water soluble complex compound. This bluish-green compound is washed into the ring zone with water. The sample rings are then compared with standard rings in the usual manner. Glycine, alanine, asparagine, aspartic acid and glutamic acid were determined with reasonable accuracy (about ±5% relative).

Ćelap and coworkers also applied ring colorimetry to the semiquantitative determination of sugars, phenols and alkaloids. The necessary number of drops of the solution of the sugar are washed with water into the ring zone, followed by 1 drop of a hydrochloric acid–alcohol solution of resorcinol. The filter paper is then heated for 20 min to 125° in a drying oven. Stable brown-yellow rings are formed and compared in the usual manner with standard rings. Fifteen μg of sugar are sufficient for preparing the 3 rings. Glucose, mannose, galactose, fructose, sorbose, arabinose, xylose and rhamnose have thus been determined.[36]

For the determination of phenols, the sample drop is transported to the ring zone, followed by 2 drops of a $1M$ sodium hydroxide solution. The stable brown rings are developed by heating the filter papers for 1 min at 120°. Catechol, resorcinol, hydroquinone, pyrogallol, phloroglucinol and *p*-nitrophenol are cited as examples for this procedure. About 4 μg of the respective phenols are needed for the determination.[37]

Alkaloids are determined by the following reaction. The filter paper bearing the alkaloid concentrated in a ring zone, is bathed in a 1 % phosphomolybdic acid solution in nitric acid, then thoroughly rinsed in water. Subsequently, the filter is immersed in a 1 % tin^{II} chloride solution in hydrochloric acid, again washed with water and finally dried at 105°. Stable blue rings are produced which can easily be compared. The determinations were performed with 10–50 μg of nicotine, atropine, cinchonine, quinine, narcotine, morphine, codeine, aconitine, strychnine and brucine.[38]

The accuracy of the 3 methods just presented is very satisfactory; the errors are of about the same order as in the determinations of inorganic ions.

The microdetermination of caffeine has been investigated by Ordoveza and West[39] for use in air pollution studies. Solutions of acetylacetone in sodium hydroxide and of *p*-dimethylaminobenzaldehyde in hydrochloric acid are used to develop blue rings with caffeine. The standard scale is stable for about 3 days. Detailed studies have been carried out in order to establish the best conditions for the reaction and to eliminate interferences from other constituents likely to be collected from the atmosphere during the sampling procedure. As little as 0.5 μg of caffeine can be determined with an average error of 3 %.

TRACE ANALYSIS

Already some years ago Feigl and West[40] pointed out the possibility of using the ring oven method in trace analysis.

Ackermann[41] investigated heavy metals in alkali and alkaline earth salt solutions by precipitation of their hydroxides or sulphides and filtration through a specially designed filtering device, offering only a very small filtration area. The precipitate collected on the small filter paper disc is then separated and identified on another filter paper by means of the ring oven technique. As little as 10^{-3} ppm of copper and iron in salt solutions could be identified. The author mentions that by this technique it was shown that the well known autoxidation of alkali iodides is caused by traces of heavy metals.

Whereas in the method just mentioned the collection of traces of heavy metals is based on the so-called "Punktflockung", on the coagulation of the colloidal precipitate on the fibres of the paper itself (Mahr and Klamberg[42]), Schulek and coworkers[43,44,45] employed oxycellulose for the collection of traces of metals from extremely dilute solutions. The suspended oxycellulose fibrils, bearing the metals, are collected on a sintered-glass filter stick (5-mm diameter), where they form a little disc which is subsequently placed in the middle of a filter paper. On the ring oven, the various ions can be separated and identified in the usual way. About 20 ions were studied. The concentration of the ions in the original solutions was between 0.001

and 0.1 ppm. From 3 to 5 mg of oxycellulose were applied for their collection.

Two other publications can perhaps also be regarded as contributions to this field: investigations of impurities in filter paper[46] (*cf.* monograph, p. 67) and the detection of traces of lead in alloys and in prehistoric bronzes.[47] Because these two publications do not contribute basically new methods to the ring oven technique itself, no details need to be given here.

AIR POLLUTION STUDIES

During the last few years, the ring oven method has been used to study and control air pollution. The analysis of air borne particulates, including aerosols, is a very important problem of chemical analysis. Especially in industrial areas it is of significance for public health and hygiene to control the impurities in air.

Although relatively large amounts of sample can be collected over extended periods of time through the use of high volume samplers or continuous sample collecting equipment, it is desirable to handle smaller samples collected during brief sampling periods. It is likewise important that rather small amounts of certain constituents can be isolated, concentrated, identified and determined semiquantitatively in the presence of major amounts of innocuous accompanying air borne sample material.

The ring oven enables these conditions to be fulfilled and can therefore be used in this field with advantage. Its use in this context has already been suggested some years ago (*cf.* monograph, p. 66).

Samples collected by impaction or electrostatic precipitation can be taken into solution and drops of the resulting sample solution subjected to the ring oven technique in the usual way. However, samples of air borne particulates are mostly collected in air pollution studies by sucking air through special filters, membrane filters, glass fibres, nylon, rayon, *etc.* The identification and estimation reactions must be carried out on ordinary filter paper, because the surface of the other filter materials is not very suitable for colour reactions or for separations with a satisfactory degree of sensitivity. Therefore, the sample substances need to be transferred from the sampling filters to ordinary filter paper. This question of transferring substances from one filter to another could be of general interest and not only in air pollution studies.

A triangular portion (about 10 mm per side) of the filter material, having on its surface the collected particulates, is cut out for analysis. The triangle is placed on a filter paper and is fixed in place to ensure its position during subsequent operations and the quantitative transfer of the sample from the filter medium to the paper.

If membrane filters (such as "Millipore" filters), which consist of cellulose acetate, have been used for the collection of the samples, the fixation of the little triangle can be accomplished very simply by moistening the filter paper with a drop of acetone. The triangular piece of the membrane filter is placed on it (with the sample-bearing surface down) and held in position for a few sec. Enough of the cellulose acetate dissolves in the acetone to cause a cementing action.

The filter paper, together with the triangle, is placed upon the ring oven, but upside-down, so that washing can start on the surface of the paper rather than on the membrane filter (Fig. 4). Dissolution of the sample and its transfer into the ring zone is accomplished by washing with an appropriate solvent (0.1*M* hydrochloric acid, ammonia solution, *etc.*). All of the sample components are quantitatively concentrated in a sharply outlined ring zone. This ring is cut into sectors, on which the various identification tests are performed.

In the case of samples collected on other filtration media, such as linen, cotton, nylon, glass-fibre filters, or paper, again a triangular portion of the sample is cut out and must be fixed to the round filter paper using tiny dots of glue. Ordinarily, 6 spots of glue ("Duco-cement", "UHU" or a slurry of cellulose acetate in acetone) applied to the circumference of the triangle are sufficient.

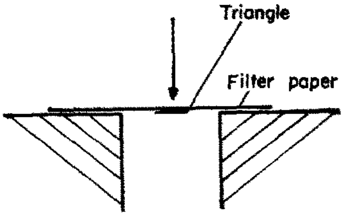

FIG. 4

These methods for transfer, concentration and analysis of collected air borne particulates have been described by West, Weisz, Gaeke and Lyles.[16] These authors also give a number of spot tests for identification of the pollutants. The quantitative determination of iron and aluminium is carried out by dissolving the sample collected on paper strips (using a low flow rate dust sampler) in a defined volume of 0.05*M* hydrochloric acid. In this sample solution, the metals are determined by ring colorimetry in the usual way. Four-hundred atmospheric samples have been analysed by this procedure. Accuracy, precision and speed were found to be satisfactory compared with conventional methods.

Methods for the estimation of antimony,[17] beryllium,[15] selenium[18] and caffeine[39] for application in air pollution studies have been worked out by West and coworkers. These methods have already been mentioned in appropriate sections of the review.

Huygen[29] described the determination of sulphate and sulphur dioxide in air. The filter paper used for the collection of sulphur dioxide is moistened with a 10% solution of potassium hydroxide or potassium carbonate and dried; sulphuric acid mist and sulphate particles in air are collected on plain filter paper (Whatman No. 1). The filter papers are clamped between circular plastic discs with centred holes in order to restrict the effective diameter to 15 mm. After the collection, the loaded filter papers are placed directly on the ring oven and the pollutants are washed to the ring zone with 0.1*M* hydrochloric acid (which contained, in the case of sulphur dioxide, 1% of hydrogen peroxide in order to oxidise it to sulphate). The reaction with barium chloride and potassium permanganate is carried out (as described above under *Anions*) to render the ring visible. The ring is then compared with standard rings for quantitative evaluation. The author obviously applied only 1 ring for comparison with the standard scale and therefore the accuracy of this method is only about ±25%. This is not surprising, because it has already been shown (*viz.* monograph) that 3 rings prepared from suitable drop numbers of sample solution have to be prepared and compared with the standard scale in order to obtain results with a degree of accuracy between ±5 and 8%.

This fact now shows the difficulty so far encountered in this type of work. One can either dissolve the collected particulates from the sampling material, such as filter papers, in a defined volume and then prepare the necessary 3 rings from varying drop numbers. Alternatively, the sample collected on the filter can be washed directly on the ring oven into the ring zone, if necessary (*e.g.*, a non-paper medium used for sampling) applying the transfer procedure described above. In this case, however, only 1 ring is available and obviously the averaging technique of ring colorimetry cannot be used; the results are not as precise as desirable in many cases.

The first technique, namely, dissolving the collected material from the sampling medium and preparing 3 sample rings, yields, of course, more precise results, but much more of the material to be determined needs to be collected than is actually used in preparing the 3 rings. Alternatively, the sample would have to be dissolved in a very small but known volume of, say, some 10 μl, which is not easily practicable.

It seems possible to overcome this difficulty by sucking the air simultaneously through at least 3 restricted areas of different but known size of the filter material. The ratio of the "sample spots" thus achieved should be such that 3 of them, after having been extracted to the ring zone and developed with suitable reagents, cover a wide range of the respective standard scale used for comparison. Thus, it would be possible to transfer the collected material directly to the ring zone without previous dissolution and to have, nevertheless, the 3 rings necessary for comparison. Only very small amounts of the pollutant need to be collected and that, on the other hand, means that only a shorter sampling period would be necessary. This could be of some importance in many practical instances.

An alternative approach might be to collect the pollutants on filter material and to cut out 3 circular or triangular pieces of different but well defined size, the areas of which should have a suitable ratio from one to the other, then to transfer the collected material from these small pieces to the ring zone of 3 separate filter papers.

Practical experiments, which we plan to carry out in the near future, will serve to evaluate these techniques.

RADIOACTIVE SUBSTANCES

In the monograph, the application of the ring oven method to the analysis of radioactive substances has already been described, but only with a few qualitative experiments. It was pointed out that autoradiography of the rings should provide a method for the semiquantitative determination of active substances. This suggestion has now been verified and two basically different methods for semiquantitative determinations are currently available and will be reviewed here.

The simpler approach to the quantitative determination is as follows. Prepare a standard scale by making rings from 1, 2, 4, 6, 8 and 10 drops of a standard solution of a radioactive isotope, expose the rings to X-ray film for sufficient time and develop the rings. Then prepare and autoradiograph under identical conditions 3 rings with varying numbers of sample drops. Compare the unknown ring autoradiographs with the standard scale and calculate the concentration of the unknown solution as in chemical ring colorimetry.

This method gives good results, but it is rather time consuming. In ring colorimetry 3 rings made from different drop numbers always have to be compared with the standard scale (*viz.* monograph).

In order to find suitable drop numbers, a ring with 1 drop is always made first and compared with the standard scale. From this preliminary result, the numbers of test drops for the other two rings are derived. In ordinary chemical ring colorimetry this is done very quickly, but in autoradiography one must first make an autoradiograph of the one-drop-ring, which takes, of course, several hr, before one can decide the drop numbers to be applied for the other two rings.

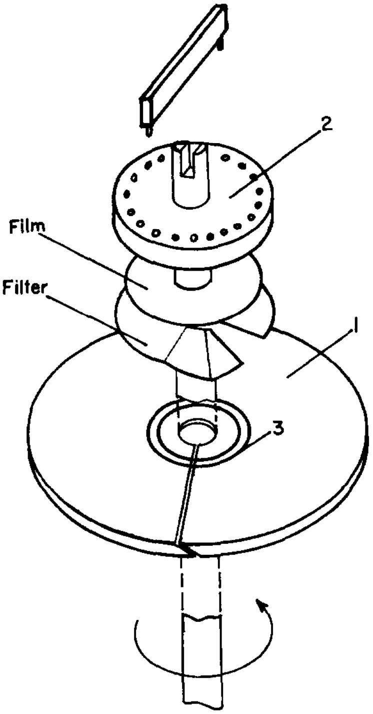

FIG. 5.—Exposure apparatus:

1—Steel plate with slit, on which the filter bearing the active ring is placed and one of the radially cut edges inserted into the slit.

2—Heavy steel plate fitted with fine steel needles on the lower side; these needles firmly fix the filter and film together.

3—Narrow groove to receive tips of the steel needles.

This has lead to another approach. In carrying out the procedure in the way mentioned above, one in fact neglects an essential possibility of autoradiography, namely, utilisation of the law of reciprocity. Two blackenings of a photographic film from radioactive substances are identical if the products of intensity and exposure time are likewise identical ($i.t$ = constant). The method to be reviewed here now makes use of this principle.[48]

The radioactive substance in the sample drop is washed into the ring zone and fixed there by a suitable precipitant. The filter paper bearing the "active ring" is provided with a central hole and cut along a radial line. It is then placed on a slit plate in an exposure apparatus (Fig. 5) and a piece of X-ray film placed on top. The paper and film are held firmly together, but during a slow rotary motion the paper gradually passes through the slit plate while the film remains above the plate. Hence the action of the active ring on the film is stopped.

One rotation takes 12 hr and the film is then developed. It shows an autoradiograph with stepwise increasing density, corresponding to exposure times from 0 to 12 hr.

The rotary motion should not be carried out linearly, for instance with the aid of a clockwork drive, because if a linearly increasing blackening of the ring autoradiograph is to be achieved, the various exposure times (for the various parts of the ring) have to follow a geometric series and not an arithmetic one. Therefore the rotary motion is carried out in 50 single steps, using a gear-wheel and a magnetic switch (not shown in Fig. 5). At different times an electrical contact gives an impulse to the magnet, which in turn moves the gear-wheel one step further. The various times are regulated by a simple additional switch apparatus, which delivers the necessary electrical contacts to the magnetic switch.

If the exposure time for the first step is t min, the time for the second step is $t.k$, for the third $t.k^2$ and so on. The exposure time for the last step, *i.e.*, for the last little segment of the ring, is therefore $t.k^{49}$ min; this is the maximum exposure time, and so also the time for a complete rotary motion of the film + filter. This total exposure time has been chosen to be 12 hr, the time for the first step t is about 10 min and k is $\sqrt[8]{2}$ (= 1.0905). This means that every eighth step has exactly double the exposure time of the first one, because $(\sqrt[8]{2})^8 = 2$. The "ring chrono-autoradiograph" is then nothing but a circular stepped grey wedge.

In this way, chrono-autoradiographs are prepared from 1, 2, 4, 8 and 10 drops of a standard solution of a radioactive isotope. From 1 drop of the unknown solution a chrono-autoradiograph is likewise prepared. Evaluation of the sample ring chrono-autoradiograph is made by comparing it with various (usually 3 or 4) standard ring chrono-autoradiographs.

The unknown autoradiograph is placed almost on top of, but separated by 1–2 mm from one of the standards and turned (clockwise or anticlockwise) until the best coincidence of blackening is observed. The number of steps (50 for the total ring) through which the sample chrono-autoradiograph had to be turned is noted. This is best done by illuminating the two rings from below and applying a simple dial, of which the circle is divided into 50 sectors (equal to the number of steps in the exposure apparatus).

As an example, suppose the unknown ring had to be turned clockwise 6 steps to give the same appearance as the standard ring. This obviously means that the activity of the sample solution is higher than that of the standard solution, because it gave at a shorter exposure time already an equal degree of blackening. The difference is 6 steps, which means the activity is $(\sqrt[8]{2})^6 = 1.495$ times that of the standard solution.

Because drop numbers can be varied and also the exposure times (one is not bound to 12 hr: 6, 24, 48 or other multiples of 12 hr could be used), the range of activities which can be measured is extremely wide. A very simple arithmetical treatment gives the ratio of the activities of the unknown and the standard solution. In the calculations the different rotation times and drop numbers have, of course, to be taken logically into account. As long as the factor k is the same, all sample rings can be compared with the same standard scale, irrespective of the rate of the rotation in the exposure apparatus. Because it would surpass the scope of this review to describe the arithmetical evaluations in detail, the reader is referred to the original publication[48] for this information.

It is also possible to compare a sample autoradiograph derived from a different active isotope than that from which the standard scale has been prepared. In this case, the result has to be multiplied by a suitable isotope conversion factor, which has been determined experimentally by a single standardisation. So far ^{59}Fe, ^{32}P, ^{235}U, ^{60}Co, ^{137}Cs, ^{95}Zr, ^{90}Sr, ^{144}Ce and ^{106}Ru have thus been determined over a wide range of concentrations, down to nano-curie and even less.

In a second publication,[49] the precision and sensitivity of this method are discussed and detailed procedures for the determination of the conversion factors are given (cobalt/caesium, cobalt/zirconium, cobalt/strontium, cobalt/cerium, cobalt/ruthenium). Chrono-autoradiography in its many aspects is summarised in a further publication.[13]

These methods have been applied to the investigation of very dilute radioactive solutions and waste waters. The dilute solutions are concentrated on the ring oven itself, using a simple glass apparatus which delivers sample solution continuously to the filter paper on the ring oven. The "active rings" are then chrono-autoradiographed as described above. The detection limits were found to be of the order of nano-curies or even less, using a total exposure time of only 6 hr.[50]

An exposure apparatus for chrono-autoradiography has also been devised which allows a continuous rotation instead of a stepwise one, as is the case in the apparatus just described. The rotation must not, of course, be linear, for reasons already mentioned. Therefore, a programme curve disk takes care of the necessary exponential rotational course.[51]

As stated above, the simplest method for the determination of radioactive substances is the direct autoradiography of sample rings, but the problem is here to ascertain suitable drop numbers of the unknown solution for preparation of the necessary 3 sample rings. A newer method has been described, in which this difficulty was overcome without any special exposure device.[52]

From a standard solution of an active isotope, standard rings with 1, 2, 4, 6, 8, 10, 13 and 20 drops are prepared and exposed to X-ray film for 20 hr. It is, of course, essential that the standard solution has a suitable activity (a_{St}) in order to obtain a well differentiated standard scale. Sample rings are prepared from the unknown solution with 1, 4, 8, 16 and 20 drops (of the same volume as the standard drops, of course) and each of them is "sandwiched" between two pieces of X-ray film and exposed (weighted with a glass-plate). After 1, 12 and 125 hr the upper film covering the sample rings made from 20, 16 and 8 drops, respectively, is developed. The upper films serve only for "piloting experiments" to ascertain the necessary exposure time. For the final comparison, the second (underlying) films are used.

The drop numbers and exposure times have been chosen so that always at least three of the 5 sample rings must fall within the standard scale, if the concentration (activity) of the unknown solution is between a fiftieth and fifty-fold that of the standard solution ($1/50\ a_{\mathrm{St}} - 50\ a_{\mathrm{St}}$). This is a limitation, but for most practical purposes a concentration range of the sample solution from 1:2500 is certainly sufficient.

The resulting ring autoradiographs are compared with the standard autoradiographs as usual. The calculation is simple:

$$\frac{a_{\mathrm{S}}}{a_{\mathrm{St}}} = \frac{\Sigma z_{\mathrm{St}}}{\Sigma z_{\mathrm{S}}} \cdot \frac{t_{\mathrm{St}}}{t_{\mathrm{S}}}$$

where a_S/a_{St} = the ratio of the activity of sample solution to standard solution,

Σz_{St} = the total number of drops of the standard rings to which the three sample rings have been aligned,

Σz_S = the total number of drops from which the 3 sample rings have been prepared,

and t_{St} and t_S = the exposure time for standard and sample ring autoradiographs, respectively.

It is also possible to chose other values for the exposure time of the standard scale as well as for the sample rings, and other drop numbers. A different range of concentration of the unknown solutions can be covered by this method.

Several radioactive isotopes have thus been determined with a satisfactory degree of accuracy ($\pm 10\%$): ^{45}Ca, ^{137}Cs, ^{110}Ag, ^{204}Tl and ^{90}Sr/Y.

If the difference of the exposure time of the standard scale and the sample rings is too great (*e.g.*, 20 — 120 hr), then the "fading" effect enhances the degree of error and the blackening of the longer exposed film becomes weaker than it should be. This can easily be avoided (or at least greatly reduced) by autoradiographing at a temperature of $-20°$ in a cool box.

Whereas all of these methods aim to determine radioactive substances themselves, in the procedure to be described next radioactive isotopes are used for the determination of inactive substances. An isotope dilution method in combination with the ring oven technique has been worked out, which allows the determination of submicrogram amounts of various ions. Only 1 drop of a rather dilute solution of the respective active isotope is needed.[53]

To the solution (2 or 3 drops) of an ion (x μg), an always constant amount (a μg) of the same ion, labelled with an active isotope of this ion, is added. With a constant amount of a suitable reagent, part (b μg) of the total amount $x + a$ is precipitated and separated on filter paper on the ring oven. The amount b is collected in the inner ring zone (14-mm diameter), whereas the rest ($x + a - b$) is transported to the outer ring zone. The separations are carried out with the aid of the auxiliary ring described above.[1] The impulses (cpm) corresponding to b and $x + a - b$, respectively, are determined by a suitable counting device (Geiger-Müller counter) after the filter paper has been cut by a pair of scissors.

It is also possible to carry out the reverse procedure: to precipitate the total $x + a$ in the inner ring and to add a certain amount of a reagent, which dissolves b μg of the precipitate. The amount b is then washed to the outer ring zone. Under identical conditions, a series of solutions of known concentrations of the ion are treated, the ratios of the two impulse rates (for b and $x + a - b$) are determined and plotted graphically *versus* the concentrations, thus giving a standard curve. The unknown solution is treated in exactly the same way, and the evaluation of the results is done graphically. It is, of course, important that the solutions are mixed as uniformly as possible. This is carried out in a blood mixing pipette.

In this way, calcium [+ EDTA, $(NH_4)_2HPO_4$], phosphate (+ $CeCl_3$, aqueous NH_3) and iron [+ $K_4Fe(CN)_6$] have been determined in the range 0·1 — 1 μg/μl with a satisfactory degree of accuracy. It should likewise be possible to carry out the measurement of the activity by autoradiography. The advantage of this method is obviously that only very small activities need to be applied, so that the technique can be used in an ordinary chemical laboratory without any danger.

Hilton and Reed[71] recently determined caesium-137 in irradiated uranium solutions using the following technique. A drop of sample solution was placed on a preformed precipitate of iron^{III} hydroxide at the centre of a filter paper. This precipitate adsorbed unwanted radioactive components. Caesium-137 was then washed, on the ring oven, with aqueous ammonia and water into the ring zone, where it was subsequently evaluated by γ-ray scintillation spectrometry. Apart from the advantages of speed, simplicity and negligible use of shielding, the method was precise and did not need any determination of the yield because a calibrated standard was always analysed under the same conditions as the sample. The authors suggested the ring oven technique in conjunction with γ-ray spectrometry should prove effective for determining many radionuclides in complex mixtures.

It seems that the ring oven method could be used also for educational purposes in the field of radiochemistry with advantage, because it allows experiments to be carried out with extremely small amounts of radioactive substances.

IN COMBINATION WITH OTHER TECHNIQUES

Several methods have already been mentioned, both in the monograph and in the present review, which are based on combinations of the ring oven method with other well established analytical procedures, *e.g.*, autoradiography, paper chromatography, electrographic sampling.

Biró[54] applied the ring oven method in connection with electrographic sampling of metallic specimens in a similar way to that already described by Stephen and by Nall (*cf.* monograph). Application of the ring oven method and especially its combination with electrographic sampling in the analysis of metals has been recently reviewed in detail by Ottendorfer.[55]

Mooney[56] described an interesting method which might be generally applicable, namely, combination of the ring oven technique with cation exchange and emission spectrography. The sample drop is spotted on a small circular disk (9-mm diameter) of cation exchange paper (Whatman CM 50) and dried. The disk is then placed on an ordinary filter paper on the ring oven and the anions washed with water to the ring zone, where they can be identified in the usual manner. Cations are either detected spectrographically by placing the disk directly in a graphite electrode for the d.c. arc method, or they are eluted from the ion-exchange paper into the ring zone of another filter paper, using $3M$ nitric acid as a solvent. In this "cation ring zone" the various metal ions are either detected by conventional chemical identification reactions or, in a sector, again spectrographically. Some of the metals which are present as anions (such as molybdate and chromate) are to be found, of course, already in the first ring zone, together with the other anions. The practical cation capacity of the ion-exchange paper and the sensitivety of the spectrographic determination for a number of metals have been studied. So far, only a rather limited number of examples for this technique has been communicated, but it is to be hoped that the author will continue with his interesting work.

CONCENTRATION OF SUBSTANCES IN THE FORM OF A STRAIGHT LINE

In the ring oven method, the concentration of the soluble substances contained in a sample drop takes place in the form of a sharply developed ring of 22-mm diameter; this causes a concentration effect of about 3–10 fold. It is obvious that a ring oven having a smaller bore hole diameter would enable a still higher concentration effect to be achieved. However, it would also give a ring with a smaller circumference. Because the ring oven method has now been developed for separations and semiquantitative determinations, too small a ring would give difficulties in this respect. With a smaller circumference of the ring, the number of sectors into which it can be cut for various identification procedures must logically decrease.

Within the last few years, several authors have described methods of concentrating substances on filter paper strips which result in short straight lines. Farr and Chaney[34] used for their method of determining proteins a modified ring oven, by which the substances are concentrated along a line. Schwarz-Bergkampf[57] described a very simple tool (gas-heated) for the accumulation procedure. Biró[58,59] published his "line oven", which consists essentially of two heating blocks, which can be pushed against each other, one serving for concentration of the sample constituents (as usual in the ring oven method) and the other, suitably positioned, serving to protect "lines" which had been previously developed, against the solvent.

Reimers[60] described a "rod oven", which does not seem to bring about any new possibilities at all.

It has been shown[61] that the ring oven in its original form can also be used advantageously for the concentration of substances along a short straight line. The sample drop is spotted on a filter paper strip of 6-mm (or even less) width. This strip is placed across the ring oven so that the spot lies between the middle and the edge of the bore hole. Using a capillary washing pipette with a suitable solvent, the soluble substances are then concentrated in the form of a short (6 mm or less, depending on the width of the paper strip) line. By suitable movement of the filter paper strip on the ring oven and by selection of the appropriate fixation reagents and solvents, the components contained in the sample drop can be separated from each other and concentrated in parallel lines on the paper strip, as with the other newer described concentration devices.

LITERATURE

The ring oven method has been frequently reviewed, and only a few of these articles need be quoted here. These reviews have, without doubt, contributed much to the growing interest in this field of microchemistry. German,[62,63] English,[64,65] Finnish,[66] Spanish[67] and Italian[68] papers have summarised the method.

In several text books and hand books of analytical chemistry, the ring oven method has been described, *e.g.*, in Feigl's *Spot Tests in Inorganic Analysis*,[72] in *Standard Methods of Chemical Analysis* edited by Welcher.[73]

Amongst the many comments on the monograph there is to be found a rather negative one.[69] The critic, who preferred to remain anonymous, was under the misapprehension that the ring oven technique was a form of paper chromatography and that it is by no means. He believed that the then limited number of publications did not justify the compilation of the monograph. It is to be hoped that a comparison of the number of publications on this subject then and at present will prove the contrary.

FUTURE DEVELOPMENTS

In order to make this present review as complete as possible, it seems to be necessary to mention studies which are currently being carried out. Only those can be quoted here, of course, which derive from the laboratories of the reviewer or of colleagues who were so kind as to communicate with him about their present work in this field.

Ring autoradiography and the isotope dilution method will be applied to more ions. A systematic qualitative separation scheme for a greater number of radioactive substances contained in one single drop is at present under investigation.

A qualitative and semiquantitative scheme for toxicological analysis will soon be available. Ring colorimetric methods for a number of dyes[70] and other organic substances and for the noble metals[70] are likewise under investigation.

Many new reactions both for organic and inorganic substances will be worked out for use with the ring oven and so contribute to the wider use of this technique. Air pollution studies are being continued. The method will be applied in the field of testing foodstuffs, especially in the dairy industry.

These few newer applications will, it is to be hoped, show that the ring oven method is being still further developed. The reviewer would be glad to learn of any information at present unknown to him and cordially invites colleagues who work in this field to communicate with him.

Zusammenfassung—Eine Übersicht über neue Entwicklungen in der Ringoftentechnik wird gegeben.

Résumé—On présente une revue des développements récents dans la technique du four annulaire.

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APPLICATION OF CATION-SENSITIVE GLASS ELECTRODES TO THE STUDY OF ALKALI METAL COMPLEXES—II*

USE OF A POTENTIAL COMPARISON METHOD

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Summary—Formation constants for alkali metal-citrate and -malate complexes have been evaluated by cation-sensitive glass electrodes. Use of a potential comparison method was found to be beneficial in improving the reliability and accuracy of such measurements. Formation constants for alkali metal-malate complexes agree well with the literature data; corresponding values for citrate complexes have not previously been published.

INTRODUCTION

In an earlier paper[1] we demonstrated the usefulness of cation-sensitive glass electrodes in the study of weak alkali metal complexes. The accuracy of the reported measurements for the formation constants of alkali metal-malate complexes was primarily limited by experimental problems inherent in the potentiometric procedures used. A potential comparison method has now been devised which largely eliminates sources of error, such as electrode drift and variation in solution composition, yet retains the advantages gained by the use of cation-sensitive glass electrodes. Briefly, this method involves the adjustment of the alkali metal activity of a solution containing known concentrations of complexing ligands by the incremental addition of concentrated solutions of alkali metal ions or ligands until the potential of the complex-containing solution becomes exactly equal to that of a solution containing only known concentrations of alkali metal ion. From initial concentrations and volumes of metal ion or ligand solution added, the formation constants of complexes formed can be easily calculated.

EXPERIMENTAL

Apparatus

All potentiometric and pH measurements were made using a Beckman Model 76 Expanded-Scale pH meter. A Beckman #39137 cation-sensitive glass electrode *vs.* #39170 fiber junction saturated calomel reference electrode (SCE) was employed. A #41263 pH glass electrode *vs.* SCE was used for all pH determinations.

An A. H. Thomas Co. #2457 Shohl microburette of 2-ml capacity with a hypodermic syringe needle-type delivery tip (luer lock slip hub, s.g. #25) was employed in accordance with the manufacturer's directions.

Reagents

All solutions except that of malic acid were prepared by weight from reagent-grade materials, and were used without further purification.

Alkali metal chlorides: Weigh 14·6120, 29·2240 and 43·8360 g of NaCl and bring each with water to a total volume of 0·250 litre, thus preparing 1·000, 2·000 and 3·000*M* stock solutions. Serial dilutions of 0·300, 0·200, 0·100 and 0·050*M* are made. Similar 1·000*M* stock solutions of KCl, LiCl, RbCl and CsCl, with serial dilution to 0·100*M*, were prepared.

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* Part I: *Talanta*, 1964, **11**, 617.

Malic acid: (Purified powder, racemic). Weigh 33·5230 g and dilute to 0·250 litre with water to make a 1·000*M* stock solution, with serial dilutions of 0·300, 0·200, 0·100 and 0·050*M*. Stock solutions must be prepared fresh daily.

Citric acid: Weigh 52·5365 g and dilute to 0·250 litre with water to make a 1·000*M* stock solution; make serial dilutions as with malic acid.

Hydrochloric acid: Dilute concentrated hydrochloric acid (12·4*M*) with water to make 1·0 litre of 1·2*M* and 0·250 litre of 6·2*M* solutions.

THAM–HCl buffer solution: Weigh 145·3680 g of tris(hydroxymethyl)aminomethane (THAM), mix with 0·344 litres of 1·2*M* HCl, and dilute with water to total volume of 2·0 litre. This will give a solution of pH 8·45 ± 0·01, and is sufficient for 20 determinations.

Preconditioning solutions for cation-sensitive glass electrodes: Dilute 41·67 ml of 0·1*M* NaCl to 0·250 litre total volume with buffer solution.

Procedure

The following is a typical procedure used in the study of the sodium-citrate complex: pipette 10 m of 0·1*M* NaCl and 50 ml of buffer into a 100-ml beaker to make the standard solution, *s*. Pipette 10 ml of 0·1*M* citric acid and 50 ml of buffer into a second 100-ml beaker to make the test solution, *t*. Measure the pH of the solutions. The pH of $s >$ the pH of t, therefore adjust the standard with additions of 6·2*M* HCl until pH of $s =$ pH of t. Next, measure the potential of the standard solution, mv_s, and of the test solution, mv_t, with a cation-sensitive glass electrode *vs.* SCE, finding that $mv_s > mv_t$. Now titrate 1·0*M* NaCl into the test solution until $mv_s = mv_t$ on successive measurements. To determine the amount of NaCl complexes, *c*, by the citric acid apply the following:

$$\text{meq of NaCl}(t) - \text{meq of NaCl}(s) = \text{meq of NaCl}(c).$$

Assuming, for purposes of illustration, that a 1:1 complex is formed, the formation constant, K_f, of the complex can be calculated by the standard methods.

A back-titration of the above system can be performed as follows: the standard solution contains 10 ml of 0·1*M* NaCl and 50 ml of buffer: the test solution contains 0·1*M* NaCl in excess of 10 ml and 50 ml of buffer. Suitable pH measurements and adjustments are made. Potentiometric measurements show $mv_s < mv_t$. Titrate 1·0*M* citric acid into the test solution until $mv_s = mv_t$ as above.

All formation constant values reported are calculated from an average of 3 or 4 determinations. Magnetic stirring was used throughout, and all determinations were carried out at room temperature, 25·0 ± 0·5°. Pre-conditioning of the cation-sensitive glass electrode is essential if reproducible potentials are to be obtained. The pre-conditioning solution must be as similar as possible to the standard solutions employed; electrodes should be soaked for a minimum of 24 hr before use.

RESULTS AND DISCUSSIONS

General considerations

In order to treat the system quantitatively, the appropriate pH, ionic strength, and particular buffer system employed must all be taken into consideration. Citric acid[3] has $pK_1 = 3{\cdot}08$, $pK_2 = 4{\cdot}39$, and $pK_3 = 5{\cdot}49$. Thus, to study the system:

$$M^+ + A^{3-} \rightleftharpoons MA^{-2}, \quad K_f = \frac{[MA^{2-}]}{[M^+][A^{3-}]} \tag{1}$$

where M^+ is the alkali metal ion and A^{3-} is the citrate anion, the pH of the system must be greater than 5·49. The THAM-HCl buffer at pH 8·45 ± 0·01 was chosen for the following reasons:

(1) If pH $\leq$ 5, the potential developed by the cation-sensitive glass electrode is a function of pH and pM.[4]

(2) It is desirable to work in alkaline medium to ensure complete dissociation of the citric acid.

(3) A 1:1 complex, MA^{2-}, could not exist at pH 5·49.

(4) The THAM-HCl buffer cation, $(CH_3OH)_3CH_3N^+$, probably forms no complexes with citrate or malate anions.

(5) The cation-sensitive glass electrode does not respond to $(CH_3OH)_3CH_3N^+$.

(6) To maintain the ionic strength of the standard and test solutions equal and constant, a high buffer concentration is employed.

Malic acid has $pK_1 = 3{\cdot}62$ and $pK_2 = 4{\cdot}68$.[3] Thus, similar considerations apply to the system:

$$M^+ + A^{2-} \rightleftharpoons MA^-, \quad K_f = \frac{[MA^-]}{[M^+][A^{2-}]} \tag{2}$$

where M^+ is the alkali metal and A^{2-} is the malate anion. The same buffer was used to study the 1:1 malate complex, MA^-, which is assumed to be the predominant species formed.

Effect of pH

For the sodium-citrate system, a pH change from 8·30 to 8·01, over a concentration range of initial citrate concentrations from 0·1 to 0·3*M*, results in a change of $K_f = 1{\cdot}0$. At constant pH 8·00, a change in citrate concentrations from 0·1 to 0·3*M* results in a K_f change of only 0·2 (see Table I). This small change probably arises from unavoidable ionic strength variations as the ratio of buffer and ligand to metal ion is changed. It is clear, therefore, that while high buffer concentrations provide adequate control over ionic strength changes, rigid maintenance of constant pH values in all solutions is critical.

TABLE I.—EFFECT OF pH ON FORMATION CONSTANTS

System	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
NaCl + citric acid	0·1	8·30	5·0 ± 0·1
	0·2	8·17	4·3 ± 0·1
	0·3	8·01	4·0 ± 0·1
	0·1	8·00	4·2 ± 0·1
	0·2	8·00	4·1 ± 0·1
	0·3	8·00	4·0 ± 0·1
NaCl + malic acid	0·05	8·48	2·0 ± 0·2
	0·1	8·38	1·9 ± 0·1
	0·2	8·30	1·6 ± 0·1
	0·3	8·20	1·6 ± 0·1

Ratio of metal to ligand

The effect of changes in the ratio of metal ion to ligand concentration was tested over the range of initial sodium and citrate concentrations of 0·1 to 0·3*M*. Experiments carried out at pH 8·00 and constant ionic strength are summarised in Table II. Essentially, constant formation-constant values are obtained at equal metal ion and ligand concentrations, thus confirming the formation of a 1:1 complex.

TABLE II.—RATIO OF METAL ION TO LIGAND

NaCl + citric acid (pH 8·00 constant)

Initial salt and acid concn. *M*	K_{f_1}	K_{f_2}	K_{f_3}, *ml/meq*
0·1	4·2	10·9	16·8
0·2	4·1	7·7	10·4
0·3	4·0	6·1	7·8

Formation constants for the citrate and malate complexes

Formation constants for the alkali metal-citrate complex, MA^{2-}, at constant initial metal and salt concentration of $0{\cdot}1M$ and pH 8·30 ± 0·01, and for the malate complex, MA^{-}, at $0{\cdot}1M$ concentration and pH 8·35 ± 0·01, are summarised in Tables III and IV respectively. Both forward- and back-titration values agree for these complexes. The K_f values for malate complexes of sodium and caesium agree within ±0·05 with those obtained by Erickson and Denbo,[2] and represent considerable improvement over values reported in our first paper.[1] Formation constant values for alkali metal-citrate complexes have not been previously reported in the literature. It is interesting to note that the magnitudes of K_f-values for both citrate and malate complexes depend on the alkali metal ion involved, and follows the trend $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ predicted by the trend in charge metal ion radius ratios.[2]

TABLE III.—FORMATION CONSTANTS OF ALKALI METAL-CITRATES

Complex	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
LiA^{2-}	0·1	8·32	6·8 ± 0·1
NaA^{2-}	0·1	8·30	5·0 ± 0·1
KA^{2-}	0·1	8·30	3·9 ± 0·1
RbA^{2-}	0·1	8·30	3·1 ± 0·1
CsA^{2-}	0·1	8·32	2·1 ± 0·1

TABLE IV.—FORMATION CONSTANTS OF ALKALI METAL-MALATES

Complex	Initial salt and acid concn., *M*	pH	K_f, *ml/meq*
LiA^-	0·1	8·35	2·4 ± 0·1
NaA^-	0·1	8·38	1·9 ± 0·1
KA^-	0·1	8·35	1·5 ± 0·1
RbA^-	0·1	8·36	1·1 ± 0·1
CsA^-	0·1	8·35	0·7 ± 0·1

CONCLUSION

Because the potential values measured by the glass electrodes are used only as reference points to indicate when the activities of alkali metal ion in the standard and test solutions are identical, possible errors from electrode drift or temperature effects are of no consequence. In fact, the method does not even require that the electrode shows Nernstian behaviour. Dilution errors and ionic strength changes are reduced to a minimum by the use of concentrated titrants and high buffer concentrations. The accuracy with which formation constants can be determined depends, therefore, primarily on the limitations of the titrimetric technique employed. A real limit is imposed, however, by the response of the glass electrode to hydrogen ions in regions of $pH < 5$.

The potential comparison method can be used to determine formation constants of any weak complex of alkali metal cations with organic acids, if proper precautions are taken to eliminate interfering species, control pH, and maintain ionic strength. Complexes of bivalent cations should be amenable to this method when the phosphate glass electrodes of Truesdell and Pommer[5] or similar specific-ion electrodes become more widely available.

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Zusammenfassung—Bildungskonstanten von Alkalimetallkomplexen mit Zitronen- und Apfelsäure wurden mittels kationenempfindlicher Glaselektroden gemessen. Eine Potentialvergleichsmethode wurde als geeignet befunden, um die Zuverlässigkeit und Genauigkeit solcher Messungen zu steigern. Die Bildungskonstanten der Malatkomplexe stimmen gut mit Literaturwerten überein; entsprechende Werte für Citratkomplexe waren bisher nicht publiziert.

Résumé—Les constantes de formation de complexes métal alcalin-citrate et -malate ont été estimées au moyen d'électrodes de verre catio-sensibles. On a trouvé que l'emploi d'une méthode de comparaison de potentiel est avantageuse, car elle améliore la sûrete et la précision de telles mesures. Les constantes de formation des complexes métal alcalin-malate sont en bon accord avec les données de la littérature; les valeurs correspondantes des complexes citriques n'ont pas été publiées antérieurement.

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PHOTOMETRIC TITRATIONS—IX*

DTPA TITRATION OF ZINC IN PRESENCE OF CADMIUM AND OTHER METALS

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Summary—Zinc can be titrated in the presence of large amounts of cadmium in the following manner. The sample is neutralised and buffered to pH 5·0 with an acetate buffer. Potassium iodide (up to about 60% *w/v*, depending on cadmium concentration) and Xylenol Orange as indicator are added and the titration is performed photometrically at about 570 mμ with DTPA as titrant. Correct results have been obtained with Cd/Zn mole ratios up to 3300. Interferences and tolerable limits of concentrations of some other metal ions have been investigated.

Masking by means of the formation of soluble complexes is the most convenient and practical method of eliminating interferences in chelometric titrations. Generally, moderate concentrations of ligands which form highly stable complexes are preferred. Thus, 1:1 complexes, whose stabilities are enhanced by the chelate effect, or 1:n complexes of very high stabilities are usually employed. There are only a few exceptions where high concentrations of ligands which form rather weak 1:n complexes have been used. The most notable example is the masking of thorium *via* the formation of sulphato complexes[1] (log $K_{Th(SO_4)_2}$ = 5·6.)[2]

It seemed of interest to investigate more closely the possibilities of "low stability masking" and, as a first result, the masking of cadmium with iodide was achieved.[3] That investigation revealed that cadmium can be successfully masked by high concentrations of iodide (*ca.* 5*M*) against reaction with some chelons and metallochromic indicators. Zinc is little affected by iodide, and can be titrated at pH 5 in the presence of cadmium to a visual end-point with Xylenol Orange as indicator. The application of the method is limited, however, in that only rather small amounts of lead, copper, calcium and magnesium can be tolerated and that the deterioration of the quality of the end-point with increasing cadmium concentration sets the maximum Cd/Zn mole ratio at about 300. A photometric technique should allow end-point detection over a more extended range than the visual method and has therefore been applied to the system.

EXPERIMENTAL

The absorbance curves of Xylenol Orange and its zinc and cadmium complexes at pH 5·0 are shown in Fig. 1. In solutions containing 10 or more per cent *w/v* of potassium iodide, the cadmium-Xylenol Orange complex is essentially completely dissociated. The maximum absorbance difference between the zinc-Xylenol Orange complex and the free indicator occurs at about 572 mμ.

Some preliminary experiments indicated that zinc could be successfully titrated with EDTA to a photometric end-point in the presence of up to about a 3000-fold excess of cadmium. With much cadmium present, however, prolonged drift of the galvanometer implied that the titration reaction was quite slow. Neither addition of ethanol or acetone nor changing the concentrations of buffer,

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* Part VIII: *Mikrochim. Ichnoanalyt. Acta*, in the press.

dye or iodide improved the situation. Other chelons were therefore investigated as titrants for the method and DTPA (diethylenetrinitrilopenta-acetic acid) was found to be satisfactory. With DTPA as titrant, the titration reaction is fast except near the end-point; there, however, because of the extrapolative nature of the method, no data are needed. It also proved possible to titrate zinc in the presence of large excesses of cadmium despite the fact that the DTPA complex of cadmium is more stable than that of zinc ($\log K_{CdY} = 19{\cdot}0$, $\log K_{ZnY} = 18{\cdot}0$),[3] a situation less favourable than in the case of EDTA ($\log K_{CdY} = \log K_{ZnY} = 16{\cdot}5$).[3]

Below pH 5, the degree of dissociation of the zinc-Xylenol Orange complex increases rapidly with decreasing pH. Only slightly above pH 5, the rate of the titration reaction slows considerably and, in high concentrations of potassium iodide, the indicator begins to change to its red form whose absorbance curve is very similar to that of the zinc Xylenol Orange complex. A pH of 5·0 was therefore selected for the titration. A Xylenol Orange concentration of 0·01 mg/ml in the titration solution was found to be satisfactory.

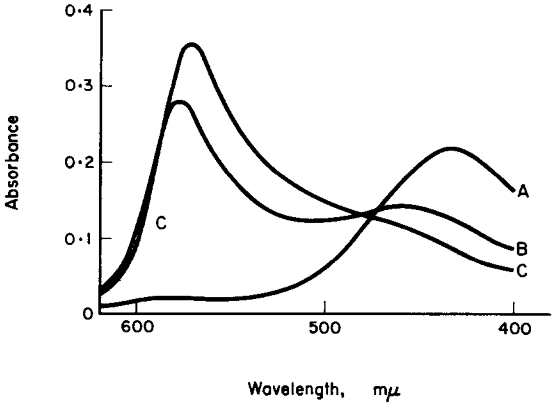

FIG. 1.—Absorbance curves of Xylenol Orange (XO) and its zinc and cadmium complexes at pH 5:

A: free XO,
B: XO + excess Cd,
C: XO + excess Zn.

Reagents

All reagents were of the highest available purity except potassium iodide, for which U.S.P. grade was found to be adequate. Only de-ionised water was used. A 0·1000*M* zinc solution was prepared by dissolving 6·358 g of zinc metal (99·99% purity) in nitric acid and diluting to 1 litre. Approximately 0·1*M* DTPA was obtained by suspending 39·3 g of the acid in water, adding sufficient sodium hydroxide to bring about dissolution and diluting to 1 litre. This solution was standardised *versus* the zinc solution at pH 5 with Xylenol Orange as indicator. $10^{-3}M$ DTPA and $5 \times 10^{-4}M$ zinc solutions were prepared by appropriate dilution of the respective stock solutions. An acetate buffer of pH 5·0 was obtained by dissolving 68 g of sodium acetate trihydrate in about 700 ml of water, adjusting the pH to 5·00 with concentrated hydrochloric acid and diluting to 1 litre. The indicator solution consisted of 50 mg of Xylenol Orange dissolved in 10 ml of water. Potassium iodide solution, 100% *w*/*v*, was prepared by dissolving 250 g of U.S.P. grade potassium iodide in sufficient hot water to make about 240 ml, filtering the hot solution, cooling and diluting to 250 ml. The indicator and DTPA solutions were stored in polyethylene bottles.

Apparatus

The phototitrator described by Flaschka and Sawyer[4] was employed with a glass heat filter mounted in the light path.[5] An interference filter with a nominal wavelength of 568 mμ was used. All titrations were performed in a glass cell of 2-cm light path and 60-ml capacity.

Procedure

Accurately measured amounts of metal solutions were delivered into the titration cell; the resulting solution was neutralised when necessary. About 5 ml of buffer and 10–25 ml of potassium iodide solution were added. The solution was then diluted to about 40 ml, the cell placed in the phototitrator and the latter adjusted to indicate a transmittance of 105–110%. Two drops of indicator solution were added and the titration was performed in the usual manner, using $10^{-3}M$ DTPA as titrant.

RESULTS AND DISCUSSION

The results of several titrations of zinc, alone and in the presence of cadmium and some other metals, are presented in Table I. The tendency to positive errors with increasing amounts of cadmium is probably because of trace impurities, most likely zinc, in the cadmium used.

With increasing amounts of cadmium present, the titration curve degenerates, as indicated in Fig. 2. Solutions with a Cd/Zn ratio of 3300 could, however, be successfully titrated in contrast to the visual method in which the maximum ratio was about 300.

With the photometric end-point, the situation with regard to other interferences also improves considerably. Calcium and lead can be tolerated in greater than a 600-fold molar excess. Magnesium was tested up to 3000-fold excess and even higher amounts should not interfere. Mercury is masked completely by iodide and does not interfere when present in any reasonable amount. A Cu/Zn mole ratio of about 200

TABLE I.—PHOTOMETRIC TITRATION OF ZINC, ALONE AND IN THE PRESENCE OF SOME OTHER METALS

Zn taken, *μg*	$1{\cdot}01_4 \times 10^{-3}M$ DTPA, *ml*			Metal added, *mg*	Mole ratio of metal:Zn	KI, %*w*/*v*
	Calc.	Found	Diff.			
131	1·97	1·97	±0·00			30
131	1·97	1·95	−0·02			30
131	1·97	1·97	±0·00			63
229	3·45	3·47	+0·02			30
262	3·94	3·95	+0·01			30
262	3·94	3·98	+0·04			63
248	3·81	3·82	+0·01	Cd 282	660	63
98	1·48	1·48	±0·00	Cd 169	1000	63
262	3·94	3·90	−0·04	Cd 450	1000	63
163	2·47	2·53	+0·06	Cd 280[a]	1000	50
248	3·81	3·84	+0·03	Cd 564	1320	63
131	1·97	2·00	+0·03	Cd 337	1500	50
131	1·97	2·02	+0·05	Cd 450	2000	63
131	1·97	2·00	+0·03	Cd 562	2500	63
98	1·48	1·52	+0·04	Cd 562	3300	63
163	2·47	2·47	±0·00	Ca 20	200	50
98	1·48	1·49	+0·01	Ca 40	670	50
163	2·47	2·47	±0·00	Mg 122	3000	50
196	2·96	3·00	+0·04	Pb 124	200	50
105	1·58	1·61	+0·03	Pb 207	630	50
98	1·48	1·46	−0·02	Bi 0·4	1	50
229	3·45	3·52	+0·07	Bi 4	6	50
131	1·97	2·01	+0·04	Bi 6	15	50
163	2·47	2·47	±0·00	Cu^{II} 32[b]	200	50
196	2·96	2·98	+0·02	Cr^{III} 3	20	50
131	1·97	1·97	±0·00	Hg^{II} 320	800	50
203	3·06	3·07	+0·01	Al 0·3[c]	3	50
235	3·55	3·57	+0·02	Al 0·3[d]	3	50
163	2·47	2·45	−0·02	Al 1[d]	20	50

[a] Solution 0·06*M* in tartrate.
[b] Iodine removed with thiosulphate.
[c] Solution 0·05*M* in sulphosalicylic acid.
[d] Spatula tip full of Tiron added.

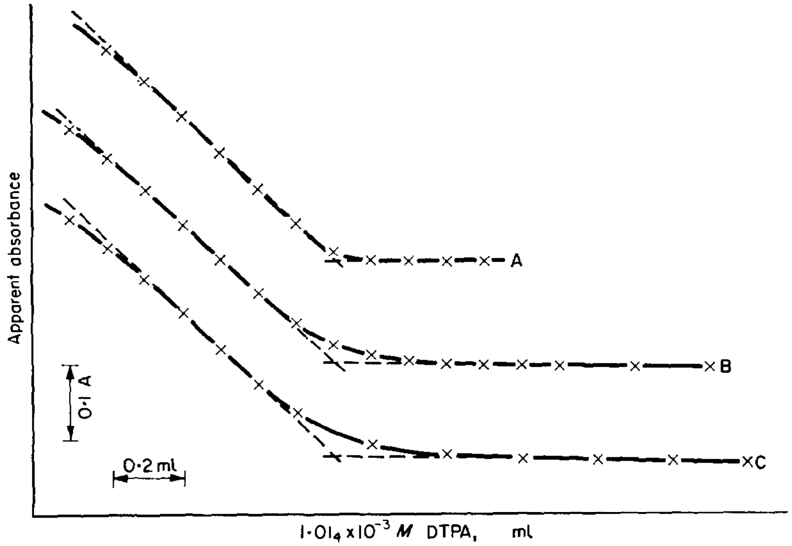

FIG. 2.—Influence of cadmium concentration on the titration curve:
A: Cd/Zn = 0,
B: Cd/Zn = 1500,
C: Cd/Zn = 3300.

can be tolerated. Aluminium, if masked by Tiron, can be present in about 20-fold excess; chromium and bismuth can be tolerated to about the same extent. The addition of tartrate (*ca.* 0·05*M*) does not interfere, but does not materially aid in the masking of bismuth.

Cobalt, iron^{II}, manganese, nickel and vanadate interfere by complete or partial cotitration. Iron^{III} blocks the indicator. Gallium and indium appear to cotitrate, even in the presence of tartrate; the indium interference is not removed by chloride.

Acknowledgment—This work was supported by a grant from the National Science Foundation, which aid is most gratefully acknowledged.

Zusammenfassung—Zink kann in Gegenwart beträchtlicher Mengen an Kadmium in folgender Weise titriert werden. Die Probelösung wird neutralisiert und mit einem Azetatpuffer von pH 5 versetzt. Kaliumjodid (bis zu 60 g per 100 ml, je nach der Kadmium-Konzentration) und Xylenolorange-Indikator werden zugegeben und die Titration wird sodann in üblicher Art durchgeführt. Es wird bei 570 mμ gearbeitet; DTPE dient als Titrationsmittel. Korrekte Ergebnisse werden bis zu einem Cd/Zn Molverhältnis von etwa 3300 erhalten. Störungen und erlaubte Konzentrationen einiger anderer Metallionen wurden untersucht.

Résumé—On peut doser le zinc en présence de grandes quantités de cadmium de la façon suivante. L'èchantillon est neutralisé et tamponné à pH 5,0 avec un tampon à l'acétate. On ajoute de l'iodure de potassium (jusqu'à environ 60 % poids/volume, en fonction de la concentration en cadmium) et de l'indicateur xylénol orange, et le dosage est mené photométriquement, à environ 570 mμ, au moyen de DTPA. On a obtenu des résultats corrects avec des rapports molaires Cd/Zn atteignant 3300. On a étudié les interférences et les limites de concentration tolérables de quelques autres ions métalliques.

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ANALYTICAL USES OF BROMANILIC ACID

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Summary—Bromanilic acid (2,5-dibromo-3,6-dihydroxyquinone) precipitates barium, calcium and strontium quantitatively from weakly acid solution, and forms a coloured complex with zirconyl ions in perchloric acid solution. The complex exhibits maximum absorbance at a wavelength of 335 mμ. Beer's law is obeyed in the range from 0·0 to 3·5 ppm of zirconium. Optimum results are obtained in solutions 2·8*M* in perchloric acid. The effect of various diverse ions has been investigated. Hafnium gives results identical with zirconium. Other interfering ions are Fe^{III}, Th^{IV}, UO_2^{II}, Ti^{IV}, phosphate, oxalate, fluoride and sulphate. Errors caused by varying amounts of these ions have been determined. A procedure for the determination of zirconium is given. Bromanilic acid is a more sensitive reagent than chloranilic acid for the determination of zirconium, and can be used over a slightly greater range.

INTRODUCTION

CHLORANILIC acid has been used as a reagent for the determination of calcium,[6,14,18] strontium[14] and barium.[6,17] The corresponding bromo-compound, bromanilic acid (2,5-dibromo-3,6-dihydroxy-1,4-benzoquinone), has not received much attention as an analytical reagent, and therefore has been studied in the hope of finding a reagent more sensitive and more selective than chloranilic acid.

Precipitation of barium, calcium and strontium

In the determination of calcium, strontium and barium[6,14,17] with chloranilic acid a known excess of the reagent is added. This forms a precipitate with the above ions, and the excess is then measured colorimetrically. The method is limited in usefulness because many cations interfere. The reaction of bromanilic acid with these ions has been studied.

Ultraviolet spectrophotometric determination of zirconium

Many reagents have been used for the colorimetric determination of zirconium.[2,4,5,8,13,15,16] One of the most sensitive is chloranilic acid, investigated by Thamer and Voigt,[17] who showed that low concentrations of zirconium (2×10^{-6}–$5 \times 10^{-5}M$) could be determined with accuracies within 1%. The zirconium chloranilate complex shows maximum absorbance in the ultraviolet region at 330 mμ. Frost-Jones and Yardley[6] measured the absorbance of the same complex at 525 mμ and obtained results similar to those of Thamer and Voigt, but the sensitivity was less at 525 mμ than at 330 mμ. The present investigation examined bromanilic acid to find if it could be used for the spectrophotometric determination of small amounts of zirconium.

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EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Model DU Spectrophotometer using 1·000-cm quartz cells.

Synthesis of reagent

Bromanilic acid was prepared from *p*-phenylenediamine, which was brominated, and oxidised with nitric acid to form bromanil. This was hydrolysed to form bromanilic acid. Procedures are given in the literature.[8,10,12]

Analysis of the purified compound gave the following: found: C, 24·07; H, 0·69; Br, 53·61; calculated for $C_6H_2O_4Br_2$: C, 24·16; H, 0·67; Br, 53·69. Bromanilic acid is a dark-red crystalline powder which dissolves to the extent of 1·5 g per litre in water to give a deep-red solution.

Solutions

Bromanilic acid: saturated aqueous and $2 \times 10^{-4}M$: 0·080 g of bromanilic acid was dissolved in 1 litre of distilled water to prepare the $2 \times 10^{-4}M$ solution.

Ammonium chloranilate: 5·0 g of bromanilic acid were dissolved in the calculated amount of dilute aqueous ammonia and diluted to 1 litre with water.

Zirconium perchlorate: 0·353 g of pure recrystallised zirconyl chloride octahydrate was dissolved in 235 ml of 72% perchloric acid (G. Frederick Smith Chemical Company) and then fumed to expel all hydrochloric acid. The product was cooled, and diluted to 1 litre with water, making a solution containing 0·1 mg of zirconium per ml. A second solution, $2 \times 10^{-4}M$ in zirconium and $2{\cdot}8M$ in perchloric acid, was prepared in a similar manner using 0·064 g of zirconyl chloride and 235 ml of 72% perchloric acid and diluting to 1 litre.

Hafnium perchlorate: 0·157 g of hafnium tetramandelate was heated to fumes with 5 ml of concentrated nitric acid and 5 ml of 72% perchloric acid. The residue was dissolved in 230 ml of 72% perchloric acid, and diluted to 1 litre with distilled water. The resulting solution was $2 \times 10^{-4}M$ in hafnium and $2{\cdot}8M$ in perchloric acid.

Other perchlorates, used in interference studies, were obtained from the G. Frederick Smith Chemical Company, U.S.A.

Procedures

Calcium, strontium and barium: Standard solutions of the nitrates were prepared by taking a known amount and diluting to 25 ml with distilled water. The solutions were heated to approximately 90°, and to each were added 40 ml of a 0·5% solution of ammonium bromanilate, dropwise, with stirring. (Ammonium bromanilate was used as precipitant because it is more soluble than the free acid.)

The precipitates were allowed to settle for about 15 min, and were then transferred to sintered-glass filters, dried for about 2 hr at 110°, and weighed.

General: A saturated aqueous solution of the reagent was added to solutions of various cations and anions.

RESULTS AND DISCUSSION

Calcium, strontium and barium: The results of the precipitations are given in Table I. In calculating the theoretical weights of the precipitates it was assumed that 1 ion of alkaline earth metal combines with 1 bromanilate ion to give compounds such as $CaC_6O_4Br_2$.

No further gravimetric studies were made, because many other cations form precipitates with the reagent (see next section), thereby limiting its usefulness.

General: In neutral or weakly acid solution precipitates were formed with the following: Ag^{I}, Hg_2^{II}, Hg^{II}, Pb^{II}, Bi^{III}, Cu^{II}, Cd^{II}, Sb^{III}, Sn^{II}, Mn^{II}, Zn^{II}, Ni^{II}, Co^{II}, Ca^{II}, Sr^{II}, Ba^{II}.

In strongly acid solution no precipitates were formed, but the following gave coloured solutions: Fe^{II}, Fe^{III}, Zr^{IV}, Hf^{IV}, Ti^{IV}, Th^{IV}, UO_2^{II}. The complexes of Ti^{IV}, Th^{IV} and UO_2^{II} were much lighter in colour than those formed with Fe, Zr and Hf.

On the basis of these tests it was decided that it would be useful to investigate

TABLE I.—PRECIPITATION OF BARIUM, STRONTIUM, AND CALCIUM BROMANILATE

Sample	Wt. of calcium compound, *g*	Wt. of strontium compound, *g*	Wt. of barium compound, *g*
1	0·2091	0·1101	0·0793
2	0·2099	0·1089	0·0781
3	0·2081	0·1086	0·0779
Average	0·2090	0·1092	0·0784
Calcd. wt.	0·2096	0·1094	0·0789

further the use of the reagent for the colorimetric determination of zirconium and hafnium.

Investigation of the zirconium-bromanilate complex

Job's method[11] of continuous variations, and the subsequent study made by Vosburgh and Cooper,[19] served to determine the nature of the complex formed by zirconium and bromanilic acid. A series of solutions was prepared in which the sum

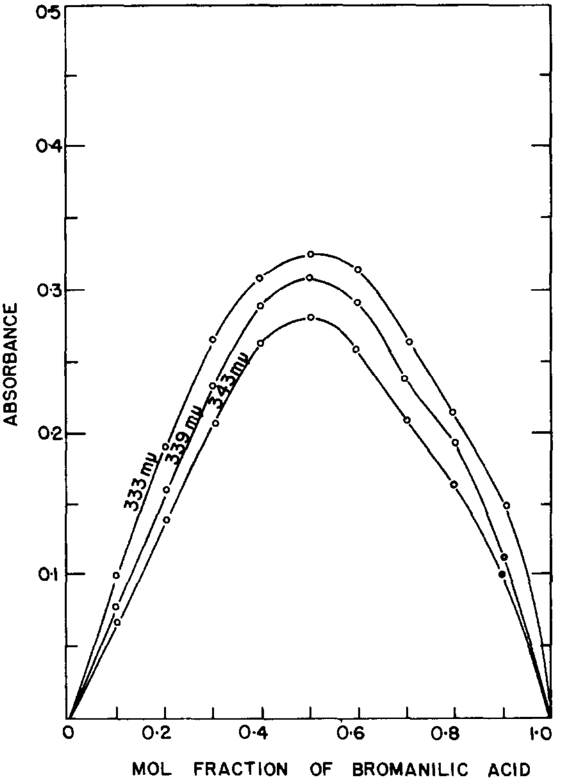

FIG. 1.—Identification of the zirconium bromanilate complex.

of the concentrations of the two reactants (zirconium perchlorate and bromanilic acid) was kept constant at 1·0 × $10^{-4}M$ but their ratio was changed. The concentration of perchloric acid was kept constant at 2·8*M*. The difference in absorbance between the measured values and those values that would have been observed at the same wavelength in case of no reaction was calculated according to the method of Vosburgh and Cooper. Fig. 1 shows this absorbance as a function of the ratio of the reactants at three selected wavelengths. Because a definite maximum was observed at $x = 5$ ($x/10$ = fraction of bromanilic acid), the formation of a 1:1 complex between zirconium and bromanilic acid was indicated. The shoulders on the right of the curves (Fig. 1) indicate that one or more higher complexes may be present to some extent, but this does not alter the usefulness of the method. Fig. 2 gives the absorption spectra of $2 \times 10^{-4}M$ bromanilic acid, and of solutions $1 \times 10^{-4}M$ in zirconium or in hafnium and $2{\cdot}8M$ in perchloric acid containing excess bromanilic acid.

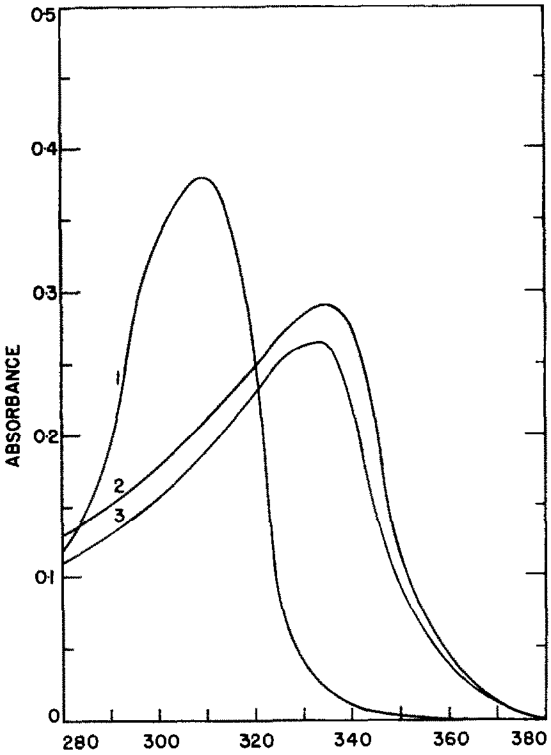

FIG. 2.—Absorption spectra:
1—bromanilic acid; 2—zirconium bromanilate complex;
3—hafnium bromanilate complex.

Solutions containing zirconium bromanilate complex at the concentrations used in the above experiments were stable, forming no precipitate even after several days. In solutions greater than $2 \times 10^{-2}M$ in zirconium a light blue precipitate formed on standing.

Hafnium perchlorate solution ($2 \times 10^{-4}M$) behaved in the same manner as the zirconium perchlorate solution. The absorbance maximum for the hafnium bromanilate complex occurred at the same wavelength as that for zirconium bromanilate complex.

Conformity to Beer's law

Bromanilic acid solution (15 ml of $2 \times 10^{-4}M$) was added to each of a number of 100-ml volumetric flasks. Standard zirconium perchlorate solution was then added in definite amounts varying from 0·05 to 0·60 mg of zirconium. Enough perchloric acid and distilled water were then added to make up 100 ml of solution which was 1*M* in perchloric acid. Absorbance measurements were made at wavelengths of 335 and 340 mμ as shown in Fig. 3. The reference solution consisted of $2 \times 10^{-4}M$ bromanilic acid in 2·8*M* perchloric acid. The wavelength of 335 mμ is recommended, because at this value the complex has its maximum absorbance and bromanilic acid has negligible absorbance.

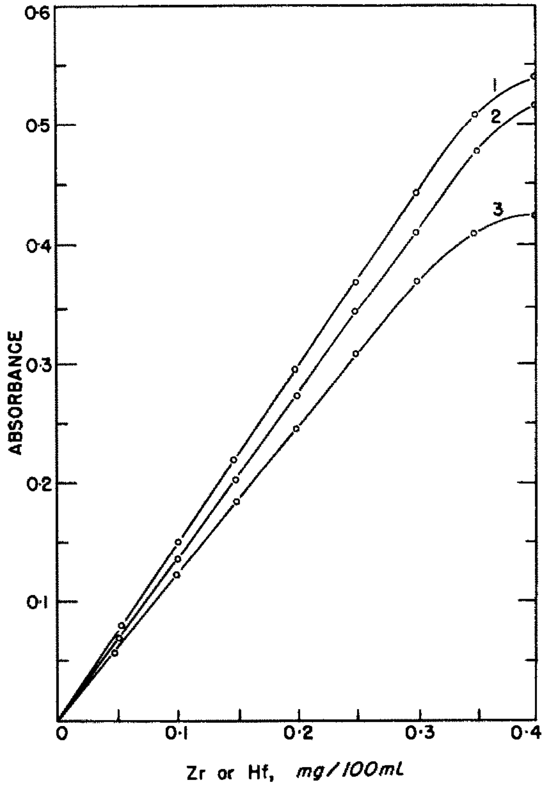

FIG. 3.—Standard curves for zirconium and hafnium:
1—zirconium at 335 mμ;
2—zirconium at 340 mμ;
3—hafnium at 335 mμ.

The standard curves shown in Fig. 3 indicate conformity to Beer's law in the concentration range 0·0–0·35 mg of zirconium in 100 ml. This covers a slightly greater range then chloranilic acid.[16]

The hafnium solutions also obeyed Beer's law (Fig. 3). Therefore, it is not possible to differentiate between zirconium and hafnium with this reagent and the method gives the sum of these two elements.

Effect of acid concentration

Bromanilic acid in water gives a purple colour which is quenched by addition of perchloric acid, hence the effect of varying the concentration of perchloric acid upon the absorbance of the complex was investigated. Consistent results were obtained in solutions 2·5*M*–3·5*M* in perchloric acid. High results are obtained in solutions less than 2*M* in acid and low results in solutions greater than 3·5*M*.

Effect of time

After mixing of the zirconium solution with the bromanilic acid reagent 15 min of standing were found to be sufficient to obtain accurate results. The absorbance did not change, even after 24 hr.

Table II.—Effect of diverse ions

Diverse ion	Added as	Wt. of diverse ion expressed as % of wt. of zirconium	Error, %
Fe^{III}	$Fe(ClO_4)_3$	10	2·0
		25	2·0
		50	2·0
		100	3·0
Th^{IV}	$Th(NO_3)_4$	10	2·0
		25	2·0
		50	3·0
		100	3·2
UO_2^{II}	$UO_2(C_2H_3O_2)_2$	10	2·0
		25	2·0
		50	3·3
		100	3·5
Ti^{IV}	$TiCl_4$	10	2·0
		25	3·0
		50	4·0
		100	4·8
Cr^{III}	$Cr(ClO_4)_3$	100	0·0
		500	2·2
Co^{II}	$Co(ClO_4)_2$	100	0·0
		500	3·1
PO_4^{3-}	Na_2HPO_4	10	2·0
		25	2·0
		50	2·1
		100	3·1
$C_2O_4^{2-}$	$Na_2C_2O_4$	10	2·0
		25	2·0
		50	10·0
		100	12·1
F^-	NaF	10	2·0
		25	3·6
		50	8·0
		100	10·1
SO_4^{2-}	Na_2SO_4	10	2·0
		25	3·9
		50	13·2
		100	20·2

Effect of diverse ions

To study the interference of diverse ions, absorbance measurements were made at 335 and 340 mμ on solutions containing 2 mg of zirconium per litre and varying concentrations of the diverse ion. Those ions that caused interference in the determination of zirconium are listed in Table II. Al^{III}, Ca^{II} and alkali metals showed no interference even when present in five-fold excess. Similarly, chloride, nitrate and acetate ions, added as sodium salts, showed no interference in this concentration.

Recommended general procedure

Bring the sample into solution by a suitable procedure. Add a measured excess of 72% perchloric acid, and evaporate down to copious fumes. Cool and dilute with water, then take an aliquot which does not contain more than 0·35 mg of zirconium. Transfer to a 100-ml volumetric flask, and add 15 ml of $2 \times 10^{-4}M$ bromanilic acid and sufficient 72% perchloric acid to make the final solution 2·8M in perchloric acid upon dilution. Shake and set aside for 15 min. Measure the absorbance at 335 mμ in 1·000-cm quartz cells, and determine the amount of zirconium from a standard curve.

Zusammenfassung—Bromanilsäure, 2,5-Dibromo-3,6-dihydroxychinon, fällt Barium, Calcium und Strontium quantitativ aus schwach saurer Lösung und bildet in überchlorsaurer Lösung mit Zirkonylionen einen farbigen Komplex mit einem Absorptionsmaximum bei 335 mμ. Das Beersche Gesetz gilt zwischen 0,0 und 3,5 ppm Zirkonium. Die besten Ergebnisse erzielt man in 2,8 m Überchlorsäurelösung. Der Effekt verschiedener Fremdionen wurde untersucht. Hafnium gibt dieselben Ergbnisse wie Zirkonium. Ferner stören Eisen(III), Thorium (IV), UO_2^{2+}, Ti(IV), Phosphat, Oxalat, Fluorid und Sulfat. Die durch verschiedene Mengen dieser Ionen verursachten Fehler wurden ermittelt. Eine Arbeitsvorschrift zur Zirkonbestimmung wird angegeben. Bromanilsäure ist empfindlicher bei der Zirkonbestimmung als Chloranilsäure und ist in etwas größeren Bereich anwendbar.

Résumé—L'acide bromanilique, ou 2,5-dibromo-3,6 dihydroxyquinone, précipite quantitativement le baryum, le calcium et le strontium à partir de solutions faiblement acides, et forme un complexe coloré avec les ions zirconyle en solution perchlorique. Le complexe présente un maximum d'absorption à 335 mμ. La lio de Beer est respectée entre 0,0 et 3,5 p.p.m. de zirconium. Les résultats optimaux sont obtenus dans solutions 2,8 M en acide perchlorique. L'influence de divers ions a été étudiée. Le hafnium donne des résultats identiques au zirconium. Les autres ions interférants sone Fe(III), Th(IV), UO_2(II), Ti(IV), phosphate, oxalate, fluorure et sulfate. On a déterminé les erreurs causées par des quantités variables de ces ions. On donne une technique de dosage du zirconium. Pour le dosage du zirconium, l'acide bromanilique est un réactif plus sensible que l'acide chloranilique, et il peut être utilisé dans un intervalle légèrement plus grand.

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THE DETERMINATION OF ESTER GROUPS BY ETHANOLYSIS

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Summary—Changes in boiling point, following the ethanolysis of an ester, give information about the number of ester groups present per molecule, the saponification equivalent, and, in the case of a polymeric ester, the degree of polymerisation. Methods of calculating the results are discussed and illustrative results are presented. The method is simple and rapid to apply. It yields results of only moderate accuracy, which, are however, sufficient for many purposes.

THEORY

WHEN an ester is dissolved in a large excess of boiling ethanol in the presence of a basic catalyst (*e.g.*, sodium ethoxide), ethanolysis proceeds to completion.[1-3] The examples to be considered are:

(i) $A(O{\cdot}CO{\cdot}R)_n + n\,EtOH \rightarrow A(OH)_n) + n\,RCO{\cdot}OEt$;

(ii) $R(CO{\cdot}OA)_n + n\,EtOH \rightarrow R(CO{\cdot}OEt)_n + n\,A(OH)$;

(iii) $HO(AO{\cdot}CO{\cdot}RCO{\cdot}O)_nA{\cdot}OH + 2n\,EtOH \rightarrow (n + 1)\,A(OH)_2 + n\,R(CO{\cdot}OEt)_2$.

All the solutions are considered to be sufficiently dilute to allow the change in the concentration of uncombined ethanol to be neglected.

Equations (i) and (ii) represent the ethanolysis of esters formed by the combination of a monobasic acid with an n-functional alcohol, and a polybasic acid with a monohydric alcohol, respectively. Equation (iii) is the reaction between ethanol and a polymer formed from a dihydric alcohol and a dibasic acid. Disregarding the ethanol molecules, the changes particularly attendant upon these reactions are: in cases (i) and (ii) from 1 to $n + 1$, and in the third example from 1 to $2n + 1$.

When these reactions are allowed to take place in an ebulliometer, the boiling point elevations before and after the reactions will be in the above ratios (the ethanol content may be regarded as sensibly constant). It is assumed that the original ester, the liberated alcohol and the ethyl esters are all non-volatile relative to ethanol. Thus, in principle, a method is provided for counting the number of ester groups per molecule. Because solutions of esters with molecular weights higher than *ca.* 700 are frequently non-ideal, and the elevations observed are subject to an apparent systematic zero error, the detailed calculations in individual cases are not always straightforward. These calculations are dealt with in the following sections.

RESULTS AND DISCUSSION

The symbols employed have the following meanings:

w = weight of original ester added to ebulliometer;

T_o = initial boiling point elevation;

T_f = elevation after ethanolysis;

K = ebulliometric constant for the appropriate volume of ethanol or other solvent;
M_{T_0} = molecular weight calculated from initial elevation;
M_s = molecular weight calculated from the slope of the linear part of the graph of elevation *vs.* w (in ethanol or other solvents);
M_n = molecular weight calculated by assuming that the number of ester groups per molecule is known;
n = number of ester groups per molecule;
S_e = saponification equivalent of ester found ebulliometrically;
S_h = saponification equivalent found by hydrolysis with KOH followed by back titration of the excess alkali.

Three sets of results are presented. The first two illustrate the general applicability of the method and the accuracy attainable. A number of glycerides and edible fats were investigated because methods for their characterisation are well-known and are available for comparison. Moreover, these mixtures are peculiarly subject to the errors inherent in ebulliometry. The results provide an opportunity for discussing the critical treatment of data of this kind. The third set of results illustrates the application of the method to a polymeric material, a field in which it may prove to have most usefulness.

Table I illustrates the dependence of w/T_0 on concentration, and the correction achieved by employing Kw/M_s in place of T_0. The variation of w/T_0 for the higher triglycerides arises from a number of factors, the two most important being association (which does not occur in acetone), and an error arising from their surface activity, which will be the subject of a separate publication. The fact that w/T_f is

TABLE I.—ETHANOLYSIS OF ESTERS

Concentration, *mg/ml*	$(T_f/T_0) - 1$	n	M_{T_0},	M_n	M_s	S_e	S_h
				Castor oil			
5·29	1·48	2·99	584	956	955[a]	320	307
52·41	2·81	3·05	898	942		312·5	
				Tristearin			
20·83	1·81	3·13	558	816	840[a]	269	276
36·74	2·35	3·07	685	823		274	
32·60	—[b]	3·04	—	831		276	
				Tripalmitin			
23·16	2·68	3·02	757	821	825[a]	273	269
27·84	2·42	3·06	700	814		270	
38·32	2·60	3·03	735	816		272	
51·20	3·08	3·04	825	818		271	
23·25	—[b]	3·11	—	805		265	
				Glyceryl tribenzoate			
21·83	3·02	2·95	405	403	401	136	135·4
30·70	2·89	3·02	388	400		133	
				Diethyleneglycol distearate			
18·69	1·73	2·07	527	596	616	300	310
31·22	1·79	2·06	557	598		301	

[a] Determined in acetone. [b] Ester added to sodium ethoxide solution.

independent of concentration indicates that the low molecular weight ethyl esters and the glycerol are producing almost ideal boiling point elevations. This is also shown by the relative constancy of M_n and its agreement with M_s. In Table I the following relationships have been employed:

$$n = (T_f M_s/Kw) - 1;$$

$$M_n = (n + 1)Kw/T_f \text{ (assuming } n \text{ to be known, } e.g., \text{ 3 for the triglycerides);}$$

$$S_e = Kw/(T_f - Kw/M_s).$$

Table II contains a similar set of figures obtained for a series of edible fats. The somewhat low figures for n probably result from the presence of unsaponifiable material, including any free fatty acid; 1% of free acid would result in 0·1 units change in n. The acid and any other unsaponifiable material will increase T_0 without having a proportional effect on T_f. Because the free acids have a molecular weight about one third that of the glyceride, 1% by weight is equivalent to 3 moles %, or a 3% increase in T_0 relative to T_f, hence a 0·1-unit change in n. Figures for the free acidity are given in Column 5. The standard deviation, $\pm\sqrt{\delta/n - 1}$, between S_e and S_h for all the results in Tables I and II is ±2·0%, and in each case n provides an unambiguous count of the number of ester groups per molecule.

TABLE II.—ETHANOLYSIS OF EDIBLE FATS

	M_s	n	S_e	S_h	Acidity, %
Cocoa Butter	845	2·90	292	290	1·1
Coberine	854	2·97	287	290	0·13
Illipe Butter	845	2·80	302	292	2·8
Cocoa Shell Butter	864	2·92	296	294	0·15
Hardened Palm Kernel Oil	674	2·94	229	231	1·0
Extracoa	680	2·87	237	227	0·2

In Table III are collected a number of results obtained for samples of polydiethylene adipate. The formula for these polymers was given as:

$$HO{\cdot}(CH_2)_2O{\cdot}(CH_2)_2[O{\cdot}CO{\cdot}(CH_2)_4CO\ (CH_2)_2O(CH_2)_2]_nOH$$

so that $M = 216n + 106$, and could be calculated if n (the degree of polymerisation) were known. The number of moles of product formed per mole of polymer is $2n + 1$, hence:

$$T_f/T_0 = 2n + 1 \quad \text{and} \quad (T_f - T_0)/2T_0 = n$$

Thus, it is possible to find n and M without weighing the sample. For this series of polymers the systematic error in boiling point referred to in the theoretical section amounted to 0·008° (calculated from resistance changes, which are the actual measurements made), which must be deducted from the observed values of T_0; when these are thus corrected they give the figures for n in Column 1. Column 2 lists M_n, the molecular weight calculated from the degree of polymerisation.

T_f is related to the molecular weight and n by the equation:

$$T_f = (2n + 1)Kw/M.$$

Therefore $Kw/T_f = M/(2n + 1) = (216n + 106)/(2n + 1)$. This quantity varies between 107·6 for $n = 2$ and 108 for $n = 10$; the error involved in assuming that it is constant at 108 is less than the experimental error of the method, hence:

$$K' = T_f(108)/w.$$

This quantity is found in practice to be almost constant. K' measured in this way is higher than K obtained by employing low molecular weight compounds as standards. The polymer molecular weights agree, however, with those found from n; these are listed as M_e in Column 3. In Column 4 are the molecular weights found by chemical assay of the terminal hydroxyl groups.

TABLE III.—ETHANOLYSIS OF POLYDIETHYLENE ADIPATE

n	M_n	M_e	M_{OH}
4·25	1026	1050	1005
6·35	1542	1470	1385
8·0	1830	1820	1875
8·45	1930	1950	2310
9·15	2086	2100	2750

The method is only of moderate accuracy ($r = \pm 2\%$) when compared with conventional techniques. Its principal utility arises from the circumstance that it is both rapid and simple to apply. Thus, in laboratories which are not regularly engaged in the analysis of fats and waxes it permits a quick, if admittedly rough, characterisation, and often the information thus obtained would be sufficiently accurate for many purposes. It may also be employed for the counting or detection of ester groups in substances of unknown structure. Finally, its use in the polyester field may provide alternative and additional information to that available from end-group assay, a method which itself is liable to some uncertainty.

EXPERIMENTAL

The ebulliometer was a commercially available instrument based upon that described by the author.[4] Two ebulliometers were placed in opposite arms of a Wheatstone bridge to compensate for barometric changes.

The essential precaution for obtaining consistent results is the exclusion of moisture. The ethanol used was dried by means of magnesium ethylate,[5] and stored over Hi-Drite, a form of anhydrous calcium sulphate.* The sodium ethoxide was prepared by dissolving 0·5 g of metallic sodium in 20 ml of the dry ethanol. Ten ml of ethanol were used in the ebulliometer, and 1 g of Hi-Drite was added to the solvent; this removed traces of moisture added with the sample and ensured that any water present remained at a low and constant concentration.

Up to five additions of approximately 0·1 g of ester were made and the elevations recorded. If a linear plot of T_0 versus concentration was obtained, the slope was used to calculate M_e. When curvature persisted, M_e was found in another solvent.

The ethoxide was introduced by collecting a drop on a platinum spiral attached to a glass rod, and immersing the spiral in the boiling solution. Usually 3 drops were added, and this was sufficient to bring the reaction to completion within 20 min. When the reading on the galvanometer had remained constant for 5 min it was assumed that the reaction was complete, and T was recorded. A further 3 drops of ethoxide solution were then added, and the small elevation deducted from that previously recorded. (This correction never amounted to more than 2% of the total elevation.)

Acknowledgement—The results quoted in Table II are based on results obtained by G. M. Pierce, Dip.Tech., as part of a project carried out in this department. The fats were kindly supplied by Messrs. J. S. Fry and Sons Ltd., Sommerdale, Bristol, England.

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* Hi-Drite, Ltd., 17 New Bond Street, London W.C., England.

Zusammenfassung—Die Änderung des Siedepunkts nach Äthanolyse eines Esters liefert Informationen über die Anzahl von Estergruppen in einem Molekül, das Verseifungsäquivalent und im Fall eines polymeren Esters über den Polymerisationsgrad. Methoden zur Berechnung der Ergebnisse werden diskutiert und zur Illustration einige Ergebnisse angegeben.

Résumé—Les variations de point d'ébullition qui résultent de l'éthanolyse d'un ester donnent des renseignements sur le nombre de groupes ester présents dans la molécule, sur l'équivalent de saponification et, dans le cas d'un ester polymère, sur le degré de polymérisation. On discute des méthodes de calcul des résultats et on présente des résultats à titre démonstratif.

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SHORT COMMUNICATION

Lead tetra-acetate in anhydrous acetic acid as an oxidising agent

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EARLIER investigations[1] of oxidation-reduction titrations in acetic acid medium have been extended to an examination of reactions of lead tetra-acetate, which are described in the present communication. Lead^{IV} was first employed in the inorganic field by Tomiček *et al.*,[2] and quite recently[3] a kinetic study of the oxidation of Co^{II}, Ce^{III} and Mn^{II} acetates has been carried out.

EXPERIMENTAL

Reagents

Stock solution of Pb^{IV}: An 0·05*M* lead tetra-acetate solution was prepared by dissolving in glacial acetic acid the salt obtained by the method of Bailar.[4] The concentration was determined iodometrically in aqueous solution.

Reducing agents: Solutions in acetic acid of Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, $Hg_2(ClO_4)_2$, NH_4SCN, all about 0·05*M*, were prepared from chemically pure salts. The solvent used was analytical-reagent acetic acid without further purification. Its content of water is less than 0·3%.

Apparatus

Potentiometric titrations were performed using a Metrohm model E 353 apparatus, fitted with an aqueous calomel cell as reference electrode. This electrode was connected to the titration cell through an aqueous K_2SO_4 saturated agar bridge, one arm of which terminated in an asbestos plug, and was constantly maintained immersed in glacial acetic acid.

The amperometric apparatus was that described previously.[1]

RESULTS

The results of titrations are tabulated in Table I.

Sodium sulphite is easily oxidised in the cold by lead tetra-acetate in the presence of 1*M* sodium acetate, and quantitative results which differ from the theoretical value by less than 1% are obtained. The molar ratio between oxidant and reductant is 1:1. The course of the titration can be followed potentiometrically or amperometrically. In the latter case the curve obtained is characteristic of the titration of an irreversible system with a reversible one. In the absence of sodium acetate the rate of the reaction is extremely low. The reaction does not occur in the presence of perchloric acid.

Iron^{II} perchlorate is easily oxidised by lead tetra-acetate if either sodium acetate or perchloric acid is present; the equivalence point corresponds to the molar ratio $Pb^{IV}:Fe^{II} = 1:2$. By the amperometric method, at a potential difference (ΔE) of 0·3 v, the curve obtained shows that the titration involves a reaction between two reversible systems. The equivalence point determined by either method is in agreement with the theoretical value.

In the presence of sodium acetate, although precautions are taken to avoid the oxidant action of oxygen dissolved in the solvent, the error is relatively high (3%); potentiometrically, a lowering of the oxidation-reduction potential of the system Fe^{III}/Fe^{II} is observed.

The oxidation of *arsenic trichloride* is carried out in anhydrous acetic acid in the presence of perchloric acid. During the titration a turbid solution forms because of the precipitation of lead^{II} chloride. When the molar ratio oxidant:reductant is 1:1, the equivalence point of the titration is reached, according to the equation:

$$Pb^{IV} + AsCl_3 \rightarrow PbCl_2 + As^{V} + Cl^-.$$

Further addition of Pb^{IV} causes the precipitate of $PbCl_2$ to dissolve. With $Pb^{IV}:AsCl_3 = 5:2$ the solution becomes transparent, and the potentiometric curve shows a second jump. The dissolution of $PbCl_2$ during the second part of the titration is the result of oxidation by lead tetra-acetate of Cl^- to Cl_2 according to the reaction:

$$PbCl_2 + Pb^{IV} \rightarrow 2\,Pb^{II} + Cl_2.$$

Table I.—Lead tetra-acetate in the titrimetric determination of some reducing agents

Reducing agent	CH_3COONa, *M*	$HClO_4$, *M*	Taken, *mg*	Found, *mg*	Error *mg*	Error %
SO_3^{2-}	1		8·56	8·56	—	—
	1		8·81	8·80	0·01	−0·1
	1		17·61	17·45	0·16	−0·9
	1		13·20	13·20	—	—
Fe^{2+}	0·1		10·44	10·19	0·25	−2·4
	0·1		8·71	8·48	0·23	−2·6
	0·1		4·36	4·24	0·12	−2·7
		0·7	6·59	6·63	0·04	+0·6
		0·7	13·18	13·40	0·22	+1·6
		0·9	19·77	19·88	0·11	+0·5
As^{3+}	1		4·42	4·35	0·07	−1·6
	1		3·53	3·45	0·08	−2·2
	1		6·18	6·10	0·08	−1·3
		1	2·20	2·20	—	—
		1	4·42	4·44	0·02	+0·4
		1	5·32	5·33	0·01	+0·2
SCN^-	1		18·56	18·27	0·29	−1·5
	1		37·11	36·51	0·40	+1·1
	1		55·67	54·82	0·15	+0·3

At the second equivalence point the presence of elementary chlorine in the solution has been proved by bubbling nitrogen into two containers in series, the first containing the solution under examination and the second a dilute solution of fluorescein and potassium bromide. The formation of red eosin in the latter demonstrates the presence of the molecular halogen in the former. The reaction proceeds more slowly in a warm solution of 1*M* sodium acetate, but the first equivalence point (the only one visible under such conditions) can still be easily determined.

In the amperometric titration, the corresponding curve is characteristic of an irreversible system titrated with a reversible one. During the titration the solution remains transparent on account of the solubility of $PbCl_2$ in the acetic acid added with the 1*M* sodium acetate.

Ammonium thiocyanate can be oxidised by Pb^{IV} in warm, anhydrous acetic acid solution; the reaction is extremely slow but quantitative results are obtained if 1*M* sodium acetate is present. At the equivalence point the molar ratio oxidant:reductant is 3:1. The reaction between Pb^{IV} and SCN^- leads to the formation of CN^- and SO_4^{2-} ions. The sulphate ion, reacting with Pb^{II} from reduction of the Pb^{IV}, forms an easily appreciable precipitate of $PbSO_4$.

The amperometric titration gives a curve characteristic of a titration between an irreversible and a reversible system.

In the presence of perchloric acid the reaction is very slow, and quantitative results cannot be obtained.

Mercurous perchlorate cannot be oxidised, and *antimony trichloride* is oxidised incompletely in perchloric acid solution.

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Summary—A systematic study of the oxidation-reduction titration by lead tetra-acetate of various inorganic ions in anhydrous acetic acid medium is described. Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN and $HgClO_4$, all in the presence either of $HClO_4$ or of CH_3COONa, have been investigated. The reactions were followed by potentiometric and amperometric techniques.

Zusammenfassung—Es wird eine systematische Untersuchung der Redox Reaktion zwischen Blei tetraacetat und Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN und $HgClO_4$ beschrieben. Der Verlauf der jeweiligen Reaktion, mit $HClO_4$ oder CH_3COONa, wurde potentiometrisch und amperometrisch verfolgt.

Résumé—Une étude systématique a été effectuée sur les titrations redox du acétate plombique en milieu acétique anhydre, avec divers composés minéraux. Les réducteurs Na_2SO_3, $Fe(ClO_4)_2$, $AsCl_3$, $SbCl_3$, NH_4SCN et $HgClO_4$ tous en presence ou de $HClO_4$ ou CH_3 COONa, ont été etudiés. La réduction du l'acétate plombique a été suivie potentiometriquement et amperometriquement.

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LETTERS TO THE EDITOR

Nucleation and precipitation of silver chloride solutions

SIR,

Klein, Gordon and Walnut,[1] studying the crystallisation of supersaturated solutions of silver chloride, suggested that de-ionised water from the ion-exchange column they used for purification in some of their experiments contained an impurity which inhibited nucleation, but which was removed, by adsorption, when their solutions were passed through a membrane filter. Nancollas and Purdie[2] have recently compared the results of Klein, Gordon and Walnut with those of Davies and Jones,[3] who used distilled water for their experiments, and they mention the different methods of water purification employed as a possible source of the difference between the critical supersaturation ratios quoted by these authors. We believe, however, that this difference is caused by the other different experimental techniques employed, because even when using distilled water, without filtration, Klein, Gordon and Walnut still find a significantly higher value for the critical supersaturation ratio. We also believe that the effects that Klein, Gordon and Walnut observed in their own experiments are more simply explained on the basis of the known absence from de-ionised water of the nucleating particles present in ordinary distilled water than on the basis of hypothetical impurity in the de-ionised water. Evidence of the difference between these two kinds of water can easily be obtained by passing a light through the two liquids in a darkened room, when no scattered light is visible to the eye from particles in water from a good quality mixed-bed ion-exchange column.[4] We have used this property for preparing particle-free solutions for work with solutions of radioisotopes of very high specific activity which adsorb on to particulate matter in solution.[5]

Klein, Gordon and Walnut[1] showed that nucleation of silver chloride was easier (*i.e.*, took place at lower supersaturation) with the use of laboratory distilled water than with de-ionised or redistilled water which had been filtered through a membrane filter, and easier with such filtered water than with de-ionised water, unfiltered. The difference between unfiltered distilled and unfiltered de-ionised water is explained simply, in our view, by the particle-free nature of the de-ionised water; we suggest that the effect of the membrane filter may have been to bring both kinds of water to the same standard of cleanliness, by removing the particulate matter originally in the distilled water, but also contributing some particles in both cases from adventitious dirt and possibly slight disintegration of the filter material. Thus, the critical supersaturation ratio is virtually the same for either kind of filtered water (1.71–1.74), being higher than the value for distilled water (1.44) and lower than that for de-ionised water (2.04). We have found that it is easy to contaminate water and solutions with particles by the use of a filtration procedure intended to clean them, and such processes should always be monitored by visual observation of scattered light to check that no particles are being introduced from the receiving vessels or the filter material.

The theory that an increased critical supersaturation ratio is an indication of higher purity, rather than of the presence of an "anti-nucleating" impurity, is consistent with other results in this field, such as those of Collins and Leinweber[6] (quoted by Nancollas and Purdie[2]) on the critical supersaturation ratio of barium sulphate.

Klein, Gordon and Walnut[1] showed in support of their theory that the presence of eosin did inhibit silver chloride precipitation in their experiments, but this is not very convincing evidence, in that (*a*) there is no supporting information on the impurity content of their de-ionised water, (*b*) the theory does not explain the difference they observed between unfiltered and filtered distilled water, and (*c*) we have found that eosin adsorbs strongly on a mixed-bed ion-exchange column.

Although it is not easy to disprove the theory that an organic impurity from the resin column caused the effects observed, it is suggested that the known facts about the filtration properties of ion-exchange columns are sufficient to explain all the phenomena observed.

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15 *May* 1964

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An international language?

SIR,

WOULD it not be a good idea, and in keeping with the international nature of *Talanta*, to accept and encourage articles written in some international language such as Esperanto or Interlingua?

I confess that I know nothing at all about Esperanto and very little about Interlingua. However, I have seen articles written in the latter language which I have been able to read, without a dictionary, with very little difficulty. I believe that dictionaries of Interlingua are available. If this is correct, I, for one, would be very happy to spend an extra hour or two when I submit my next contribution translating it into Interlingua.

The arguments in favour of Interlingua instead of English as a universal language of science are chiefly two, in my opinion. The learning of English requires considerable effort in regard to spelling, whereas Interlingua has no irregularities either in spelling or grammar. Secondly, national pride will always cause some people to prefer their native language over English or any other living language. In contrast to this, I should hope that any scientist would take pride in presenting his work in a universal language.

It may be argued that Interlingua, which is very similar to Spanish, is helpful only to persons who know one of the languages derived from ancient Latin. This is not true. A Russian or a Japanese could learn Interlingua more easily than English, French or German because of the aforementioned irregularities in the latter languages.

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COPRECIPITATION STUDIES OF SOME TERVALENT METAL IONS WITH ALUMINIUM TRIS-(8-HYDROXYQUINOLATE)

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Summary—The coprecipitation of tracer quantities of radioactive scandium, yttrium, cerium and indium with milligram-quantities of aluminium has been studied. The aluminium was precipitated as the tris-(8-hydroxyquinolate) by slow isothermal evaporation of aqueous acetone solutions. In the presence of ammonium acetate less than 0·5% of the scandium, yttrium or cerium coprecipitates. The fraction of tracer entrained is approximately independent of the fraction of the aluminium precipitated. Surface adsorption of tracer on the glass container or on the precipitate does not occur even when all of the acetone had been removed. Milligram-quantities of yttrium and cerium give gelatinous precipitates from similar systems containing acetone (aluminium absent); the dried yttrium precipitate has the composition $Y(C_9H_6NO)_2{\cdot}OCOCH_3$. Even milligram-quantities of yttrium, when present, tend to be rejected by the aluminium precipitate. In the absence of acetate but under conditions where milligram-amounts of yttrium would precipitate, for 10–90% precipitation of the aluminium, yttrium coprecipitation ranges from 1 to 6%. Removal of all of the acetone results in considerable surface adsorption of the tracer. From acetate solutions fractional precipitation of indium as tracer in the range 10 to 90% is only slightly different (lower) than the corresponding fractional precipitation of the aluminium. D and λ, the coefficients calculated assuming a homogeneous and a logarithmic distribution, respectively, within the crystals, are approximately equal and constant. Milligram-amounts of indium give a granular precipitate by the slow evaporation procedure from acetate solutions.

Recently a method has been described for the precipitation of aluminium[1] and other metal ions[2] as 8-hydroxyquinolates by slow isothermal evaporation of solvent from a buffered aqueous acetone system containing all of the reactants. The method is claimed to give aluminium tris-(8-hydroxyquinolate) comparable in particle size and in purity to that obtained by controlled hydrolysis of 8-acetoxyquinoline[3] in solutions containing aluminium. Slow isothermal evaporation of solvent followed immediately by filtration usually results, as do homogeneous methods of precipitation,[4] in coprecipitated impurity following a logarithmic (Doerner-Hoskin's) distribution in the precipitate if isomorphous replacement of the major by minor constituent is possible or if anomalous mixed crystal formation occurs.[5]

The acetone, in the method referred to above, presumably only serves to solvate the 8-hydroxyquinolates of aluminium or other metal ions which would normally precipitate from solution in its absence. It seemed of interest, therefore, to examine

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the coprecipitation of tracer quantities of other tervalent metal ions with aluminium precipitated by this method. Accordingly, scandium, yttrium, cerium and indium were chosen for this study and their distributions between the solution and the precipitate were followed by using radioactive isotopes in conjunction with suitable counting equipment. Distributions of tracer in each system were determined for various fractions of aluminium precipitated, and the coefficients, D and λ, appropriate to a homogeneous and logarithmic distribution, respectively, were calculated from the relations

$$\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{cryst.}} = \mathrm{D}\left(\frac{\text{tracer}}{\text{carrier}}\right)_{\text{soln.}} \tag{1}$$

and

$$\log\left(\frac{\text{total tracer}}{\text{tracer in soln.}}\right) = \lambda \log\left(\frac{\text{total carrier}}{\text{carrier in soln.}}\right) \tag{2}$$

Under the conditions employed, partial or complete precipitation of macro amounts of these elements (as 8-hydroxyquinolates) might be expected to occur (Table II).

EXPERIMENTAL

Reagents

Unless otherwise stated, reagents were of analytical reagent grade.

8-Hydroxyquinoline. A fresh 4% solution was prepared in acetone every 2 days.

Acetone. Some experiments were carried out using reagent grade acetone but most were performed with technical solvent acetone (redistilled) without any apparent effect on the results.

2M Ammonium acetate. 154 g of ammonium acetate were dissolved in 1 l. of water.

Aluminium solution. Potassium aluminium sulphate was dissolved in water to give a solution containing about 1 mg of aluminium/ml. It was standardised using 8-hydroxyquinoline.[6]

Radioactive isotopes. These were obtained from the Radiochemical Centre, Amersham, England. Yttrium-91 and cerium-144/praseodymium-144 were "carrier free" in dilute hydrochloric acid but scandium-46 and indium-114m (obtained as chlorides) contained inactive isotopes of these elements. Each stock solution was diluted with 0·1*M* hydrochloric acid to reduce the radioactivity to a level suitable for use in the procedure outlined below.

Apparatus

Yttrium-91, cerium-144/praseodymium-144 and indium-114m were counted as liquid samples in a Geiger-Müller counter of the annular type (20th Century Electronics type M6H). Scandium-46, also in a liquid form, was determined using a γ-scintillation counter consisting of a sodium iodide (thallium activated) crystal (1·5 in. diam. × 1 in. deep) in conjunction with a photomultiplier tube, a single channel pulse-height analyser and the usual scaling equipment. The photopeaks corresponding to the 0·89- and 1·12-MeV γ-rays were used together, for counting purposes.

General procedure

Ten ml of aluminium solution and 2 ml of tracer solution were pipetted into a 250-ml pyrex-glass beaker. Forty ml of ammonium acetate, 60 ml of acetone and 5 ml of 8-hydroxyquinoline solution were added in that order. The initial radioactivity was measured by counting 10 ml of such mixtures in the Geiger-Müller counter when yttrium, cerium or indium were used as tracers. A 5-ml sample was taken for counting scandium solutions with the scintillation counter.

The beakers were immersed in a thermostat at 50 ± 0·5° and the contents stirred continuously. At various stages of the precipitation a beaker was removed and the precipitated aluminium tris-(8-hydroxyquinolate) collected in a weighed sintered glass crucible (porosity No. 4), washed well with cold water, dried at 130° and weighed. A weighed portion (about 70–90%) of the precipitate was transferred to a beaker and dissolved in 4 ml of 4*M* hydrochloric acid and 15 ml of acetone. Ten ml of 2*M* ammonium acetate were then added and either 5 ml (for scandium) or 10 ml of the mixture counted.

The usual corrections for paralysis time of the counting equipment and background counting rates were made and the percentage of tracer, *W*, coprecipitated with the aluminium was calculated from the relation

$$W = \frac{x}{yz} \times \frac{29}{117} \times 100$$

where x is the final and y the initial counting rate (corrected as described) and z is the fraction of the precipitate taken for the final count.

Because the solution composition is kept almost the same for the initial and final counts, self-absorption corrections are avoided. Corrections for departures from volume additivity were also made unnecessary by following the procedure described. In experiments with scandium and indium as tracers and when inactive yttrium was added in milligram-amounts, a correction was made for the presence of the "tracer" in order to compute the fraction of the aluminium precipitated from the weight of the precipitate. This correction was always small (less than 2% of the total precipitate weight) in experiments with scandium and indium.

RESULTS AND DISCUSSION

The results presented in Table I show that the coprecipitation of scandium, yttrium and cerium (all at very low concentrations) with aluminium is very approximately constant, independent of the fraction of aluminium precipitated, and independent of the tracer element. D and λ values are not recorded because, as would be expected from the results, they both vary considerably. Table II shows pH values for the onset and completion of precipitation of macro amounts of the tracer elements used here.

TABLE I.—COPRECIPITATION OF TRACER AMOUNTS OF SCANDIUM(III), YTTRIUM(III) AND CERIUM(III) WITH ALUMINIUM TRIS-8-HYDROXYQUINOLATE

Al pptd., %	Sc[a] copptd., %	Al pptd., %	Y[b] copptd., %	Al pptd., %	Ce[b] copptd., %
9·25	0·438	13·2	0·398	14·7	0·351
18·3	0·414	20·6	0·348	21·6	0·306
31·6	0·461	25·2	0·402	33·4	0·298
39·4	0·367	33·8	0·427	44·0	0·409
51·3	0·423	41·3	0·247	54·8	0·290
55·8	0·404	49·5	0·446	61·4	0·367
68·1	0·317	60·8	0·478	70·2	0·339
80·0	0·509	89·3	0·515	74·4	0·293
85·4	0·477	90·7	0·431	82·9	0·455
96·1	0·573	95·5	0·417	88·6	0·401
98·7	0·747	99·7	0·496	91·7	0·571
—	—	100·0	1·04	94·3	0·507

[a] $1{\cdot}2 \times 10^{-7}$ moles (0·0054 mg) of scandium present in the system during each precipitation.

[b] ^{91}Y and ^{144}Ce were 'carrier free'.

TABLE II.—pH OF PRECIPITATION OF METAL IONS WITH 8-HYRDOXYQUINOLINE

Metal complex	pH for precipitation Initial	Complete	Acetic acid–acetate conc.[a]	Ref.
$Sc(C_9H_6NO)_3{\cdot}C_9H_7NO$	3·90[b]	6·3	0·54	7
$Y(C_9H_6NO)_3$	3·84	4·78	0·07	8
$Ce(C_9H_6NO)_3$	4·44	5·55	0·08	9
$In(C_9H_6NO)_3$	2·7	—	0·08	This work

[a] Molar and approximate; calculated from data in the papers quoted.

[b] The pH at which the precipitate just dissolves.

Experiment showed that evaporation of the acetone from an aqueous acetone solution of the composition described in the general procedure above gave, on removing the precipitated metal 8-hydroxyquinolate, a filtrate having a pH about 6·3. At this pH, therefore, scandium, yttrium and cerium(III) would be expected to precipitate if present in milligram-amounts and to coprecipitate readily with aluminium. However, acetate present in high concentration in the coprecipitation experiments described may prevent or partly prevent the formation of the expected 8-hydroxyquinolates of the tracer elements although not interfering with the formation of the aluminium complex. (It may be noted that the acetate-acetic acid concentration used in much of the experimental work described here is somewhat higher than that normally employed in the direct precipitation of aluminium or by Howick and Jones[1,2] in their experiments.) Accordingly, with yttrium as tracer, additional experiments were performed in which ammonium acetate was replaced by 15 ml of 0·100*M* sodium hydroxide and 25 ml of water in the procedure already outlined. Evaporation of the acetone from a solution thus prepared gave, on separating the precipated metal complexes, a filtrate having a pH of about 9·5. Table III gives the results of these experiments. It will be observed that whilst the percentage coprecipitation is higher than in the presence of acetate, it is still quite low, amounting to only about 1% for 10% of the aluminium precipitated and only 6% for over 90% precipitation of the carrier. The results suggest, therefore, that acetate alone is not responsible for the low coprecipitation observed. Table III (column 3) shows that for up to at least 95% precipitation of the aluminium the ratio of the fractions of yttrium to aluminium in the precipitate is very approximately constant. A similar result was obtained previously by Gordon, Peterson and Burtt[11] in a study of the coprecipitation of thallium(I) with silver chloride precipitated from homogeneous solution. Their results and those in Table III would suggest a homogeneous distribution of tracer within the carrier lattice; in neither series of experiments were either of the distribution laws [equations (1) and (2)] obeyed.

TABLE III.—THE COPRECIPITATION OF YTTRIUM-91 WITH ALUMINIUM BY ISOTHERMAL EVAPORATION OF SOLUTIONS[a]

Al pptd., %	Y copptd., %	(Y/Al)cryst. $\times 10^2$	$D \times 10^2$	$\lambda \times 10^2$
12·8	0·91	7·1	6·3	6·53
15·0	1·26	8·40	7·23	7·97
19·8	1·43	7·22	5·87	6·30
34·1	2·48	7·27	4·91	6·19
48·2	3·56	7·39	3·97	5·53
53·2	4·14	7·78	3·80	5·55
81·0	4·59	5·67	1·13	2·83
94·5	6·18	6·54	0·38	2·2
100	36·9	36·9	—	—
100	44·1	44·1	—	—

[a] Solutions prepared from 10 ml of aluminium + 25 ml of water + 15 ml of 0·100*M* NaOH + 5 ml of 8-hydroxyquinoline + 2 ml of ^{91}Y solution + 60 ml of acetone.

For complete precipitation of aluminium (Table III), the ratio of the fractions of yttrium to aluminium in the precipitate increases very considerably, suggesting that yttrium is deposited on the surface of the aluminium precipitate on complete removal of acetone. As might be expected, this deposition was not confined to the precipitate surface; appreciable and approximately constant losses occurred to the walls of the beaker as the results of experiments recorded in Table IV show. (There is an estimated uncertainty of about 5% in the values given in column 4.)

Losses from solutions containing acetate were negligible. It was demonstrated in preliminary experiments that adsorption of tracer from aqueous acetone solutions prepared according to the directions given in the experimental part (or with acetate replaced by sodium hydroxide), was negligible even after standing for 3 or 4 hr in glass beakers. (Polythene was found to be unsatisfactory for the work described in this paper because of the tendency of the aluminium precipitate to adhere to the surface.) It may, therefore, be concluded that tracer quantities of yttrium [and probably also scandium and cerium(III)] are prevented from undergoing surface adsorption on glass or on the precipitate by acetone or by acetate ions (expts. 5, 6 and 7, Table IV).

TABLE IV.—THE RECOVERY OF YTTRIUM FROM SYSTEMS CONTAINING ALUMINIUM TRIS-(8-HYDROXYQUINOLATE)

No.	% Total ^{91}Y Filtrate	% Total ^{91}Y Ppt.	% Total ^{91}Y accounted for	Duration of evaporation, *hr*
1	45	33	78	2·0
2	60	20	80	2·5
3	53	21	74	3·25
4	49	24	73	6·17
5	96	0·5	97	1·5
6	97	0·5	98	2·0
7	96	0·7	97	2·5

1, 2, 3, and 4 were performed according to the general procedure but with 15 ml of 0·100*M* NaOH + 25 ml of water replacing the 40 ml of 2*M* ammonium acetate. 5, 6, and 7 were performed according to the general procedure. Very little if any acetone remains after evaporation for 2·0 hr.

Coprecipitation experiments were performed in which varying amounts of inactive yttrium were present. Corresponding molar increases in 8-hydroxyquinoline were made to these mixtures which were otherwise prepared according to the *General procedure*. It was found that when yttrium was present in amounts greater than about 14 mg, it precipitated immediately or within minutes of adding the 8-hydroxyquinoline. The precipitates thus formed were not dispersed by further additions of either acetone or 8-hydroxyquinoline. Qualitative tests with cerium(III) in the absence of aluminium suggest that colloid formation followed by slow precipitation and possibly also oxidation sets in when lower amounts (≤ 5 mg) of this metal ion are present. On the other hand, 25 mg of aluminium do not precipitate. Scandium was not examined. Table V records results obtained with yttrium.

Following the same procedure as was used to obtain the results in Table V but omitting aluminium, gelatinous precipitates, difficult to filter, were obtained from solutions containing 25 mg of yttrium. Analysis of such a precipitate, collected, washed well with cold water and dried at 110° for 1·5 hr gave Y, 20·3% (as Y_2O_3); C, 55·3% and H, 3·47% [$Y(C_9H_6NO)_2.OCOCH_3$ requires Y, 20·4%; C, 55·1%; H, 3·47%.]. The dried solid had a brownish-yellow colour. In the absence of acetate a bright yellow precipitate was obtained and analysis showed that the dried substance was $Y(C_9H_6NO)_3$. In Table V, the percentage of the aluminium precipitated (column 2) was calculated on the assumption that the yttrium was coprecipitated as $Y(C_9H_6ON)_3$ in experiments 3 and 4 and present as $Y(C_9H_6NO)_2.OCOCH_3$ in 5, 6 and 7.

The results in Table V show that even when considerable relative amounts of yttrium are present in the solutions, the aluminium tris-(8-hydroxyquinolate) tends to exclude yttrium from the precipitate. Only when the concentration of the yttrium builds up relative to the concentration of the aluminium, either by deliberate addition of the former or through removal of the latter by precipitation, does the yttrium tend to precipitate significantly. Post-precipitation rather than coprecipitation may predominate when the larger amounts of yttrium are present (*cf.* results 4 and 5, Table V). The last two results recorded in Table III suggest that post-precipitation also occurs significantly with tracer yttrium in the absence of acetate.

TABLE V.—CO-PRECIPITATION OF MILLIGRAM-AMOUNTS OF YTTRIUM WITH ALUMINIUM

No.	Y added, *mg*	Al pptd., %	Y copptd., %
1	0·356	51·4	0·33
2	1·78	47·4	0·42
3	4·43	83·8	0·72
4	8·86	70·7	0·77
5	8·86	98·5	45·8
6	13·29	79·6	29·5
7	13·29	87·0	53·7

Attempts were made to obtain information on the distribution of tracer in precipitates obtained under conditions yielding the results reported in Tables I and III. The precipitates, while still on the crucible, were partly dissolved away with an aqueous acetone solvent mixture approximating in composition to that prepared initially and yielding the precipitate on evaporation except that the metal ions were absent. Typical results are recorded in Table VI.

The results suggest that in the presence of acetate the tracer may be distributed throughout the crystals or perhaps concentrated near the centres. In the absence of acetate results 4 and 5 suggest (when compared with results from Table III) that some surface adsorption may be occurring. However, these conclusions are based on the assumption that preferential leaching of one of the components does not take place, an assumption which may not be valid when the solubilities of the species involved are different and when non-equilibrium conditions exist during the dissolution process.

According to Geilmann and Wrigge,[12] indium is quantitatively precipitated as the tris-(8-hydroxyquinolate) from sodium acetate-acetic acid solutions. Moeller[10] has shown that this complex extracts completely from solutions containing some acetic acid into chloroform at a pH of approximately 3·2. Complete precipitation of milligram-amounts of indium would be expected at or above this pH and, provided acetate did not interfere, tracer quantities of indium would therefore coprecipitate readily with aluminium, precipitated according to the procedure used in investigating the other tracers. The results presented in Table VII show that coprecipitation is such that, just a slightly lower fractional precipitation of tracer occurs for a given fractional precipitation of aluminium. There is some indication (Table VII) that the fraction of indium precipitated increases relative to that of the aluminium when precipitation of the latter is nearly complete, particularly at lower acetate concentrations. The extent of coprecipitation is otherwise little affected by change in the amount of acetate present over the range investigated. (The pH may also change slightly in these experiments.) As would be expected under these circumstances if isomorphous substitution occurs in the crystal both D and λ are approximately equal and constant; these results are very different from those obtained with scandium, yttrium and cerium(III).

TABLE VI.—DISTRIBUTION OF TRACER IN THE CARRIER PRECIPITATE

No.	Tracer	Al pptd., %	Al[a] left on washing, %	Y[a] left in ppt., %
1[b]	Sc	54·9	35·6	0·374
2[b]	Y	65·7	58·4	0·327
3[b]	Ce	61·4	41·3	0·252
4[c]	Y	59·7	29·3	1·19
5[c]	Y	72·2	48·7	1·92

[a] Expressed as percentages of the total added originally.
[b] Obtained from an acetate medium.
[c] Obtained in the absence of acetate.

TABLE VII.—COPRECIPITATION OF INDIUM[a] WITH ALUMINIUM

Ammonium acetate added, [b]*M*	Al pptd., %	In copptd., %	D	λ
0·20	34·6	29·9	0·806	0·838
0·20	54·5	52·7	0·930	0·951
0·20	71·4	68·5	0·871	0·923
0·20	92·3	92·0	0·96	0·97
1·0	20·1	17·8	0·861	0·874
1·0	24·0	19·7	0·777	0·799
1·0	41·7	39·4	0·909	0·928
1·0	66·7	60·1	0·752	0·835
1·0	81·4	77·1	0·770	0·876
1·0	91·0	90·0	0·89	0·96
2·0	12·8	10·2	0·774	0·787
2·0	14·4	12·0	0·811	0·822
2·0	23·9	19·7	0·781	0·803
2·0	24·9	20·7	0·787	0·809
2·0	26·0	21·3	0·770	0·797
2·0	39·2	34·7	0·824	0·856
2·0	65·4	59·4	0·774	0·849
2·0	77·2	71·1	0·726	0·840
2·0	90·7	87·1	0·69	0·86

[a] 4·6 × 10^{-6} mole (0·53 mg) per sample.
[b] 40 ml of the concentration stated here; otherwise the procedure outlined under *Experimental* was followed.

This difference in behaviour would appear to arise from structural differences between the complexes produced in the solutions. Both aluminium and indium yield a tris-(8-hydroxyquinolate) complex from solutions containing acetate ion in the concentration range used in the work described here. It was found that milligram-amounts of indium (and incidentally also gallium) can be precipitated by isothermal evaporation of aqueous acetone solutions containing acetate with results similar to those obtained with aluminium. The other metal ions behave differently; in the presence of much acetate, mixed acetate-8-hydroxyquinolate complexes are probably formed as has been shown for milligram-amounts of yttrium. Evidence in support of this view is provided by the work of Ishimori,[13] who studied the partition of tracer quantities of yttrium between an aqueous acetate or tartrate (not specified which) phase at pH 8·6 and a chloroform phase containing 8-hydroxyquinoline. He found that the yttrium distribution depended only on the square of the reagent concentration and concluded that the species extracting had the composition $Y(C_9H_6ON)_2X$, where X is a monovalent anion.

The difference in behaviour is possibly associated with the ability or inability of the heterocyclic nitrogen atom of 8-hydroxyquinoline to act, in complex formation, as a donor in competition with oxygen from acetate ions or even water. A heterocyclic nitrogen atom acts as a strong donor for indium(III) because $[In(phen)_3]^{3+}$ can be precipitated (with a suitable anion) from aqueous solutions by *o*-phenanthroline (phen).[14] An aluminium[15] and, independently, rare-earth[16] complex ions of the form $M(phen)_3{}^{3+}$ have been isolated as perchlorate and thiocyanate salts, respectively, from ethanolic solution. Whilst the aluminium complex ion has been shown to be stable in polar solvents the rare-earth complex ions are said to break up. Only oxygen, it appears, is a satisfactory donor in chelate formation for the rare-earth(III) ions;[17] the formation (stability) constants of the complexes with 8-hydroxyquinoline are thus likely to be somewhat lower than for aluminium or indium. (Relative measurements have not been reported.) In the absence of acetate which does complex significantly with rare-earth ions, if the normal complex, $Y(C_9H_6ON)_3$, is formed, coprecipitation might be expected to occur to a greater extent than is observed (Table III). However, even assuming that a 1:3 complex is formed, it may be that the nitrogen donors failed to displace co-ordinated water readily from the hydration sphere of the metal ion, thus giving a reaction of the form

$$M(H_2O)_x{}^{3+} + 3(C_9H_6ON)^- \rightleftharpoons M(C_9H_6ON)_3(H_2O)_{x-3} + 3H_2O$$

where x, if only the primary hydration sphere is considered, is probably 6. The observation[8] that yttrium is not extracted from slightly acid aqueous solutions containing 8-hydroxyquinoline into chloroform but that $Y(C_9H_6NO)_3$, when isolated and dried, readily dissolves in the latter solvent provides support for this suggestion. For similar reasons, scandium(III) may take up an extra molecule of 8-hydroxyquinoline, giving $Sc(C_9H_6ON)_3.C_9H_7ON$ in the solid, when a sufficient concentration of this reagent is present (unlikely in the experiments described here) in such a way that only its oxygen atom co-ordinates, as has recently been shown[18] by an X-ray structural examination, to be the case for $UO_2(C_9H_6ON)_2.C_9H_7ON$.

Whatever structures these complexes assume, however, the results presented here suggest that the growing aluminium tris-(8-hydroxyquinolate) crystals are sensitive to the incorporation of more than a small fraction, even of very low levels, of impurities in the form of other tervalent-metal ions, which may exist predominantly in the solution from which the crystals are growing, in a form containing 8-hydroxyquinoline but other than $M(C_9H_6ON)_3$. (M represents the tracer metal ion.) This appears to be so notwithstanding the lower solubilities of macro amounts of the tracer ions (at least for yttrium and cerium) relative to that of aluminium in the medium from which precipitation is occurring.

Acknowledgement—We are grateful to Mr. T. F. Holmes of the Chemistry Department for performing the C and H analyses.

Zusammenfassung—Die Mitfällung von Tracermengen von radioaktivem Scandium, Yttrium, Cer und Indium mit Milligrammengen Aluminium wurde untersucht. Aluminium wurde als Tris(8-hydroxychinolat) durch langsames isothermes Abdampfen wäßriger acetonhaltiger Lösungen gefällt. In gegenwart von Ammoniumacetat wird weniger als 0,5% von Scandium, Yttrium oder Cer mitgefällt. Der Anteil mitgefallten Tracers ist von dem gefällten Aluminiumanteil ziemlich unabhängig. Oberflächenadsorption von Tracer am Glas oder am Niederschlag findet nicht statt, auch wenn alles Aceton abgedampft ist. Milligrammengen Yttrium und Cer geben aus acetonhaltigen Lösungen schleimige Niederschläge (in Abwesenheit von Aluminium); der getrocknete Yttriumniederschlag hat die Zusammensetzung $Y(C_9H_6NO)_2OCOCH_3$. Auch Milligrammengen Yttrium werden vom Aluminiumniederschlag nicht aufgenommen. In Abwesenneit von Acetat, aber unter Bedingungen, unter denen Milligrammengen Yttrium ausfallen würden, liegt die Mitfällung von Yttrium bei 10–90 prozentiger Ausfällung von Aluminium zwischen 1 und 6%. Wenn alles Aceton abgedampft wird, findet beträchtliche Oberflächenadsorption des Tracers statt. Die teilweise Ausfallung von Indium als Tracer zwischen 10 und 90% aus acetathaltigen Lösungen ist nur wenig geringer als die entsprechende teilweise Ausfällung von Aluminium. Unter der Annahme einer homogenen beziehungsweise einer logarithmischen Verteilung in den Kristallen berechnete Koeffizienten D und λ sind ungefähr gleich und konstant. Milligrammengen Indium geben bei der Abdampfmethode aus acetathaltiger Lösung eine körnige Fällung.

Résumé—On a étudié la coprécipitation des scandium, yttrium, cérium et indium radioactifs, à la concentration des traceurs, avec des quantités d'aluminium de l'ordre du mg. L'aluminium a été précipité à l'état de tris-(8-hydroxyquinolinate) par évaporation isotherme lente de solutions hydroacétoniques. En présence d'acétate d'ammonium, moins de 0,5% du scandium, de l'yttrium ou du cérium coprécipitent. La fraction de traceur entraînée est approximativement indépendante de la fraction d'aluminium précipitée. Il ne se produit pas d'adsorption en surface du traceur, ni sur le récipient en verre, ni sur le précipité, même lorsque toute l'acétone a été éliminée. Des quantités d'yttrium et de cérium de l'ordre du mg donnent des précipités gélatineux à partir de systèmes similaires contenant de l'acétone (l'aluminium étant absent); le précipité d'yttrium, sec, a la composition $Y(C_9H_6NO)_2\text{-}OCOCH_3$. Même des quantités d'yttrium de l'ordre du mg, lorsqu'elles sont présentes, tendent à être rejetées par le précipité d'aluminium. En l'absence d'acétate, mais dans des conditions où des quantités d' yttrium de l'ordre du mg précipiteraient, pour une précipitation de l'aluminium allant de 10 à 90%, la coprécipitation de l'yttrium se situe entre 1 et 6%. L'élimination de toute l'acétone a pour conséquence une adsorption en surface considérable du traceur. A partir de solutions d'acétate, la précipitation fractionnée de l'indium à l'état de traceur, dans le domaine 10 à 90%, n'est que légèrement différente (plus faible) que la précipitation fractionnée correspondante de l'aluminium. D et λ, les coefficients calculés en supposant des distributions respectivement homogène et logarithmique, à l'intérieur des cristaux, sont approximativement égaux et constants. Des quantités d'indium de l'ordre du mg donnent un précipité granulaire, par la technique d'évaporation lente, à partir des solutions renfermant de l'acétate.

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DETERMINATION OF SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM IN STANDARD SILICATE ROCKS, G–1 AND W–1, BY NEUTRON-ACTIVATION ANALYSIS*

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Summary—Neutron-activation analysis results for four rare earth elements in standard silicate rocks, G-1 and W-1, are reported. An anion-exchange method for the separation of scandium, yttrium, samarium and lanthanum in good radiochemical purity has been developed. The method is based on the chromatographic elution of these elements from a Dowex 1 × 8 (nitrate form) resin column using methanol-nitric acid mixtures. The results obtained by this method are compared with values already available.

INTRODUCTION

The relative abundances of the individual rare earths in terrestrial as well as meteorite samples are of geochemical interest, because they have been used as an argument for the existence of abundance rules.[1] However, the reliability of analytical data for these elements, even on "Standard Rocks," seems to be far from satisfactory as evident from the summaries of values by Ahrens and Fleischer[2] and Fleischer and Stevens.[3] The methods which have been generally used for their determinations are spectrographic. Many of the rare earth elements are well suited for neutron-activation analysis so that this technique has been used for their determination.[4–11] The present paper describes the procedure employed for the determination of scandium, yttrium, samarium and lanthanum in the standard rocks G-1 and W-1.

Nuclear data

The principles and techniques of neutron-activation analysis have been reviewed in the literature and will not be repeated here. The data[12,13] relating to the activation of the elements under consideration are given in Table I.

Based on the information shown in Table I, ^{46}Sc, ^{90}Y, ^{153}Sm and ^{140}La have been chosen as suitable isotopes for the determinations of these elements.

EXPERIMENTAL

Reagents

All reagents were of recognised analytical purity.

Carriers for lanthanum, samarium, yttrium and scandium. Oxides of purity ⩾99·9% of individual elements were ignited and dissolved in nitric acid so as to give solutions containing 10·0 mg of metal/ml.

Standards. Standards of the above elements, containing 100.0 μg/ml, were prepared by dissolving spec-pure oxides in nitric acid. In the case of scandium the purity was only 99·9%.

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TABLE I.—NUCLEAR DATA RELATING TO THE ACTIVATION OF SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM

Target nuclide	Product nuclide by (n, γ) reaction	Half-life	Saturation specific activity for a flux of $1{\cdot}0 \times 10^{12}$n. cm^{-2}. sec.$^{-1}$, *dpm/μg*	Mode of decay	Gamma-ray energy, *MeV*	No. of photons per 100 disintegrations
^{45}Sc	^{46}Sc	84·0 d	9.6×10^{6}	Beta	0·885	100
				(100)	1·12	100
^{89}Y	^{90}Y	64·2 h	$4{\cdot}9 \times 10^{5}$	Beta	1·73	0·002
				(100)		
^{144}Sm	^{145}Sm	340·0 d	$<1{\cdot}5 \times 10^{4}$	EC	0.061	12·1
				(100)	0·485	0·003
^{152}Sm	^{153}Sm	47·0 h	$8{\cdot}9 \times 10^{6}$	Beta	0·069	2·3
				(100)	0·084	1·2
					0·103	33
					0·178	0·02
					0·530	0·06
^{139}La	^{140}La	40·2 h	$2{\cdot}1 \times 10^{6}$	Beta	0·328	35
				(100)	0·487	44
					0·815	40
					0·890	9
					1·59	88
					2·6	0·9

Ion-exchange resin. Dowex 1 × 8 analytical grade resin of mesh size 50–100 was regenerated in nitrate form and used when required. The resin was pre-equilibrated with the proper methanol-nitric acid mixture overnight before use.

Methanol-nitric acid mixtures. Analytical reagent grade nitric acid was standardised by titrating with standard alkali and suitably diluted to give 7·0, 1·0 and 0·1*M* nitric acid. The eluants were prepared by diluting aqueous nitric acid, of the molarity indicated, with methanol to give the appropriate percentage composition. Thus, 10% 1·0*M* nitric acid-methanol is obtained by diluting 10·0 ml of 1·0*M* nitric acid to 100·0 ml with methanol. These mixtures were prepared fresh when required.

Oxalic acid. Saturated aqueous solution.

Apparatus

Ion-exchange columns. Conventional ion-exchange columns, 30·0 cm × 8·0 mm, with stopcocks to regulate flow rates were used.

Counters. Beta activities were counted using a Geiger-Müller counter. Gamma activities were measured using a single channel analyser connected to a scintillation head consisting of a 1·5″ × 1″ NaI (Tl activated) crystal coupled to a E.M.I. 9536 photo tube and cathode follower.

Irradiation

For the determination of samarium and lanthanum 50·0-mg samples were irradiated for 24–40 hr. For yttrium and scandium, 200·0 mg samples were irradiated for 24–40 hr. The samples were sealed in Polythene capsules. Standards were prepared by evaporating aliquots of the standard solution varying between 1 and 10 μg on Polythene sheets. These were sealed and irradiated with the samples, in the "Apsara" Swimming Pool Reactor of the Atomic Energy Establishment Trombay, at a flux of 1×10^{11} n. cm^{-2}. sec.$^{-1}$ A cooling of 24 hr was needed before determining yttrium, samarium and lanthanum; for scandium the cooling period was 2 weeks.

Radiochemical separation

Isolation of rare earths as a group. A weighed amount of irradiated sample (25·0 mg for lanthanum and samarium and 100·0 mg for yttrium and scandium) was treated with hydrofluoric acid in a platinum dish to expel silica. A suitable aliquot of the carrier solution, containing 10–15 mg of the element being determined, was added to the dish and evaporated to dryness. The mass was fused with potassium bisulphate and taken up in 5% sulphuric acid. The rare earth activities were isolated as a group by at least three cycles of hydroxide and fluoride separation.[14] The hydroxides were finally dissolved in nitric acid and the solution evaporated to dryness on a water bath. The residue was taken up in the appropriate methanol-nitric acid mixture for ion-exchange separation.

Ion-exchange separation. The ion-exchange separation is based on the data published by Faris and Warton.[15] Their values indicate that in these solvent mixtures scandium elutes first from the resin. The heavy earths from lutecium to terbium with yttrium move almost together, followed by gadolinium to lanthanum in that order. Eluants were prepared and their suitability was established by using the carrier for the element of interest and tracers for those from which separation was desired. The composition of the eluants used and details of the elution behaviour of the individual elements are given in Table II.

TABLE II.—COMPOSITION OF ELUANTS AND DETAILS OF SEPARATION[a]

Element	Sorption[b]	Removal of heavier rare earths	Elution of element	Elements retained on column
Scandium	10·0 ml of 2·5% 7·0*M* nitric acid–methanol	—	30·0 ml of 2·5% 7·0*M* nitric acid–methanol	All rare earths including Y
Yttrium	10·0 ml of 2·5% 7·0*M* nitric acid–methanol	30·0 ml of 2·5% 7·0*M* nitric acid–methanol (Sc)	50·0 ml Of 10·0% 1·0*M* nitric acid–acid–methanol (Lu to Tb with Y)	Elements lighter than Gd retained on column
Samarium	10·0 ml of 10% 1·0*M* nitric acid–methanol	40·0 ml of 10% 1*M* nitric acid–methanol (Lu to Tb with Y), followed by 20·0 ml of 10% 0·7*M* nitric acid–methanol (Gd to Eu)	50·0 ml of 10% 0·5*M* nitric acid–methanol (Sm)	Elements lighter than Sm retained on column
Lanthanum	10·0 ml of 10% 1·0*M* nitric acid–methanol	40 ml of 10% 1*M* nitric acid–methanol (Sc + Lu to Tb), followed by 50 ml of 10% 0·05*M* nitric acid–methanol mixture (Gd to Ce)	50 ml of 0·01*M* nitric acid (La)	

[a] Flow rates: 0·5 ml/min for sorption step and 0·5–0·8 ml/min for subsequent elutions.

[b] The residue of nitrates after chemical treatment is dissolved in the given volume of the eluant.

The solution obtained after ion-exchange separation was evaporated on a water bath, the residue dissolved in water and the oxalates of yttrium, samarium and lanthanum precipitated. Scandium was precipitated by 8-hydroxyquinoline. The precipitates were filtered using a demountable filtration unit, washed with water, dried and mounted for counting.

Counting and chemical yield

Scandium. ^{46}Sc activity was determined by counting the photopeak activities at 0·89 and 1·12 Mev.

Yttrium. ^{90}Y activity was measured through an aluminium absorber (182 mg.cm^{-2}). In the absence of an absorber, a long lived activity, possibly terbium or ytterbium was observed. Consideration of the nuclear data[12,13] of the heavy rare earths which are likely to accompany yttrium in the ion-exchange separation shows that an appreciable interference in the determination of yttrium, counted through an absorber, can only come from ^{166}Ho. The observed half-lives of the samples indicate that there is no significant contamination by an element with a shorter half-life (Fig. 2).

Samarium. ^{153}Sm activity was determined by beta counting. The radiochemical purity of samarium was established by following the half-life. The gamma spectrum of samarium isolated from the samples (Fig. 2) shows that there is no significant contamination by other nuclides.

Lanthanum. ^{140}La activity was determined by beta counting and gamma counting using the 0·487-MeV photopeak. The photopeak activity decayed with the expected half-life. The beta activity decay curve showed an impurity, presumably neodymium, which was resolved (Fig. 1).

The chemical yield was determined by igniting the precipitates as oxides.

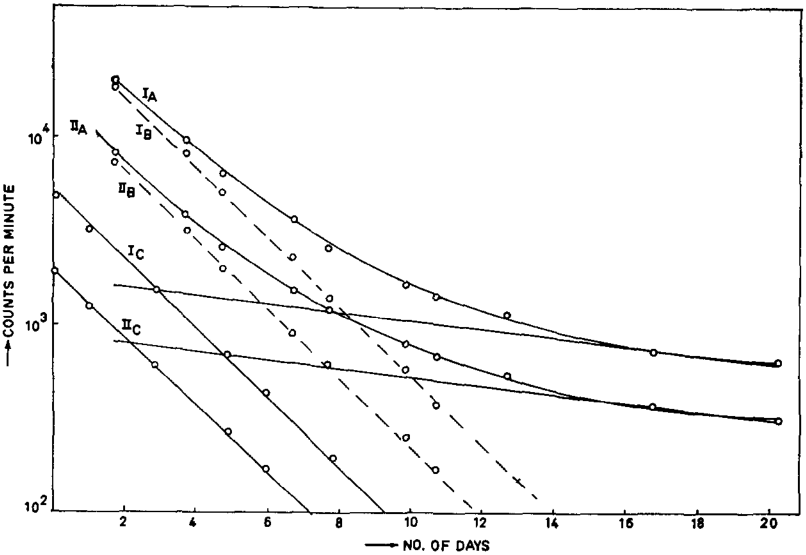

FIG. 1.—Decay curves of ^{140}La:
$\mathrm{I_A}$—Gross β-decay of lanthanum fraction from G-1, $\mathrm{I_B}$—β-Decay of lanthanum fraction from G-1 after correcting for tail, $\mathrm{II_A}$—Gross β-decay of lanthanum fraction from W-1, $\mathrm{II_B}$—β-Decay of lanthanum fraction from W-1 after correcting for tail, $\mathrm{I_C}$—γ-Decay of lanthanum fraction from G-1, $\mathrm{II_C}$—γ-Decay of lanthanum fraction from W-1.

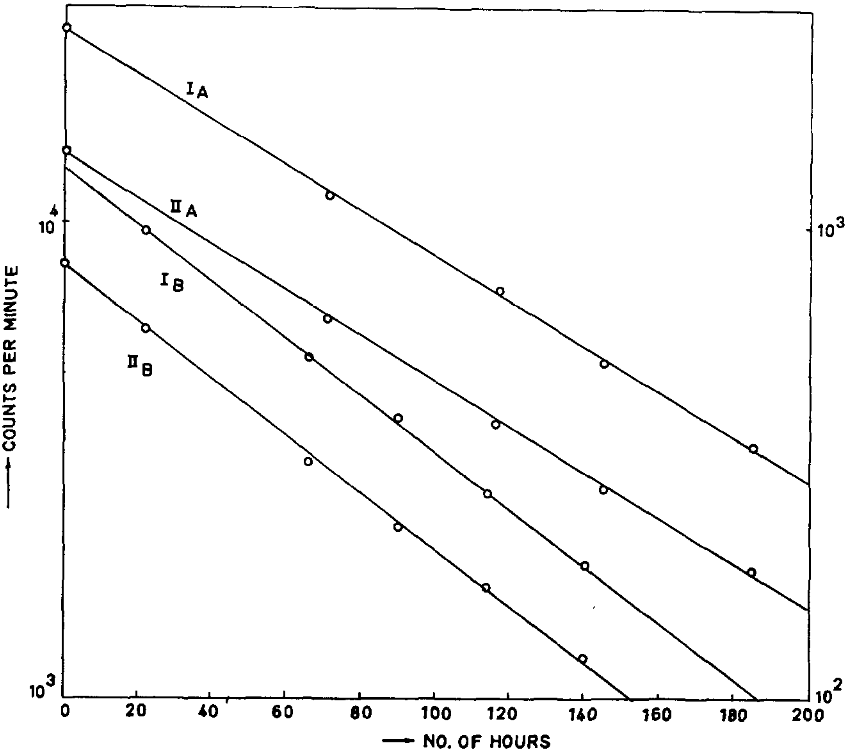

FIG. 2.—Decay curves of ^{90}Y and ^{153}Sm:
$\mathrm{I_A}$—Yttrium from W-1, $\mathrm{I_B}$—Samarium from G-1, $\mathrm{II_A}$—Yttrium from G-1, $\mathrm{II_B}$—Samarium from W-1.
($\mathrm{I_A}$ and $\mathrm{II_A}$, R·H·S: $\mathrm{I_B}$ and $\mathrm{II_B}$, L·H·S.)

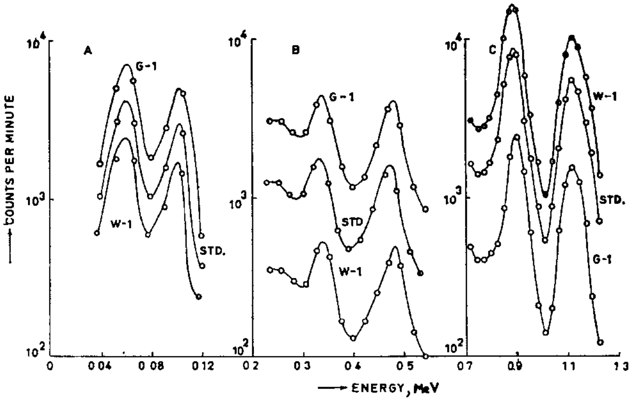

FIG. 3.—Gamma spectra of ^{153}Sm, ^{140}La and ^{46}Sc: A—Samarium, B—Lanthanum, C—Scandium.

TABLE III.—RESULTS FOR SCANDIUM, YTTRIUM, SAMARIUM AND LANTHANUM IN G-1 AND W-1

Element	G-1		W-1		Remarks
	Concentration, *ppm*	Measured half-life, *hr*	Concentration, *ppm*	Measured half-life, *hr*	
Scandium	(a) 2·96	—	(a) 32.7	—	(a) Based on 0·885 MeV γ-ray
	2·98	—	31·2	—	
	(b) 2·92	—	(b) 34·4	—	(b) Based on 1·12 MeV γ-ray
	3·12	—	34·4	—	
	3·0		33·3		Mean
Yttrium	13·1	64·5	26·2	65·5	β-measurement through an (182·0 mg.cm^{-2}) Al absorber
	13·8	65·0	26·7	66·0	
	13·1	66·5	27·9	64·5	
	12·1	62·0	27·5	60·0	
	13·0		27·1		Mean
Samarium	12·5	49·0	7·0	48·5	
	13·8	49·0	6.4	50·0	
	13·2	50·0	6·4	49·5	
	13·2		6·6		Mean
Lanthanum	132	40·5	19·1	40·5	Based on β^- activity measurement
	135	40·5	20·8	40·5	
	126	39·0	21·4	40·0	
	136	39·0	22·8	39·5	
	132		21·0		Mean
	116	40·7	16·0	39·0	Based on 0·487 MeV γ-ray
	126	41·5	16·2	39·8	
	123	41·0	21·4	40·0	
	136	41·5	22·2	41·0	
	125		19·0		Mean

TABLE IV.—COMPARISON OF RESULTS OBTAINED WITH PUBLISHED RESULTS FOR G-1 AND W-1

Element		Present method, *mean ppm*	Published results				
			Neutron activation, *ppm*	Reference	Recommended values, *ppm*		Range of values, *ppm*
					A.F.[8]	F.S.[8]	
Scandium	G-1	3·0	2·8	6	4	3	2·7 to 13
			2·7	7		3	
	W-1	33·4	34·0	6	43	33	25 to 120
			34·0	7			
			31·0	17			
Yttrium	G-1	13·0	12·5	11	21	21	10 to 30
	W-1	27·1	23·8	11	35	35	30 to 50
Samarium	G-1	13·2	11·0	7	11		—
			8·6	11			
	W-1	6·6	5·1	7	5		—
			3·8	11			
Lanthanum	G-1	132	141·9	10	150	120	60 to 430
		125	122·0	7			
			113·0	8			
			102	11			
	W-1	21	27	7	30		
		19	13	8		30	5 to 32
			11·7	11			

RESULTS AND DISCUSSION

The results obtained for the four elements are given in Table III.

The mean values for lanthanum, in which both beta and gamma measurements were used, show a difference between the two procedures of 6% for G-1 and 10% for W-1. The number of measurements does not permit the assignment of any significant cause for this difference.

In Table IV, the mean values obtained by the present method are compared with those recommended and those obtained by other workers using the technique of activation analysis.

Taylor and Ahrens[16] have recommended these samples as standards for spectrographic analysis, whilst others[18,19] have expressed doubts regarding their very homogeneity.

It may be noted from Table IV that the reported values show a large spread for any given element. Hence a comparison of results becomes difficult. However, the present results are in good agreement with other results obtained by activation analysis.

While the method permits resolution of elements having close half-life values, it is not expected to separate individual members of the rare earth series, because an unusually large excess of an element modifies the elution behaviour of the adjacent elements. The advantages claimed for the method are satisfactory precision, rapidity, simplicity of operation and use of commonly available reagents. There should be few difficulties in applying the method to other minerals and ores, and work along these lines is in progress.

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Zusammenfassung—Ergebenisse der Neutronenaktivierungsanalyse für vier seltene Erden in den Standard-Silikatgesteinen G-1 und W-1 werden angegeben. Eine Anionenaustauschmethode zur Abtrennung von Sc, Y, Sm und La in guter radiochemischer Reinheit wurde entwickelt. Die Methode beruht auf der chromatographischen Elution dieser Elemente von einer Säule mit Dowex 1 × 8 (NO_3^--Form) mittels Methanol-Salpetersäure-Mischungen. Die Ergebnisse dieser Methode werden mit bereits zugänglichen Daten verglichen.

Résumé—On décrit les résultats de l'analyse par activation de neutrons pour quatre éléments des terres rares dans les roches aux silicates, étalons G-1 et W-1. On a élaboré une méthode par échange d'anions pour séparer Sc, Y, Sm et La dans un état de pureté radiochimique satisfaisant. La méthode est basée sur l'élution chromatographique de ces éléments, à partir d'une colonne de résine Dowex 1 × 8 (forme NO_3^-), au moyen de mélanges méthanol-acide nitrique. On compare les résultats obtenus par cette méthode aux données déjà existantes.

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AN EXAMINATION OF THE ATOMIC ABSORPTION SPECTROSCOPY OF SILVER

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Summary—Silver in aqueous solution in the range 1–10 ppm is determined by direct atomic absorption spectroscopy in an air/propane flame at 3281 Å. Many potential interferences are examined; only thorium, iodate, tungstate and permanganate cause interference when present in 1000-fold mole-ratio excess. Silver can also be determined without interference from any known ion in the range 0·1 down to 0·01 ppm in aqueous solution following an extraction of the silver as its di-n-butylammonium salicylate into methyl isobutyl ketone. The extract is submitted directly to absorptiometry in the flame. The solvent enhancement effect is shown to be caused principally by an increase of atomisation relative to aqueous solution.

THE advent of atomic absorption spectroscopy has led not only to a simplification in the preparation of a sample for analysis, but also to the determination of traces of metals which have hitherto been very difficult to determine by their emission in flames. One such metal is silver, and methods for its analysis in trace amounts have usually been based on spectrophotometry and the use of the organic reagents dithizone,[1] *p*-dimethylaminobenzylidenerhodanine[1] and, latterly, pyrogallol red.[2] The last-mentioned reagent, used in conjunction with a selective extraction system[3,4] for silver ions, possesses the advantages of selectivity, sensitivity, stability and reproducibility. However, subsequent evaluation of the reaction mechanism,[5] together with the lack of specificity, indicates that there are some limitations to its wider application.

The use of atomic absorption spectroscopy as an analytical technique is now well established[6] and it has been reviewed by Elwell and Gidley.[7] Application of the technique to the analysis of trace amounts of silver was first described by Lockyer and Hames.[8] These workers produced calibration curves from 1·0 to 10 ppm of silver and they examined the effects of some other noble metals, *viz.*, gold, platinum, palladium and rhodium, on the determination.

Traces of silver (<10 ppm) are of vital concern in many areas, such as effluent analysis. It was, therefore, the purpose of the following investigation to examine the possibilities of applying atomic absorption spectroscopy to such complex problems.

The apparatus used by the authors was the commercially available Hilger and Watts Uvispek (H700) spectrophotometer and its atomic absorption attachment. Using the optimum instrument control settings (see *Apparatus*), it was found that down to 1 ppm of silver in an aqueous solution could be easily determined. Furthermore, a plot of absorbance against concentration of silver (in ppm) produced a straight line calibration curve from 1 to 10 ppm of silver and its extension passed through the origin (Fig. 1A). The plot above the 10-ppm level of silver curved off slowly towards the abscissa (absorbance zero).

INTERFERENCES

The absorbance depends upon the rate of atomisation or the amount of material, in the form of droplets, reaching the flame. Thus, it is necessary in such an investigation to consider those substances which could give rise to physical changes in the solution to be atomised as well as direct chemical interferences.

Cations

The effect was observed upon an aqueous solution $5 \times 10^{-5}M$ in silver nitrate (5·394 ppm of silver) of about a 1000-fold mole excess, relative to silver, of a number of metal nitrates. No interference was noted from Al, Ba, Be, Bi, Ca, Cd, Ce^{III}, Co, Cr, Cu^{II}, Fe^{III}, Hg^{II}, K, La, Li, Mg, Mn^{II}, Na, NH_4^+, Ni, Pb, Sn^{IV}, Sr, Tl^I, Zn and Zr. Other workers[8] have already shown that there is no interference from a similar excess of the noble metals Au, Pt, Pd and Rh.

Only thorium was found to interfere, causing a reduction in the absorbance of approximately 15%. This was suspected to be caused by the formation of a refractory oxide of thorium. Wilson[11] reports interference from relatively large amounts of aluminium in his determination of silver in aluminium alloys.

Inorganic anions

No interference was observed from a 1000-fold mole excess, relative to silver, of the sodium, potassium or ammonium salts of $B_4O_7^{2-}$, Br^-, Cl^-, ClO_3^-, ClO_4^-, CN^-, CO_3^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, I^-, MoO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, SCN^-, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$ and VO_3^-.

Only iodate, permanganate and tungstate were found to interfere. Iodate decreased the absorbance by *ca.* 80%, permanganate by *ca.* 15% and tungstate by *ca.* 6%. The interferences, especially with iodate, are caused by the formation of precipitates which immediately settle out of solution. Provided that the precipitate is in an attenuated finely divided form, for example silver chloride, then there is no reduction in the expected absorbance.

Organic anions

The sodium or potassium salts of acetate, formate, oxalate, tartrate, phthalate and citrate were also investigated at a 1000-fold mole excess, but none was found to interfere.

Acids

Hydrochloric, sulphuric, nitric, phosphoric and acetic acids were examined by adding 10-ml aliquots of each concentrated acid to 5 ml of a $10^{-3}M$ solution of silver nitrate, followed by dilution to 100 ml with distilled water. The silver content of such solutions was 5·394 ppm.

There was no interference from hydrochloric and nitric acids, but sulphuric and phosphoric acid caused a reduction in absorbance, whilst acetic acid caused an increase. The reduction in absorbance (*ca.* 20% in both instances) is caused by the increased viscosity of the solution, which gives rise to a reduced rate of atomisation. The increase in absorbance (*ca.* 36%) with acetic acid is caused by what is commonly called the "organic solvent effect". This is an enhancement in absorbance observed upon the addition of an organic solvent which is miscible with the aqueous solution under investigation. The over-all effect seems to be an increased rate of atomisation. This effect is discussed below under "*The organic solvent effect*".

Organic solvents miscible with water

The absorbance of an aqueous solution $5 \times 10^{-5}M$ in silver nitrate was compared with that of solutions $5 \times 10^{-5}M$ in silver nitrate and 10% with respect to the organic solvents acetone, dioxan, ethanol, ethylene glycol, formaldehyde, glycerol, isopropyl alcohol, methanol, methyl ethyl ketone and pyridine.

Glycerol gave a reduction in absorbance because of an increase in the viscosity of the solution and a subsequent reduced rate of atomisation. All of the remaining solvents produced, however, a considerable enhancement, especially isopropyl alcohol and methyl ethyl ketone (*ca.* 43% in each instance).

Surface active agents

Gelatin was chosen as a typical surface active agent and its effect was examined in a manner similar to that of *Organic solvents miscible with water.* Although only a slight enhancement was given, it was sufficient to indicate that a lowering of surface tension can increase the rate of atomisation.

"The organic solvent effect"

The reduction or enhancement in the absorbance, from the addition of certain organic solvents miscible with an aqueous silver-containing solution, was further investigated by considering the variations in the volume of different solvents actually fed into the burner as a fine spray.

First, a known volume of distilled water was converted into a fine spray by the vapour chamber attachment under the usual optimum conditions. The total time for the complete consumption of the distilled water was recorded, together with the volume of liquid not converted into a fine spray. This latter measurement was made by attaching a measuring cylinder to the waste outlet of the spray chamber. A similar experiment was then repeated with methyl ethyl ketone and a 50% aqueous/glycerol solution. The means of a number of readings obtained are shown in Table I.

TABLE I

Solvent system	Distilled water	Methyl ethyl ketone	50% Aqueous glycerol
Volume used, *ml*	10·0	10·0	6·5
Volume recovered, *ml*	8·4	4·8	5·0
Volume atomised, *ml*	1·6	5·2	1·5
Time taken, *sec*	310	235	1200
Rate, *ml/sec* (throughput $\times 10^2$)	0·516	2·213	0·125
Throughput ratio relative to distilled water	1·00	4·29	0·24

Thus, the rate of atomisation of methyl ethyl ketone is about four times that of distilled water, whilst that of 50% aqueous glycerol is about four times less. Consequently, the differences in the absorbance produced by these systems, containing the same concentration of silver, should be in these same ratios if the rate of atomisation is the most important factor. In fact, for the systems containing 3·236 ppm of silver, distilled water gave an absorbance value of 0·080, methyl ethyl ketone a value of 0·313 and 50% aqueous glycerol a value of 0·019. This represents a ratio of 1:3·9:0·24.

It is, therefore, apparent that the increase or decrease in the absorbance observed with different solvents, provided there is no chemical interference, is mainly caused by an increased or reduced rate of atomisation. Although these results are very approximate, the conclusions reached agree well with the more elaborate experiments described by Elwell and Gidley.[7]

Extraction of Silver

The extraction of silver into an organic solvent before absorption measurements should cause an increase in the over-all sensitivity because of a concentration of silver in the organic phase and a further increase in sensitivity from the "organic solvent effect". It was, therefore, decided to examine the application of a selective extraction system (di-n-butylamine/salicylate ion-association system)[3,4] for silver ions to the determination of silver by atomic absorption spectroscopy.

Preliminary experiments showed that by extracting 1- to 5-ml aliquots of a $10^{-4}M$ silver nitrate solution with 10 ml of hexone reagent "A", it was possible to determine silver accurately down to at least 0·2 ppm. By extracting from larger volumes of an aqueous silver-containing solution with hexone reagent "B", it was possible to determine silver down to 0·01 ppm. The efficiency of this latter extraction system has been investigated and confirmed radiochemically.[4]

Fig. 1 shows the two calibration curves obtained for the range 1–10 ppm of silver in aqueous solution and after extraction with hexone reagent "A". Fig. 2 shows the calibration curve obtained over the range 0·01–0·1 ppm of silver after extraction of 1- to 10-ml aliquots of a $10^{-4}M$ silver nitrate solution in 1 litre of aqueous solution with hexone reagent "B".

The partial co-extraction of mercury^{II} with silver was also investigated and the results obtained showed that, provided a sufficient excess of anthranilic acid diacetic acid (AADA) was present to complex completely all of the mercury, there was no interference from a *ca.* 1000-fold mole excess.

The instrument control settings employed in this work were as described under *Apparatus*, but with one exception. The propane pressure was reduced slightly when organic solvents were employed so as to give a non-luminous and non-turbulent flame.

DISCUSSION

Atomic absorption spectroscopy compares very favourably with other techniques, particularly with regard to ease of operation, sensitivity, reproducibility of result and an almost complete lack of interference from extraneous cations and anions. The precision of a determination has been reported[7] to be of the order of 2% and because of its high specificity, accuracies are also high. The sensitivity obtained for silver, following extraction, is at least as high as that of any of the alternative methods

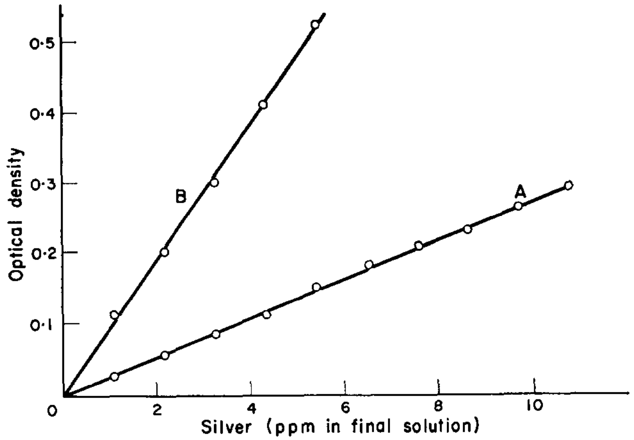

FIG. 1.—Calibration curves for silver determination:
A—normal procedure for 1–10 ppm of silver in aqueous solution;
B—procedure for 1–5 ppm of silver (in 10 ml of solution) after extraction with 10 ml of hexone reagent "A".

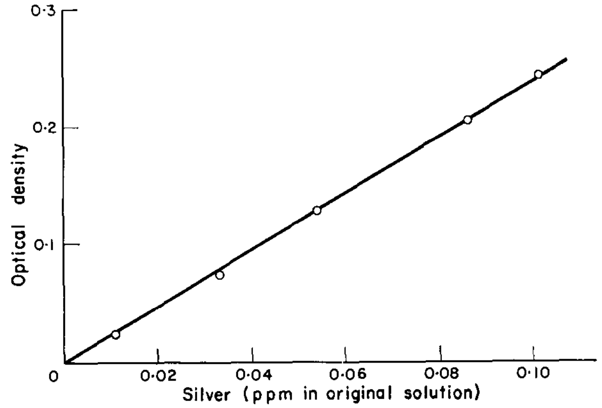

FIG. 2.—Calibration curve for extraction of silver
[normal procedure for 0·01–0·1 ppm of silver (in 1 litre of solution) after extraction with 50 ml of hexone reagent "B".]

of determination. In addition, we have observed interference from few other ions. Although the silver samples examined by the authors have all been in solution-form, it should nevertheless be possible to work directly with solid samples by employing an atomisation technique, such as cathodic sputtering.[9]

EXPERIMENTAL

Determinations in Aqueous Solutions

The working range is 1–10 ppm of silver (absorbance 0·026 to 0·270), but this can be reduced to 1–5 ppm with 50% aqueous/isopropyl alcohol solutions. Of the 27 cations and 30 anions examined, only thorium, iodate, permanganate and tungstate interfered.

Apparatus

Hilger and Watts Uvispek (H700) spectrophotometer and its atomic absorption attachment: The attachment consisted of a vapour chamber, a burner and a silver hollow-cathode lamp (FL 161), together with the appropriate power packs. The flame employed was a regulated supply of compressed air and propane.

The optimum instrument control settings were determined with a $10^{-4}M$ aqueous solution of silver nitrate (10·788 ppm of silver). The settings, listed below, were constantly checked, and were employed throughout the entire investigation:

Lamp current: 8 mA (setting 2 on power pack),
Wavelength: 3281 Å,
Slit width: 0·1 mm,
Uvispek sensitivity: setting 8, input sensitivity X5,
Air pressure to atomiser: 17·8 lb./in.^{2},
Propane pressure to burner: sufficient to give a non-luminous, non-turbulent flame.

Reagent

$10^{-3}M$ *Silver nitrate solution.* Prepared by dilution of a standard $10^{-1}M$ solution (B.D.H. Ltd.):

$$1 \text{ ml of } 10^{-3}M \text{ AgNO}_3 \equiv 107{\cdot}9\ \mu\text{g of Ag.}$$

Procedure

Calibration curve (1–10 ppm: *see Fig.* 1A). Pipette 1- to 10-ml aliquots of $10^{-3}M$ silver nitrate solution into 100-ml volumetric flasks and dilute to the mark with distilled water. Switch on the instrument and leave for about 1 hr to attain equilibrium. Next adjust the instrument control settings to their optimum or required positions, then spray distilled water through the flame for about 1 min. Set the spectrophotometer to read zero absorbance and spray the first silver solution. Measure the absorbance, then spray distilled water for a further min, resetting the spectrophotometer controls if necessary. This sequence of operations must be carried out after spraying each silver solution.

Determinations. Proceed as under *Calibration curve* if the sample is in aqueous solution. If substances are present which are likely to reduce the absorbance (*e.g.*, glycerol, sulphuric acid, *etc.*) or enhance it (*e.g.*, organic solvents), then new standard solutions must be prepared containing the same concentration of these substances and another calibration curve prepared. The concentration of silver is read from the calibration curve.

Determinations in Organic Media

The working range in organic media is normally 1–5 ppm of silver,[10] but by using the di-n-butylamine/salicylate extraction system as a means of concentration it is possible to determine silver down to 0·01 ppm in an original aqueous solution. There are no cationic interferences because of the selective nature of the ion-association extraction system, and in addition those anions compatible with silver in aqueous solution will also not interfere.

Reagents

$10^{-4}M$ *Silver nitrate solution.* Prepared as above:

$$1 \text{ ml of } 10^{-4}M \text{ AgNO}_3 \equiv 10{\cdot}79\ \mu\text{g of Ag.}$$

Hexone reagent "A". 3·2 g of salicyclic acid and 30 ml of di-n-butylamine dissolved in and diluted to 1 litre with methyl isobutyl ketone.

Hexone reagent "B". As reagent "*A*", but with 70 ml of di-n-butylamine.

$10^{-1}M$ *Anthranilic acid diacetic acid* (*AADA*) *solution.* Neutralised with sodium carbonate.

$5M$ *Sodium nitrate solution.* 42·5 g of analytical reagent grade sodium nitrate dissolved in and diluted to 100 ml with distilled water.

20% *Sodium acetate solution.* 20 g of analytical reagent grade sodium acetate trihydrate dissolved in and diluted to 100 ml with distilled water.

Procedure

Calibration Curve (0·01–0·1 ppm: *see Fig.* 2). Pipette 1- to 10-ml aliquots of the 10^{-4} silver nitrate solution into 2-litre separating funnels, treated with a protective silicone film, and make up with distilled water to *ca.* 1 litre. Add 5 ml of 20% sodium acetate solution (to give a nearly neutral solution), 5 ml of $5M$ sodium nitrate solution, 0·4 ml of $10^{-1}M$ AADA solution and 50 ml of hexone reagent "B". Shake by continuous inversion for 1 min and chill the separating funnels thoroughly in ice-water to obtain a clear solution (*ca.* 10 min). Run off the lower aqueous layer, then transfer the organic phases (now less than 40 ml) to 50-ml volumetric flasks. Wash the funnels with 5 ml of methyl isobutyl ketone and add to the volumetric flasks. Finally, make up to the mark with methyl isobutyl ketone.

Proceed with the absorbance measurements as under *Determinations in Aqueous Solutions*, but with reduction of the propane pressure to obtain a non-luminous, non-turbulent flame on spraying the hexone extract.

Hexone reagent "A" (10 ml) is used for the determination of silver in the range 1–5 ppm (Fig. 1B). A similar procedure to the above is followed with the exception that chilling of the solvent layers and subsequent dilution of the extract is no longer necessary. The volume of the aqueous phase employed was 10 ml.

Acknowledgement—We are grateful to the Department of Scientific and Industrial Research for the provision of the optical and electrical equipment used in this study.

Zusammenfassung—1–10 ppm Silber in wäßriger Lösung wird durch direkte atomare Absorptionsspektroskopie in einer Luft-Propan-Flamme bei 3281 Å bestimmt. Viele mögliche störungen werden untersucht; nur Thorium, Jodat, Wolframat und Permanganat stören in tausendfachem molarem Überschuß. 0,1–0,01 ppm Silber kann auch ohne Störung von irgendeinem Ion in wäßriger Lösung bestimmt werden, wenn es vorher als Di-n-butylammoniumsalicylat in Methylisobutylketon extrahiert wird. Der Extrakt wird direkt zur Absorptionsmessung in die Flamme gegeben. Es wird gezeigt, daß die Verbesserung durch das Lösungsmittel im wesentlichen auf besserer Zerstäubung als in wäßriger Lösung beruht.

Résumé—On dose l'argent en solution aqueuse, entre 1 et 10 ppm, par spectroscopie d'absorption atomique directe, dans une flamme air/propane, à 3281 Å. On examine de nombreuses interférences possibles; seuls, le thorium, l'iodate, le tungstate et le permanganate interfèrent, lorsqu'ils sont présents à une concentration molarie 1000 fois plus importante. On peut aussi doser l'argent sans interférence d'aucun ion connu, en solution aqueous, de 0,1 jusqu'à 0,01 ppm après extraction de l'argent, sous forme de di-n-butyl-ammonium salicylate, par la méthyl isobutyl cétone. L'extrait est soumis directement à l'absorptiométrie dans la flamme. On montre que l'effet d'exaltation du solvant est dû principalement à un accroissement de l'atomisation, par rapport à la solution aqueuse.

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SHORT COMMUNICATIONS

Absorptiometric study of ammonium aurintricarboxylate as a reagent for palladium^{II}

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INTRODUCTION

AMMONIUM aurintricarboxylate (Aluminon, AAC) has been used extensively as a chromogenic reagent and as a metallochromic indicator for metal ions. In earlier papers from these laboratories, metal chelates of AAC with copper, iron, uranyl, thorium and beryllium have been described and their use in colorimetric analysis has been suggested.[1-5]

Many colour reactions and photometric methods are available for the determination of palladium.[6-11] In the present work the photometric determination of palladium^{II} and the properties of the Aluminon chelate formed have been examined. This reagent has a greater sensitivity than several others and is more tolerant of foreign metals, especially those of the platinum group.

EXPERIMENTAL

Reagents

Standard palladium solution: Prepared by dissolving an accurately weighed amount of Johnson Matthey's Specpure palladium^{II} chloride in hydrochloric acid.

Aluminon solution: Prepared by dissolving a pure preparation of the reagent (B.D.H. Indicator) in water.

Apparatus

A Unicam SP 500 spectrophotometer was used for absorbance measurements. For colorimetric measurements, a Klett-Summerson photoelectric colorimeter (test-tube model) was used. The pH was measured with a Leeds and Northrup line-operated pH meter.

Conditions of study

All experiments were performed at 25°. The total volume of the mixtures prepared for the measurements was 25 ml, and the pH was adjusted to 4·0 by the addition of sodium hydroxide or hydrochloric acid. The ionic strength of the system was maintained at $0{\cdot}1M$ with sodium perchlorate.

Palladium^{II} reacts with AAC at pH 4·0 (λ_{max} 520 mμ), giving an intense violet colour (λ_{max} 560 mμ). At relatively high concentrations of palladium and AAC a flocculent precipitate separates out. The colour intensity is stable for at least 72 hr. The ratio Pd:AAC is 1:2 by the continuous variation method (Fig. 1) and also by the slope ratio and mole ratio methods.

Effect of pH on chelate

The chelate is stable between pH 3·5 and 6·0, as shown by the constancy of λ_{max} within this range. However, the absorbance is constant only between pH 3·8 and 5·5.

Effect of temperature on colour intensity of chelate

The intensity of the colour increases with rise in temperature and decreases when the temperature is lowered. This increase in colour intensity may be attributed to AAC, whose own colour intensity increases with temperature. The colour intensity of the complex, however, remains constant for a considerable length of time at any given temperature and the readings are reproducible.

Conformity to Beer's law

Beer's law is obeyed over the range 0·14–7·7 ppm of palladium.

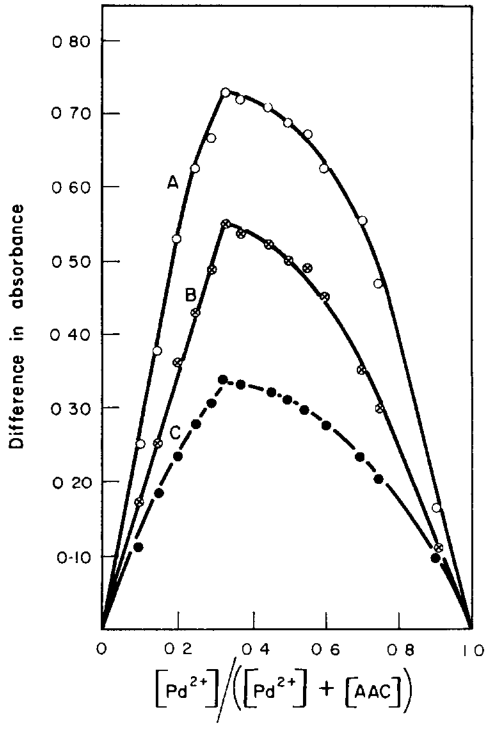

FIG. 1.—Determination of composition of complex by the method of continuous variation at 560 mμ (pH 4·0; μ 0·1*M*)
Concentrations of the interactants (equimolecular)
A: $3{\cdot}33 \times 10^{-4}M$
B: $2{\cdot}50 \times 10^{-4}M$
C: $1{\cdot}67 \times 10^{-4}M$

Sensitivity

The sensitivity of the colour is 0·026 μg. cm^{-2} for log $I_0/I = 0{\cdot}001$. The range of most accurate measurement is 1·0–5·0 ppm of palladium.

Effect of diverse ions

Various ions were tested for their influence on the colour reaction. Fe^{II}, Fe^{III}, Cu^{II}, Cr^{III}, Be^{II}, Zr^{IV}, Th^{IV}, Ga^{III}, In^{III}, Ge^{IV}, Al^{III}, Ca^{II}, Mg^{II} and UO_2^{II} interfere in all concentrations; common anions, like sulphate, nitrate, chloride, bromide, acetate, *etc.*, do not interfere in large excess. Diverse ions were added to the solutions containing 4·26 ppm of palladium and the colour was developed by adding a 3-fold concentration of AAC. The tolerance limits for the various foreign ions were taken as those concentrations which affects the absorbance by less than ±2%. The results are summarised in Table I.

Evaluation of equilibrium constant

In this procedure the equilibrium constant for the reaction $Pd^{2+} + 2H_6R \rightleftharpoons Pd(H_{6-n}R)_2 + 2nH^+$ is defined as

$$K = \frac{[Pd(H_{6-n}R)_2]}{[Pd][H_6R]}\,.$$

The effect of dissociation of the reagent is ignored, and to obtain the usual equilibrium constant this one must be multiplied by $[H]^{2n}$.

log K (K = equilibrium constant at pH 4·0, 0·1*M* ionic strength and 25°) for the reaction was determined by the method of Dey *et al.*,[1,3] as well as by the mole ratio method, and the values were found to be 9·8 and 9·6, respectively.

TABLE I.—EFFECT OF DIVERSE IONS ON THE COLOUR INTENSITY

Concentration of palladium chloride = $4\cdot00 \times 10^{-5}M$
Concentration of AAC = $1\cdot33 \times 10^{-5}M$
pH of the mixtures = $4\cdot0 \pm 0\cdot2$
Klett filter No. 54 used

Foreign ion	Added as	Tolerance limit, *ppm*
Ni^{II}	$NiSO_4$	20
Co^{II}	$Co(NO_3)_2$	58
Ru^{III}	$RuCl_3$	50
Rh^{III}	$RhCl_3$	25
Os^{VIII}	OsO_4	15
Ir^{IV}	$IrCl_4$	60
Pt^{IV}	K_2PtCl_6	20
Au^{III}	$AuCl_3$	40

Recommended procedure for the determination of palladium

The use of AAC as a reagent for the colorimetric determination of palladium^{II}, when present alone in minute quantities, may be recommended. The solution should be suitably diluted or concentrated so as to contain 1–5 ppm of palladium. Introduce a 4-fold excess of freshly prepared AAC solution and maintain at constant temperature for 0·5 hr for the development and equilibration of colour. The pH should be adjusted to 4·5. The colour intensity may then be measured either with a colorimeter using a suitable filter (Klett No. 54) or a spectrophotometer at 560 mμ, and compared with a calibration curve prepared under the same conditions.

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Chemical Laboratories
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KAILASH N. MUNSHI
ARUN K. DEY

Summary—A new colorimetric method for the determination of bivalent palladium with ammonium aurintricarboxylate (Aluminon) is described. The method involves the formation of a violet chelate of palladium-Aluminon at pH 4·0. The colour reaction has a sensitivity of 0·026 μg. cm^{-2} for log $I_0/I = 0\cdot001$, and obeys Beer's law over the range 0·14–7·7 ppm of palladium. The effects of pH, time, order of addition of the reagents, temperature, and diverse ions have been investigated, and a procedure for the microdetermination of palladium is described. The composition of the complex has been confirmed by three different methods as 1:2 (metal:reagent), and an equilibrium constant of $10^{9\cdot8}$ was found by the method of Dey *et al.* at pH 4·0, temperature 25° and ionic strength 0·1*M*.

Zusammenfassung—Eine neue kolorimetrische Methode zur Bestimmung von zweiwertigem Palladium mit Ammonium-aurintricarboxylat (Aluminon) wird beschrieben. Bei pH 4,0 bildet sich ein violettes Palladium-Aluminon-Chelat. Die Farbreaktion hat eine Empfindlichkeit von 0,026 μg. cm^{-2} für log $I_0/I = 0{,}001$, und das Beersche Gesetz wird zwischen 0,14 und 7,7 ppm Palladium befolgt. Der Einfluß von pH, Zeit, Reihenfolge der Zugabe der Reagentien, Temperatur und verschiedenen Fremdionen wurde studiert und eine allgemein anwendbare Arbeitsvorschrift für die Mikrobestimmung von Palladium mit Aluminon beschrieben. Die Zusammensetzung des Komplexes wurde mit den drei üblichen Methoden als 1:2 (Metall:Reagens) ermittelt; die nach der Methode von Dey *et al.* berechnete Stabilitätskonstante ist $10^{9{,}8}$ bei pH 4,0, 25°C und der Ionenstärke 0,1.

Résumé—On décrit une nouvelle méthode colorimétrique de dosage du palladium bivalent au moyen d'aurinetricarboxylate d'ammonium (Aluminon). La méthode met en jeu la formation d'un chélate palladium-Aluminon, coloré en violet, à pH 4,0. La réaction colorée a une sensibilité de 0,026 μg. cm^{-2} pour $\log I_0/I = 0{,}001$, et obéit à la loi de Beer entre 0,14 et 7,7 ppm de palladium. Les effets du pH, du temps, de l'ordre d'addition des réactifs, de la température, et de divers ions ont été étudiés, et on décrit une méthode générale de microdosage du palladium. La composition 1:2 (métal:réactif) du complexe a été confirmée par trois méthodes différentes et la constante de stabilité $10^{9,8}$ à pH 4,0, à la température de 25°C et à la force ionique 0,1*M*, a été calculée par la méthode de Dey *et coll.*

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Direct titration of iron(III) with disodium diaminocyclohexanetetra-acetate

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NUMEROUS methods have been proposed for the direct titration of iron with disodium ethylenediamine-tetra-acetate (EDTA). In most cases, Tiron, salicylic acid, sulphosalicylic acid or thiocyanate ion is used as the indicator. Each of these indicators has certain advantages and disadvantages. For example, Tiron gives an easily distinguishable end-point, but an exceptionally large concentration of the indicator is needed.[3,10] The end-point using thiocyanate indicator is sharp (and can be improved by extraction of the iron-thiocyanate complex into organic solvents),[2,6] but the competitive effect of thiocyanate ion leads to variable results for iron.[6] Chrome Azurol S also gives a good end-point, but in this case the titration results are always high by 0·5% or more.[7] Sulphosalicylic acid does not give a satisfactory colour change in the titration of milligram-amounts of iron.[4] Variamine Blue B is also a good indicator, but it cannot be used in the presence of trace amounts of copper.[5]

The best indicators for iron are those that show a large difference in the colour of the free and complexed forms, because the indicator transition must be seen over the yellow background colour of the iron(III) complex. A preliminary investigation of common indicators showed that screened thiocyanate and Chrome Azurol S gave the sharpest end-points in the titration of milligram-amounts of iron. Therefore, these two indicators were chosen for the examination of the titration of iron with disodium 1,2-diaminocyclohexanetetra-acetate (DCTA).

One would expect better results for titrations of iron in acid solutions using DCTA instead of EDTA because of a larger conditional constant for the iron-DCTA complex. Přibil[8] has reported that iron can be determined by titration with DCTA, but no indication of either the precision or accuracy of the method is given. Clearly, a more detailed investigation was necessary to show that the direct titration with DCTA gives reliable results. The purpose of this paper is to report on the precision and accuracy of the direct titration using screened thiocyanate and Chrome Azurol S as indicators. In addition, the interference of small amounts of some metals (aluminium, cobalt, nickel, manganese and copper) has been examined.

Résumé—On décrit une nouvelle méthode colorimétrique de dosage du palladium bivalent au moyen d'aurinetricarboxylate d'ammonium (Aluminon). La méthode met en jeu la formation d'un chélate palladium-Aluminon, coloré en violet, à pH 4,0. La réaction colorée a une sensibilité de 0,026 μg. cm^{-2} pour log $I_0/I = 0{,}001$, et obéit à la loi de Beer entre 0,14 et 7,7 ppm de palladium. Les effets du pH, du temps, de l'ordre d'addition des réactifs, de la température, et de divers ions ont été étudiés, et on décrit une méthode générale de microdosage du palladium. La composition 1:2 (métal:réactif) du complexe a été confirmée par trois méthodes différentes et la constante de stabilité $10^{9,8}$ à pH 4,0, à la température de 25°C et à la force ionique 0,1*M*, a été calculée par la méthode de Dey *et coll.*

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EXPERIMENTAL

Reagents

Disodium 1,2-diaminocyclohexanetetra-acetate (DCTA). Obtained from Hach Chemical Co. and purified by treatment of a boiling solution of the salt with activated charcoal.

Iron(III) solutions. Prepared both from electrolytic iron (G. F. Smith) and reagent grade iron(III) chloride (Baker and Adamson, 99·5% min. assay). Iron solutions used in the thiocyanate method were prepared from electrolytic iron using only a very slight excess of perchloric acid. The dissolution was accomplished by using dilute perchloric acid and heating gently over a steam plate. Vigorous heating led to the formation of an intractable red residue. This problem is not encountered if a large excess of perchloric acid is used.

Erio Green. Used as the screening agent and incorporated into the DCTA titrant. A sufficient amount of the dye (G. F. Smith Co.) was present to give an absorbance of 0·50 at 575 mμ using a 1-cm cell.

Chrome Azurol S. Obtained from Hach Chemical Co. and used without further purification.

Procedure

In titrations using the thiocyanate end-point, the iron sample was mixed with the thiocyanate solution at an acid pH (*ca.* 2·6), then the mixture diluted with water to pH 3·1–3·3. Attempts to neutralise very acidic iron solutions with dilute base solutions inevitably led to low results. This is believed to be caused by the formation of hydroxy complexes in regions where local excess of base is established when the base is added dropwise. Titration with DCTA is continued until the solution becomes bright green. By incorporation of the screening agent into the titrant, the concentration of Erio Green remains constant relative to the iron content, and the colour change is less variable with iron content.

The titration of iron using Chrome Azurol S presents no particular difficulties. The pH of the sample solution is adjusted to 1·3–2·0 with perchloric acid and the solution heated to 60–70°. One drop of 0·3% indicator is added and the titrant added until the violet colour changes to green. Four or five more drops of indicator are added, and the titration continued until the solution is bright yellow-orange. It is helpful to have some estimate of the iron content, because it is possible to add the bulk of the titrant before heating, and thus the solution is in the proper temperature range when the end-point is approached.

RESULTS

Thiocyanate ion indicator

The work first centered around the effect of indicator concentration on the titration results. This was of interest in that the titration with EDTA shows a large variability with thiocyanate concentration.[6] On the basis of the difference in conditional constants for the formation of EDTA and DCTA complexes of iron, one would expect the best results at pH 3. At pH 3·5 or higher, the hydrolysis of iron would lead to unsatisfactory results.

TABLE I.—VARIATION OF TITRATION RESULTS WITH THIOCYANATE CONTENT[a]

SCN^-, *M*	0·02*M* DCTA used,[b] *ml*	Standard deviation, *ml*
0·01	11·47	0·02
0·02	11·47	0·02
0·04	11·47	0·02
0·10	11·48	0·02
0·20	11·47	0·02

[a] Each entry is the average of 6 analyses; initial pH 3·2–3·1.

[b] Iron(III) sample taken in each case is 10·02 ml and calculated amount of DCTA required is 11·47 ml.

Tables I and II summarise the results of titrations at an initial pH of 3·1–3·2. The titration is essentially independent of the concentration of thiocyanate, at least over the concentration range studied, and independent of the iron concentration over the range 0·1–0·3 mmole of iron/100-ml sample. When a correction was applied for the known amount of iron(II) in the iron(III) stock solution, the amount of iron taken for analysis and that found agreed to within 0·1%. The determination of iron using thiocyanate indicator is dependent upon the initial pH of the solution, and is

TABLE II.—VARIATION OF TITRATION RESULTS WITH AMOUNT OF IRON AT CONSTANT THIOCYANATE CONCENTRATION OF 0·04M[a]

0·02M Fe taken, *ml*	0·20M DCTA used,[b] *ml*	Standard deviation, *ml*
5·00	5·71	0·01
10·00	11·45	0·02
15·00	17·18	0·01

[a] Each entry is the average of 6 analyses.
[b] Calculated DCTA required is 11·45 ml/10·00-ml iron sample.

stoichiometric only above pH 3. Attempts to use buffers always led to low results because of complex formation of the buffer with iron(III) ion. This use of a buffer undoubtedly accounts for some of the variability of results obtained by Lydersen and Gjems.[6] Under the controlled conditions employed above, the pH change upon titration is not sufficiently large to give appreciable errors and it is not necessary to employ a buffer system. Although the method is capable of good accuracy, it is exceedingly difficult (in practice) to free the iron sample from excess acid and thus this aspect severely limits its use.

Chrome Azurol S indicator

In view of the results of the thiocyanate titrations, it was certain that titration with DCTA in the pH region 2–3 would be much more precise and accurate than that with EDTA. Hence, work was concentrated on titrations with DCTA at the lowest possible pH where good results could be obtained. Preliminary experiments indicated that this lower limit is about pH 1·25.

Table III summarises the results of the titration of iron with 0·01M DCTA. In each case, the sample was taken to fumes before titration to oxidise any residual iron(II). The agreement with the known amount of iron taken for analysis shows that the direct method gives very good results.

TABLE III.—DIRECT AND INDIRECT TITRATION OF IRON WITH DCTA AT pH 1·25–1·50 USING 0·1005-MMOLE SAMPLES

	Titrant required,[a] *ml*	
	Direct	Indirect
	10·66	10·67
	10·67	10·66
	10·64	10·67
	10·65	10·64
	10·66	
Average	10·66	10·66
Fe found, *mmole*	0·1004	0·1004

[a] 0·009421M DCTA.

The relative standard deviation for both titration methods is the same. Table IV shows the results that are obtained with 0·02M DCTA over a range of iron contents. It was found that the maximum amount of iron that can be determined with Chrome Azurol S indicator is approximately 1 mmole/100-ml sample volume because of the interfering colour of the iron-DCTA complex.

The most interesting results were those for titrations in the presence of other metal ions. In contrast to the observation of Musil and Theis,[7] milligram-amounts of aluminium react with Chrome Azurol S to give a violet colour at pH 1·3, which obscures the end-point for the iron titration. At pH 3 the molar extinction coefficient is about 30,000. Milligram-amounts of copper and nickel interfere in the titration, as would be expected from the values of the alpha function $\left(\frac{\text{free metal ion}}{\text{total metal}}\right)$ for these elements.[8] Manganese would not be expected to interfere, but the addition of 0·04 mmole

TABLE IV.—DIRECT TITRATION OF IRON AT pH 1·25–1·50 WITH 0·01959*M* DCTA

Fe taken, *ml*	Average DCTA required, *ml*	Standard deviation, *ml*	Relative standard deviation, *ppt*
5·00	4·80[a]	0·006	1·3
10·00	9·60[a]	0·016	1·7
15·00	14·40[a]	0·009	0·6
20·00	19·20[a]	0·006	0·3
25·00	23·98[b]	0·022	0·9
50·00	47·96[a]	0·033	0·7

[a] Average of 4 analyses.
[b] Average of 6 analyses.

of manganese to 0·1 mmole of iron(III) led to results that were 0·3 % low. The cause of the interference by manganese could not be ascertained. No interference was observed for small amounts of cobalt(II). The addition of chloride ion as hydrochloric acid has no effect on the iron determination as long as the pH is greater than 1·3. Chloride ion added as sodium chloride has no effect on the titration at 0·1*M* levels. Table V shows that an increase in the ionic strength by addition of sodium nitrate does not lead to an appreciable change in stoichiometry.

TABLE V.—EFFECT OF ADDITION OF SODIUM NITRATE ON TITRATION OF IRON WITH DCTA AT pH 1·25–1·35

$NaNO_3$, *M*	0·009421*M* DCTA required, *ml*
0·000	10·66
0·040	10·67
0·080	10·65
0·20	10·62
0·40	10·63

0·1005 mmole of iron taken in each case.

The end-point transition using Chrome Azurol S is much more easily determined than that of thiocyanate ion or sulphosalicylic acid. This and the fact that the conditions for use of the thiocyanate indicator are so restrictive, makes Chrome Azurol S the preferred indicator for the direct titration of iron.

In view of (1) the simplicity of the direct method using Chrome Azurol S, (2) the superior accuracy compared to the direct EDTA titration, and (3) a precision that is comparable to one of the best indirect titration methods, the direct titration of iron with DCTA is highly recommended.

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Summary—The direct titration of iron(III) with disodium 1,2-diaminocyclohexanetetra-acetate using thiocyanate ion and Chrome Azurol S as indicators has been studied in detail. Good results can be obtained with thiocyanate indicator if the pH of the iron(III) solution is adjusted to 3·0–3·2 by simple dilution. The addition of a buffer or a dilute solution of a strong base to adjust the pH to the desired range always leads to low results. Chrome Azurol S is the preferred indicator because the colour transition is much more distinct and because titrations are possible in relatively acid solutions (pH 1·25). Up to 50 mg of iron/100-ml sample may be determined with a relative standard deviation of only 2 parts per thousand.

Zusammenfassung—Die direkte Titration von Eisen(III) mit Dinatrium-cyclohexadiamintetraacetat mit Rhodanid und Chromazurol S als

Indikatoren wurde in ihren Einzelheiten studiert. Gute Ergebnisse mit Rhodanid erhält man, wenn man durch einfache Verdünnung den pH der Eisenlösung auf 3·0–3·2 einstellt. Zugabe eines Puffers oder einer verdünnten Lösung einer starken Base zur pH-Einstellung gibt stets zu niedrige Ergebnisse. Chromazurol S ist als Indikator vorzuziehen, da der Farbumschlag schärfer ist und Titrationen in ziemlich sauren Lösungen (pH 1·25) möglich sind. Bis 50 mg Eisen in 100 ml Probe lassen sich mit einer relativen Standardabweichung von nur 2‰ bestimmen.

Résumé—On a étudié en détail le dosage direct de l'ion ferrique au moyen de cyclohexanediamine tétracétate disodique en utilisant, comme indicateurs, l'ion thiocyanate et le Chrome Azurol S. On peut obtenir de bons résultats avec l'indicateur au thiocyanate si le pH de la solution ferrique est ajusté entre 3·0 et 3·2 par simple dilution. L'addition d'un tampon ou d'une solution diluée de base forte pour ajuster le pH dans la zone désirée conduit toujours à des résultats faibles. On préfère l'indicateur Chrome Azurol S, car le virage de couleur est beaucoup plus net, et les dosages sont possibles en solutions relativement acides (pH 1·25). On peut doser jusqu'à 50 milligrammes de fer dans un échantillon de 100 millilitres, avec un écart type relatif de deux pour mille seulement.

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The preparation of cerium–IV hydroxide from ammonium hexa-nitratocerate by employing kinetically controlled precipitation through urea hydrolysis

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THE recovery of pure cerium-IV chemicals from thorium-freed monazite cerium-thorium sands involves the isolation of the cerium from the remaining rare earths by conversion to ammonium nitratocerate $(NH_4)_2Ce(NO_3)_6$.[1] A practical cerium-IV reagent which can be converted to sulphatoceric acid, $H_2Ce(SO_4)_3$, in sulphuric acid solution, for use as a standardised titrant, has previously been described.[1] The procedure involves the precipitation of $Ce(OH)_4$ by addition of a saturated aqueous solution of pure ammonium nitratocerate to a large excess of aqueous ammonia, followed by filtration of insoluble $Ce(OH)_4$, and washing this with water to eliminate ammonium salts. By this process the hydroxide is soluble in hot dilute sulphuric acid. If this $Ce(OH)_4$ is air dried, it forms a horny solid which must be ground to pass a 100-mesh sieve. The procedure here described for producing $Ce(OH)_4$ by kinetically controlled precipitation, employing urea, offers a much more practical preparation of ceric hydroxide, and avoids the difficult drying and grinding operation previously required.

Procedure

Add 1 pound of pure ammonium nitratocerate to a solution containing 1 pound of urea and 10 ml of concentrated nitric acid in a volume of 600 ml, in a 2000-ml covered Pyrex beaker, at boiling temperature. The resulting solution is dark red in colour and crystal clear. Keep the solution boiling briskly, adding water to replace that lost as vapour.

Indikatoren wurde in ihren Einzelheiten studiert. Gute Ergebnisse mit Rhodanid erhält man, wenn man durch einfache Verdünnung den pH der Eisenlösung auf 3·0–3·2 einstellt. Zugabe eines Puffers oder einer verdünnten Lösung einer starken Base zur pH-Einstellung gibt stets zu niedrige Ergebnisse. Chromazurol S ist als Indikator vorzuziehen, da der Farbumschlag schärfer ist und Titrationen in ziemlich sauren Lösungen (pH 1·25) möglich sind. Bis 50 mg Eisen in 100 ml Probe lassen sich mit einer relativen Standardabweichung von nur 2‰ bestimmen.

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The boiling temperature after 30 min is approximately 110° and the colour of the solution is beginning to decrease. At 40 min the colour is dark orange; foaming to the extent of 25 mm results from the evolution of carbon dioxide from the urea breakdown. At 45 min precipitation begins, the precipitate being orange in colour. At 60 min the precipitate is lemon yellow and the solution temperature is 112°. At 75 min the precipitate is still lemon yellow, and foam is still being produced. At 90 min the reaction is complete, the solution is colourless, and the precipitate is grey-white.

Allow the reaction mixture to cool, and transfer the solution and precipitate to two polyethylene wide-necked 250-ml bottles with screw caps. Place the bottles in a pair of centrifuge trunion cups, and separate the precipitate from the parent solution by 5 min rotation at 1500 rpm and 250 mm displacement from the centre of rotation. (Trunion cups #844 of a No. 2 International Instrument Company centrifuge may be employed.) Pour off supernatant solution (pH approximately 12), add 150 ml of water to each bottle, stir well and repeat this centrifugal separation 5 or 6 times until the washings no longer give an ammonia test.

Transfer the $Ce(OH)_4$ thus prepared to a sheet of polyethylene and spread it out in a thin layer. The product air-dries in a few hours to give a finely divided pulverulent product. The yield is theoretical (approximately 37·95% of the weight of hexanitratocerate taken as raw material).

The finished product is readily soluble in hot dilute sulphuric acid to give a crystal clear solution that is stable on storage, and that may be heated to boiling without decomposition. It is not soluble in cold concentrated nitric or perchloric acid except after extremely long periods of storage.

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Summary—The preparation of cerium-IV hydroxide by kinetically controlled precipitation through use of the hydrolysis of urea and its reaction with ammonium hexanitratocerate is described. The air-dried product thus obtained is of fine-mesh particle size and is readily soluble in hot dilute sulphuric acid to form solutions of sulphatoceric acid, $H_2Ce(SO_4)_3$, for oxidimetric titrations.

Zusammenfassung—Die Darstellung von Cerhydroxyd durch kinetisch kontrollierte Fällung mittels Dissoziation von Harnstoff und Reaktion mit Ammoniumnitratocerat wird beschrieben. Das so erhaltene Produkt ist nach Trocknung an der Luft sehr feinkörnig und leicht in heißer verdünnter Schwefelsäure löslich, wobei sich als titrimetrisches Oxydationsmittel geeignete Lösungen von Sulfatocersäure $H_2Ce(SO_4)_3$ bilden.

Résumé—On décrit la préparation de l'hydroxyde cérique par précipitation contrôlée cinétiquement, en utilisant l'hydrolyse de l'urée et la réaction avec l'hexanitratocérate d'ammonium. Le produit ainsi obtenu, séché à l'air, se présente en particules fines et est aisément soluble en acide sulfurique dilué chaud, formant des solutions d'acide sulfatocérique $H_2Ce(SO_4)_3$; celles-ci sont utilisées comme oxydant pour titrages.

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Talanta, 1964, Vol. 11, p. 1275. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

"Deionised" or "deioned"?

SIR,

In past years, the terms "deionisation" (of water, hydrogen peroxide, *etc.*) and "deionised" (of water, *etc.*)[1–7] have occurred widely in world scientific literature in connection with the extensive use of ion-exchangers in science and industry (in particular for ion-exchange water purification).

In our opinion, these expressions are not well chosen for the following reasons. In fact, the term "ionisation of water" has meant the following quite definite equilibrium for a long time:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

Thus, the term "deionisation of water" denies ionisation, *i.e.*, denies process (1), which is incorrect: in reality, "extraction of ions" should be implied, *i.e.*, the removal of ionic impurities (*e.g.*, heavy metals) from water or hydrogen peroxide in the course of the ion-exchange purification of these substances.

This specific error occurs in the scientific literature of many languages, among them English (deionisation, deionised), German (Entionisierung, Deionisierung, entionisiertes), French (dé[s]ionisation, déionisé), Russian (деионизация, деионизированный), and also in Hungarian, Dutch, Spanish, Italian, Ukrainian, Czech, Swedish, and others. In addition to this, in English scientific literature, widespread synonyms used are "desalting", "demineralisation" (of water, *etc.*), "ion-exchange water", "demineralised water", *etc.*[1] Similar variations in this respect are observed in other languages.

It would seem more appropriate to use the expressions "deionation" and "deioned", which are shorter, and—an important point!—they express the crux of the matter more clearly and precisely. Analogous simplifications and more accurate definitions of these terms could easily be devised for other languages, and as a result of it we would find in the German language "Entionierung" and "entioniertes", in Russian "деионирование" and "деионированный" (*cf.*[8]), in Ukrainian "деіонування" and "деіонований", in French "dé(s)ionation" and "déioné", in Czech "deionace", and "deionovaný", in Swedish "avjonerat" and "avjonering", *etc.*

Surely the main thing of everything of this suggestion is not so much in the rejecting of these two unnecessary letters -is-, to which we have already become accustomed, as in terminological precision. But for precision and accuracy: *Amicus Plato, sed magis amica veritas!*

Acknowledgement—Many thanks are due to my friends Dr. A. A. Bugayevsky for his interest and helpful criticism, and Mrs. H. G. Klausnitzer for the English translation.

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18 *March* 1964.

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TALANTA REVIEW*

RADIOMETRIC TITRATIONS

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Summary—A review of radiometric titrations is presented.

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* For reprints of this review see publisher's announcement at the end of this issue.

1. INTRODUCTION

THE present paper aims at surveying the basis, the possibilities in, and the present state of radiometric titrations. Nearly all the papers published in this field from 1941, when this method was first developed, to the end of 1963 have been covered.

To the best of our knowledge, no review paper on this subject has so far been published in the literature. However, radiometric methods in general, and the general analytical applications of radioactive isotopes, have been discussed in quite a large number of reviews. In these only relatively small space has been devoted to radiometric titrations, and the descriptions have mainly been limited to an incomplete survey of earlier communications.

In the present review, several papers published in less readily available journals, or not available at all, have been covered in a relatively detailed manner. An attempt has been made by the present authors to discuss in a reasonably homogeneous form these less-known papers and the other better known material. This should facilitate the spread and further development of the method.

2. END-POINT DETERMINATION BY RADIOMETRY

In the course of a radiometric titration, in order to determine the end-point, the radioactivity of the solution is chosen as the "property" which is followed. Under identical conditions of measurement, changes in radioactivity are proportional to the concentration of the labelled component. Thus, on plotting the changes in the radioactivity of some of the reactants or reaction products during the titration against the quantity of titrant added, the end-point is indicated by the point of intersection of two straight lines on the titration curve.

Measurement of the radioactivity of substances, as a "property" followed during titration, can be carried out with an extreme accuracy, reliability and sensitivity, using a Geiger-Müller (GM) tube or one of the scintillation methods described in the literature. This procedure offers the particular advantage that, quite in contrast with other instrumental methods of end-point indication, the magnitude of the property being measured can be altered as desired, even when titrating extremely low concentrations. This is because the magnitude is determined exclusively by the specific activity of the radioactive isotope used for labelling.

Another important advantage of the method is the possibility of its easy automation. The technique of measuring radioactivity has been so far developed in other, non-analytical aspects to such an extent that the knowledge can also be applied in the case of radioanalytical methods without any difficulty. Although there are still only relatively few results in this field, in our opinion the process of automation would appear to represent one of the main trends in the development of radiometric titrations in the future.

In addition, it should be mentioned that end-point determination by radiometry can also be applied, without any further modification, in coloured, turbid or corroding media, because the actual measurement of radioactivity is not affected by these conditions.

3. "PHASE SEPARATION" AND ITS IMPORTANCE IN RADIOMETRIC TITRATION

As already mentioned, changes in the radioactivity of one of the reactants or reaction products are followed during radiometric titrations. This necessitates that the radioactivity of the component being followed should be measured "alone", *i.e.*, separated from that of the other partners of the system. This is one of the central problems in radiometric titrations. In effect, of all the reaction types applied in titrimetric analysis, the separation of phases only occurs in the case of titrations based on precipitate formation; in the case of other reaction types, separation can only be carried out using some auxiliary method or process.

On account of the great importance of phase separation, it will be discussed in detail in the present review, and the description of the various possibilities available in this respect will form a fundamental part of the discussion.

Phase separation is closely correlated with another problem in radiometric titration of equal importance—the continuity of the course of a titration. This must be particularly emphasised because, in order to evolve a suitable method of titration, not only must a reasonable possibility of phase separation exist, but the method chosen must be suitable for the application of continuous separation instead of merely batchwise operation.

4. RADIOMETRIC TITRATION BASED ON PRECIPITATION

Many reactions based on precipitation are known, apart from those applied in neutralisation analysis. However, with the exception of argentometric and mercurimetric titrations, reactions based on precipitate formation are rarely used in titrimetry. This is a direct result of the lack of adequate visual or instrumental methods of end-point indication.

The significance of radiometric titrations consists mainly in its capability of indicating the end-point, even in precipitation reactions of analytical importance for which no adequate visual indicators are available. A pronounced disadvantage of visual precipitation titrations against acid-base titrations, for example, is that different indicators are required for nearly every reaction. In radiometric titrations, on the other hand, it is possible to determine several substances by only one labelled titrant (which at the same time also serves as an indicator).

4.1. *Mathematical analysis of titration curves*

The theoretical problems of radiometric titrations and the mathematical analysis of the titration curves have been discussed in detail by Duncan and Thomas,[1] and by Jesenák and Tölgyessy.[2–4]

In evolving the theory of radiometric titrations based on precipitate formation, Jesenák and Tölgyessy start with the analogy between these titrations and amperometric titrations.[5]

On titrating a solution which contains cation A^+ with a titrant containing anion B^-, with the formation of a precipitate AB of poor solubility (with a solubility product L_{AB}), according to the reaction

$$A^+ + B^- \rightleftharpoons AB \qquad (1)$$

the correlation between the concentration of the ion A^+ and the amount of titrant added is expressed by the equation

$$\gamma^2 - \frac{\gamma_0 v_0 - c_0 v}{v_0 + v}\gamma - L_{AB} = 0 \qquad (2)$$

where γ_0 = the initial concentration of cation A^+ (normality),
γ = the concentration of cation A^+ during titration (normality),
c_0 = the concentration of titrant referred to B^- ion (normality),
v_0 = the initial volume of titrant (litres),
and v = the amount of titrant added (litres).

If

$$\frac{\gamma_0 v_0 - c_0 v}{v_0 + v} = Q \tag{3}$$

then

$$\gamma = \tfrac{1}{2}(Q + \sqrt{Q^2 + 4L_{AB}}) \tag{4}$$

Similarly, the concentration of B^- ion, c, is given by the equation

$$c = \tfrac{1}{2}(-Q + \sqrt{Q^2 + 4L_{AB}}) \tag{5}$$

and the sum of the concentrations of the two ions, $\gamma + c$, is given by

$$\gamma + c = \sqrt{Q^2 + 4L_{AB}} \tag{6}$$

In radiometric titrations, three types of titration curve may be obtained. The shape of the titration curve depends on whether the titrant itself, or the titrated solution, or both, are actually radioactive.

(*a*) When the solution to be titrated is active and the titrant is inactive, the activity of the supernatant solution shows a decrease during titration proportional to the formation of precipitate. At the equivalence point, the actual activity of the solution is determined by the solubility of the precipitate.

Because the radioactivity of the solution is directly proportional to the concentration, *i.e.*,

$$\gamma_0 = k \,.\, I_0$$

where I is the activity expressed by the number of impulses per minute

and $$\gamma = k \,.\, I$$

on substitution into equation (2), the equation

$$I^2 - \frac{kI_0 v_0 - c_0 v}{k(v_0 + v)} I - \frac{L_{AB}}{k^2} = 0 \tag{7}$$

is obtained.

In Fig. 1, the theoretical titration curve described by equation (7), referred to the conditions specified in the figure, is shown.

(*b*) When the solution to be titrated is inactive and the titrant is active, the activity of the solution is determined at the beginning of titration by the solubility product of the precipitate formed during titration, and the activity does not rise until the equivalence point is reached. However, on attaining this point, the activity of the solution increases markedly on the addition of further portions of active titrant.

On substituting $c = k \,.\, I$ into equation (5), the equation

$$I^2 + \frac{\gamma_0 v_0 - c_0 v}{k(v_0 + v)} I - \frac{L_{AB}}{k^2} = 0 \tag{8}$$

is obtained.

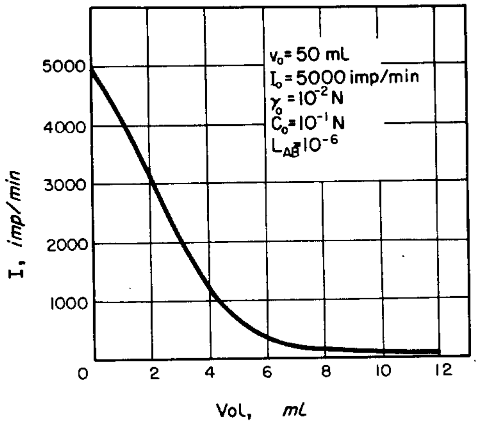


FIG. 1

The titration curve described in such conditions is shown in Fig. 2.

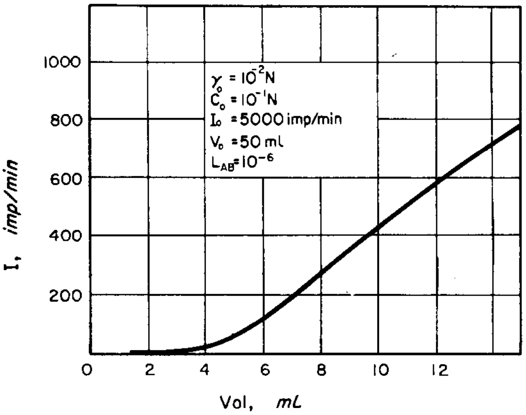


FIG. 2

(*c*) When both the titrated solution and the titrant are active, the activity of the solution decreases during titration, and subsequently rises. The equivalence point is determined by the minimum value of the curve.

If

$$\gamma_0 = k_1 I_{1,0},$$

$$\gamma = k_1 I_1,$$

and

$$c = k_2 I_2$$

the relative activity measured during the titration will be

$$I = \frac{1}{2}\left[R\left(1 - \frac{k_1}{k_2}\right) + \sqrt{R^2 + \frac{4L_{AB}}{k_1^{\,2}}} + \sqrt{\left(\frac{k_1}{k_2}R\right)^2 + \frac{4L_{AB}}{k_2^{\,2}}}\right] \tag{9}$$

where

$$R = \frac{k_1 I_{1,0} v_0 - c_0 v}{k_1(v_0 + v)} \tag{10}$$

In some cases, equation (9) can be simplified:

1. If $k_1 = k_2 = k$, *i.e.*, if the ratio of the activities of the solution to be titrated and of the titrant corresponds to the ratio of their concentrations, equation (9) can take the simplified form

$$I = \sqrt{R^2 + \frac{4L_{AB}}{k^2}} \tag{11}$$

In Fig. 3, the titration curve described by these conditions is presented.

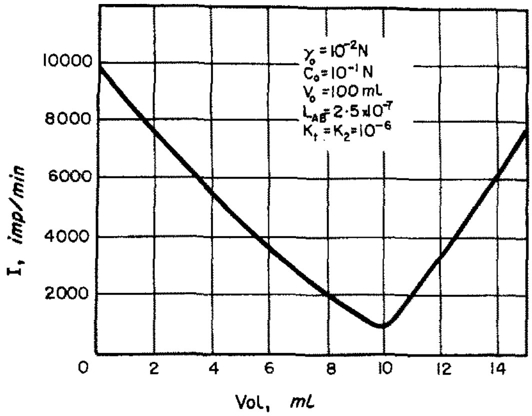


FIG. 3

2. If k_1 is negligible compared with k_2, *i.e.*, if the activity of the titrated solution markedly exceeds that of the titrant, the simplified form reads

$$I \approx \frac{1}{2}\left[R + \sqrt{R^2 + \frac{4L_{AB}}{k_1^2}}\right] \tag{12}$$

3. If, on the other hand, k_2 is negligible compared with k_1, equation (9) can be simplified to

$$I \approx \frac{1}{2}\left[-\frac{k_1}{k_2}R + \sqrt{\left(\frac{k_1}{k_2}R\right)^2 + \frac{4L_{AB}}{k_2^2}}\right] \tag{13}$$

4.2. *End-point determination by extrapolation method, and simplified techniques*

In radiometric titrations, the correlation of the activity of the solution and the quantity of titrant added is plotted as a graph. The end-point is indicated by the break in the curve.

The determination of the end-point with the aid of the titration curve (whose plotting requires 6 readings) used to last about 40–50 min. The speed of the determination depends on the nature of the precipitate formed and on the rate of its sedimentation. It is also possible to detect the end-point using only 2 points on the titration curve. In this case, the time required for the determination is reduced to 8–10 min.[6–10] Jesenák and Tölgyessy[2,3,11] have discussed in detail the mathematical analysis of end-point determination by the extrapolation method.

(*a*) *On titrating an active test solution with an inactive titrant*, the number of ml required to reach the end-point (V_{ex}) can be calculated by the formula

$$V_{ex} = \frac{I_0 \cdot V_1}{I_0 - I_1} \tag{14}$$

where V_1 is the number of ml of titrant added when the activity of the solution decreases to $I_1(V_1 < V_{ex})$, and I_0 is the initial activity of the solution (Fig. 4).

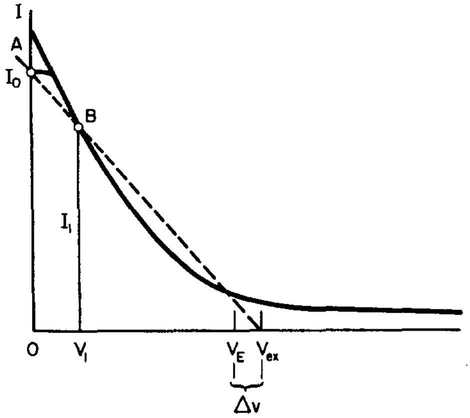


FIG. 4

When the number of ml of titrant added is given as a ratio related to the real equivalent consumption (V_E),

$$v_1 = k \, . \, V_E \quad ,$$

and the relative error of the determination by the extrapolation method, δ, is given by

$$\delta = \frac{V_E - v_{ex}}{V_E} = \left(1 - \frac{K \, . \, I_0}{I_0 - I_1}\right) \tag{15}$$

On titrating a radioactive test solution with an inactive titrant, the correlation of the concentration of the labelled ion γ with other parameters of the determination can be derived from equation (2), using values in the literature:[11]

$$\gamma^2(v_0 + v) - \gamma\gamma_0 v_0 + \gamma c_0 v - L_{AB}(v_0 + v) = 0 \tag{16}$$

and, because the radioactivity of the labelled ion is proportional to the concentration ($\gamma = k \, . \, I$), the changes in activity can be expressed by

$$\gamma_0{}^2 v_0 I^2 + \gamma_0{}^2 v I^2 - \gamma_0{}^2 v_0 I_0 I + \gamma_0 c_0 I_0 I v - L_{AB} I_0{}^2 v_0 - L_{AB} I_0{}^2 v = 0 \tag{17}$$

Because the graph of activity against the number of ml of titrant added does not give a straight line, the determination of the equivalence point by the extrapolation method is accompanied by an error which increases with an increase in the solubility product, L_{AB}, of the precipitate formed, and with an increase in the ratio v/v_0.

In order to check the validity of equation (17), Jesenák and Tölgyessy[11] titrated Tl^+ ion labelled with ^{204}Tl using $0{\cdot}1N$ Br^- solution as titrant. They also calculated the course of the titration curves under the given conditions of titration according to equation (17), using the following values: $\gamma_0 = 10^{-2}M$-$6 \times 10^{-2}M$; $v_0 = 5 \times 10^{-2}$ litre; $c_0 = 0{\cdot}1M$; $I_0 = 10^3$ imp./min; $L_{TlBr} = 2 \times 10^{-6}$ mole^2/litre^2. The titration curves obtained in this way are shown in Fig. 5. It can be seen that the experimental results are in a fair accordance with the calculated values (the experimental results are denoted by circles). Fig. 5 also shows the curves which connect the identical values of relative error of determinations by the extrapolation method, calculated using equations

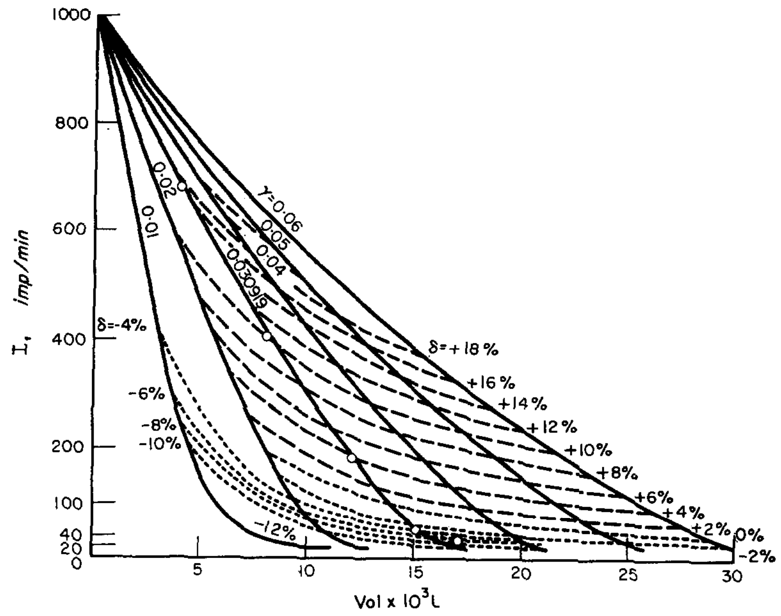


Fig. 5

(15) and (17). The dependence of the values of these errors on the volumes of titrant added and on the concentration of the test solution are shown by Fig. 6. It can be seen that relative errors may attain quite appreciable values. The errors did not show the minimum values at the ratio of $I/I_0 = 0{\cdot}5$ at which extrapolation is suggested in the literature.[7] Thus, it appears advisable in radiometric titrations to check the error of the extrapolation method or to evaluate the titration on the basis of equation (17).

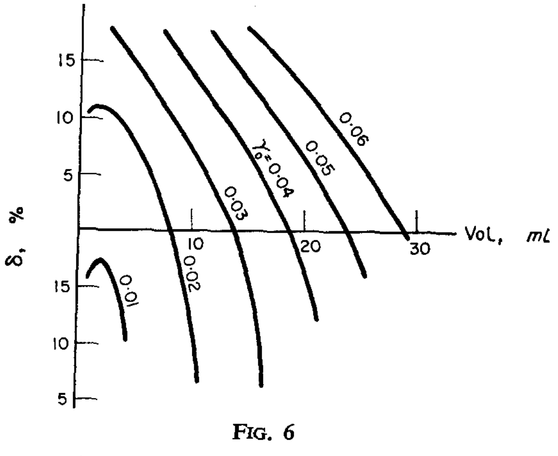


Fig. 6

Because the evaluation of equation (17) is rather cumbersome, we suggest the use of the following method. Equation (17) can also be expressed in a dimensionless form with the aid of the simplexes

$$J = \frac{I}{I_0}, \qquad V = \frac{v}{v_0}$$

and of the criteria

$$C = \frac{\gamma_0}{\sqrt{L_{AB}}}, \qquad C_c = \frac{c_0}{\sqrt{L_{AB}}}$$

leading to the equation

$$C_\gamma^2(J^2 + VJ^2 - J) + C_c VJC_\gamma - (1 + V) = 0 \tag{18}$$

Serial determinations can be carried out by maintaining, during the measurements,

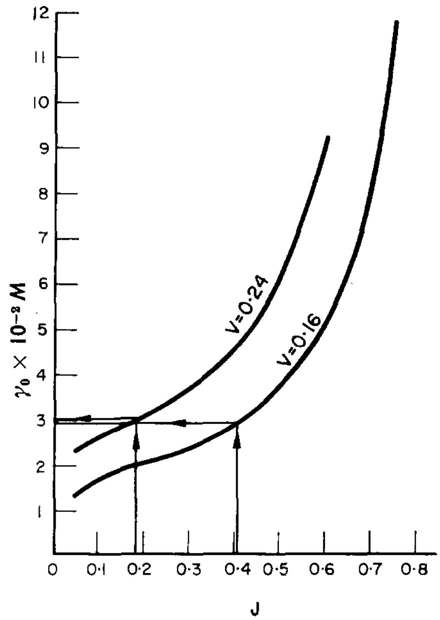


Fig. 7

constant values of V and C_c. In this case, equation (18) yields the correlation

$$C_\gamma = F(J)_{V,C_c} \tag{19}$$

or

$$\gamma_0 = G(J)_{V,C_c} = \sqrt{L_{AB}} \cdot F(J)_{V,C_c} \tag{20}$$

the application of which to the determination of Tl^+ ions, described by adding two standard volumes of titrant to the test solution, is shown in Fig. 7. The exact concentration of the test solution can be read directly from Fig. 7.

The error in the extrapolation method is

$$\delta = \frac{1 - (K - J)}{1 - J} \tag{21}$$

This method offers the advantage of maintaining c_0, v_0, v and L_{AB} at constant values in serial determinations. The value of J ($J = I/I_0$) is obtained from the activity of the test solution and from the activity measured on the supernatant liquid after forming a precipitate by addition of a standard amount of titrant. Then the concentration of the test solution is read from the graph plotted using equation (18).

(*b*) *On titrating an inactive test solution with an active titrant*, the number of ml required to attain the equilibrium point can be calculated by the formula

$$v_{\mathrm{ex}} = \frac{V_1 I_2 - V_2 I_1}{I_2 - I_1} \tag{22}$$

In this case, an excess of titrant, V_1, is first added to the test solution, and the activity of the solution, I_1, is determined. On adding a second volume of titrant, v, where $V_2 = V_1 + v$, the activity of the solution, I_2, is again measured (Fig. 8).

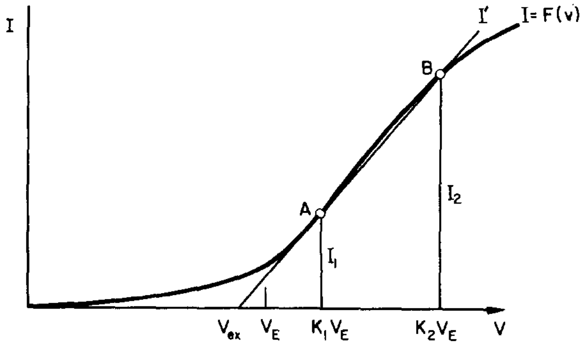


FIG. 8

In this case, according to Fig. 8, the relative error of the determination will be

$$\delta = \frac{V_{\mathrm{E}} - V_{\mathrm{ex}}}{V_{\mathrm{E}}} = \frac{I_2(1 - K_1) - I_1(1 - K_2)}{I_2 - I_1} \tag{23}$$

In addition, Jesenák and Tölgyessy[11] evaluated the derived dimensionless equations using an electronic computer, type ZRA I. Thus, the course of the curve of precipitate formation, of the dilution curve, and of the error of the linear extrapolation was calculated for a wide field of varying parameters in order to follow the effect of the single parameters in precipitation reactions of analytical importance.

4.3. *Methods of phase separation and technique of titration*

The fundamental prerequisite for the possibility of carrying out a radiometric titration is the ability to separate the initial radioactive reagents from the radioactive reaction products. This, however, as already previously mentioned, is possible only in the case when the reaction products are present in a different phase from that of the initial substances. This condition is met in precipitation reactions where the reaction product precipitates from the liquid medium in a solid form, *i.e.*, the radioactive indicator is converted from an aqueous phase into solid phase. In all such operations described in the literature, phase separation has been achieved by filtration, centrifuging or flotation.

4.3.1. *Filtration methods:* In the simplest case, the precipitate formed on titration can be separated from the solution by filtration through filter paper. This method was used, for example, by Moeller, Terril and Seal[12] to determine chloride ion in various waters.

The first apparatus applying phase separation by filtration to radiometric titration was designed by Langer.[13] This is shown in Fig. 9. On titration, after the addition of a certain amount of titrant, the supernatant liquid is sucked up by the suction device into the glass mantle, and the activity of supernatant liquid is measured by a GM counter. After returning this liquid to the bulk solution, another portion of titrant is added to the test solution, and the whole process is repeated.

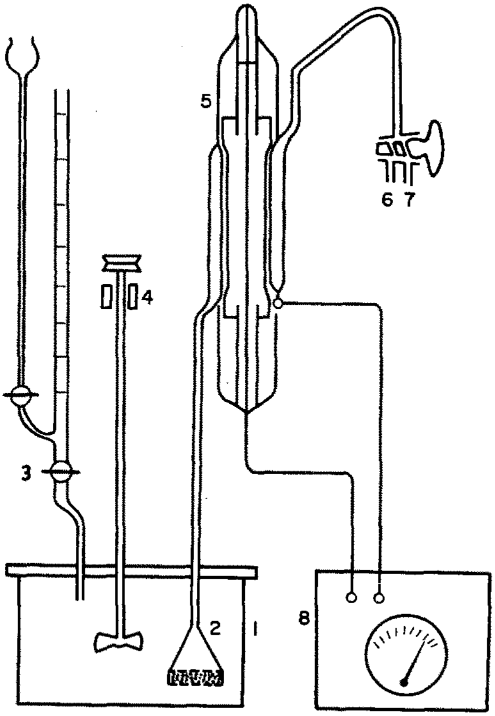


Fig. 9.—Apparatus for radiometric titrations based on precipitate formation, according to Langer.[13]

1. Titration flask	5. GM counter
2. Suction device with filter	6. To rubber bulb
3. Burette	7. To suction pump
4. Stirrer	8. Rate-meter

The apparatus shown in Fig. 10 was used for radiometric titrations by Sirotina and Alimarin.[14]

The apparatus used by Tölgyessy and Schiller[15] is shown in Fig. 11.

A conventional apparatus for amperometric titration was modified and adapted to radiometric titration by Aylward and co-workers.[16] The dropping mercury electrode was removed from the original apparatus, and it was replaced by a filter tube.

During titration, volume changes take place, arising from the addition of titrant. The measured impulse values have, therefore, to be corrected for the volume change occurring during titration. The correction value is obtained by multiplying the measured impulse values by the correction factor, k', where

$$k' = \frac{V_0 + V_1}{V_0} \tag{24}$$

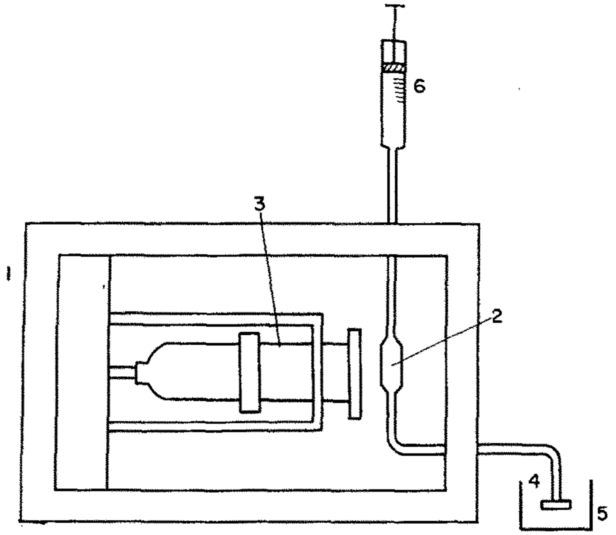


FIG. 10.—Apparatus for radiometric titrations based on precipitate formation, according to Sirotina and Alimarin:[14]

1. Lead mantle	4. Glass filter
2. Glass container	5. Titration flask
3. GM counter	6. Sprayer

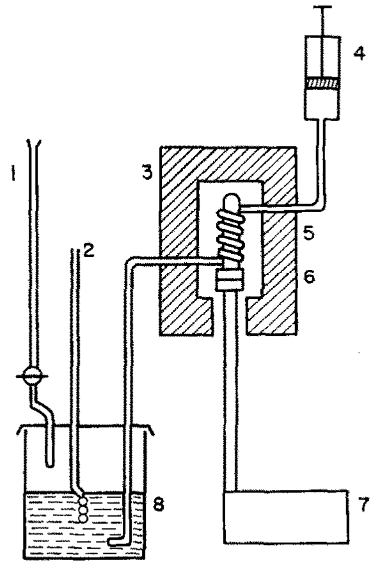


FIG. 11.—Apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Schiller:[15]

1. Burette	5. Glass spiral
2. Stirrer	6. GM counter
3. Lead mantle	7. Rate meter
4. Sprayer	8. Glass tube with glass filter

V_0 being the original volume, in ml, of the test solution and V_1 the number of ml of titrant added.

4.3.2. *Centrifuging method:* A shortcoming of the filtration methods is the glass tube ending in a glass filter, which is frequently clogged by fine-grain precipitates. This drawback is, however, eliminated in the centrifuging method evolved by Korenman and co-workers.[17] In this method, identical amounts of the test solution are transferred into several centrifuge tubes, various amounts of the titrant are added, and the tubes are then filled up to the same volume with distilled water. The precipitate formed is then sedimented by centrifuging, 0·5–1·0-ml portions of the supernatant liquid are transferred by a pipette to filter paper, and, after drying the paper strips, the radioactivity of the preparations is measured. The titration curve is plotted using the values obtained. The Frieseke Hoepfner Automat apparatus, type FH 49 proved to be particularly suitable[18] for rapid determinations by the centrifuging method. In this apparatus, the circular dry filter papers are placed in the cavity of the rotating sample-exchanger disc, and their activity is automatically measured. A titration curve is plotted on the basis of the registered values of activity.

4.3.3. *Flotation method:* Flotation was used with success by Braun, Galateanu and Maxim[19,20] for phase separation in radiometric precipitation titrations. On applying flotation, solid particles suspended in water are separated from the liquid by the effect of air bubbled through the system in a vigorous flow. The particles adhere to the inner free surface of the air bubbles which, on rising, carry the solid as well. In this case the system consists of three phases: gas (air bubbles), liquid (water) and solid (solid particles of the substance). The same circumstances are also present in radiometric titrations, but, the gas phase is replaced by a liquid phase immiscible with water (organic liquid). On stirring or shaking the system, the two phases are converted to an unstable emulsion of the organic compound in water. Because of adhesive forces, the particles of the precipitate adhere to the drops of the organic compound, and finally separate at the interface of the two liquids. The measurement of activity is easier when the labelled component is present in the upper phase. Because in a titration the activity of the aqueous layer is being measured, it is desirable to use organic compounds with a specific gravity exceeding that of water.

4.3.4. *Automation of the titration:* The problem of automation of precipitation titrations is discussed in several papers.[1,21–23]

Tölgyessy and Sajter[23] evolved a procedure and an apparatus for automatic titrations which automatically adds the titrant and registers the titration curve. The titrant is added to the test solution at a steady rate, and a precipitate of low solubility is formed. The circulation of the supernatant liquid through the filter plate in the titration flask, into the glass mantle of the GM counter measuring the liquid, and back again into the titration flask, is achieved by a laboratory micropump. The GM counter is attached to a rate-meter, and the activity values indicated by this rate-meter are continuously registered by an adequate registering device. This apparatus is shown in Fig. 12.

In another paper[22] the same authors suggested a method for automatic radiometric titrations carried out to the equivalence point. This technique is particularly useful for the serial determination of substances present in approximately identical amounts. Before carrying out the actual determination it is necessary to plot the titration curve with a sample in order to obtain the radioactivity of the supernatant

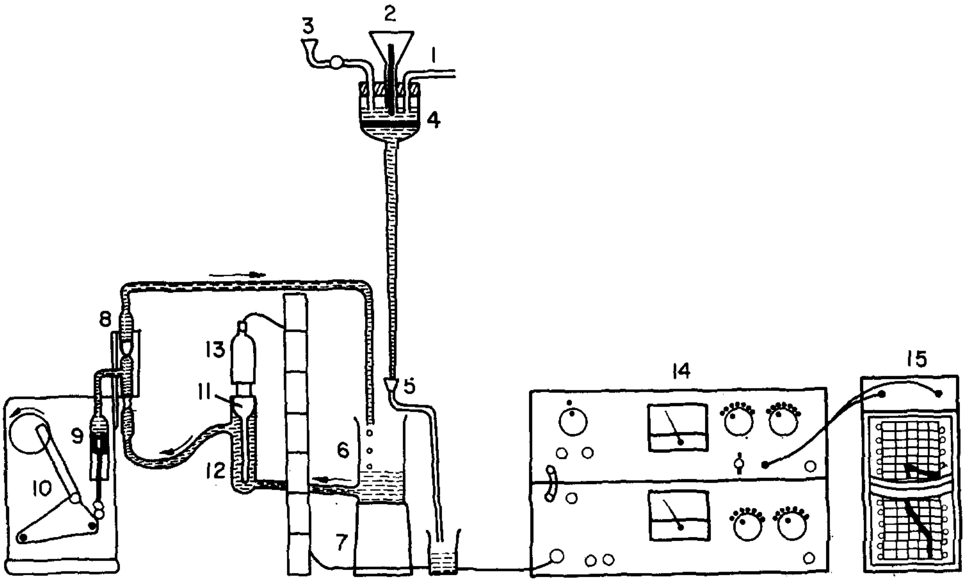


FIG. 12.—Automatic apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Sajter:[21]

1. Glass tube attached to suction device
2. Container
3. Funnel
4. Flask with titrant
5. Funnel for removing waste titrant
6. Titration flask with filter attachment
7. Stirrer
8. Mercury valve
9. Sprayer
10. Electromotor with transmissions
11. GM counter
12. Glass mantle
13. Sonde
14. Rate-meter
15. Registration device

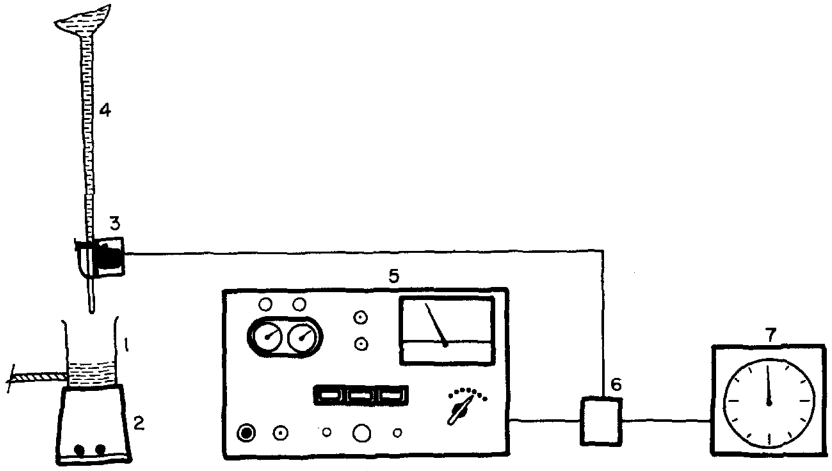


FIG. 13.—Automatic apparatus for radiometric titrations based on precipitate formation, according to Tölgyessy and Sajter:[22]

1. Titration flask
2. Stirrer
3. Electromagnetic valve
4. Polyethylene tubing
5. Rate-meter
6. Relays
7. Timer

liquid at the equivalence point. This method is essentially similar to the previous technique in which the titration curves are automatically registered. The only differences lie in the measurement of the radioactivity and in the determination of the equivalence point. In titrations of this type, the time from first adding the titrant to attaining the equivalence point is measured by an electric stop-watch which is automatically started and stopped by a rate-meter. The addition of titrant is also similarly controlled. If the activity of the supernatant liquid decreases to a previously set value, the addition of titrant is interrupted, and the electric stop-watch is stopped. The apparatus is shown in Fig. 13. The polyethylene tubing (4) through which the titrant is added is closed by an electromagnetic valve (3). This, in turn, is controlled through a relay (6) by a Soviet rate-meter of type TISS. With a steady rate of addition of titrant and knowing the time of addition, the volume of titrant consumed can be determined. When a burette, or another calibrated flask, is used for titration, no stop-watch is necessary because the volume of titrant consumed can be read directly.

The automatic apparatus eliminates subjective errors, and it permits an increase in the accuracy of the determination and a reduction of the time required for the titration to about 5–8 min.

4.4 *Determination of several components together*

Methods suitable for the determination of several substances in the presence of each other can be classified in five groups.[9,10,17,24,25,26]

4.4.1. *Radiometric titration of two substances by two titrations and one active titrant:* (*a*) This method lends itself to the determination of two substances in the presence of each other only when both substances yield poorly soluble precipitates with the same titrant. Two portions of identical volume of the solution to be titrated are used in this type of determination. The combined amount of both substances is first determined in a portion of the test solution by titration with active titrant. Then in another portion of the test solution of identical volume, one of the substances is precipitated by a selective reagent. The precipitate is removed by filtration (or sedimentation without filtration), and the other substance to be determined is measured by titration with the active titrant. The quantity of both substances can be calculated from the results of the two titrations. For example, to determine zinc and lead ions present together, a portion of the test solution is titrated with labelled potassium ferrocyanide solution. The amount of titrant consumed gives the combined content of zinc and lead. Subsequently, lead is precipitated from another portion of the test solution with sulphuric acid, and the zinc content of the residual solution is determined by radiometric titration. The lead content can be calculated from the difference in the two titrations.[18,25]

(*b*) As a variant of this technique, two oxidation states of the same substance can be determined in the presence of each other (*e.g.*, iodine and iodide), one of which gives with the titrant a precipitate of poor solubility. In this method, as in the previous case, two portions of identical volume of the test solution are used. In the first portion, using an active titrant, the amount of that component is determined which gives a poorly soluble precipitate with the titrant. Then, in the other portion of the test solution, by an appropriate oxidation or reduction, the second component is converted to the same oxidation state as the first, and both components are determined together. For example, to determine iodine and iodide present together, the amount of iodide ion is first measured by titration with a solution of $^{204}Tl_2SO_4$. In another portion of the test solution, iodine is reduced to iodide with sodium thiosulphate solution, and the total amount of iodide is determined.[27]

4.4.2. *Radiometric titration of two substances by two inactive titrants:* The substances to be determined are labelled by adequate radio-isotopes, and then consecutively titrated with selective titrants. For example, to determine sulphate and iodide present together, the test solution is labelled with $^{131}I^-$ and $^{35}SO_4^{2-}$ ions, *i.e.*, with the isotopes ^{131}I and ^{35}S. Then barium chloride as titrant is added to the test solution. The activity of the supernatant liquid will decrease with the precipitation of sulphate ion up to the first end-point, after which the activity will show a constant value. Silver nitrate as titrant is then added to the test solution. The activity of the supernatant liquid will then decrease with the precipitation of iodide ion. After the second end-point, the activity of the solution will be determined only by the solubility of barium sulphate and silver iodide. By plotting the course of titration, the end-points can be read from the curve obtained.[9,25]

4.4.3. *Radiometric titration of two substances by one active titrant:* Two substances can be determined together with an active titrant when the substances to be determined form precipitates with the titrant at various pH values, as in the determination of two ions by Busev and Byrko.[26,28] One of the ions is completely precipitated at pH 14, and the other ion at a lower pH value. Another example is the determination[26] of Tl^{3+} and In^{3+}, with 1-dithiocarboxy-5-phenylpyrazoline labelled with ^{35}S as titrant. The Tl^{3+} ion is first titrated at pH 14. At the end-point the activity of the supernatant liquid rises, because of the excess titrant. On adjusting the pH value of the solution to 7 the In^{3+} ion precipitates, and the activity remains constant, being determined by the solubilities of the thallium and indium complexes. After complete precipitation of the indium, the activity of the solution will again rise.

4.4.4. *Radiometric titration of two substances by one inactive titrant:* Two substances can be titrated with an inactive titrant when the substances form with the titrant poorly soluble precipitates of markedly differing solubility products. The solution is labelled with an appropriate radioisotope for the substance which gives the more soluble precipitate. The end-point can then be determined by calculation.[9,25]

The course of titration is shown in Fig. 14. Three values of activity are required for the calculation of the two end-points by equations (25) and (26):

$$V_{1_{ekV}} = (V_2 - V_1)\frac{I_0 - I_1}{I_2 - I_1} + V_1 \tag{25}$$

$$V_{2_{ekV}} = (I_0 - F)\frac{V_1 - V_2}{I_2 - I_1} \tag{26}$$

The technique of this determination is as follows. First the original activity, I_0, of the labelled test solution is measured. Then V_2 ml of titrant are added in order to precipitate quantitatively the first component, and the activity of the supernatant liquid, I_2, is measured. After adding a further amount, v ml, of titrant, where $V_1 = V_2 + v$, the activity, I_1, is measured. F is the activity of the solution at the second end-point.

For example, to determine sulphide and iodide ion the test solution is labelled with radioactive iodine (as $^{131}I^-$), and titration is carried out with a solution of silver nitrate as titrant. On adding the titrant, the activity of the solution does not change while sulphide ion is present in the solution. After the precipitation of the sulphide ion, the precipitation of iodide ions (together with ^{131}I) leads to a decrease of activity in the solution. From the values obtained a titration curve is established. The end-points can be read from this curve or can be determined by calculation.

4.4.5. *Radiometric titration of three substances by one inactive titrant:* Three substances, in fact, can be determined with an inactive titrant if the substances give with the titrant poorly soluble precipitates of markedly different solubility products.

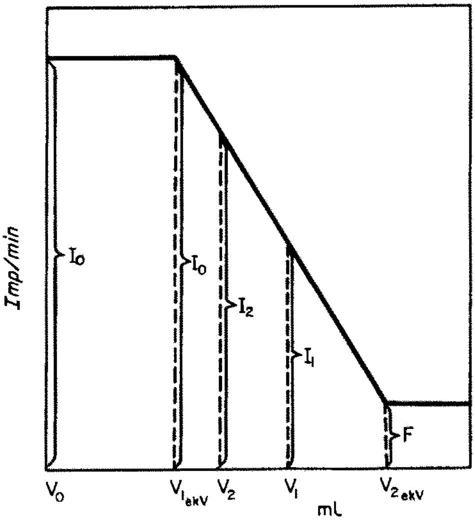


FIG. 14

In determinations of this type, radioisotopes suitable for the two components with the least and greatest solubilities, *i.e.*, those which precipitate first and last, are applied for labelling the solution.

4.5. *Practical applications*

In the field of precipitation titrations the majority of the methods are based on the precipitation reactions which are most frequently used in the normal determination of inorganic substances. In this way, the following elements and compounds have been determined: silver,[7,9,15,18,43,60] lead,[18,57] mercury,[15] copper,[15,16,18,42] cadmium,[34] zinc,[17,18,26,28,34,35,36] iron,[45] cobalt,[50] nickel,[60] calcium,[29,32] barium,[9] magnesium,[13] palladium,[15,55] thallium,[14,28,51,52,61] zirconium,[51,52,53] beryllium,[51,52,54] niobium,[56] tantalum,[56] uranium,[13] rare earth metals,[46–49] phosphates,[9,13,31] chromates,[18] carbonates,[18] sulphates,[9,12,29–32] oxalates,[18,57,59] chlorides,[7,9,12] bromides,[7,9] iodides,[9] cyanides,[9,57,59] sulphides,[18] fluorides,[18,44] ferrocyanides,[9] iodates,[18] molybdates,[31] sulphocyanides,[9] and inorganic drugs.[63] By the methods already described, several substances have also been determined in the presence of each other, such as the pairs iodide-chromate,[25] iodide-iodine,[27,29,30] sulphate-iodide,[9,25] calcium-lead,[25] zinc-cadmium,[34] zinc-copper,[17] sulphide-iodide,[25] lead-zinc[25] and thallium-indium.[26] Among organic compounds, the following can be included: quinine,[37–40] hyoscyamine,[40,41] morphine,[40,41] strychnine,[40,41] 8-hydroxyquinoline,[38,39] amidopyrine,[37,39] purines and barbiturates,[64] sulphamides,[57] alkaloids[58,62] and other organic drugs.[65]

4.6. *Increasing the sensitivity of radiometric titration based on precipitate formation*

The sensitivity of titrations based on precipitate formation is known to be of the order of magnitude of mg. This limit of sensitivity appears to follow from the basis of the method itself, being actually determined by the solubility product of the precipitate formed during titration.

Braun and Tölgyessy[69] have evolved several methods for increasing the sensitivity of titrations of this type.

4.6.1. *Radiometric titration on ion exchangers:* The radiometric titration of iodate ions by a silver nitrate solution labelled with ^{110}Ag has been carried out by Braun, Maxim and Galateanu.[70] This titration was conducted by the conventional technique. Because the solubility product of silver iodate is rather low, the titration cannot be carried out in very dilute solutions. However, when the iodate ions have previously been bound by anion exchangers added to the system, it is possible to conduct the titration even in $10^{-4}M$ solutions. The precipitate forms on the surface of the particles of ion exchanger where the ion to be titrated is present in an enriched form.

4.6.2. *Radiometric titration by separation with a collector:* The radiometric titration of zirconium by a PO_4^{3-} titrant labelled with ^{32}P was described in 1956 by Alimarin and Gibalo,[53] together with a technique suitable for the titration of mg-amounts. If, during the titration, after the addition of each new portion of titrant (PO_4^{3-}), solutions of silver nitrate and sodium iodide are added to the system from two separate burettes, the silver iodide precipitate which forms carries with it, as a collector, the traces of zirconium phosphate not still precipitated. In this way, minute amounts of zirconium can be titrated, *e.g.*, about 10 μg of zirconium can be determined with an error of about $\pm 5\%$.[71]

4.7. *Radiometric titration based on precipitation in non-aqueous media*

The radiation intensity of radioactive isotopes does not depend on the solvent used. It was proved by Chernyi, Vail and Izmailov[83] that organic acids and their salts can be titrated readily in a medium of methanol, acetone or dioxan-methanol by silver ions labelled with ^{110}Ag. The sensitivity of the method is increased by using a non-aqueous solvent in which the precipitate formed during titration is less soluble than in water. The same authors titrated calcium butyrate and sodium benzoate in a methanolic medium, valeric and caproic acid in a medium of methanol-dioxan, and halogen salts of quaternary ammonium bases in an acetone medium.

5. RADIOMETRIC TITRATION BASED ON COMPLEX FORMATION

It is known that titration methods based on complex formation (complexometry) and especially on the formation of chelate complexes (chelatometry) play an appreciable role in titrimetric analytical processes. In the past decade, this field has been extended greatly by a series of novel complex forming agents (complexones) which have made possible the simple solution of many complex analytical problems. Parallel with the development of practical methods, the theoretical basis of titrations based on complex formation has been evolved. In addition to visual methods based on colour indicators, which are doubtlessly simpler and quicker, much attention has been paid to instrumental methods of end-point indication. These latter offer possibilities, on the one hand of automating the processes, and, on the other hand of determining micro and submicro concentrations.

So far, only a relatively small number of papers have dealt with the problem of radiometric end-point indication in titrations based on complex formation. This is mainly because of the difficulties of phase separation. In this type of titration, in complete contrast to those based on precipitate formation, separation of phases does not follow from the method itself (*i.e.*, from the course of the reaction). Instead, the separate measurement of the radioactivity of the reaction partners or reaction products can only be carried out by an auxiliary but proper separation process, such as extraction of the reaction product or products by a solvent immiscible with water, separation by ion exchange or, finally, the use of solid indicators.

5.1. *Phase separation by solvent extraction*

The field of application of radiometric titrations has been appreciably extended by the use of phase separation by solvent extraction.[72–74] In general, the reaction products (chelate complexes) are extracted. The prerequisite of the application of this technique is that the complex formed during titration should be insoluble in water but readily soluble in an organic solvent. Obviously, the complex formed must meet the requirements of stability which apply to any in complexometry.[75] A considerable number of organic chelating agents have been proved to meet these requirements, *e.g.*, dithizone, 8-hydroxyquinoline, diethyldithiocarbamate, *etc.* However, the sensitivity of this method should also be considered. In the case of radiometric titrations based on precipitate formation the lower limit of sensitivity is determined by the solubility product of the precipitate, and this limit can be lowered only by special methods (*cf.* paragraph 4.6.). The sensitivity of radiometric titrations based on complex formation, with solvent extraction, however, depends only on the order of magnitude of the impurities present and on the specific activity of the radioactive isotope applied for labelling, because of the high stability of the complexes.

As has been proved by Duncan and Thomas,[73] in the radiometric titration of silver traces by extraction with dithizone, the sensitivity of the method attains that of activation analysis.

5.1.1. *Determination of equivalence point:* In general, the equivalence point is determined from graphs.[73,74] Obviously, radioactivity can be measured both in the aqueous and in the organic phase, and in consequence, the results are more accurate. In addition, the point of equivalence can be determined by calculation, although this method necessarily produces higher errors.[72] The accuracy of the result, taking into account other conditions, such as the stability of the complex, the pH value, the presence of interfering ions, and a good separation of the phases, depends, in the end, on the exact measurement of radioactivity.

From the aspect of labelling, two cases can be distinguished: either the component to be determined is labelled, according to the amount present, by larger or smaller quantities of its (possibly) carrier-free isotope; or a labelled titrant is used. The first case exists, for example, when mercury ion labelled with ^{203}Hg is titrated in the presence of carbon tetrachloride, with dithizone as titrant (dissolved in carbon tetrachloride). An example of the second case is the titration of thiocyanate ion with a solution of cobalt nitrate, labelled with ^{60}Co.

In practice, cases can occur where no radioactive isotope of the element to be determined, suitable for labelling, is available. Then the isotope of another element may be used, provided that the complex formed by this auxiliary element with the titrant possesses the same stability as that of the ion to be determined. If this is impossible, the so-called non-isotope method can be used, which is based on the following principle. When Me_1 ion is to be titrated with the complexing agent, A, this titration can be carried out with labelled Me_2 ion also present in the solution. These latter should react with A only when A has already reacted with all the Me_1 ion present. Consequently, in the titration curve the activity will be constant till the whole of the Me_1 ion is titrated, and then, when Me_2 ion enters the reaction, activity will increase or decrease depending on whether the radioactivity of the organic phase or that of the aqueous phase is followed. The volume of A consumed by Me_1 ion is indicated in the titration curve by a sharp break. This principle was first applied almost simultaneously by Korenman and co-workers[72] and by Duncan and Thomas[73] to radiometric titration by extraction.

Another possibility is utilised by the so-called indirect technique of extractive radiometric titration. This is used when the rate of the reaction between the ion to be determined and the chelating titrant is low. By adding excess of titrant, the reaction is generally speeded up. Consequently, by adding chelating titrant in excess to the solution of the ion to be titrated, and then an excess of an element which reacts instantaneously with the titrant, the excess of this last can be measured by titration with the chelating titrant using extractive radiometry, and the amount of ion originally to be determined can be calculated from the volume of titrant consumed.

5.1.2. *Theoretical basis of radiometric titration by solvent extraction:* The theoretical problems of radiometric titration by solvent extraction are discussed in detail in a paper by Duncan and Thomas.[1] On extracting metal complexes with organic solvents there occur the following equilibria:

$$\begin{aligned} \overline{\mathrm{HL}} &\rightleftharpoons \mathrm{HL} \\ \mathrm{HL} &\rightleftharpoons \mathrm{H^+} + \mathrm{L^-} \\ \mathrm{M^+} + \mathrm{L^-} &\rightleftharpoons \mathrm{ML} \\ \mathrm{ML} &\rightleftharpoons \overline{\mathrm{ML}} \end{aligned}$$

where HL represents the non-dissociated complexing agent (weak acid), and $\overline{L}$ represents the portion of component L present in the organic phase.

Denoting the partition coefficient of the complexing agent by P_{HL},

$$P_{\mathrm{HL}} = \frac{[\overline{\mathrm{HL}}]}{[\mathrm{HL}]} \tag{27}$$

the partition coefficient of the complex ML formed on titration by P_{ML},

$$P_{\mathrm{ML}} = \frac{[\overline{\mathrm{ML}}]}{[\mathrm{ML}]} \tag{28}$$

the dissociation constant of the ligand by K_a,

$$K_a = \frac{[\mathrm{H^+}][\mathrm{L^-}]}{[\mathrm{HL}]}\,. \tag{29}$$

the stability constant of the complex ML by K,

$$K = \frac{[\mathrm{ML}]}{[\mathrm{M^+}][\mathrm{L^-}]} \tag{30}$$

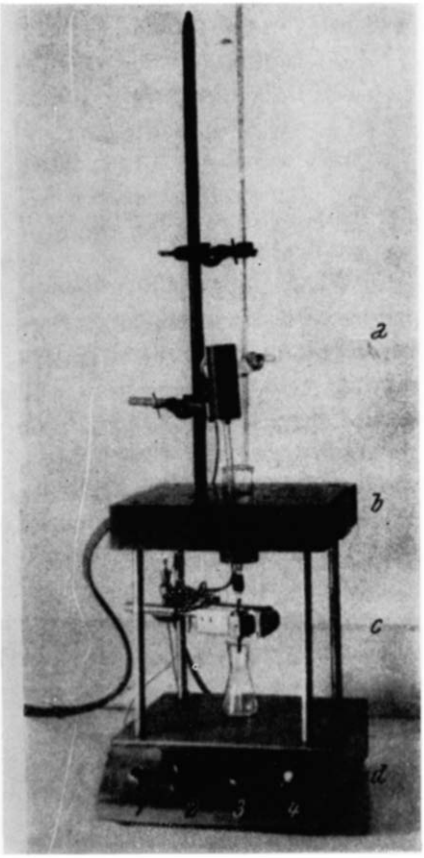


FIG. 15.—Semi-automatic apparatus for radiometric titrations based on complex formation, suitable for phase separation by solvent extraction, according to Spitzy.[74]

the volume of the solution containing the radioactive ions M^+ by v_0 (ml); the original concentration of these ions in the aqueous phase by $[M^+]_0$; and the volume of the organic solvent immiscible with water (which contains HL in the original concentration $[\overline{HL}]_0$) by v (ml); it can be derived that

$$v^2(KP_{ML}K_aR[\overline{HL}]_0) + vv_0\{K\,.\,K_aR(P_{ML}(R-1)[M^+]_0 + [\overline{HL}]_0) \\ + P_{HL}[H^+](R-1)\} + v_0^2(R-1)\{K\,.\,K_aR[M^+]_0 + [H^+] + K_a\} = 0 \quad (31)$$

where $R = (a_{M^+}/a^0_{M^+})$ is the ratio of the initial total activity of the solution to the total activity measured in a given period of titration. This relatively complicated equation can be simplified if the following conditions hold:

(*a*) the values of K and P_{ML} are relatively high;

(*b*) the values of $[\overline{HL}]_0$ and $[M^+]_0$ are low and of the same order of magnitude (dilute solutions);

(*c*) the pH of the aqueous phase remains constant so that $[H^+] \ll K\,.\,K_a[M^+]_0$, *i.e.*, on attaining equilibrium, only a negligible amount of unreacted HL remains in the aqueous phase;

(*d*) P_{ML} and P_{HL} are of the same order of magnitude.

On simplifying, the following equation is obtained:

$$v = \frac{v_0[M^+]_0(1-R)}{[\overline{HL}]_0} \quad (32)$$

which is valid for all the radiometric titrations by solvent extraction so far described in the literature.[1] When it is impossible to extract the complex ML quantitatively from the aqueous phase (the value of P_{ML} or K is low or that of $[H^+]$ is high), instead of a straight line, a curved titration graph will be obtained. With knowledge of the values of K_a, $[H^+]$ and P_{HL}, it is possible to calculate the values of K, P_{ML} and $[M^+]_0$ from three points of the graph.

5.1.3. *Titration apparatus and technique of titration:* Titrations are carried out by Korenman and co-workers[72] in glass-stoppered test-tubes carrying a volume scale. Identical volumes of the test solution are transferred to the test-tubes by pipette, the pH value of the solution is adjusted with a buffer solution, and increasing amounts of titrant are added. Then the test tubes are filled up with an organic solvent (that used for dissolving the chelating titrant) to the mark. After shaking in a shaking machine for 15 min, the test-tubes are centrifuged 1–2 min to promote separation, and the radioactivity of aliquots taken from both the aqueous and the organic phase are measured in a liquid counter. The titration curve is established from the results obtained.

Titrations are carried out by Duncan and Thomas[73] in a separatory funnel, and the activities of aliquots withdrawn from the aqueous phase are measured after each new addition of titrant and shaking. In both cases the titration is intermittent and rather cumbersome and lengthy. So far it has not been possible to evolve a continuous process for solvent extraction. In consequence the automatisation of the titration has been delayed. Spitzy[74] has developed an apparatus which automatically separates the two phases after shaking and thus markedly accelerates the course of titration (Fig. 15), but the problem of continuous titration still remains unsolved.

5.1.4. *Methods:* In the papers published so far, the applicability of the method has mainly been proved by model experiments. The advantages and drawbacks of the method can be evaluated by the published results. Duncan and Thomas[73] titrated traces of mercury labelled by ^{203}Hg at pH 1·0 and traces of cobalt labelled with ^{60}Co at pH 6·7, using a solution of dithizone as titrant. Similarly, traces of zinc[72] labelled with ^{65}Zn and traces of silver[74] labelled with ^{110}Ag can be determined by titration with dithizone. In Fig. 16 the curves of the radiometric titration of cobalt and mercury,

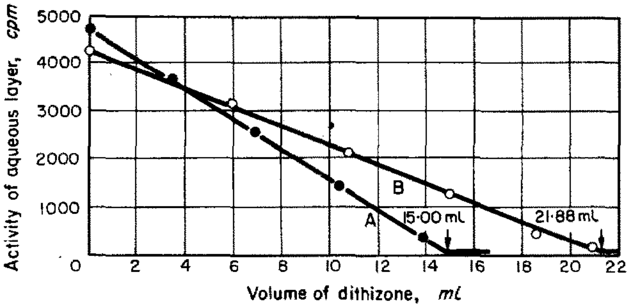


FIG. 16.—Curve of the radiometric titration of cobalt (^{60}Co, A) and mercury (^{203}Hg, B) ions with a dithizone solution in carbon tetrachloride as titrant, according to Duncan and Thomas.[73]

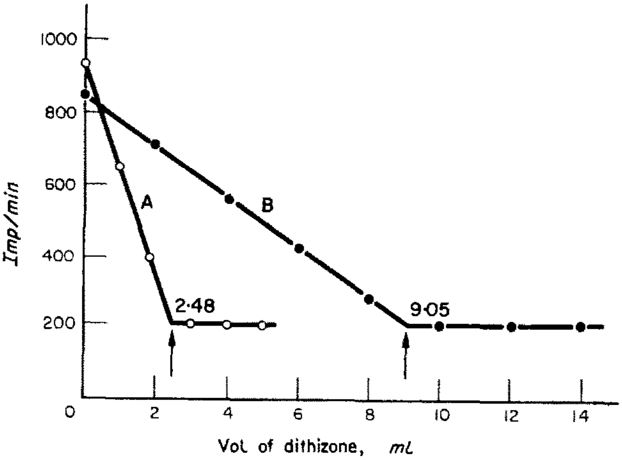
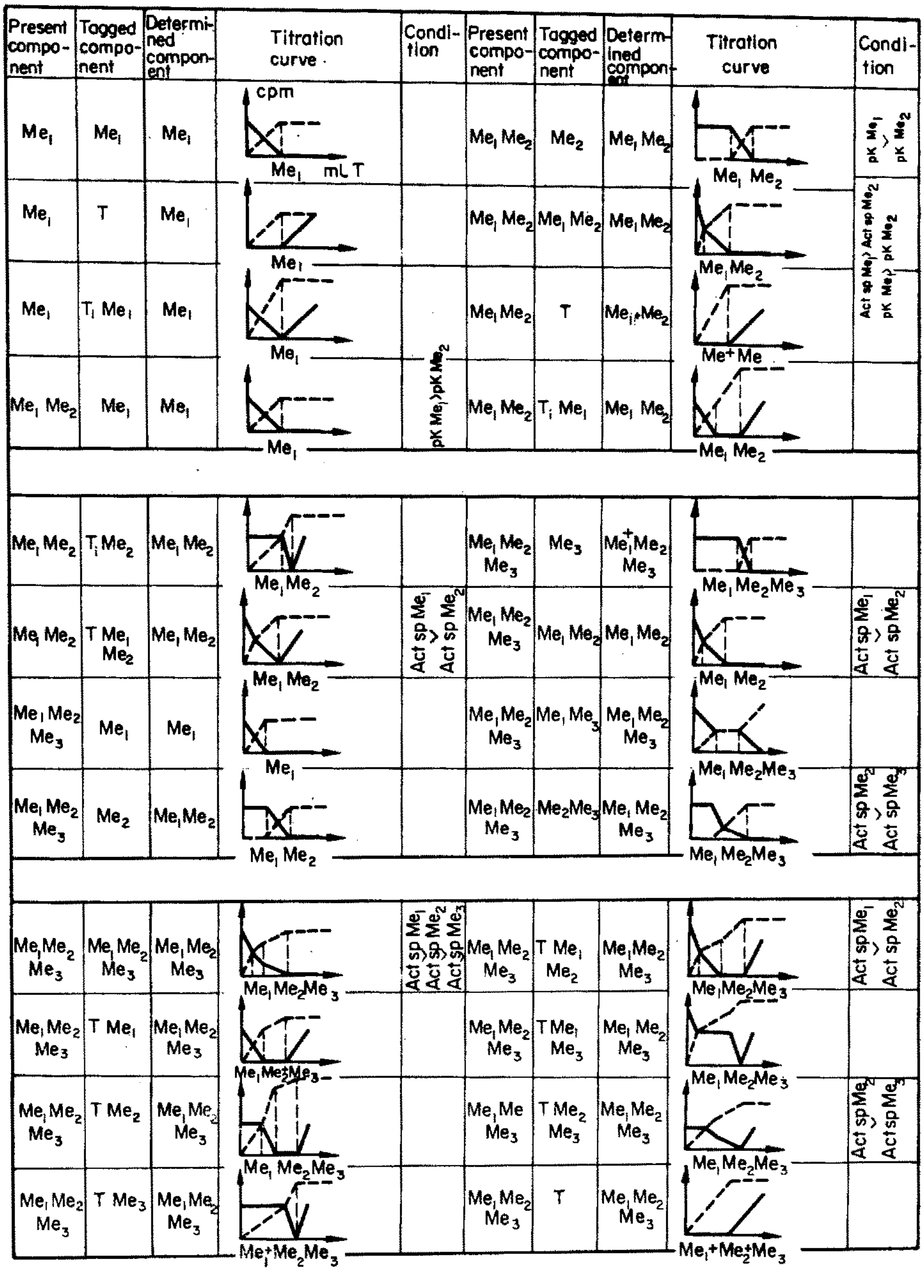


FIG. 17.—Curve of the radiometric titration of silver (^{110}Ag) and zinc (^{65}Zn) ions with a dithizone solution in carbon tetrachloride as titrant, according to Spitzy.[74]

obtained by extraction with dithizone, are shown; Fig. 17 shows the curves for the dithizone titration of silver and zinc.

5.1.5. *Determination of several components together:* The theoretical possibilities of radiometric titration by extraction, for the determination of several components together, are shown in Fig. 18, and include the use of non-isotopic methods, active titrants or different specific activities. Because Fig. 18 is prepared only as a guide, only numbers of components not exceeding three were taken into account. But similar theoretical conclusions can also be drawn for the determination of four, five or more ions. All the results published in the literature can be classified in one of the types shown in Fig. 18. However, the examples given in Fig. 18 do not include all the possibilities of simultaneous determination. For example, selective titrations can



Present component	Tagged component	Determined component	Titration curve	Condition	Present component	Tagged component	Determined component	Titration curve	Condition
Me_1	Me_1	Me_1	cpm Me_1 mL T		Me_1 Me_2	Me_2	Me_1 Me_2	Me_1 Me_2	pK Me_1 > pK Me_2
Me_1	T	Me_1	Me_1		Me_1 Me_2	Me_1 Me_2	Me_1 Me_2	Me_1 Me_2	Act sp Me_1 > Act sp Me_2 pK Me_1 > pK Me_2
Me_1	T_1 Me_1	Me_1	Me_1	pK Me_1 > pK Me_2	Me_1 Me_2	T	Me_1+Me_2	Me+Me	
Me_1 Me_2	Me_1	Me_1	Me_1		Me_1 Me_2	T_1 Me_1	Me_1 Me_2	Me_1 Me_2	
Me_1 Me_2	T_1 Me_2	Me_1 Me_2	Me_1 Me_2	Act sp Me_1 > Act sp Me_2	Me_1 Me_2 Me_3	Me_3	$\overset{+}{Me_1}$ Me_2 Me_3	Me_1 Me_2 Me_3	
Me_1 Me_2	T Me_1 Me_2	Me_1 Me_2	Me_1 Me_2		Me_1 Me_2 Me_3	Me_1 Me_2	Me_1 Me_2	Me_1 Me_2	Act sp Me_1 > Act sp Me_2
Me_1 Me_2 Me_3	Me_1	Me_1	Me_1		Me_1 Me_2 Me_3	Me_1 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	
Me_1 Me_2 Me_3	Me_2	Me_1 Me_2	Me_1 Me_2		Me_1 Me_2 Me_3	Me_2 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Act sp Me_2 > Act sp Me_3
Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Act sp Me_1 > Act sp Me_2 > Act sp Me_3	Me_1 Me_2 Me_3	T Me_1 Me_2	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Act sp Me_1 > Act sp Me_2
Me_1 Me_2 Me_3	T Me_1	Me_1 Me_2 Me_3	Me_1 Me_2+Me_3		Me_1 Me_2 Me_3	T Me_1 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	
Me_1 Me_2 Me_3	T Me_2	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3		Me_1 Me Me_3	T Me_2 Me_3	Me_1 Me_2 Me_3	Me_1 Me_2 Me_3	Act sp Me_2 > Act sp Me_3
Me_1 Me_2 Me_3	T Me_3	Me_1 Me_2 Me_3	Me_1+Me_2 Me_3		Me_1 Me_2 Me_3	T	Me_1 Me_2 Me_3	Me_1+Me_2+Me_3	

FIG. 18.—Alternative possibilities of radiometric titration based on complex formation and carried out by solvent extraction (theoretical possibilities of determining one, two or three components).

Me_x: metal ion to be determined
T: titrant
Act. sp.: specific activity

——: activity of aqueous phase
– – –: activity of organic phase

also be carried out by varying the pH, by using auxiliary complexing or demasking agents, *etc.*

Examples of published methods include that developed by Duncan and Thomas[73] for the determination of traces of cobalt and zinc in the presence of each other, using ^{60}Co and the non-isotope method. The curve published by Duncan and Thomas is shown in Fig. 19. A similar principle was applied by Korenman and co-workers[72] to the determination of traces of mercury and zinc, and of traces of copper and zinc, using ^{65}Zn. However, the titrations must be conducted at two different pH values. Similarly, the non-isotope method and titrations at two different pH values have been applied by Spitzy[74] to the determination of traces of silver and zinc, using ^{65}Zn.

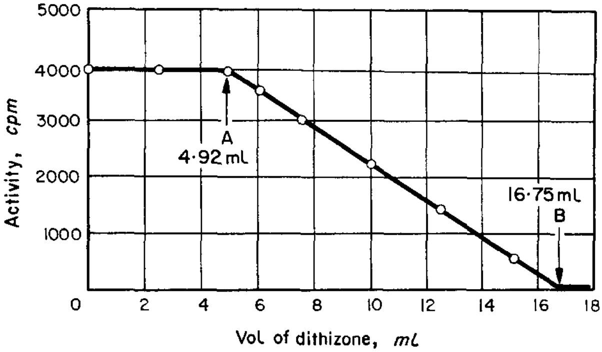


FIG. 19.—Curve of the radiometric titration of cobalt (B) and zinc (A) ions with a dithizone solution in carbon tetrachloride as titrant and with the non-isotope method, according to Duncan and Thomas.[73]

Spitzy has developed another method[74] for the titration of three components occurring together. Thus, for example, traces of mercury, silver and zinc were titrated by labelling with ^{203}Hg and ^{65}Zn, and conducting titrations at two pH values. The

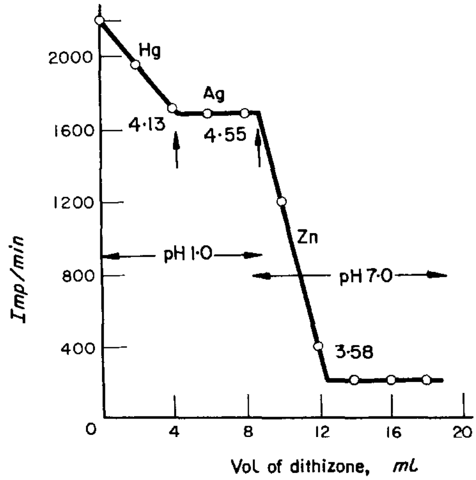


FIG. 20.—Curve of the radiometric titration of mercury, silver and zinc ions with a dithizone solution in carbon tetrachloride as titrant, and with the non-isotope method, according to Spitzy.[74]

titration curves of these three ions are shown in Fig. 20. In all the mentioned cases a carbon tetrachloride solution of dithizone served as titrant.

The application of indirect titrations has still to be mentioned. This method has been applied by Spitzy[74] for the titration of traces of palladium. The solution, containing palladium, was extracted with an excess of a dithizone solution of known concentration. The organic phase was then treated with a solution containing a known amount of ^{110}Ag. On shaking, some of the silver was bound by that part of the dithizone which did not react with the palladium. After separating the organic phase, the residual silver was titrated with dithizone. The quantity of dithizone consumed by the palladium was then calculated from the ratio of the added solutions, of known concentration and volume, to the volume of the dithizone solution consumed by the silver.

5.2. *Phase separation using solid indicators*

A novel possibility of radiometric titrations based on complex formation has been evolved by Braun, Maxim and Galateanu.[76,70] The principle of the method, based on the use of "solid indicators" is as follows. A cation, M^{2+}, is titrated with the complexing anion, A^{2-}, according to the reaction:

$$M^{2+} + A^{2-} \rightleftharpoons (MA)$$

The end-point of this titration reaction is determined with the use of the tagged cation, M_i^{*2+}, present in the system. The cation, M_i^{*2+}, is originally present as the slightly soluble precipitate, $M_i{}^*B$ (solid indicator). The prerequisite of end-point indication is that the cation, M_i^{*2+}, should react with the complexing agent, A^{2-}, only when all the M^{2+} ion (to be titrated) has already reacted. The complexing process of the cation, M_i^{*2+}, is characterised by the dissolution reaction:

$$M_i{}^*B + A^{2-} \rightleftharpoons (M_i{}^*A) + B^{2-}.$$

In order to carry out the above titration, the following conditions must be met: (*a*) the inequality

$$pK(MA) > pK(M_i{}^*A)$$

must exist between the stability constants of the complexes (MA) and $(M_i{}^*A)$;

(*b*) the ratio of the stability constant of the complex, $(M_i{}^*A)$, to the solubility product of the precipitate, $M_i{}^*B$, must be chosen in a way that the excess of the complexing agent added during titration should dissolve the precipitate.

A certain amount of labelled $M_i{}^*B$ precipitate is added to the solution of M^{2+} ion to be titrated, in a titration flask; the solution is then titrated with the complexing titrant, A^{2-}, and during titration the radioactivity of the solution separated from the precipitate is measured; the radioactivity remains low, as long as the solution contains free M^{2+} cation. When all the M^{2+} cation has been converted into complex, the excess complexing agent will react with the cation, M_i^{*2+}, and this leads to the dissolution of the precipitate, $M_i{}^*B$. Consequently, the radioactivity of the solution will increase in proportion to the amount of A^{2-} added. The titration curve is shown in Fig. 21. The sensitivity of the method is limited, on the one hand, by the stability of the complex used in the titration reaction, and, on the other hand, by the solubility and specific activity of the solid indicator. With properly chosen conditions, minute amounts can be titrated. In addition, this method appears to be suitable for automation.

These principles permit end-point indication by radiometry in complexometric titrations.[71,76,77] Methods have been evolved for the radiocomplexometric determination of calcium, strontium, magnesium, copper and zinc, using solid silver iodate labelled with ^{110}Ag as indicator.

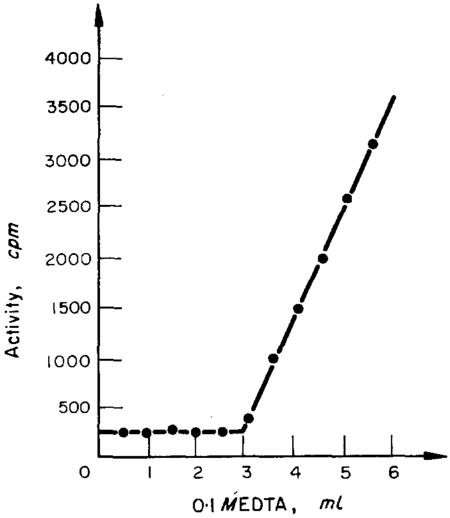


FIG. 21.—Curve of the radiocomplexometric titration of calcium ions using silver iodate as solid indicator.

5.2.1. *Possibilities of this method: direct, indirect and back-titrations:* By using solid indicators the complexometric titration of a great number of ions becomes possible. The direct titration of calcium, strontium, magnesium, copper and zinc has already been mentioned. Back-titration can be applied when, for example, the solid indicator acts only at a high pH value where the titrated ion will be hydrolysed, or when the reaction between the titrated ion and the complexing agent is slow, as in the complexometric titration of aluminium.[78] In this titration, a known excess of EDTA is added to the solution of the titrated ion at a low pH value, the system is boiled, and the pH value is adjusted to about 10. A suspension of ^{110}AgIO$_3$ as solid indicator is then added. Excess EDTA completely dissolves this indicator. Then the solution is back-titrated with a solution of calcium nitrate. The excess of EDTA is bound by the calcium ions, and the radioactivity of the solution remains constant at a high level. When the excess of EDTA is consumed, ^{110}Ag$^+$ is replaced in the $(AgY)^{3-}$ complex by Ca^{2+} because

$$\mathrm{p}K(\mathrm{AgY})^{3-} < \mathrm{p}K(\mathrm{CaY})^{2-}.$$

The displaced ^{110}Ag$^+$ ions combine with the IO_3^- ions present in the solution, and are precipitated as ^{110}AgIO$_3$. In consequence, the radioactivity of the solution gradually decreases. When the complex $(AgY)^{3-}$ is completely decomposed by Ca^{2+} ions, the radioactivity of the solution remains constant. Aluminium complexonate is not decomposed by Ca^{2+} ions because

$$\mathrm{p}K(\mathrm{AlY})^{-} > \mathrm{p}K(\mathrm{CaY})^{2-}.$$

The titration curve is shown in Fig. 22.

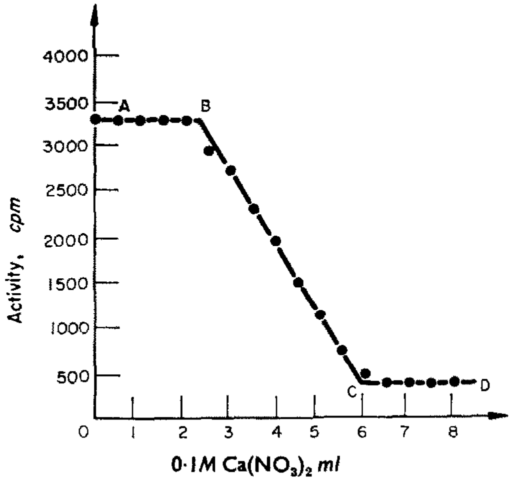


FIG. 22.—Curve of the radiocomplexometric back-titration of aluminium ions using silver iodate as solid indicator, according to Braun.[38]

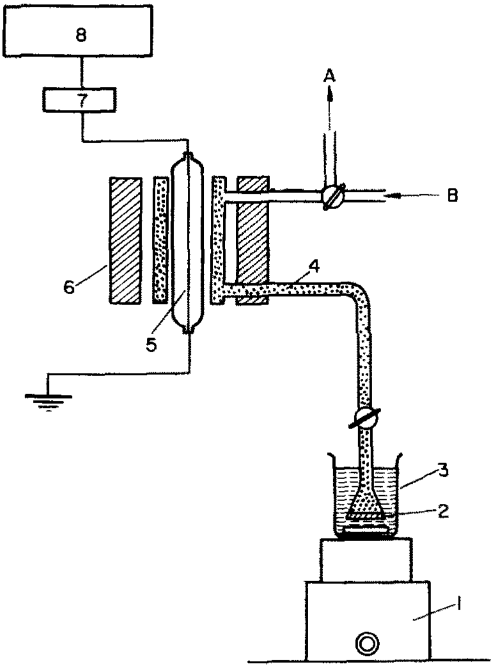


FIG. 23.—Apparatus for radiometric titration based on complex formation, carried out with a solid indicator and with phase separation by filtration, according to Braun:[82]

1. Stirrer
2. Suction tube with glass filter
3. Titration flask
4. Glass mantle
5. GM counter
6. Lead mantle
7. Pre-amplifier
8. Impulse meter

A. Air
B. Suction

In addition to these possible applications, the method also lends itself to indirect titrations, mainly for determining anions. In this case, the ion to be determined is precipitated by an excess of another ion which, by dissolving the precipitate, can be directly titrated with EDTA. This method has proved suitable, for example, for the determination of sodium through the titration of the zinc content of sodium zinc uranyl acetate, and for the determination of tungstate through the titration of the calcium content of calcium tungstate.[79]

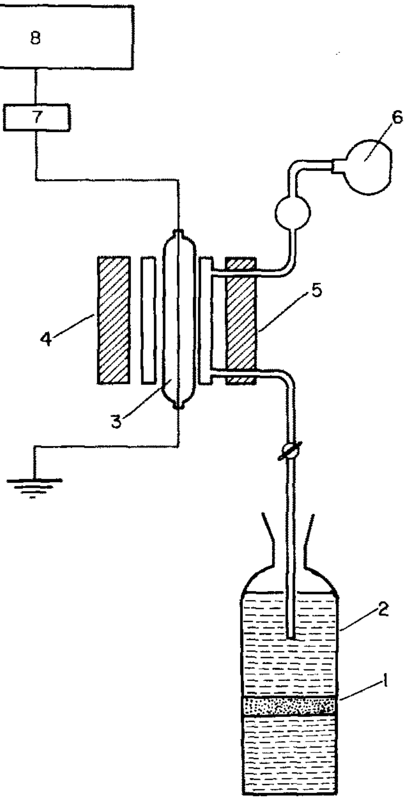


FIG. 24.—Apparatus for radiometric titrations based on complex formation, with a solid indicator and phase separation by flotation, according to Braun:[82]

1. Precipitate
2. Titration flask
3. GM counter
4, 5. Lead mantle
6. Suction device with rubber bulb
7. Pre-amplifier
8. Rate meter

5.2.2. *Titration devices and technique of titration:* Titration devices for solid indicators do not differ much from the conventional types of apparatus used in other radiometric titrations. If the solid indicator is applied during titration as a suspension, phase separation can be carried out by filtration, centrifuging or flotation. The apparatus used for phase separation by filtration is shown in Fig. 23. For the flotation method for phase separation, the equipment shown in Fig. 24 can be used.[19] Because in these cases phase separation is carried out intermittently, the titration process is not continuous. After each addition of titrant, phase separation must be carried out (filtration, centrifuging or flotation), followed by measurement of the radioactivity. The next addition of titrant can only take place after these operations. This discontinuity is a common drawback of all titration methods described, and is a hindrance to the possibility of automation. However, the method applying solid indicators can make continuous titrations possible when the indicator is introduced, in a form fixed to the fibres of filter paper instead of as a suspension, $^{110}AgIO_3$ as indicator can be precipitated within the fibres of chromatographic filter paper. This filter paper, fixed on a support, is transferred to the titrated solution during titration. No phase separation is then necessary, and titration can be carried out as a continuous operation[84] or it can be made completely automatic.

5.3. *Phase separation by ion exchangers*

Recently, Starý, Růžička and Zeman[80] showed that in radiometric titrations using EDTA, phase separation can also be carried out by ion exchangers. This method is based on the formation of negatively charged or neutral chelates which can easily be separated from the excess of unreacted metal by cation exchangers. The end-point is indicated by the measurement of the radioactivity of the eluates. As in other methods of radiometric titration, either the isotope or the non-isotope technique may be applied. The optimum pH values of this titration can be calculated on the basis of theoretical considerations suggested by Starý and Růžička.[81] According to this theory, ions forming very stable chelates, such as Co^{3+}, Zr^{4+}, Fe^{3+}, In^{4+}, Th^{4+}, *etc.*, can be titrated at pH values of 2–3, even with 10^{-6}–$10^{-7}M$ EDTA solution.

Less stable complexes can only be titrated at much higher pH values. By this technique, these authors succeeded in titrating microgram quantities of indium. By the non-isotope method it was possible to determine even 0·5 μg of cobalt by titration. The only drawback of the method is that the titration, as in other radiometric titrations, can only be conducted as an interrupted operation in the way described by these authors.

6. RADIOMETRIC TITRATION BASED ON REDOX REACTIONS

Among the methods of titrimetric analysis, redox titrations are of great importance because a great number of multivalent elements can be titrated successfully with an oxidant or a reductant.

Indication of the end-point of titrations of this nature by radioactive isotopes was until recently impossible by recognised techniques. In redox titrations all the components of the reaction remain in the same phase. Consequently, it is impossible to measure separately the radioactivity of the reactants and of the reaction products. This problem was solved by Braun[82,19] using labelled liquid amalgams. The principle can be instanced by considering bivalent Me^{2+} ion, which is titrated with a solution of the quadrivalent oxidising agent, Ox^{4+}, according to the reaction:

$$Me^{2+} + Ox^{4+} \leftrightharpoons Me^{3+} + Ox^{3+}$$

When a liquid amalgam, $Me_i{}^*Hg$, with a labelled metal atom, is also present in the system to be titrated, and this amalgam is capable of reducing the oxidising agent, Ox^{4+}, then on titration, after oxidation of all the Me^{2+} ion, the oxidising agent will react with the amalgam. During the reduction process an amount of labelled $Me_i{}^{*2+}$ ion equivalent to the amount of the oxidising agent will be liberated from the amalgam. The reduction reaction reads:

$$\downarrow Me_i{}^{*2}Hg + 2Ox^{4+} \rightleftharpoons \downarrow Hg + Me_i^{*2+} + 2Ox^{3+}.$$

The titration curve is shown in Fig. 25. At the beginning of titration radioactivity is low, and it remains constant till all the ion to be titrated is consumed (AB in Fig. 25). On adding further amounts of titrant, reaction with the amalgam follows (BC in Fig. 25), and the radioactivity of the solution shows a linear rise. The point of intersection of the two straight lines gives a readily evaluable end-point. Using this principle, Braun titrated ascorbic acid, as a model experiment, with a solution of Fe^{3+}, in the presence of zinc amalgam labelled with ^{65}Zn.

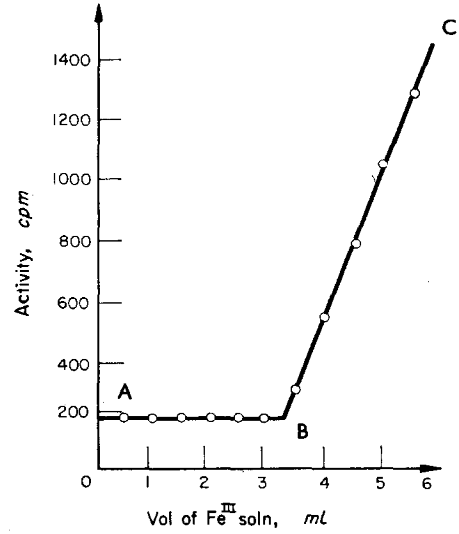


FIG. 25.—Curve of the radiometric titration in a redox reaction, with phase separation by amalgam, according to Braun.[82]

7. RADIOMETRIC TITRATION BASED ON ABSORPTION OF β-RADIATION AND ON ITS SCATTERING

β-rays, on passing through a substance, interact with it and gradually lose their energy and alter their direction. This phenomenon has been utilised for titration purposes.

7.1. *Radiometric titration based on scattering of β-rays*

An appreciable part of the scattered β-particles follow a reverse direction, *i.e.*, are back-scattered from the medium in question. The over-all effect of β-ray scattering depends on the atomic number of the examined substance, on the maximum energy of the β-radiation and on the thickness of the substance being examined (for solutions, on the concentration of the substance being examined). This phenomenon was utilised by Tölgyessy and Varga[66] to enable them to evolve a method of radiometric titration based on β-ray scattering combined with precipitate formation. In a titration of this type the titration curve shows the intensity of back-scattered β-radiation plotted against the amount of titrant added. Three alternatives are possible:

(*a*) the solution contains an element or several elements of high atomic number and the titrant has elements of low atomic number, *e.g.*, the titration of Ag^+ ions with hydrochloric acid. During titration, the intensity of β-radiation back-scattered from the solution decreases, because of the decrease in concentration of the element of higher atomic number (though precipitation of this element);

(*b*) the solution contains elements of lower atomic number and the titrant has elements of higher atomic number (*e.g.*, the titration of Cl^- ions with silver nitrate). During titration, the intensity of the back-scattered β-radiation slightly diminishes until the end-point is reached, and then increases markedly;

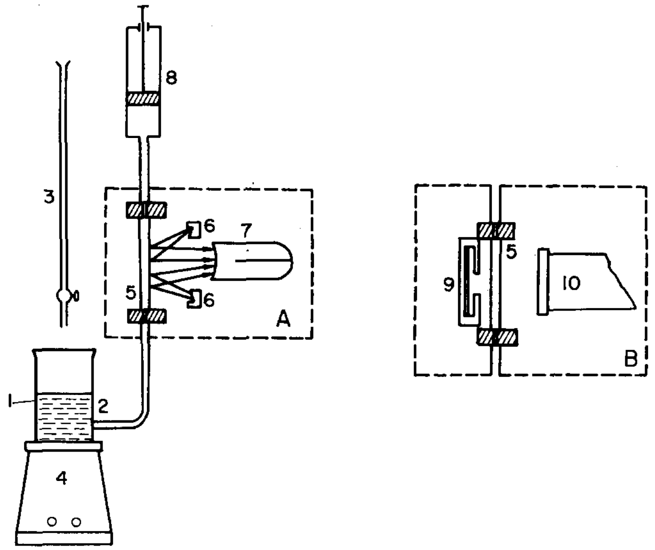


FIG. 26.—Apparatus for radiometric titrations based on β-radiation scattering (A) and β-radiation absorption (B), according to Tölgyessy, Varga, Dillinger and Braun[66,67,68]

1. Titration flask
2. Glass filter
3. Burette
4. Stirrer
5. Measuring cuvette
6. Ring-shaped radiation source
7. GM counter
8. Sprayer
9. Closed β-radiation source
10. Scintillation counter

(*c*) both the solution and the titrant contain elements of high atomic number. The intensity of the scattered β-radiation decreases until the end-point is reached, then rises.

In these titrations the conventional filtration and centrifuging methods have been applied. The experimental apparatus is shown in Fig. 26(A). The windows of the measuring cuvette (5) are of polyethylene. This cuvette is placed before the ring-shaped source of β-radiation (6), (^{204}Tl). The β-radiation back-scattered by the solution placed in the measuring cuvette is measured by a GM counter, (7), with an end window. The titration curve of Ag^+ ions with $0{\cdot}1M$ hydrochloric acid is shown in Fig. 27. Ferrocyanide ions have been titrated with $0{\cdot}1N$ lead nitrate by the same authors, using the same technique.

7.2. *Radiometric titration based on absorption of β-radiation*

The absorption of β-radiation has been utilised by Tölgyessy, Dillinger and Braun[67,68] for end-point indication in titrations based on precipitate formation and extraction. In these titrations, either the solutions to be examined, or the titrant, or

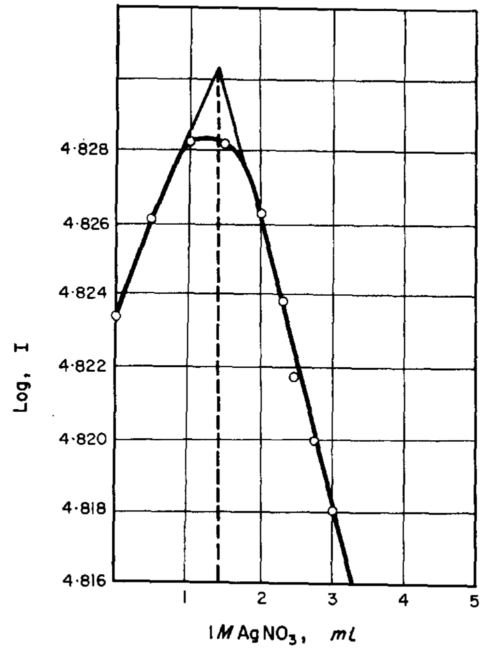


FIG. 27

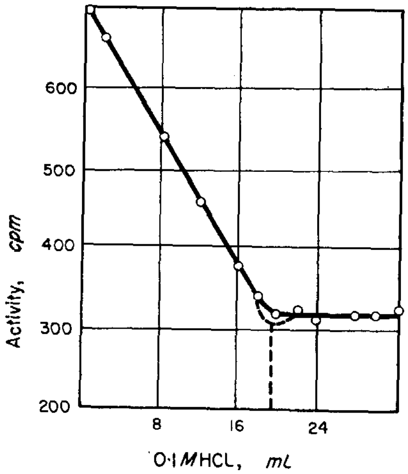


FIG. 28

both, should contain elements of high atomic number. The titration curves show the measured radiation intensities (expressed by the logarithm of the number of impulses observed in unit time) plotted against the amount of titrant. The curves show the reverse shape to that of the normal radiometric titration curves.

In titrations based on precipitate formation the usual filtration and centrifuging methods have been used; in titrations based on extraction centrifuging methods have been used. In the filtration method, the apparatus shown in Fig. 26(B) was used. On one side of the measuring cuvette (made of Plexiglass and equipped with polyethylene windows), a closed β-radiation source (^{90}Sr) of 1 mC activity was located, and on the other side a scintillation counter which was attached to an automatic measuring apparatus. Fig. 28 shows the curve obtained on titrating 25 ml of a solution containing chloride ion with 1·0*M* silver nitrate. In this determination the error was ±1·5%. These novel titration methods offer the advantage over the radiometric titration processes described earlier that a closed radiation source is used, and therefore the method is markedly freer from radiation hazards. In addition, the titration process lends itself readily to automation.

8. OTHER APPLICATIONS OF RADIOMETRIC TITRATION

Radiometric titrations have been applied with success by several authors in processes not directly analytical. Only a few papers have been published in this field, but the results attained are fairly promising and they should stimulate further experiments of this type.

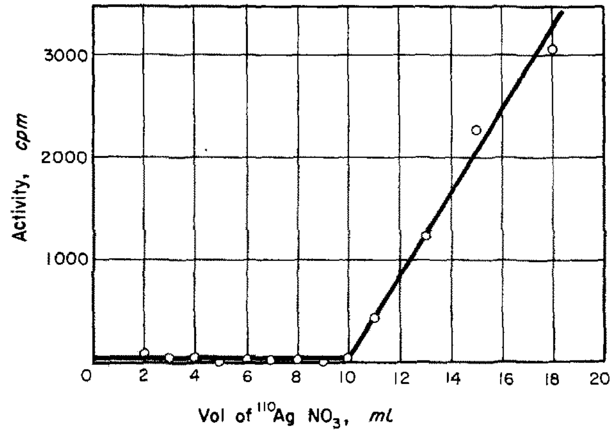


FIG. 29

8.1. *Determination of structure of compounds*

The composition of solutions of silver and cobalt tungstate has been studied by Bradhurst, Coller and Duncan[84] at various pH values, using radiometric titrations. It can be seen in Fig. 29 that on titrating a solution of sodium tungstate at pH 6·2–7·8 with a silver nitrate solution labelled with ^{110}Ag, a titration curve with a sharp break is obtained. The ratio Ag:W can easily be calculated from the end-point. The dependence on pH of the ratio Ag:W, calculated on the basis of titrations carried out at various pH values, is shown in Fig. 30, which proves that the method furnishes information on the composition of the various condensed tungstate ions present in the solution. Shinagawa, Matsuo and Yoshida[85] succeeded in establishing the composition of the complex triphenylselenonium iodobismuthite by a similar method, showing that the compound corresponds to the formula $[(C_6H_5)_3Se].[BiI_4]$.

8.2. *Investigation of coprecipitation*

Coprecipitation of various labelled compounds has been investigated, using radiometric titration, by Alimarin and Sirotina,[86] who studied in detail the coprecipitation of ^{204}Tl with AgI, AgCl, AgSCN and PbI precipitates, the titration of silver and thallium with ^{204}TlI, and that of lead and silver with CrO_4^{2-}. The results have proved, among other things that the non-isotope method lends itself to use in

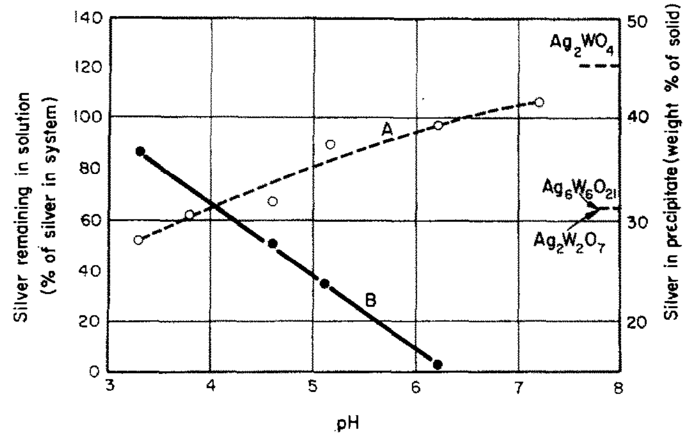


FIG. 30

radiometric titrations not only when isomorphic precipitates are formed, but also when anomalous mixed crystals develop in the solution.

8.3. *Determination of solubility product*

A method has been evolved by Duncan[87] for the determination of solubility product by radiometric titration. If a solution of volume v, which contains N^- ion at a concentration of $[N^-]_0$, is added to another solution of volume v_0, which contains the radioactive ion M^+ at a concentration of $[M^+]_0$ and which possesses a radioactivity of a_0 (impulses per minute), and if the solubility product is $S = [M^+][N^-]$, where $[M^+]$ and $[N^-]$ are the equilibrium concentrations of M^+ and N^- ion with the precipitate MN, then according to Duncan, the equation

$$Sv^2 + vv_0\{2S - [N^-]_0 \cdot [M^+]_0 R\} + v_0^2\{S + [M^+]_0^2 R(1 - R)\} = 0 \qquad (33)$$

can be derived, where $R = a/a_0$ and a is the residual activity of M ions in the solution after precipitation. The titration curve actually reflects the changes of R plotted against v. With the aid of equation (33) it is possible to calculate the value of S from any point along the curve. For details the reader is referred to the original paper.

Zusammenfassung—Eine Übersicht von radiometrischer Titration wird gegeben.

Résumé—On présente une revue de titrage radiométrique.

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COLORIMETRIC DETERMINATION OF VANADIUM WITH XYLENOL ORANGE

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Summary—A highly selective colorimetric method for vanadium^{V}, based on its colour reaction with Xylenol Orange, is described. In the presence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA) this method is almost specific for vanadium, because other elements are screened, and do not interfere in moderate amounts.

The well-known metallochromic indicator Xylenol Orange[1,2] (XO) has also been proposed for the colorimetric determination of a number of metals, including zirconium,[3–5] hafnium,[6] uranium,[7,8] iron,[9] bismuth,[10–12] zinc,[13] cerium and rare earths,[14] niobium[15,19] and, indirectly, for fluorine.[16] It is evident that Xylenol Orange shows but slight selectivity, except for the reaction with zirconium, which occurs in acidic solutions (0·5–1·0 *M* nitric acid). For other metals it can be used only in special cases, *e.g.*, after separation of the respective metal, *etc.*

Recently, two colour reactions of Xylenol Orange with vanadium have been described. Janoušek[17] studied the reaction of vanadium^{V} at pH 4, and recommended it for the colorimetric determination of vanadium after its separation by ion exchange. Otomo[18] studied a similar reaction with vanadium^{IV} at pH 2·8 in the presence of ascorbic acid. Some elements can be masked with fluoride, but high concentrations of fluoride interfere with the colour reaction. Strong complexing agents, such as ethylenediaminetetra-acetic acid (EDTA),[19] ethyleneglycoltetra-acetic acid (EGTA), diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexa-acetic acid (TTHA), completely suppress the colour reaction of vanadium with Xylenol Orange and therefore cannot be used for screening of interfering elements. We have found that 1,2-diaminocyclohexanetetra-acetic acid (DCTA) has only a very small effect on the colour reaction. Preliminary experiments have shown that conditions for a highly selective determination of vanadium^{V} in the presence of DCTA are very simple. Our experience obtained in this respect is described in the present paper.

EXPERIMENTAL

Reagents

0·001*M solution of Xylenol Orange:* Prepared by dissolving 0·83 g of about 80% reagent (Chemapol, Prague, Czechoslovakia) and diluting to 1 litre with distilled water.

0·05*M DCTA solution:* Prepared by dissolving 17·73 g of 1,2-diaminocyclohexantetra-acetic acid (Geigy, Basel, Switzerland) in 130–150 ml of hot 1*M* sodium hydroxide and diluting it, after cooling, to 1 litre.

0·05*M EDTA solution:* Prepared by dissolving 18·61 g of ethylenediaminetetra-acetic acid disodium salt (Chemapol, Prague, Czechoslovakia) in 1 litre of water.

2 × 10^{-4}*M ammonium vanadate solution:* Prepared by dissolving 0·0234 g of NH_4VO_3 (Lachema, Brno, Czechoslovakia) in 1 litre of water.

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Buffer solution (pH about 4·5): Prepared by dissolving 200 g of ammonium acetate in 200 ml of acetic acid and diluting to 1 litre.

0·05*M solutions of salts* of Fe^{III}, Al, Th, Co^{II}, Cr^{III}, Bi, Cd, Ce^{III}, La, Ca, Sr, Ba, Mg, Mn^{II}, Sc, Pr, Nd, Cu^{II}, Tl^{III}, Ni^{II}, Hg^{II}, In, Ga, Ti^{IV}, Pb, UO_2^{2-}, CrO_4^{2-}, MoO_4^{2-}, solid tartaric acid, sodium fluoride, ammonium phosphate, citric acid and oxalic acid were used for the interference studies.

All reagents were of reagent-grade purity.

Apparatus

Spectral grating spectrophotometer: Jouan (Paris, France); 350–1100 mμ.

Pulfrich photometer with photoelectric attachement Elpho II: (VEB Carl Zeiss, Jena, E. Germany).

Recording spectrophotometer: Leres type T2D (Bagneux, Seine, France); 200–2500 mμ.

pH-meter with glass electrode: Multoscop V (Laboratorní přistroje, Prague, Czechoslovakia).

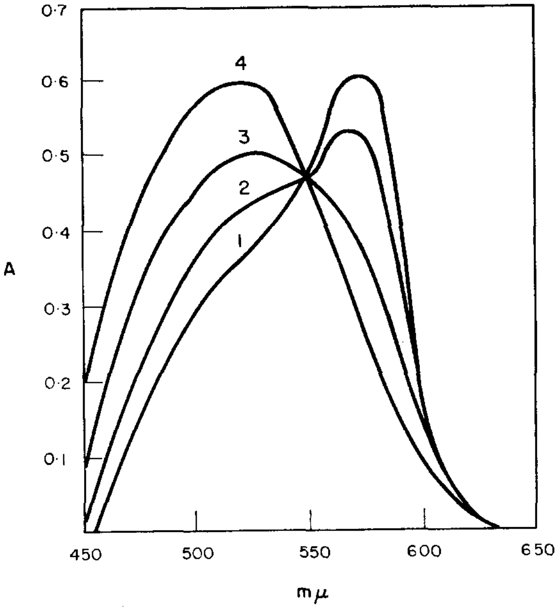

FIG. 1.—Absorption spectrum of the vanadium^V-Xylenol Orange complex for different excesses of Xylenol Orange: (1) XO:V^{5+} = 1·5:1; (2) 2:1; (3) 4:1; (4) 10:1.

RESULTS AND DISCUSSION

Structure of vanadium^V complex with Xylenol Orange

In a slightly acidic medium and with a low concentration of Xylenol Orange (up to the ratio X0:V^{5+} = 1:1) an intense violet colour is formed with vanadium^V, but with higher concentrations the coloration is red-orange (Fig. 1). From the absorption curves it is apparent that a number of complexes can be formed, their formation depending on the total concentration of Xylenol Orange. The existence of two complexes has been proved by the molar ratio method, measuring the absorbance at 520 mμ and 590 mμ (Fig. 2): one with a molar ratio of 1:1 > V:(XO), and absorption maximum at 590 mμ; and a second with a molar ratio 1:2, V:$(XO)_2$, and absorption maximum at 520 mμ.* The molecular extinction coefficients have been calculated from the above results (ε_{590} = 20,000 and ε_{520} = 13,000), classifying this coloration as

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* A maximum at 430 mμ shows the probable existence of further complexes. This maximum disappears, however, after a few min. No other maxima have been observed in the ultraviolet region.

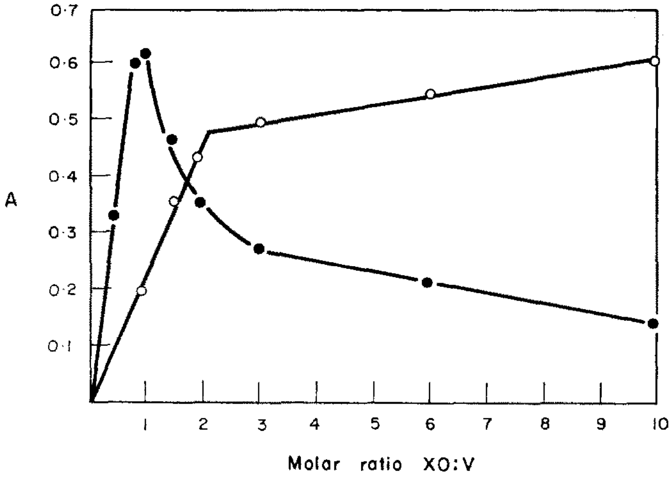

FIG. 2.—Influence of the excess of Xylenol Orange on the absorbance of the vanadium^V-Xylenol Orange complexes:
●—590 mμ,
○—520 mμ.

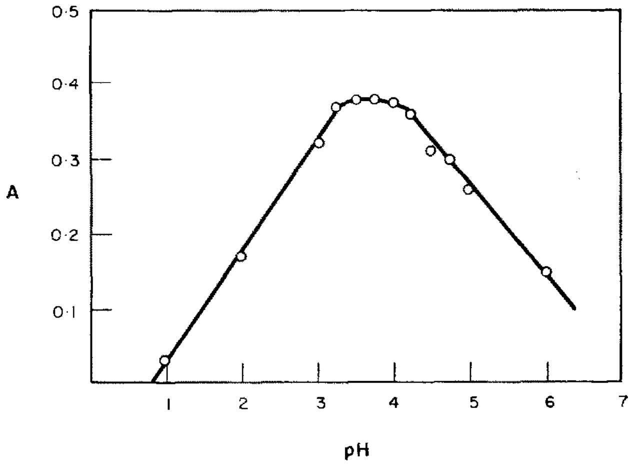

FIG. 3.—Dependence of the absorbance of the vanadium^V-Xylenol Orange complex on pH (1 μmole V^{5+}; 5 μmole XO; 550 mμ).

one of the most sensitive reactions for vanadium.[17] The coloration develops within 30 sec and remains stable for at least 24 hr. Absorbance measurements are carried out most conveniently at the isosbestic point (550 mμ): the absorbance is independent of the quantity of reagent added only at the isosbestic point. The optimum pH-range for the formation of the complex is 3–5 (Fig. 3).

Influence of DCTA on stability of the complex

From a detailed study of the colour reaction of vanadium with Xylenol Orange, it has been found that DCTA has some influence. In the presence of DCTA only one complex is formed—$V(XO)_2$ (Fig. 4). The absorbance in the presence of DCTA depends on the pH up to 4·5. Above this value however, it is effectively constant.

The coloration develops slowly, reaching a maximum within 10 min after the addition of Xylenol Orange (at room temperature). The absorbance does not attain the same value found in the absence of DCTA, but it is reproducible under identical conditions. The decrease in absorbance corresponds to the concentration of DCTA. Furthermore, even DCTA bound to other metals affects, according to the metal involved, the absorbance of the colour reaction with vanadium. This is obviously because of the equilibrium between DCTA complexes. The results for vanadium were in all cases lower. The equilibrium can, however, be shifted completely in favour of the colour reaction with vanadium by means of a considerable increase in the concentration of Xylenol Orange. With a 50-fold excess, the absorbance reaches about the same value as in the absence of DCTA (Fig. 4), and within certain limits of concentrations, it is quite independent of the nature of other metals present. It should be stressed that the absorbance at the isosbestic point (550 mμ) is less influenced by the presence of DCTA than is the maximum (520 mμ) of the absorption curve. Hence, we recommend that absorbance measurements in the presence of DCTA also be carried out at 550 mμ.

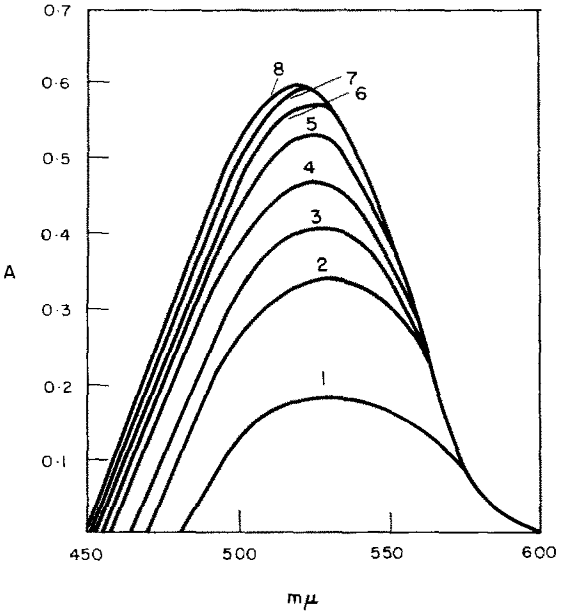

FIG. 4—Absorption spectrum of the vanadium^V-Xylenol Orange complex for different excesses of Xylenol Orange in the presence of DCTA: (1) XO:V^{5+} = 1:1; (2) 3:1; (3) 5:1; (4) 10:1; (5) 20:1; (6) 30:1; (7) 40:1; (8) 50:1.

The calibration curve must always be constructed at the same concentration of DCTA and against a blank solution containing the same concentration of Xylenol Orange. In the presence of coloured ions we prepare a blank from an aliquot of the test solution, adding EDTA, which prevents the formation of all coloured metal complexes with Xylenol Orange. The influence of foreign ions has been ascertained by the following procedure.

To 5–10 ml of slightly acidic solution, containing 5–50 μg of vanadium,$^{\mathrm{V}}$ add 5 ml of 0·05*M* DCTA solution, 5 ml of buffer solution (pH 4·5) and 5 ml of 0·001*M* Xylenol Orange solution, and dilute to 50 ml. After 10 min measure the absorbance of the solution on a spectrophotometer at 550 mμ or on a Pulfrich photometer in a 5-cm cell (filter S 53) against the same concentration of Xylenol Orange, or against an aliquot solution to which the same amount of EDTA has been added instead of DCTA. The concentration of Xylenol Orange in this blank has also to be maintained constant.

Some results of the determination of vanadium$^{\mathrm{V}}$ in the presence of common elements are given in Table I.

TABLE I.—Determination of vanadium$^{\mathrm{V}}$ in the presence of other elements

	Foreign ion, μmole	Molar ratio	Vanadium V^{5+}, μg		Differences, μg
			Taken	Found	
None		—	10	9·3	−0·7
		—	20	19·7	−0·3
		—	30	30:7	0·7
Fe^{3+}	100	1:500	10	12·5	2·5
	200	1:1000	10	12	2
Al^{3+}	100	1:500	10	10·5	0·5
	150	1:750	10	11·5[a]	1·5
Ca^{2+}	100	1:500	10	10·7	0·7
Mg^{2+}	100	1:500	10	10·5	0·5
Sr^{2+}	100	1:500	10	11	1
Ba^{2+}	100	1:500	10	12·5	2·5
Mn^{2+}	100	1:500	10	9·5	−0·5
Pb^{2+}	100	1:500	10	10	0
Zn^{2+}	100	1:500	10	11·6	1·6
Hg^{2+}	100	1:500	10	11·5	1·5
Cu^{2+}	100	1:500	10	12[b]	2
Ni^{2+}	100	1:500	10	9·3[b]	−0·7
Bi^{3+}	100	1:500	10	11	1
In^{3+}	100	1:500	10	9	−1
La^{3+}	100	1:500	10	12	2
Sc^{3+}	100	1:500	10	10·6[b]	0·6
Nd^{3+}	100	1:500	10	9[b]	−1
Cr^{3+}	50	1:250	10	9	−1
ZrO^{2+}	50	1:250	10	9·7[a,c]	−0·3
Tl^{3+}	50	1:250	10	10·7	0·7
Pr^{3+}	50	1:125	20	20·7[b]	0·7
Co^{2+}	50	1:125	20	21·6[b]	1·6
Ga^{3+}	12	1:62	10	11·3[a]	1·3
Th^{4+}	12	1:62	10	11·6[a]	1·6
Ti^{4+}	5	1:25	10	10·3[a,d]	0·3
UO_2^{2-}	3	1:15	10	9·8[a]	−0·2
CrO_4^{2-}	100	1:500	10	11·5[b]	1·5
WO_4^{2-}	5	1:25	10	10[a,e]	0
MoO_4^{2-}	0·4	1:2	10	9·6[a]	−0·4
$(NH_4)_2HPO_4$—50 mg			10	10·3	0·3
Tartaric acid—50 mg			10	9·5	−0·5
Citric acid—50 mg			10	9·5	−0·5
Oxalic acid—50 mg			10	0·1	−9·9
NaF—50 mg			10	11·5	1·5

[a] Maximum ratio of V^{5+}: Me.

[b] Measured against the same concentration of the coloured ion and 5 ml of 0·05*M* EDTA.

[c] Previously boiled at pH 0·5.

[d] In presence of 50 mg of tartaric acid.

[e] In presence of 50 mg of $(NH_4)_2HPO_4$.

Zusammenfassung—Eine hochselektive kolorimetrische Bestimmungsmethode für fünfwertiges Vanadium auf Grund der Farbreaktion mit Xylenolorange wird beschrieben. In Gegenwart von 1,2-Diaminocyclohexantetraessigsäure (DCTA) ist diese Methode für Vanadin fast spezifisch, da alle Elemente maskiert werden und in mäßigen Mengen nicht stören.

Résumé—Une méthode colorimétrique très sélective pour le dosage du vanadium pentavalent basée sur la réaction colorée qui se manifeste en présence d'orange de xylénol est décrite. En présence d'acide diamino-1,2-cyclohexane-tétracétique (DCTA) la méthode est presque spécifique du vanadium, car tous les autres éléments sont protégés et ne sont pas gênants s'ils sont en quantité modérée.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XV*

DETERMINATION OF INDIUM AND GALLIUM IN THE PRESENCE OF EACH OTHER WITHOUT THE USE OF A SCREENING AGENT

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Summary—The different complexation reaction of indium and gallium with TTHA (triethylenetetraminehexa-acetic acid) is utilised for the complexometric determination of these elements in mixtures. With EDTA and TTHA indium forms complexes of normal composition (1:1); gallium, however, forms a 2:1 complex with TTHA. To one aliquot of test solution an excess of EDTA is added, to another the same amount of TTHA. Both solutions, after adjustment of pH to 5–5.5, are titrated with zinc solution using Xylenol Orange as indicator. From the consumption of zinc solution in the two titrations the amounts of indium and gallium are easily calculated.

WHEN systematically studying TTHA (triethylenetetraminehexa-acetic acid) as a titrimetric reagent we paid attention to the determination of indium and gallium in their mixtures. Today these elements are no longer considered as less common metals, because their practical importance in the electronic industry is steadily rising. Both elements can be easily determined by an EDTA titration, but not in the presence of each other, because with EDTA they form complexes of about the same stability ($pK_{InY} = 24{\cdot}9$, $pK_{GaY} = 20{\cdot}3$). From previous experiments[1] we concluded that indium and gallium behave differently in complex formation with TTHA. Over the whole range of pH indium forms a complex of normal composition (1:1), while gallium under the same conditions forms only a 2:1 complex (Ga_2Y). This has now been utilised as the basis of a specific determination over a wide concentration range.

EXPERIMENTAL

Reagents

0·05M TTHA solution. Prepared by dissolving 24·723 g of triethylenetetraminehexa-acetic acid (J. R. Geigy, Basel, Switzerland) in 100–120 ml of 1*M* sodium hydroxide with warming and diluting to 1 litre. The factor is controlled by titration against a weighed amount of metallic zinc (dissolved in nitric or hydrochloric acid), using Xylenol Orange as indicator. It needs to be emphasised that TTHA forms a 2:1 complex with zinc, and the consumption in the titration with zinc solution drops to one-half in comparison with that of EDTA.

Solutions of indium and gallium. Prepared by dissolving the two metals in 20 ml of hot hydrochloric acid (1:1).

Other solutions and reagents include 0·05*M* EDTA, 0·05*M* zinc chloride, 1*M* hydrochloric acid, solid urotropine and 0·5% Xylenol Orange.

Determination of Indium and Gallium with EDTA

Indium can be titrated directly with EDTA in hot solution at pH 3–5, using Xylenol Orange as indicator; under the same conditions, however, gallium blocks the indicator. The sum of the two

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* Part XIV: *Talanta*, 1964, **11**, 1197.

metals, can, therefore, only be determined indirectly, *e.g.*, at pH 5–5·5 with an excess of EDTA and back-titration by zinc solution and Xylenol Orange.

Procedure

To the acid solution containing gallium and indium, add a sufficient amount of 0·05*M* EDTA, adjust the pH to 5–5·5 with solid urotropine and heat nearly to boiling. After the addition of Xylenol Orange, titrate with 0·05*M* zinc solution to an intense red colour.

TABLE I.—SIMULTANEOUS DETERMINATION OF INDIUM AND GALLIUM

Taken, *mg*		Back-titn., *ml*		Back-titn., *ml*		Found, *mg*		Difference, *mg*	
In	Ga	0·05*M* EDTA	0·05*M* Zn	0·05*M* TTHA	0·05*M* Zn	In[b]	Ga[c]	In	Ga
57·38	3·20	15·09	4·10	15·00	9·08	56·98	3·66	−0·40	+0·46
5·74	31·96	20·13	9·87	15·00	18·82	5·30	32·56	−0·44	+0·60
28·69	15·98	12·08	2·42	15·00	15·41	28·35	16·35	−0·34	+0·37
5·74	3·20	5·03	3·08	5·00	7·05	5·68	3·34	−0·06	+0·14
57·38	31·96	25·16	5·98	25·00	20·98	56·57	32·56	−0·81	+0·60
114·76	3·20	25·16	4·19	25·00	≃9[a]	—	—	—	—
5·74	63·92	25·16	5·90	15·00	9·69	5·96	63·52	+0·22	−0·40

[a] High concentration of In.

[b] In = [(EDTA − Zn) − Ga(in ml)]3·486 mg.

[c] $$\text{Ga} = 2\left[(\text{EDTA} - \text{Zn}) - \left(\text{TTHA} - \frac{\text{Zn}}{2}\right)\right] 5{\cdot}738\ \text{mg.}$$

Determination of Indium and Gallium with TTHA

Procedure

To another equal aliquot of the test solution add the same amount of 0·05*M* TTHA as EDTA used above, then carry out the back-titration with zinc solution as previously described.

Calculations

First titration. The sum of gallium- and indium-EDTA complexes corresponds to the consumption of A ml of 0·05*M* EDTA.

Second titration. Let the sum of gallium- and indium-TTHA complexes correspond to the consumption of B ml of 0·05*M* TTHA. In both cases the consumption is calculated on the basis of a back-titration of excess EDTA or TTHA with zinc solution. (In the second titration zinc forms a 2:1 complex with TTHA and its consumption is twice that compared with EDTA.)

For determination of the total consumption of TTHA to complete complexation of gallium and indium, the consumption of the zinc solution has to be divided by two. This means that the consumption of gallium in the analysed solution equals 2(A ml of 0·05*M* EDTA − B ml of 0·05*M* TTHA).

1 ml 0·05*M* EDTA (TTHA) ≡ 5·380 mg of indium or 3·486 mg of gallium.

DISCUSSION

The above method of determination of indium and gallium is given intentionally for their pure solutions, because the principle of their determination is quite new. The application of this method opens new possibilities for the determination of indium and gallium, even in the presence of other elements which may be present in different materials of practical importance (alloys, semiconductors, monocrystals of the Ga–In–As system, *etc.*). Because indium forms only a 1:1 complex with TTHA, while other heavy metals, such as zinc, cadmium, lead and copper, form 2:1 complexes, the determination of indium can be carried out in a similar way to that described in this paper. On the other hand, however, gallium can be determined by the "double titration" in the presence of all metals forming 1:1 complexes with TTHA.

Zusammenfassung—Die verschiedene Komplexbildung von Indium und Gallium mit EDTA und TTHA (Triäthylentetraminhexaessigsäure) wird zur komplexometrischen Bestimmung beider Elemente nebeneinander verwertet. Indium bildet mit EDTA und TTHA 1:1-Komplexe, Gallium jedoch mit TTHA einen 2:1-Komplex. Die Methode beruht auf folgendem: Zu einem aliquoten Teil der Lösung wird überschüssige EDTA gegeben, zu einem andern dieselbe Menge TTHA. Beide Lösungen werden nach Einstellung des p_H auf 5–5.5 mit Zinklösung und Xylenolorange als Indikator titriert. Aus dem Zinkverbrauch bei beiden Titrationen läßt sich die Menge von Indium und Gallium leicht berechnen.

Résumé—On ulitise les réactions de complexation différentes que donnent l'indium et le gallium avec l'EDTA et le TTHA (acide triéthylènetétramine hexacétique) pour le dosage complexométrique des deux éléments dans leurs mélanges. L'indium forme avec l'EDTA et le TTHA des complexes de composition normale 1:1, cependant que le gallium forme, avec le TTHA, un complexe 2:1. La méthode est basée sur le mode opératoire suivant: à une partie aliquote de la solution, on ajoute un excès d'EDTA, et à une autre la même quantité de TTHA. On dose les deux solutions, après avoir ajusté le pH à 5–5,5, au moyen d'une solution de zinc en présence de xylénol orange. On peut aisément calculer les teneurs en indium et gallium à partir des quantités de solution de zinc consommées dans les deux dosages.

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SEMI-MICRO DETERMINATION OF SILICON AND PHOSPHORUS IN FLUORINATED ORGANIC MATERIALS

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Summary—A method for the colorimetric determination of silicon and phosphorus in fluorinated organic compounds is outlined. After mineralisation of the material by fusion with sodium peroxide, silicon is determined as silicomolybdenum blue and phosphorus as phosphovanadomolybdate. Mean recoveries of 101·3% (standard deviation 1·64) for silicon and 100·9% (standard deviation 2·02) for phosphorus were obtained.

IT was suggested in an earlier publication[1] that the interference by fluorine in the determination of silicon in organic materials could be overcome by the addition of boric acid before precipitation of silica. This was later found to be not universally applicable, especially when larger quantities of fluorine were present.

It was known that fluorine could be determined in compounds containing silicon[2] and/or phosphorus[3,4] and that phosphorus could be determined in compounds containing fluorine[5] and/or silicon.[1] Schwarzkopf and Henlein[2] proposed two procedures for the determination of silicon in fluorinated organic compounds. Neither could be used if phosphorus was also to be determined, because phosphate is precipitated with lead chlorofluoride[3] and with oxine silicomolybdate.[6] The methods for determination of silicon in the presence of fluorine proposed by Shell and Craig[7] and by Harel *et al.*[8] were considered inappropriate for adaptation.

PRELIMINARY INVESTIGATIONS

Separation of silica after complexing fluoride with aluminium[9] was moderately successful, but insufficiently reliable for the present purpose. Determination of silica after precipitation of calcium fluoride[10,11] was moderately successful but tedious. Separation of silicate from fluoride with zinc oxide[12] was found to give the required precision.

The above procedures depend on the gravimetric determination of silicon as silica, with its attendant poor gravimetric factor and tendency to produce slightly low results. Chumachenko and Burlaka[13] have suggested that an empirical factor might be used to overcome the latter defect, but this expedient is hardly justifiable. Improved gravimetric factors are achieved by precipitation of silicon as the silicomolybdate of an organic base, but such complexes are slightly soluble, and the phosphomolybdates are simultaneously precipitated. In spite of a statement to the contrary,[14] it was found that the precipitation of the quinoline-silicomolybdenum blue complex was also accompanied by quantitative precipitation of the phospho complex. In the absence of phosphate, this was found to be an excellent method for silicon determination, although an empirical factor (0·0117) had to be used.

Greenfield[15] has proposed a colorimetric method for determination of silicon in minerals containing phosphorus and fluorine. Silicomolybdate is reduced under rigorously controlled conditions without reduction of phosphomolybdate. It was confirmed that no interference was caused by the amounts of fluorine and phosphorus that might be expected to occur with the silicon in organic compounds.

A colorimetric procedure, using the phosphovanadomolybdate complex, was recommended by Dunn[16] for determination of phosphorus in organic compounds. It was established that no interference was caused by the quantities of fluorine and silicon expected (*cf.* Lew and Jakob[17]).

EXPERIMENTAL

Analysis of organic materials

Using our usual technique for peroxide bomb fusion,[6] incomplete decomposition of some organosilicon compounds has occurred, but it has been found that fusion with sodium peroxide in a nickel "fluorine" bomb[18] at 500° is effective. This technique, although possibly not essential, was used in this work.

Using triphenylsilanol as a standard compound, low recoveries of silicon were obtained if Greenfield's procedure was applied directly to the bomb leachings. Satisfactory recoveries were, however, obtained when Wilson's method[19] for complete conversion to orthosilicate was applied to the bomb leachings before determination of silicon.

Procedure

Place a little sodium peroxide in the bottom of a "fluorine" bomb, and add the weighed organic sample, containing 1–5 mg of silicon and 1–4 mg of phosphorus, followed by sufficient sodium peroxide to give a total of 1 g of peroxide. Seal the bomb, and heat it in a muffle furnace at 500° for 15 min, swirling the molten contents after 10 min and also when the bomb is removed from the furnace.

Cool and open the bomb, washing any peroxide adhering to the cap into a platinum dish. Wipe the outside of the bomb with a clean tissue, and lay it on its side in the platinum dish. Add water until the bomb is half covered, place a watch glass over the dish and heat on a hot-plate, occasionally rolling the bomb gently, until effervescence ceases and the solution comes to the boil. Remove the dish from the hot-plate and allow to cool. Rinse the underside of the watch-glass and the bomb, collecting the washings in the dish.

Run 9 ml of 4*M* hydrochloric acid into a 250-ml Polythene beaker, and pour the alkaline contents of the dish into the acid, stirring well. Rinse the dish, collecting the washings in the beaker.

Add 15 ml of 1*M* sodium hydroxide solution and allow the solution to cool. Adjust the pH back to 7 with 2*M* hydrochloric acid, using a pH meter. Add 34·0 ml of 4*M* hydrochloric acid from a burette, stir well and allow to cool. Filter the contents of the beaker through a paper-pulp pad into a 250-ml volumetric flask, rinse the beaker and pad, and dilute to the mark with water. Transfer the sample solution to a Polythene bottle.

Into each of two dry 250-ml beakers, marked "test solution" and "compensating solution", pipette 50 ml of 1% ammonium molybdate solution. Then make the additions shown in Table I after the times indicated:

TABLE I

Time, *min*	Test solution	Compensating solution
0	20 ml of sample solution	60 ml of 1 + 1 HCl (burette) followed immediately by 10 ml of 1% $SnCl_2$ (pipette) and 20 ml of sample solution (pipette)
5	60 ml of 1 + 1 HCl (burette)	—
15	10 ml of 1% $SnCl_2$ (pipette)	—
	Transfer a portion of each solution into a 5-mm spectrophotometer cell.	
20	Measure the optical density, at 800 mμ, of the "test solution", against "compensating solution" as blank.	

Compute the silicon content of the sample by reference to a calibration curve prepared from standard silicate solution* added to acidified blank bomb leachings, and put through the analytical process.

To a 100-ml volumetric flask add 20 ml of sample solution, about 20 ml of water and 5 ml of vanadomolybdate reagent†; make up to the mark with water.

Similarly, prepare a blank solution by substituting 20 ml of acidified blank bomb leachings for the sample solution.

Allow to stand for 20 min, then measure the optical density, at 420 mμ, of the sample solution against the blank in 2-cm cells.

Compute the phosphorus content of the sample by reference to a calibration curve prepared from standard phosphate solution‡ added to acidified blank bomb leachings and put through the analytical process.

RESULTS

Table II shows the results obtained for the analysis of triphenylsilanol and a selection of research compounds containing silicon and phosphorus, some also containing fluorine.

TABLE II.—ANALYSIS OF ORGANIC COMPOUNDS

Compound	Sample wt., *mg*	Silicon, %		Phosphorus, %		Fluorine, %
		Calc.	Found	Calc.	Found	Calc.
$C_{18}H_{16}O\ Si$	19·64	10·14	10·39	—	—	—
	25·68		10·40			
	28·56		10·12			
	29·68		10·28			
	30·73		10·28			
	40·05		10·34			
$C_{15}H_{37}O_5Si_2P$	13·25	14·60	15·02	8·05	8·46	—
	30·47		14·57		7·75	
$C_9H_{23}O_5Si\ P$	27·53	10·39	10·53	11·46	11·44	—
	27·77		10·51		11·45	
$C_{38}H_{52}O_9Si_2P_2$	31·27	7·29	7·36	8·04	8·06	—
	39·80		7·21		7·89	
$C_{15}H_{35}F_2O_3Si_2P$	15·54	14·46	14·54	7·97	8·43	9·8
	17·31		14·27		8·20	
$C_{20}H_{37}F_2O_3Si_2P$	24·05	12·52	12·68	6·90	7·11	8·4
	27·91		12·36		7·13	
$C_{28}H_{32}F_{28}O_9Si_2P_2$	42·71	4·93	5·13	5·44	5·34	46.7
	49·05		5·18		5·36	

DISCUSSION

Mean recoveries, calculated from the results in Table II, are: for silicon 101·3% (standard deviation 1·64, 18 determinations); for phosphorus 100·9% (standard deviation 3·02, 12 determinations). In spite of the possible existence of a positive bias in the method, and the tendency for some results to fall outside the normally

* Fuse 2 g of precipitated silica with 12 g of anhydrous sodium carbonate. Leach the cooled melt with water. Filter the resulting solution and dilute the filtrate to 1 litre. Store in a Polythene bottle. Standardise this solution gravimetrically.[22]

† *Preparation:* Dissolve 1·6 g of ammonium vanadate and 50 g of ammonium molybdate in 700 ml of water at about 60°, filter if not completely clear, and allow to cool. Add cautiously, with stirring, 150 ml of concentrated sulphuric acid, allow to cool and dilute to 1 litre with water.

‡ Dissolve 87·86 mg of KH_2PO_4, dried at 105° for 1 hr, in water, and dilute to 1 litre.

accepted limits (±0·3% absolute) for analysis of organic materials, we consider that these results are reasonable for these types of compound.

Attempts to determine fluorine, by the method of Belcher and West,[20] in a further portion of the solution obtained from the bomb leachings, met with limited success. Use of one of the methods proposed by Belcher and West[21] for larger quantities of fluorine, thus allowing larger portions of the leach solution to be taken, may be more successful.

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Zusammenfassung—Eine Methode zur kolorimetrischen Bestimmung von Silicium und Phosphor in fluorierten organischen Verbindungen wird skizziert. Nach Aufschluß des Materials durch Natriumperoxydschmelze wird Silicium als Silicomolybdänblau und Phosphor als Phosphovanadomolybdat bestimmt. Mittlere Ausbeuten von 101,3% (Standardabweichung 1,64) für Silicium und 100,9% (Standardabweichung 2,02) für Phosphor wurden erhalten.

Résumé—On présente une méthode de dosage colorimétrique du silicium et du phosphore dans les composés organiques fluorés. Après minéralisation du produit par fusion avec le peroxyde de sodium, on dose le silicium à l'état de bleu de silicomolybdène, et le phosphore à l'état de phosphovanadomolybdate. On retrouve en moyenne 101,3% (écart type 1,64) de silicium et 100,9% (écart type 2,02) de phosphore.

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DETERMINATION OF NON-METALLIC COMPOUNDS IN STEEL—I

APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS-EFFLUENT GAS ANALYSIS

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Summary—Differential thermal analysis can be used to identify metal carbides, nitrides and sulphides in the residues which can be chemically or electrochemically extracted from steels. Different dynamic gases can be used to produce different thermal responses, which will further aid in the identification. Monitoring changes in the thermal conductivity and/or composition of the effluent gas can also aid in this identification. Preliminary experiments in detecting changes in the composition of the effluent gas by thermal-conductivity measurement, selective absorption and coulometric titration indicate that quantitative determination of inclusion compounds extracted from steel is possible. However, the design of the sample holder must be improved to eliminate gas leaks and temperature differences between the reference and effluent gases. Future work will also be directed towards developing methods for quantitatively determining specific non-metallic compounds in mixtures extracted from steels.

INTRODUCTION

FOR many years the effect of carbide and nitride compounds on the physical and mechanical properties of steel has been recognised. For example, strain-aging, a phenomenon associated with the precipitation of iron nitride in steel, can be prevented by the addition of aluminium or vanadium, which preferentially combine with the nitrogen to form aluminium or vanadium nitride.[1,2] The precipitation of carbides is known to hinder crystal growth and thereby effect a fine microstructure and increased tensile strength.[3] Intergranular corrosion of stainless steels may be caused by depletion of chromium at the grain boundaries because of the formation of chromium carbide. To prevent this depletion, niobium or titanium is added to form a carbide in preference to that of chromium.[4] Variations in many other mechanical properties, such as hardenability, yield strength, toughness and brittleness, have been associated with the presence of compounds such as nitrides, carbides, oxides and sulphides. The analysis of steel for these compounds can, therefore, be used to aid in the development of steels with improved physical and mechanical properties.

Mixtures of compounds are isolated from steel by techniques such as electrolytic extraction,[5] acid extraction,[6] direct halogenation[7] and halogenation in an ester or alcohol medium.[8,9] Chemical analysis of these mixtures for specific compounds is difficult and sometimes impossible. Separations based on solubility in a specific reagent are not always satisfactory because the rates of solution of many of these compounds are not sufficiently different. Furthermore, reliable information on the rate of solution of many of these compounds is not available. Finally, analysis for these compounds is often complicated by their existence as very fine particles (10 mμ or less), which cannot always be isolated by normal filtration or separation techniques.[10,11,12]

The oldest method used for identification of compounds in steel is optical microscopy. Visual identification, can, however, lead to errors. Also, with this technique very fine particles cannot be seen because of insufficient resolution. In recent years more precise methods, such as X-ray diffraction, electron diffraction and electron microscopy, have been employed in conjunction with chemical-isolation and plastic-replication techniques. Although the qualitative information gained by the use of these instruments is more reliable, fine particles of titanium nitride, titanium carbide and titanium carbonitride cannot be differentiated because of their similar crystal structures. Furthermore, the methods are only semiquantitative.

Because the design of apparatus for differential thermal analysis (DTA) and effluent gas analysis (EGA) has recently been improved,[13,14,15] these techniques seemed applicable to the analysis of mixtures of compounds that are chemically extracted from steel.

In the initial work characteristic DTA curves for some of the compounds were obtained from commercially prepared synthetics, then inclusions were separated by weak-acid dissolution or anodic dissolution of the steel matrix and filtration of the residue through a 10-mμ pore size filter. The DTA-EGA results on some titanium compounds extracted from steel were compared with chemical and X-ray diffraction results.

EXPERIMENTAL

Apparatus

A Model 12BC$_2$ DTA-EGA apparatus, manufactured by the R. L. Stone Co. of Austin, Texas, U.S.A., was used for the experiments. The EGA unit was modified by replacing the conductivity cell with a Gow-Mac Model JDC-133 microvolume thermistor detector immersed in a thermally insulated oil bath. A Gow-Mac Power Supply Model 9999-D1 was used with this cell. A Pyrex Millipore filter holder, containing a 47-mm Type VF Millipore filter disk (10-mμ pore size), was used for collection of the inclusions extracted from the steels.

Reagents

Commercially prepared titanium carbide, titanium nitride, titanium carbonitride, zirconium carbide, zirconium nitride, niobium carbide and niobium nitride were used for the preliminary experiments. The identification and purity of these compounds were established by X-ray diffraction and chemical analysis.

The experimental steels used for this study contained titanium and one or more of the elements nitrogen, carbon and sulphur, as shown in Table I. The steels were prepared by vacuum melting so that very little oxygen would be present.

Procedure

DTA data were obtained by introducing 1–3 mg of sample into an R. L. Stone Model SH8A or SH9A sample holder equipped with platinum-cup thermocouples. The heating rate was 10°/min, and the thermograms of the difference in response between the reference and sample thermocouples, (ΔT, *versus* the furnace temperature) were recorded at $\frac{1}{30}$ and $\frac{1}{15}$ of the maximum sensitivity setting of the instrument for the commercial compounds and the extracted compounds, respectively. Oxygen flow rates of 5 and 40 ml/min were used for the extracted and the commercial compounds, respectively. Reagent-grade alundum, containing more than 95% of α-alumina, was used in the reference thermocouple.

EGA data were obtained by introducing a weighed sample (*ca.* 1–3 mg) to an R. L. Stone Model SH12BP sample holder equipped with platinum-cup thermocouples, and recording the difference in thermal conductivity of the effluent gases from the reference and sample sides (Δk). The attenuator was set at $\frac{1}{8}$ the maximum sensitivity for the EGA recording unless otherwise shown. The oxygen gas flow was 5 ml/min through the reference side; it varied from 5 to 8·5 ml/min in the sample side of the EGA apparatus. The heating rate was 10°/min.

TABLE 1.—PERCENTAGE COMPOSITION OF EXPERIMENTAL STEELS[a]

Element	Steel sample		
	A	B	C
C	0·22	0·21	0·049
Mn	0·015	<0·01	1·38
P	0·005	0·003	0·009
S	0·005	0·062	0·004
Si	0·017	0·006	0·052
Ni	0·036	0·027	0·036
Cr	0·012	<0·002	0·010
Ti	0·50	0·53	0·37
Sol. Al	0·004	0·003	0·004
Insol. Al	0·003	<0·002	0·002
N	0·002	0.001	0·019

[a] <0·005% of Cu, Mo, V, Zr, Nb or Ta; <0·0005% of B.

Titanium compounds were extracted from 5-g samples of the experimental steels by dissolving the steel matrix in 3% hydrochloric acid at 50° or by dissolving the steel anodically in a solution of 12·5% sodium citrate, 0·5% sodium thiocyanate, 1% potassium bromide and 0·01% hydrazine. The solution was filtered through a 10-mμ filter. One mg of the inclusion residue was scraped from the filter, weighed on a Cahn microbalance and introduced into the DTA apparatus. For several tests, the sample was introduced into the test apparatus with the portion of the filter on which it had been collected. One mg of residue was about $\frac{1}{10}$th of the inclusions isolated from steel samples A and B and $\frac{1}{80}$th of the inclusions isolated from sample C.

The titanium-bearing steels were also chemically analysed for titanium compounds to provide a comparison for the DTA-EGA results. Because the chemical analysis did not require filtration (see Appendix), none of the very fine inclusions of titanium compounds were lost. The chemically extracted titanium compounds were identified by standard X-ray diffraction techniques after collection on a 10-mμ filter.

RESULTS AND DISCUSSION

Thermograms of synthetic compounds

Characteristic thermograms were consistently obtained for the carbides and nitrides of titanium, zirconium and niobium (Fig. 1). Because the peak temperatures and the shapes of the thermograms are different for corresponding carbides and nitrides, these compounds can be distinguished in a residue containing these non-metallic compounds.

Often steels do not contain pure titanium carbide or pure titanium nitride, but rather titanium carbonitride (nitrogen-bearing titanium carbide or carbon-bearing titanium nitride of indefinite formula). The thermogram of a commercially prepared titanium carbonitride compound, containing 10% of nitrogen, 5% of carbon and 85% of titanium (Fig. 2), has some of the thermal characteristics of both the titanium carbide and the titanium nitride. Differences in the shapes of the titanium carbonitride thermogram permit identification of the carbonitride in the presence of either the carbide or the nitride.

Thermograms produced by different dynamic gases

In the thermograms for titanium carbide, titanium nitride and zirconium nitride in steam (Fig. 3), the peak temperatures are lower than those obtained in oxygen. The peak itself is higher for each of the two nitrides, but lower for the carbide. Substituting helium or vacuum for oxygen changes the type of reaction from combustion to decomposition and thus changes both the DTA and the EGA curves.

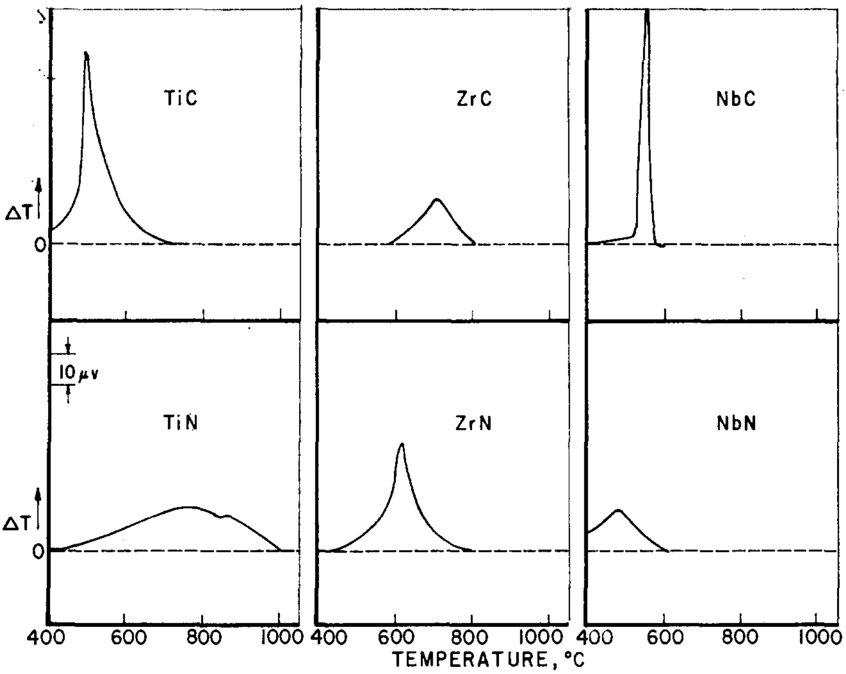

Fig. 1.—DTA recordings for carbides and nitrides of titanium, zirconium and niobium (oxygen as dynamic gas).

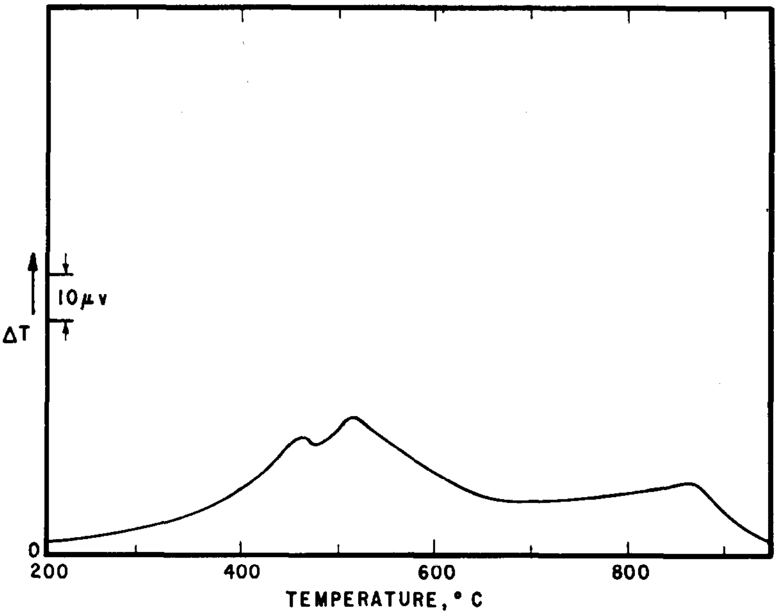

Fig. 2.—DTA recording for titanium carbonitride (85% of Ti, 5% of C, 10% of N by weight) (oxygen as dynamic gas).

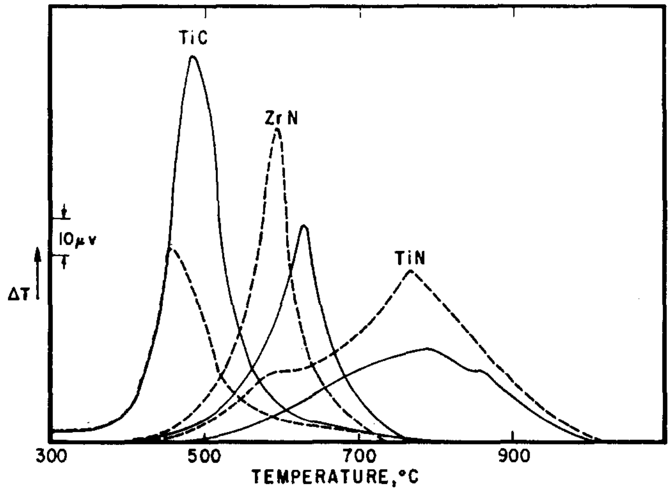

FIG. 3.—DTA recordings for titanium and zirconium nitrides and titanium carbide (oxygen or steam as dynamic gas):

—— oxygen,

– – – steam

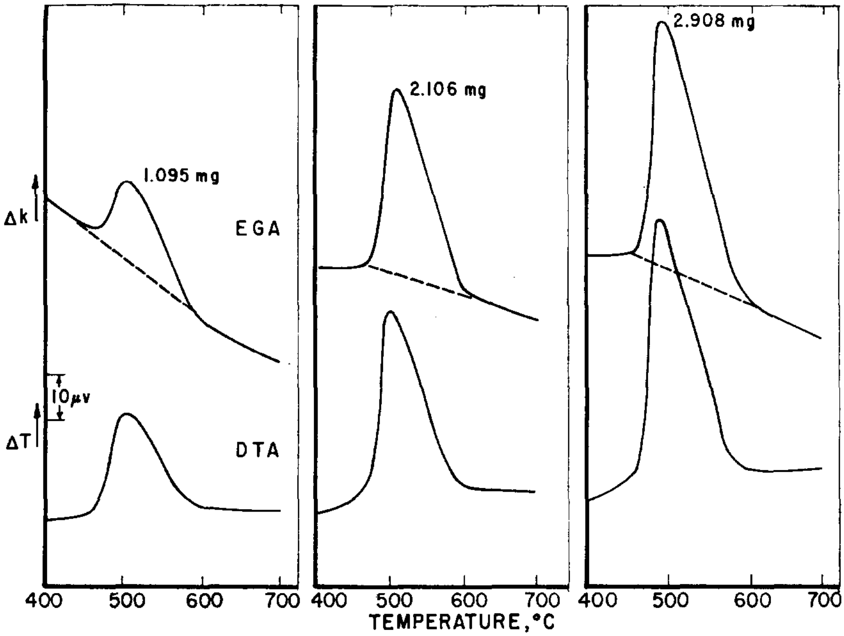

FIG. 4.—DTA-EGA recordings for different amounts of titanium carbide (oxygen as dynamic gas).

This illustrates another aid in the qualitative identification of mixtures of non-metallic compounds extracted from steel.

EGA response for titanium carbide

Fig. 4 shows the DTA and EGA curves for the combustion of 1, 2 and 3 mg of titanium carbide with oxygen as the dynamic gas in the sample and reference sides of the microvolume thermistor detector. The area above the dotted line represents the difference in thermal conductivity between oxygen containing carbon dioxide from combustion of the sample and pure oxygen from the reference side. The EGA base line drifted because of a temperature imbalance between the reference gas and the sample gas and a continuously changing gas flow rate in the sample side of the thermistor. A plot of the area representing the thermal-conductivity response against the amount of titanium carbide (Fig. 5) shows that, in spite of the base-line drift, good quantitative results are obtained. Elimination of the temperature imbalance between the reference and sample gases and the sample-holder leaks that contribute to the changing flow rates should improve the base line.

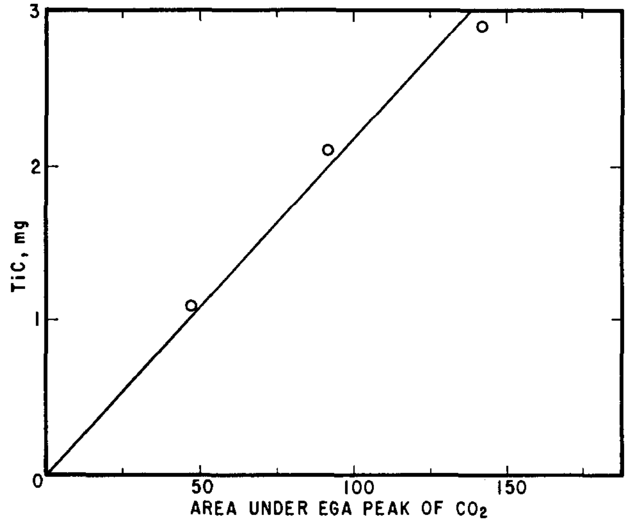

Fig. 5.—Amount of titanium carbide *versus* relative area under EGA curves (planimeter reading) for carbon dioxide (oxygen as dynamic gas).

Table II.—Analysis of inclusions

Steel sample	Chemical results, %			X-ray results		Estimated from DTA-EGA curves	
	Ti as TiN or TiC_xN_y	Ti as TiS	Ti as TiC	Major	Minor	Major	Minor
A	0·003	0·000	0·45	TiC	TiN	TiC	TiN
B	0·000	0·080	0·37	TiC	γ-Ti_2S	TiC	γ-Ti_2S
C	0·053	0·000	0·35	TiC	None detected	TiC	TiC_xN_y

Thermograms of inclusion residues separated from steels by acid extraction

Although the differential thermograms of the residues extracted with weak hydrochloric acid from the titanium-bearing steels are more complex than those for the commercial compounds (Figs. 6, 7 and 8), they had thermal peaks that agreed with the chemical and X-ray analyses of the residues (Table II). All three steels contained titanium carbide, and the thermogram of each steel showed a titanium-carbide peak.

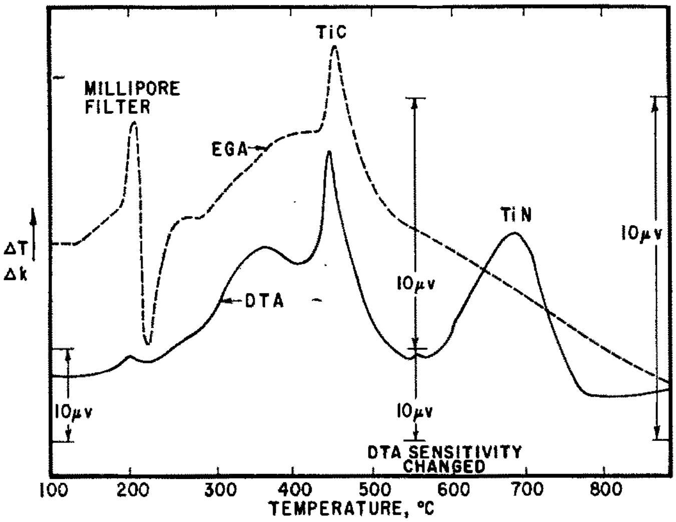

FIG. 6.—DTA-EGA recordings of membrane filter and a 1-mg sample of inclusions extracted from Steel A by weak-acid dissolution (oxygen as dynamic gas).

In addition, a thermal peak in Fig. 7 corresponds to the gamma dititanium sulphide in Steel B, and a thermal response in Fig. 8 corresponds to titanium carbonitride in Steel C. One noticeable difference in the thermograms is that the thermal peak for titanium carbide shifted from 500° for the commercial compound (Fig. 1) to 450° for the compound extracted from steel (Figs. 6–9). This shift is probably caused in part by a difference in particle size of the two titanium carbides; some of the commercial powder was 10,000 times larger than that extracted from the steel. A second possible explanation is that small amounts of other compounds in the crystal structure of the extracted titanium carbide lowered the reaction temperature. The thermal peaks for the titanium nitride in Fig. 6, for the gamma dititanium sulphide in Fig. 7 and for the titanium carbonitride plateau in Fig. 8 have also shifted.

All three differential thermograms show peaks for compounds that could not be definitely identified as titanium compounds and that might have been more complex titanium compounds or compounds containing no titanium. In addition, the doublet peaks for the titanium carbide in Figs. 7 and 8 were almost exactly reproduced on four separate thermograms of residues from two different acid extractions. Chemical tests show that carbon dioxide was evolved at each peak in the doublet. No other carbide-forming elements were present except titanium and iron. Therefore, the doublet is apparently related to the structure or the particle size of the titanium carbide.

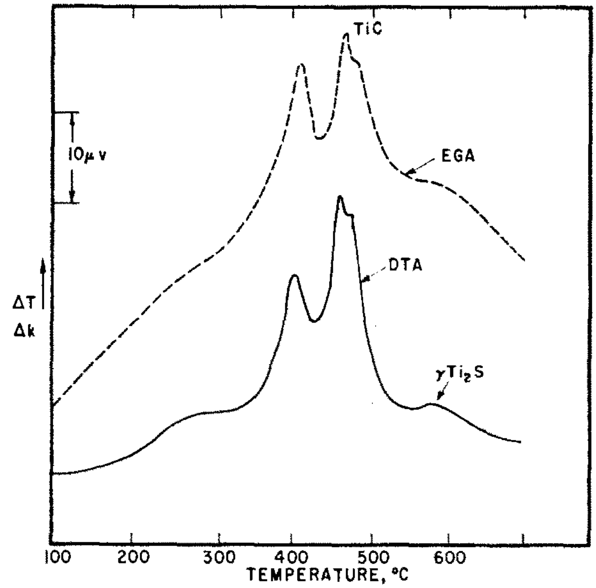

FIG. 7.—DTA-EGA recordings for 1-mg sample of inclusions extracted from Steel B by weak-acid dissolution (oxygen as dynamic gas).

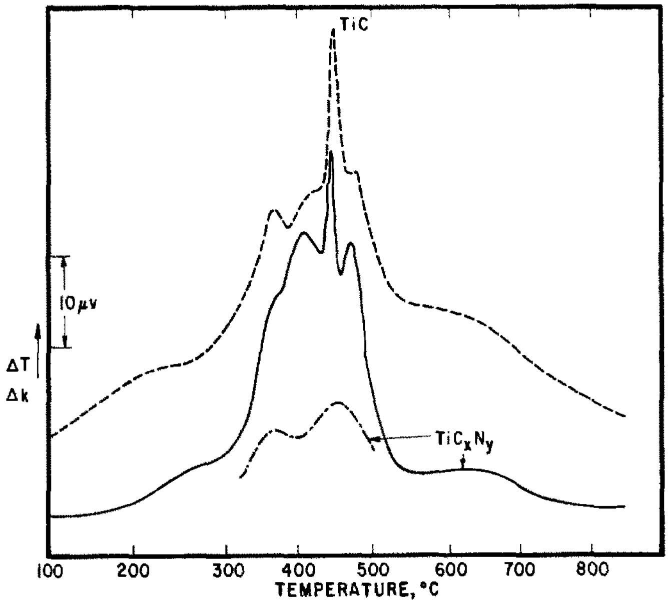

FIG. 8.—DTA-EGA recordings for 1-mg sample of inclusions extracted from Steel C by weak-acid dissolution (oxygen as dynamic gas):

--- EGA,
—— DTA,
·-·- contribution of TiC_xN_y to TiC peak.

Because the DTA-EGA response for combustion of the Millipore filter occurs below 300° (Fig. 6), the filter containing the residue can be introduced directly into the apparatus with no interference in the analysis at temperatures greater than 300°. No EGA response corresponds to the DTA peak of the titanium nitride with oxygen as the dynamic and reference gas in Fig. 6. This indicates that decomposition of the compound releases nitrogen which has a similar thermal conductivity to that of oxygen and therefore causes very little EGA response. This effect can be used to differentiate between nitrides and carbides. Because only about 0·019 mg of titanium nitride was present in the sample-holder, the DTA sensitivity was changed from $\frac{1}{15}$th to $\frac{1}{4}$th maximum at 600° so that a recognisable peak would be recorded. The sensitivity setting of only $\frac{1}{4}$ demonstrates that very small amounts of these compounds can be detected when no DTA interference is present.

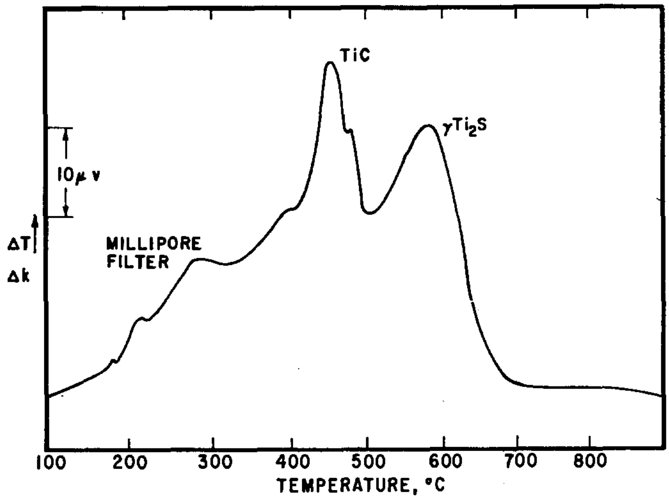

FIG. 9.—DTA recording of membrane filter and inclusions extracted from Steel B by anodic dissolution of sample (oxygen as dynamic gas).

The nitrogen found by chemical methods in the residue from Steel C was not present as TiN because the DTA peak for this compound in Fig. 6 is not present in Fig. 8. A plateau from 520 to 700° appears to fit TiC_xN_y, and a broad thermal response from 300 to 500° is characteristic of TiC_xN_y (see Fig. 2). A sharper titanium-carbide doublet peak is superimposed on the broad titanium carbonitride thermal response.

No attempt was made to calculate quantitative values for the titanium carbide in the three steels from the EGA curves because of the temperature imbalance in the gases from the sample and reference side and the gas leaks in the sample holder. However, rough estimates from assumed base lines seem to indicate that quantitative analysis of the inclusion residue can be based on the thermal conductivity of the effluent gas stream. Other methods of measuring changes in the composition of the effluent gas were also tried in a preliminary manner. Among those which seem useful are the following:

1. The removal or determination of carbon dioxide by absorption on a preweighed bulb of asbestos impregnated with sodium hydroxide.

2. The removal or determination of sulphur dioxide in the effluent stream by reaction with a solution of potassium permanganate.
3. The determination of microgram quantities of sulphur dioxide selectively and continuously by a coulometric technique wherein iodine is electrolytically generated.

In addition, these experiments and other published work indicate that selected fractions of the effluent gas could be analysed by gas chromatography and mass spectrometry.

Effect of method of extraction of inclusion compounds

Inclusions were extracted from Steel B by weak-acid dissolution and by anodic dissolution in the modified sodium citrate solution. The thermal peak for gamma dititanium sulphide is higher for the residue from the anodic extraction (Fig. 9) than for the residue from the weak-acid extraction (Fig. 7). Most of the gamma dititanium sulphide apparently dissolves under the conditions used for the acid extraction. This illustrates the importance of selecting the appropriate method of chemical isolation for specific inclusion compounds. Even low rates of solution are important because very small quantities of the fine particles, with a correspondingly large surface area, may be exposed to a dissolution medium for several days. This effect is demonstrated in Table II by the titanium sulphide results for Steel B, which were obtained from the difference in sulphur determined by the combustion and evolution methods. Very little titanium sulphide was dissolved in the few minutes necessary to evolve hydrogen sulphide in the evolution method, whereas nearly all of the gamma dititanium sulphide was dissolved in a more dilute solution of hydrochloric acid in the 2 days required to dissolve the matrix. Finally, the additional peaks and exothermic areas in Fig. 9 are from other compounds and phases in the steel, such as iron and manganese carbides and sulphides, which are chemically stable in the anodic citrate medium but not in the dilute acid medium.

APPENDIX

The following is a summary of the chemical methods used to determine the amount of the various forms of titanium in the titanium-bearing steels:

1. Dissolve a steel sample in warm 3% sulphuric acid, remove iron by mercury-cathode electrolysis, allow undissolved TiC, TiN, TiS and TiO_2 to settle, and determine the titanium in the solution by the peroxytitanic acid photometric method. The result represents the titanium in solid solution with iron in the steel (*i.e.*, titanium not combined with carbon, nitrogen, sulphur or oxygen).
2. Dissolve a second steel sample in hydrochloric acid, add perchloric acid and evaporate the solution to fumes of perchloric acid to dissolve all titanium compounds but TiO_2. Remove iron by mercury-cathode electrolysis, allow any TiO_2 to settle and determine the titanium in the solution by the peroxytitanic acid photometric method. The results represent the titanium in solid solution in the steel plus the titanium combined with carbon, nitrogen and sulphur. The difference between the titanium results obtained by procedures 1 and 2 represents the titanium combined with carbon, nitrogen and sulphur.
3. Determine sulphur by the evolution and combustion methods. The difference in the sulphur results obtained by these two methods (evolution is lower) represents the sulphur associated with the titanium and is arbitrarily calculated to TiS (the common form).
4. Dissolve a steel sample in 3% hydrochloric acid at 50° and determine the nitrogen present as iron nitride, aluminium nitride and in solid solution by the micro Kjeldahl photometric method. Dissolve another sample with potassium sulphate-sulphuric acid, heat to fumes of sulphuric acid and determine nitrogen by the same method. The difference in the nitrogen results is the nitrogen present as TiN.
5. Subtract the titanium present as TiN and TiS from the titanium value determined in procedure 2. The difference is assumed to be titanium present as TiC.

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Zusammenfassung—Mit der Diferentialthermoanalyse kann man Metallcarbide, -nitride und -sulfide in den Rückständen identifizieren, die chemisch oder elektrochemisch aus Stählen gewonnen werden können. Mit verschiedenen Trägergasen lassen sich verschiedene thermische Effekte erzielen, die bei der Identifizierung weiterhelfen. Auch Messung von Veränderungen der Wärmeleitfähigkeit und/oder Zusammensetzung des ausgetriebenen Gases kann dabei von Nutzen sein. Vorläufige Experimente zur Feststellung von Änderungen der Zusammensetzung des ausgetriebenen Gases durch Wärmeleitfähigkeitsmessung, selektive Absorption und coulometrische Titration zeigen, daß die quantitative Bestimmung aus Stahl extrahierter eingeschlossener Verbindungen möglich ist. Die Konstruktion des Probenhalters jedoch muß noch verbessert werden, um Gaseinbrüche und Temperaturdifferenzen zwischen Vergleichs- und ausgetriebenem Gas zu verhindern. Weitere Arbeiten werden ferner zum Ziel haben, Methoden zur quantitativen Bestimmung bestimmter nichtmetallischer Verbindungen in aus Stahl extrahierten Mischungen zu entwickeln.

Résumé—On peut utiliser l'analyse thermique différentielle pour identifier les carbures, nitrures et sulfures métalliques dans les résidus qui peuvent être extraits chimiquement ou électrochimiquement des aciers. On peut utiliser différents gaz dynamiques pour produire différentes réponses thermiques, qui aideront ensuite à l'identification. Le contrôle de changements dans la conductivité thermique et/ou la composition du gaz effluent peut aussi aider à cette identification. Des expériences préliminaires pour détecter des variations dans la composition du gaz effluent, par mesure de conductivité thermique, absorption sélective, et dosage coulométrique, montrent que le dosage quantitatif des composés d'inclusion extraits de l'acier est possible. Toutefois, la conception du support de l'échantillon doit être améliorée pour éliminer les fuites de gaz et les différences de température entre le gaz de référence et le gaz effluent. Les travaux futurs seront également dirigés vers le développement de méthodes de dosage quantitatif de composés non métalliques spécifiques dans des mélanges extraits d'aciers.

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SUCCESSIVE DETERMINATION OF THORIUM AND RARE EARTHS BY COMPLEXOMETRIC TITRATIONS*

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Summary—Thorium can be determined quantitatively by EDTA in the presence of the light rare earths but not in the presence of the heavy rare earths. The successive determination of thorium and heavy rare earths with diethylenetriaminepenta-acetic acid (DTPA) has been found to be feasible and is described. The direct successive determination of thorium and rare earths by combined titration with DTPA and *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) is also discussed.

VERY few workers[1,2] have reported methods for the successive determination of thorium and rare earths by complexometric titration, although there have been reports of the successive determination of thorium and rare earths by other complexometric methods (spectrophotometry, *etc.*). However, published complexometric titration methods have dealt only with the determination of thorium and the light rare earths (lanthanum to neodymium inclusive).

Complexometric titrations depend on the stability constants of complexes formed by interaction between a metal ion and the titrant, and sizable differences in these stability constants are responsible for the successful successive determination of different metals at controlled pH values.

It has been reported[1,2] that thorium may be determined accurately in the presence of light rare earths by titrating with EDTA at pH 2·5–3·0, using Xylenol Orange, Pyrocatechol Violet, *etc.*, but that the subsequent determination of the rare earths could not be accomplished because of a colour reaction of the thorium-EDTA complex at higher pH values. Přibil and Veselý[2] used diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexa-acetic acid (TTHA) successfully for the successive determination of thorium and various light rare earths.

The present authors found that, although thorium could be determined accurately by EDTA in the presence of the light rare earths, as previously reported, it was not possible to determine thorium in the presence of the heavier rare earths (samarium to lutetium inclusive) whose EDTA complexes are much closer in stability to that of thorium-EDTA. This observation prompted the authors to examine the method of Přibil and Veselý for the successive determination of thorium and the heavy rare earths.

The DTPA method was found to be suitable for determining thorium and the heavy rare earths as well as for the determination of thorium and the light rare earths. The difference was that the end-point of the titration for determination of thorium is orange instead of clear yellow, as was reported in the case of light rare earths.

Přibil and Veselý used standard lead solution as a back-titrant for determination of rare earths. We have found that, instead of adding an excess of DTPA and

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* Contribution No. 1486. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

TABLE I.—DETERMINATION OF THORIUM AND RARE EARTHS (Sm TO Lu INCLUSIVE) WITH DTPA

0·05*M* Th taken, *ml*	0·05*M* R.E. taken, *ml*	0·05*M* Th found, *ml*	Excess 0·05*M* DTPA, *ml*	Back titre with 0·05*M* Pb, *ml*	0·05*M* R.E. found, *ml*
9·65	1·995 Sm	9·65	5·65	3·65	2·00 Sm
7·72	3·99 Sm	7·75	7·25	3·26	3·99 Sm
5·79	7·98 Sm	5·80	12·20	4·27	7·93 Sm
3·86	11·97 Sm	3·85	13·15	1·10	12·05 Sm
1·93	15·96 Sm	1·95	18·05	2·06	15·99 Sm
0·965	19·95 Sm	1·00	24·00	4·08	19·92 Sm
9·65	1·97 Eu	9·65	4·35	2·40	1·95 Eu
7·72	3·95 Eu	7·75	8·25	4·32	3·93 Eu
5·79	7·90 Eu	5·80	14·20	6·34	7·86 Eu
3·86	11·85 Eu	3·90	14·10	2·25	11·85 Eu
1·93	15·80 Eu	1·95	20·05	4·27	15·78 Eu
4·83	1·93 Gd	4·80	4·20	2·25	1·95 Gd
7·72	3·85 Gd	7·75	6·25	2·35	3·90 Gd
5·79	7·70 Gd	5·80	11·20	3·48	7·73 Gd
3·86	11·55 Gd	3·90	14·10	2·52	11·58 Gd
1·93	15·40 Gd	1·95	18·05	2·63	15·42 Gd
0·965	19·35 Tb	1·00	22·00	2·66	19·34 Tb
1·93	15·48 Tb	1·95	18·05	2·54	15·51 Tb
3·86	11·61 Tb	3·90	14·10	2·50	11·60 Tb
5·79	7·74 Tb	5·80	10·06	2·35	7·71 Tb
7·72	3·87 Tb	7·75	6·25	2·40	3·85 Tb
7·72	4·02 Dy	7·75	6·25	2·10	4·04 Dy
5·79	8·04 Dy	5·80	10·20	2·16	8·04 Dy
3·86	12·06 Dy	3·90	14·10	2·10	12·00 Dy
1·93	16·08 Dy	1·95	18·05	1·97	16·08 Dy
0·965	20·10 Dy	1·00	24·00	3·84	20·16 Dy
7·72	3·92 Ho	7·75	6·25	2·26	3·99 Ho
5·79	7·84 Ho	5·80	10·20	2·35	7·85 Ho
3·86	11·76 Ho	3·90	14·10	2·35	11·75 Ho
1·93	15·68 Ho	1·95	18·05	2·45	15·60 Ho
0·965	19·60 Ho	1·00	24·00	4·46	19·54 Ho
7·72	1·86 Er	7·75	4·25	2·40	1·85 Er
5·79	3·72 Er	5·80	5·20	1·54	3·66 Er
3·86	5·58 Er	3·90	7·10	1·58	5·52 Er
1·93	7·44 Er	1·95	9·05	1·65	7·40 Er
0·965	9·30 Er	1·00	11·00	1·75	9·25 Er
7·72	3·95 Tm	7·75	5·25	1·30	3·95 Tm
5·79	7·90 Tm	5·80	9·20	1·34	7·86 Tm
3·86	11·85 Tm	3·90	13·10	1·30	11·80 Tm
1·93	15·80 Tm	1·95	18·05	2·27	15·78 Tm
0·965	19·75 Tm	1·00	21·00	1·25	19·75 Tm
8·00	4·21 Yb	8·00	6·00	1·79	4·21 Yb
6·00	8·42 Yb	6·00	10·00	1·59	8·41 Yb
4·00	12·63 Yb	4·00	14·00	1·44	12·56 Yb
2·00	16·84 Yb	2·00	18·00	1·25	16·78 Yb
1·00	12·05 Yb	1·00	23·00	1·94	21·06 Yb
0·965	18·90 Lu	1·00	24·00	5·05	18·95 Lu
0·965	1·89 Lu	1·00	4·00	2·16	1·84 Lu
1·93	18·90 Lu	1·95	23·05	4·10	18·95 Lu
3·86	11·34 Lu	3·90	16·10	4·75	11·35 Lu
5·79	7·56 Lu	5·80	14·20	6·70	7·50 Lu
9·65	3·78 Lu	9·65	10·35	6·52	3·83 Lu

TABLE II.—DETERMINATION OF THORIUM AND RARE EARTHS WITH DTPA AND HEDTA

0·05*M* Th added *ml*	0·05*M* R.E. added, *ml*	0·05*M* Th found, *ml of DPTA*	0·05*M* R.E. found *ml, of HEDTA*
2·00	13·68 La	2·00	13·70 La
4·00	10·26 La	4·00	10·30 La
6·00	6·84 La	6·00	6·90 La
8·00	3·42 La	8·00	3·45 La
2·00	8·76 Ce	2·00	8·75 Ce
4·00	6·57 Ce	4·00	6·60 Ce
6·00	4·38 Ce	6·00	4·40 Ce
8·00	2·19 Ce	8·00	2·20 Ce
2·00	14·84 Pr	2·00	14·85 Pr
4·00	11·13 Pr	4·00	11·15 Pr
6·00	7·42 Pr	6·00	7·45 Pr
8·00	3·71 Pr	8·00	3·75 Pr
2·00	15·12 Nd	2·00	15·15 Nd
4·00	11·35 Nd	4·00	11·40 Nd
6·00	7·56 Nd	6·00	7·55 Nd
8·00	3·78 Nd	8·00	3·80 Nd
2·00	15·56 Sm	2·00	15·60 Sm
4·00	11·67 Sm	4·00	11·70 Sm
6·00	7·78 Sm	6·00	7·80 Sm
8·00	3·89 Sm	8·00	3·90 Sm
2·00	15·40 Eu	2·00	15·40 Eu
4·00	11·55 Eu	4·00	11·60 Eu
6·00	7·70 Eu	6·00	7·75 Eu
8·00	3·85 Eu	8·00	3·90 Eu
2·00	14·92 Gd	2·00	14·90 Gd
4·00	11·19 Gd	4·00	11·20 Gd
6·00	7·46 Gd	6·00	7·50 Gd
8·00	3·73 Gd	8·00	3·70 Gd
2·00	15·68 Dy	2·00	15·70 Dy
4·00	11·76 Dy	4·00	11·75 Dy
6·00	7·84 Dy	6·00	7·85 Dy
8·00	3·92 Dy	6·00	3·90 Dy
2·00	15·08 Tb	2·00	15·10 Tb
4·00	11·31 Tb	4·00	11·30 Tb
6·00	7·54 Tb	6·00	7·60 Tb
8·00	3·77 Tb	8·00	3·75 Tb
2·00	15·28 Ho	2·00	15·30 Ho
4·00	11·46 Ho	4·00	11·50 Ho
6·00	7·64 Ho	6·00	7·65 Ho
8·00	3·82 Ho	8·00	3·80 Ho
2·00	7·24 Er	2·00	7·25 Er
4·00	5·43 Er	4·00	5·40 Er
6·00	3·62 Er	6·00	3·60 Er
8·00	1·81 Er	8·00	1·80 Er
2·00	15·36 Tm	2·00	15·35 Tm
4·00	11·52 Tm	4·00	11·52 Tm
6·00	7·68 Tm	6·00	7·65 Tm
8·00	3·84 Tm	8·00	3·90 Tm
2·00	15·80 Yb	2·00	15·85 Yb
4·00	11·85 Yb	4·00	11·85 Yb
6·00	7·90 Yb	6·00	7·90 Yb
8·00	3·95 Yb	8·00	3·95 Yb
2·00	14·72 Lu	2·00	14·75 Lu
4·00	11·04 Lu	4·00	11·05 Lu
6·00	7·36 Lu	6·00	7·40 Lu
8·00	3·68 Lu	8·00	3·65 Lu

back-titrating with lead solution, rare earths may be determined directly by titrating with *N*-hydroxyethylethylenediaminetriacetic acid (HEDTA) at pH 5·0–5·5.

EXPERIMENTAL

Reagents

Diethylenetriaminepenta-acetic acid (DTPA) 0·05*M* *solution.* Dissolve 19·65 g of the free acid, obtained from Geigy, in 130–150 ml of hot 1*M* sodium hydroxide solution and dilute to 1 l. with distilled water.

N-hydroxyethylethylenediaminetriacetic acid (HEDTA) 0·05*M solution.* Dissolve 13·9 g of the free acid, obtained from Geigy, in 100 ml of hot 1*M* sodium hydroxide solution and dilute to 1 l. with distilled water.

The concentrations of the above solutions were checked by titrating with standard 0·05*M* lead nitrate solution using Xylenol Orange as an indicator.

Rare earths 0·05*M solution.* Dissolve the required amount of rare earth oxide, 99·99% pure, in concentrated hydrochloric acid (c.p.) and evaporate to incipient dryness. Dissolve the residue and dilute to 1 l. in each case with distilled water. The concentrations were checked complexometrically.

Indicator solution. Dissolve 1 g of Xylenol Orange (obtained from K & K Laboratories) in 100 ml of diluted alcohol.

Other chemicals used were all of reagent grade purity.

Successive determination of thorium and rare earths (samarium to lutetium inclusive) with DTPA

Thorium can be determined by direct titration with DTPA at pH 2·5–3·0 using Xylenol Orange, in the presence of the heavy rare earths. The colour change from red to orange is quite sharp. After the titration of thorium has been completed, more DTPA is added to complex the rare earth elements, and the excess is back-titrated with standard 0·05*M* lead nitrate solution.

Procedure. Dilute solutions containing different ratios of thorium and rare earth elements (as indicated in Table I) to 150 ml with distilled water. Adjust the pH of the solutions to 2·5–3·0, using a pH meter, with either dilute nitric acid or dilute aqueous ammonia. Titrate slowly with 0·05*M* DTPA, to an orange end-point, using Xylenol Orange as indicator. Add a further amount of DTPA (in excess to that required for complexing the rare earth element), adjust the pH of the solution to 5·0–5·5 with solid urotropine, and titrate the excess DTPA with 0·05*M* lead nitrate solution to a red-violet end-point.

Successive determination of thorium and rare earths with DTPA and HEDTA

N-Hydroxyethylethylenediaminetriacetic acid (HEDTA) behaves in a similar manner to EDTA, forming 1:1 complexes with rare earths, although the stability constants are very different. Use was made of this property of HEDTA in the determination of thorium and rare earths. After the determination of thorium with DTPA, as above, the pH was adjusted to 5·0–5·5 and the rare earth content titrated directly with HEDTA. The end-point is orange. Table II shows the results of a series of determinations.

Zusammenfassung—Die quantitative Bestimmung von Thorium mit EDTA ist in Gegenwart schwerer seltener Erden nicht möglich, dagegen neben leichten seltenen Erden genau. Die Bestimmung von Thorium und schweren seltenen Erden mit DTPA ist möglich und wird hier beschrieben. Auch die direkte Bestimmung von Thorium und seltenen Erden durch kombinierte Titration mit DTPA und HEDTA wird diskutiert.

Résumé—Le dosage du thorium à l'EDTA ne peut être mené en présence de terres rares lourdes, bien qu'il puisse l'être avec précision en présence de terres rares légères. On a trouvé que l'on peut doser successivement le thorium et les terres rares lourdes au moyen de DTPA, et l'on décrit le dosage. On discute aussi des dosages successifs directs du thorium et des terres rares par titrage combiné avec le DTPA et le HEDTA.

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SPECTROPHOTOMETRIC DETERMINATION OF FLUORINE IN SILICATE ROCKS

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Summary—The rock powder is sintered with a sodium carbonate flux containing zinc oxide and magnesium carbonate, the sinter-cake leached with water and the resulting solution filtered. Fluorine is separated from the acidified filtrate by steam distillation and determined spectrophotometrically by means of a zirconium-SPADNS reagent. If a multiple-unit distillation apparatus is used, 12 determinations can be completed per man-day.

INTRODUCTION

WILLARD and Winter's[1] method, one modification of which is described by Kolthoff and Sandell,[2] has been widely used for the determination of fluorine in silicate rocks. Although sufficiently accurate, the method is too time consuming to fulfill increased requests. Shell and Craig,[3] by the introduction of a zinc-bearing flux, have simplified the preliminary separation and greatly increased its speed. Although more rapid than the troublesome thorium nitrate titration, colorimetric methods for the determination of fluoride have defects and their use has not been favoured by silicate analysts. A simple, rapid colorimetric method based on the work of others, but having none of these defects, is described in this paper. No adjustment of pH is necessary. A stable, coloured complex is formed by the addition of a single reagent to the flask containing the distillate. A special photometric technique eliminates temperature effects. Sulphuric acid may be used in the distillation.

EXPERIMENTAL

Reagents

Flux: Thoroughly mix 7 parts of sodium carbonate, 2 parts of zinc oxide, and 1 part of magnesium carbonate. (The flux is usually fluorine-free, but a blank determination should be made on each lot.)

Stock sodium fluoride solution (1·00 mg of fluoride/ml): Dissolve 10 g of reagent-grade sodium fluoride in 225 ml of water, add a few ml of hydrofluoric acid and an equal volume of methanol. Collect the salt on paper, wash it with methanol, and air dry. Fuse 3 g of the salt, pour the melt into a platinum dish and cool. Crush the sodium fluoride and quickly weigh 1·105 g. Dissolve the weighed portion in water and filter it into a 500 ml-volumetric flask. Dilute the filtrate to the mark and mix. (A solution so prepared assayed 0·996 mg of fluoride/ml when analysed by the lead chlorofluoride method.)

Standard sodium fluoride solution (0·100 mg of fluoride/ml): Dilute the above solution ten-fold.

Zirconium sulphate-sulphuric acid solution. Dissolve 13·0 g of zirconium sulphate tetrahydrate in 1 litre of 1:1 sulphuric acid and 800 ml of water. Filter the solution through a fine-porosity paper and dilute the filtrate to 2 litres. Determine the zirconium oxide content of a 10-ml portion of the solution. (Precipitate with aqueous ammonia and weigh as zirconium oxide.)

SPADNS solution: Dissolve 32 g of SPADNS [sodium 2-(*p*-sulphenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonate] in 800 ml of water. Pass the solution through a fibre-glass pre-filter and a membrane filter having 0·45-μ pores. Dilute the filtrate to 2 litres.

Zirconium-SPADNS reagent: Dilute a volume of zirconium sulphate-sulphuric acid solution containing 1·4 g of zirconium oxide to 800 ml with 1:3 sulphuric acid, add 1 litre of SPADNS solution and dilute the mixture to 4 litres. (If 12 mm × 12 mm cells are used in the colorimetry, increase the zirconium oxide content of the reagent to 1·6 g).

Procedure

Transfer 0·500 g of 100-mesh rock powder to a 25-ml platinum crucible containing 5·0 g of flux. Mix the sample and the upper part of the flux with a glass rod, then stir the mixed portion into the rest of the flux. Using an electric furnace, heat the crucible and its contents at 900° for 30 min. Allow the crucible to cool.

Add water to the contents of the crucible, loosen the cake with a stirring rod, and transfer the cake to a 50-ml beaker. Adjust the volume of the solution to 30 ml and allow the solution to stand overnight.

Crush the cake to a powder with a flat-ended stirring rod, then decant the solution through a 7-cm fine-porosity paper into a 250-ml distilling flask from the apparatus. Wash the residue twice by decantation with hot 1% sodium carbonate solution, then sluice the residue into the paper. Wash the residue 5 times with the hot sodium carbonate solution and discard the residue. Connect the flask to the condenser of the distillation apparatus.

Add 200 ml of water to the first of three 250-ml volumetric flasks (dark standard). Add 10·00 ml of standard sodium fluoride solution to the second flask, and adjust the volume to 200 ml (light standard). Place the third flask under the condenser of the distillation apparatus.

Add 250 ml of water to the steam-generating flask and bring the water to a gentle boil. Slowly add 25 ml of 1:1 sulphuric acid to the distillation flask through the steam-inlet tube. Connect the side tube of the generating flask to the steam-inlet tube of the distillation flask, and heat the solution in the distillation flask to the boil. Continue boiling at such a rate that, after 20 to 25 min, the amount of distillate is about 85 ml and the temperature of the solution is 135°. During this period, admit only enough steam to prevent bumping. Now bring the water in the generating flask to a moderate boil and adjust the flame under the distillation flask to maintain a solution temperature between 135 and 145°. Continue the steam distillation at such a rate that, in about 45 min, an additional 125 ml of distillate is collected.

Allow the distillate to stand until it attains room temperature. Add 25·00 ml of zirconium-SPADNS reagent to the distillate and to each of the standard solutions. Dilute each solution to volume and mix.

After 1 hr, measure the transmittance of the sample solution with a Beckman Model B spectrophotometer or its equivalent by the following procedure. Add light standard solution to the first of three 1 cm × 1 cm cells (Leitz), the sample solution to the second and dark standard solution to the third. Set the dark current at 0·0, then adjust the wavelength (about 585 mμ) so that the dark standard reads 25·0 ± 0·2 when the light standard reads 100·0. Adjust the dark current so that the dark standard reads 25·0 when the light standard reads 100·0 and measure the transmittance of the sample solution. Use separate portions of the standards for each measurement in a series.

If the reading is above 100·0, pipette 50 ml of the sample solution into another 250-ml volumetric flask. Dilute this portion to 200 ml and add 20·00 ml of zirconium-SPADNS reagent. Dilute the solution to the mark, mix it and measure its transmittance as before.

Prepare, in 250-ml volumetric flasks, six solutions containing from 0·00 to 10·00 ml of standard sodium fluoride solution in increments of 2·00 ml, and adjust the volume of each solution to 200 ml. Add 25·00 ml of zirconium-SPADNS reagent to each, then dilute each to volume and mix. Use the end members of the series, which are the same as the dark and light standard solutions previously mentioned, to adjust the wavelength, then measure the transmittance of the other solutions. Construct a transmittance curve from the values obtained.

To compute the fluoride content of the sample, use the transmittance curve to determine the fluoride content of the distillate and add a 3% (relative) correction.

Before re-using the distillation flask, clean it with a hot dilute solution of sodium carbonate.

DISCUSSION AND RESULTS

Silicate rocks rarely contain more than 0·2% of fluorine and almost never more than 1%. Because this method was designed for the analysis of silicate rocks, no tests were made with more than 5 mg of fluoride (1% for a 0·5-g sample); therefore statements in the following discussion may not apply to the determination of larger amounts.

It is known that the recovery of fluoride by accepted methods of steam distillation is never quite complete, and some workers have surmised that glassware adsorbs fluoride. Our experiments indicate that such adsorption occurs. If fluoride is adsorbed, the amount lost is consistent enough so that a correction can be made. Adsorbed fluoride is largely removed when the flask is cleaned with sodium carbonate solution so its effect is not cumulative. Amounts of fluoride adsorbed by or desorbed from the condenser are too small to affect the results.

The advantages of the special flux have been discussed.[4] When a sinter cake prepared with this flux is leached with water, much of the silica and alumina is retained in the residue and is removed by filtration, but enough silica and alumina are always present in the filtrate to interfere with the distillation of fluoride.

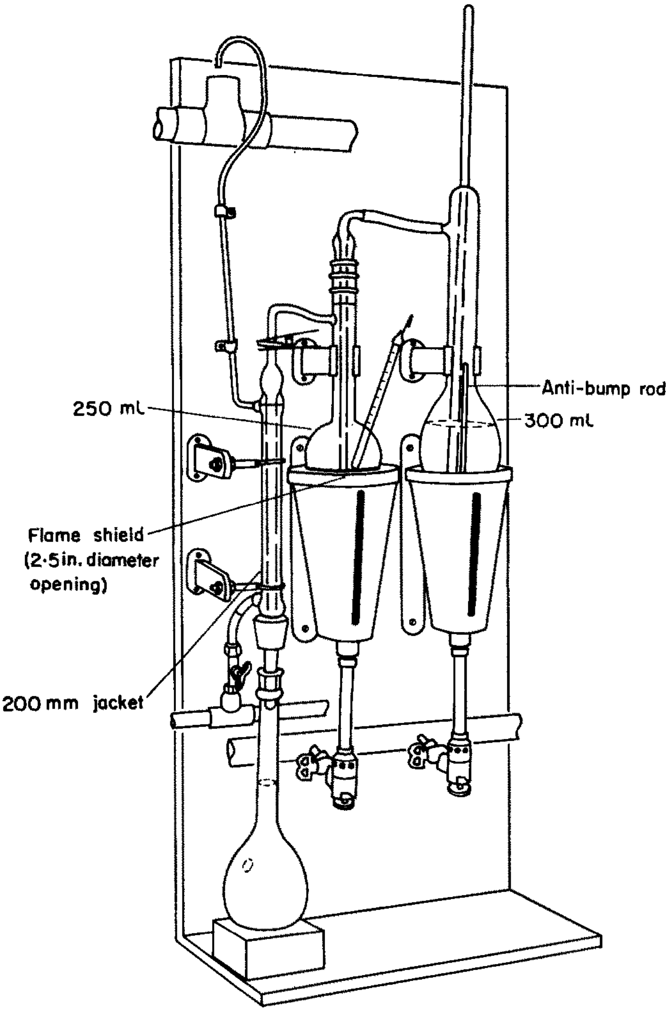

Fig. 1.—Distillation apparatus

Although limits of composition for silicate rocks cannot be defined exactly, few such rocks contain less than 35% of silica or more than 25% of alumina. Within these limits of rock composition, the alkaline filtrate never contains more than 25 mg of either silica or alumina. In the filtrate from a few uncommon samples, the amounts of either silica or alumina may be higher. Numerous experiments showed that the over-all loss caused by the presence of interfering compounds and by the adsorption of fluoride varies from about 2% to 4% (relative). If a 3% (relative) correction is applied to every analysis, the distillation error seldom exceeds 1% (relative).

Most colorimetric methods for the determination of fluoride are based upon the fading of a coloured metal-organic compound caused by the formation of a fluoride complex with the metal. Lakes of thorium or zirconium in combination with a number of organic compounds have been used for years in water analysis. The lakes we have tested are much alike: they are unstable except at low concentrations, and their use requires a close adjustment of pH.

Bellack and Shouboe[5] have described a zirconium-SPADNS chelate for use in strong hydrochloric acid solution. Our experiments confirmed their statements. If 25 ml of their combined reagent is added to the distillate, amounts of fluoride from 0·00 to 0·05% can be measured. It is desirable to extend this range so that most silicate rocks (0·0–0·2%) can be analysed without diluting the distillate. Efforts to increase the concentration of the reagent failed; precipitates always formed.

By substitution of sulphuric for hydrochloric acid, a combined reagent was prepared that gave the desired range. A plot of log transmittance against concentration is, however, slightly curved. The reagent is stable for months, perhaps indefinitely.

The transmittance of the coloured complex varies sharply with changes in temperature. Before a measurement is made, therefore, the wavelength is adjusted so that standards at the two ends of the transmittance curve have specific readings. Because of day-to-day differences in room temperature, both the slit-width and the wavelength vary, but these variations do not affect the shape of the transmittance curve. During the course of a measurement, the photometer warms the standard solutions; therefore, separate portions of the standards are used for each measurement in a series.

Sulphuric acid contained in the distillate does not interfere in the colorimetry. If the upper part of the distillation flask is shielded from the flame as shown, no more than 3 mg of sulphuric acid distil; 10 mg can be tolerated. Phosphoric acid formed from phosphates present in a rock never distils in sufficient quantity to interfere.

Table I shows the reproducibility of results obtained when 8 rock samples were analysed in triplicate. The residues from one set of samples were dried, each residue was mixed with sodium carbonate and all of the mixtures were sintered. The fluoride

TABLE I.—ANALYSIS OF ROCK SAMPLES

Set no.	Type of rock							
	Welded tuff	Diabase W1[6]	Granite G1[8]	Tuff	Andesite dike	Altered basalt	Submarine basalt	Rhyolite porphyry
	Fluorine, %							
1	0·006	0·022	0·061	0·14	0·29	0·43	0·60	0·80
2	0·006	0·021	0·060	0·14	0·29	0·42	0·59	0·79
3	0·006	0·022	0·059	0·14	0·28	0·42	0·60	0·80
Average	0·006	0·022	0·060	0·14	0·29	0·42	0·60	0·80
recoveries from residues of set no. 3	0·000	0·001	0·001	0·002	0·006	0·014	0·022	0·010

contents of the sinter cakes were determined as described in the procedure. Recoveries were small (Table I).

Zusammenfassung—Das gepulverte Gestein wird mit einer Sodaschmelze gesintert, die Zinkoxyd und Magnesiumcarbonat enthält, der Sinterkuchen mit Wassen ausgelaugt und die Lösung filtriert. Aus dem angesäuerten Filtrat wird Fluor durch Wasserdampfdestillation abgetrennt und spektralphotometrisch mit Zirkonium-SPADNS bestimmt. Mit einer Mehrfachdestillationsapparatur können 12 Bestimmungen pro Mann und Tag gemacht werden.

Résumé—La poudre de roche est frittée avec un fondant au carbonate de sodium contenant de l'oxyde de zinc et du carbonate de magnesium, la masse frittée est lixiviée à l'eau, et la solution résultante est filtrée. On sépare le fluor du filtrat acidifié par distillation à la vapeur, et dose spectrophotométriquement par un réactif zirconium-SPADNS. Si l'on utilise un appareil de distillation à unités multiples, on peut effectuer 12 dosages par journée de travail.

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SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TELLURIUM WITH *SYM*-DIPHENYLTHIOUREA

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Summary—A spectrophotometric method of determining small amounts of tellurium in acidic media with *sym*-diphenylthiourea has been studied. Tellurium is extracted almost quantitatively from 4·5–8·0*M* hydrochloric or perchloric acid solutions with a chloroform solution of diphenylthiourea, and up to 200 μg of tellurium can be determined by measuring the absorbance of the yellow complex in the chloroform phase at a wavelength between 380 and 410 mμ. The effects of diverse ions on the determination of tellurium have also been studied. It has been found that this method, with an extraction procedure, is more simple and more sensitive than the usual thiourea method in an aqueous medium.

TELLURIUM has been determined spectrophotometrically by several investigators.[1–7] The thiourea method, proposed by Nielsch,[2] is recommended as a simple and good method for the determination of tellurium in an aqueous solution. This reaction, however, takes place in an aqueous phase and the coloured tellurium complex cannot be extracted from the aqueous solution with chloroform, carbon tetrachloride, di-ethyl ether, *etc*. Moreover, the thiourea method has not such a high sensitivity. The present authors, therefore, have attempted to find a more sensitive procedure, and one suffering from fewer interferences, by means of extraction with an organic solvent.

About sixty derivatives of thiourea were tested as complex-forming reagents with metal ions by Yoe *et al.*,[8] and some of them have been applied for the determination of osmium and ruthenium,[9] but not for tellurium-IV.

Preliminary tests showed that tellurium formed yellow complexes with phenylthiourea, *sym*-diphenylthiourea, ditolylthiourea and ethylenethiourea; and the complexes with these derivatives, except that with ethylenethiourea, were extracted almost quantitatively into chloroform. The reaction of tellurium-IV with *sym*-diphenylthiourea was the most sensitive one under the experimental conditions, and also the extraction of the complex with chloroform from 4·5–8·0*M* hydrochloric acid solution could be carried out quantitatively. It was also found that when a hydrochloric acid solution of tellurium was shaken with a chloroform solution of diphenylthiourea, the complex formed was extracted simultaneously into the organic phase. Tellurium-IV can be extracted by chloroform-diphenylthiourea from perchloric acid solution. This method proposed is more simple, more sensitive, and suffers less interference than the thiourea method in an aqueous medium.

EXPERIMENTAL

Reagents

Tellurium: A stock solution (1 g of Te/litre of hydrochloric acid solution) was prepared as described in a preceding paper.[5] A solution containing 100 μg of Te per ml was obtained by dilution of the stock solution with water.

Sym-Diphenylthiourea: A commercial reagent was purified as follows: dissolve *ca.* 8 g of the reagent in 250 ml of ethyl alcohol at 70°, and filter the solution. Cool the filtrate for recrystallisation of the reagent, filter the crystals and dry the product in a desiccator. One g of diphenylthiourea was dissolved in 100 ml of chloroform.

All other reagents used in the investigation were of analytical-reagent grade.

Apparatus

Absorbance was measured with a Hitachi spectrophotometer EPU-2A, and pH was measured using a Horiba pH-meter M-3.

Procedure

(1) *Hydrochloric acid system:* Place less than 5 ml of an acidic solution, containing 10 to 200 μg of tellurium-IV, in a 20-ml graduated test-tube with a glass stopper, add 5 ml of 12*M* hydrochloric acid solution, and dilute to 10 ml with water. Mix well, and then cool it by holding in running water for 1 min. Add exactly 10 ml of diphenylthiourea-chloroform solution, shake vigorously for 1 min, transfer the mixture to a separating funnel, and separate the organic layer from the aqueous layer. Centrifuge the organic phase for 2 min. (Anhydrous sodium sulphate may be used for dehydration instead of centrifuging.) Measure the absorbance of the organic phase at 380, 390, 400, or 410 mμ in a 1-cm cell. Calculate the concentration of tellurium using a calibration curve, prepared previously.

(2) *Perchloric acid system:* Repeat Procedure (1), but using 6 ml of 9*M* perchloric acid solution (60% $HClO_4$) instead of 5 ml of 12*M* hydrochloric acid solution.

RESULTS AND DISCUSSION

Absorption curves of tellurium complexes with derivatives of thiourea

With diphenylthiourea, phenylthiourea, ditolylthiourea, ethylenethiourea and thiourea, tellurium in a solution of hydrochloric or perchloric acid in a concentration range of 4–9*M* formed yellow complexes. The tellurium complexes with diphenylthiourea, phenylthiourea and ditolylthiourea were extracted with chloroform, but not those with thiourea and ethylenethiourea. The absorbances of the tellurium complexes with the last two reagents were measured using the aqueous phase without an extraction procedure.

To a solution containing 200 μg of tellurium, 6 ml of 9*M* perchloric acid were added and the mixture was diluted to 10 ml with water. To this solution, 200 mg of one of the reagents was added. After mixing well, the tellurium complexes of diphenylthiourea, phenylthiourea and ditolylthiourea were extracted with chloroform. Absorbances of the complexes in the chloroform phase and the complexes with thiourea and ethylenethiourea in the aqueous phase were measured 1-ml cells over the range 380–500 mμ. The results obtained are shown in Fig. 1. Each complex has similar absorption, increasing in the shorter wavelength region. The absorbances of the tellurium complexes decrease in the following order under the experimental condition described: thiourea < ethylenethiourea < phenylthiourea < ditolylthiourea < diphenylthiourea.

The absorbance of the tellurium complex with diphenylthiourea in chloroform medium was about twenty times greater than that with thiourea in aqueous medium. Therefore, diphenylthiourea was used as the spectrophotometric reagent for tellurium in the further investigation.

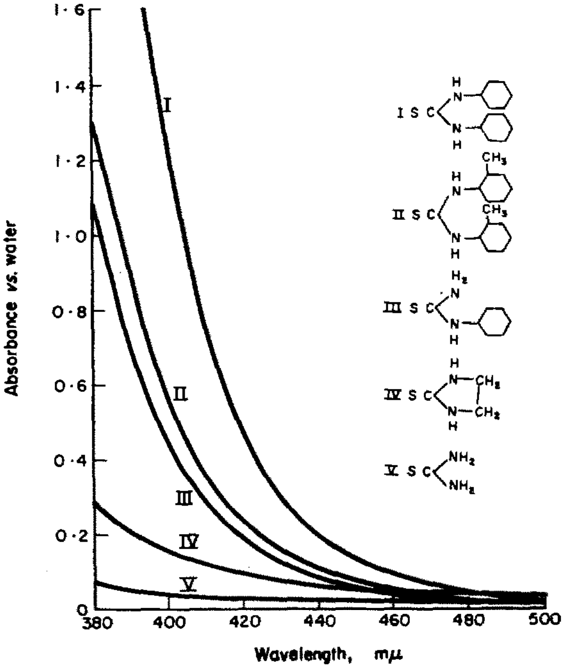

FIG. 1.—Absorption spectra of tellurium complexes with derivatives of thiourea:

I: Diphenylthiourea II: Ditolylthiourea
III: Phenylthiourea IV: Ethylenethiourea
V: Thiourea

Organic solvent

The solubility of diphenylthiourea in chloroform was several times greater than that in ethyl alcohol or in benzene; diphenylthiourea was almost insoluble in carbon tetrachloride. When an alcoholic solution of diphenylthiourea was added to a hydrochloric acid solution of tellurium, the yellow tellurium complex formed, and was extracted by chloroform. When a chloroform solution of diphenylthiourea was added to a solution of tellurium, the yellow complex formed was extracted simultaneously into the chloroform.

Effect of acid

As seen in Fig. 2, the absorbances of the tellurium complex, when extracted from 6*M* perchloric acid solution are about three times those from 6*M* hydrochloric acid solution. The effects of acid concentration on the absorbance are shown in Figs. 3 and 4. When the tellurium complex was extracted from 4·5–8·0*M* acidic solution the absorbances were always constant.

Effect of amount of reagent

Less than 0·06 g of the reagent per 10 ml of chloroform failed to produce full colour development of the complex for 100 μg of tellurium (mole ratio tellurium: diphenylthiourea *ca.* 1:330.) With more than 0·1 g of the reagent per 10 ml of chloroform the full colour development was ensured for 100 μg of tellurium. But because a solution of diphenylthiourea has absorption in the ultraviolet region (Fig. 2) a large but definite excess of the reagent should be used.

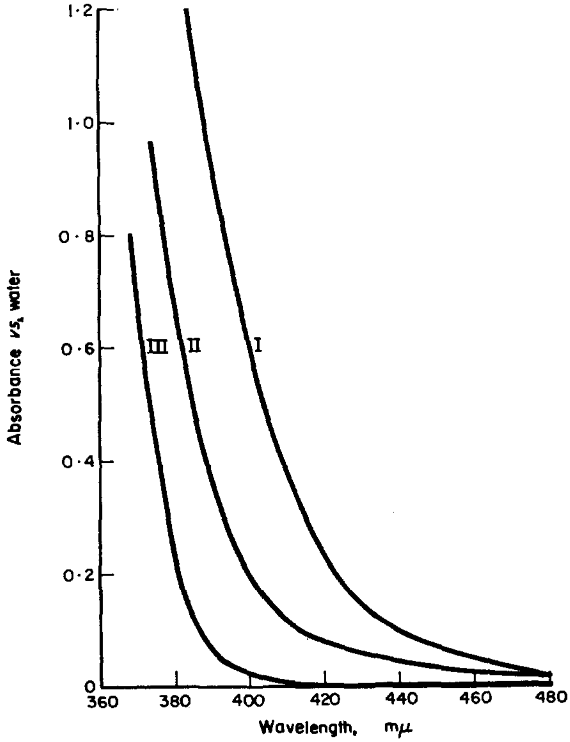

FIG. 2.—Absorption spectra of diphenylthiourea-tellurium complexes:
I: $HClO_4$ system II: HCl system
III: Blank

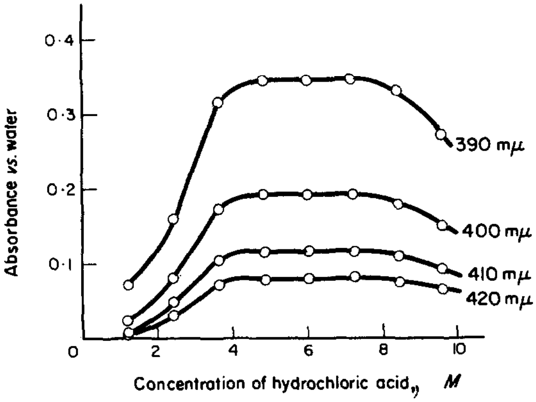

FIG. 3.—Effect of concentration of hydrochloric acid.

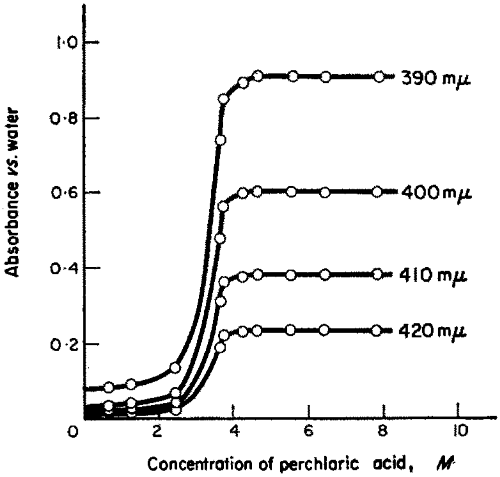

FIG. 4.—Effect of concentration of perchloric acid.

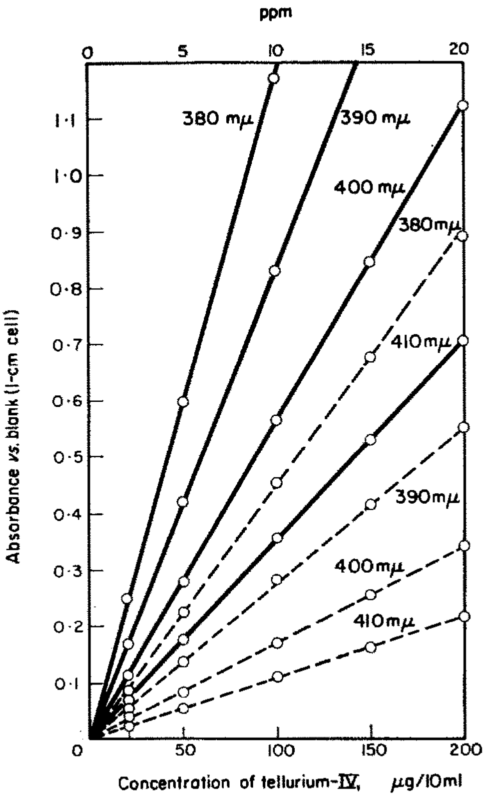

FIG. 5.—Working curves for tellurium-IV:

———— HCl system

– – – – – – $HClO_4$ system

Stability and sensitivity

The colour of the tellurium complex, developed as described, is stable for at least 90 min at room temperature, and even after 6 hr it decreases by only 3%.

Beer's law is obeyed up to 200 μg of Te/10 ml in an aqueous solution at 380, 390, 400, or 410 mμ, under the experimental conditions (Fig. 5).

The sensitivities of this reaction, by Sandell's expression,[10] are 0·022, 0·036, 0·059 and 0·09 μg of Te/cm^2 for the hydrochloric acid system; and 0·0084, 0·012, 0·018 and 0·028 μg of Te/cm^2 for the perchloric acid system.

Effect of diverse ions

The effects of a number of diverse ions on the determination of 100 μg of tellurium-IV, by Procedure (1) are summarised in Table I.

TABLE I.—EFFECT OF DIVERSE IONS
(Te 100 μg, HCl system)

Ion	Added		Te recovered, μg			
	mg	as	at 380	390	400	410 mμ
Bi^{III}	2	$BiCl_3$	101	104	107	—
Bi^{III}	1	$BiCl_3$	100	102	103	—
Cd^{II}	40	$CdCl_2$	100	100	100	101
Co^{II}	40	$CoCl_2$	102	102	102	102
Fe^{III}	0·4	$FeCl_3$	105	106	105	104
Mn^{II}	40	$MnCl_2$	100	100	101	100
Ni^{II}	40	$NiCl_2$	101	101	102	103

Large amounts of cadmium, cobalt, manganese, nickel and zinc do not interfere with the determination of tellurium. Against expectation, bismuth in an amount ten times as much as the tellurium was tolerated in the hydrochloric acid system, although in the perchloric acid system bismuth interfered with the determination. Iron-III interferes with the determination, so that it should be removed from the solution before the determination of tellurium. Because selenium-IV reacts with diphenylthiourea, no test was carried out on its interfering action.

Zusammenfassung—Die spektralphotometrische Bestimmung kleiner Tellurmengen mit Diphenylthioharnstoff in saurem Medium wurde untersucht. Tellur wird aus 4, 5–8, On salz- oder überchlorsauren Lösungen fast quantitativ mit einer Lösung von Diphenylthioharnstoff in Chloroform extrahiert. Bis 200 μg Tellur werden durch Messung der Extinktion des gelben Komplexes in der Chloroformphase zwischen 380 und 410 mμ bestimmt. Der Einfluß verschiedener Fremdionen auf die Tellurbestimmung wurde auch untersucht. Diese Extraktionsmethode ist einfacher und empfindlicher als die übliche Thioharnstoffmethode in wäßrigem Medium.

Résumé—On a étudié une méthode spectrophotométrique de dosage de petites quantités de tellurium en milieu acide, au moyen de diphénylthiourée. Le tellurium est extrait presque quantitativement, à partir de solutions 4,5 à 8,0 N en acide chlorhydrique ou acide perchlorique, au moyen d'une solution chloroformique de diphénylthiourée, et l'on peut doser jusqu'à 200 μg de tellurium en mesurant l'absorption du complexe jaune en phase chloroformique, à une longueur d'onde comprise entre 380 et 410 mμ. On a également étudié les effets de divers ions sur le dosage du tellurium. On a trouvé que cette méthode avec procédé d'extraction est plus simple et plus sensible que la méthode usuelle à la thiourée en milieu aqueux.

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SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE WITH THENOYLTRIFLUORACETONE

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Summary—A new spectrophotometric method for the determination of microgram amounts of manganese with thenoyltrifluoracetone(TTA) is described. After oxidation with sodium bromate, manganese (presumably tervalent) is extracted with 0·5*M* TTA in xylene from a 0·5*M* sulphuric acid solution. The absorbance of the organic phase is measured at 440 or 450 mμ. Beer's law is followed up to 10 μg of manganese/ml of organic phase. Except for cerium, iron and chloride, small amounts of many common elements do not interfere. Iron(III) can be removed by cupferron-chloroform extraction, and cerium by washing the TTA extract with an ammonium hydrogen fluoride-nitric acid solution.

INTRODUCTION

DURING studies[1,2] on the spectrophotometric determination of cerium with thenoyltrifluoracetone (TTA), it has been found that manganese (presumably tervalent) gives a greenish-yellow colour with TTA. On the basis of this phenomenon, a new spectrophotometric method has been developed which is suitable for the determination of 10–100 μg of manganese. The proposed method is more sensitive and selective than that involving the extraction of manganese(II) with TTA at pH 6·7–8·0.[3] The elimination of interfering elements is also reported in this paper.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Hitachi EPU-2A spectrophotometer, using 1-cm cells. A shaking machine with a time switch was used for the extractions.

Reagents

6% *w/v Cupferron solution:* Prepare fresh daily.

1*M Sodium bromate solution.*

0·5*M TTA solution:* Dissolve 45 g in 400 ml of xylene. A product of Dojindo & Co., Ltd., Kumamoto-shi, Japan, was used.

Ammonium hydrogen fluoride-nitric acid solution: 0·1*M* in ammonium hydrogen fluoride and 0·2*M* in nitric acid, stored in a polyethylene bottle.

Standard manganese solution: A standard stock solution, containing 1·00 mg of manganese/ml, was prepared by dissolving 0·100 g of pure manganese metal in 10 ml of 7*M* nitric acid and diluting to exactly 100 ml with water. Solutions of lower concentrations were prepared by diluting aliquots of the stock solution with water.

All other solutions were prepared from analytical reagent-grade compounds and metals.

Procedure: TTA-xylene extraction

Transfer the sample solution, containing 10–100 μg of manganese(II), to a small separating funnel. Add 15 mequiv of sulphuric acid and adjust the volume to 10 ml. Add 3 ml of 1*M* sodium bromate solution and allow to stand for 5–10 min. The sulphuric acid concentration should be about 0·5*M*. Add 10·0 ml of 0·5*M* TTA solution and shake the system for 10–15 min. Allow the funnel to stand for about 5 min for water droplets to separate from the organic phase. Drain off and discard the aqueous phase. Filter the organic phase through a small plug of glass wool into a 1-cm cell. Measure the absorbance of the solution at 440 or 450 mμ, using the reagent blank or xylene as the reference.

Construct a calibration curve by taking, for example, 0, 20, 40, 70 and 100 μg of manganese, adjusting the amount of sulphuric acid to 15 mequiv and the volume of the solution to 10 ml, then proceeding as described above for the TTA-xylene extraction.

Run a blank through the entire procedure.

Procedure in presence of cerium

Carry out the TTA-xylene extraction as described above. Drain off and discard the aqueous phase. To the organic phase in a separating funnel add 10 ml of ammonium hydrogen fluoride-nitric acid solution. Shake the system for 1 min. Allow the funnel to stand for about 5 min. Drain off and discard the aqueous phase. Filter the organic phase through a small plug of glass wool into a 1-cm cell. Measure the absorbance of the solution at 440 or 450 mμ against the reagent blank or xylene. The calibration curve should be prepared including the back-extraction.

Procedure in presence of iron(III): Cupferron extraction

Before the TTA-xylene extraction, transfer the sample solution, containing 10–100 μg of manganese(II), to a small (50–60 ml) separating funnel. Adjust the amount of sulphuric acid to 15 mequiv and dilute to 10 ml with water. Add 2·0 ml of cupferron solution and mix. Add 15 ml of chloroform and shake the system for 1 min. Drain off and discard the organic phase. Add 1·0 ml of cupferron solution and mix. Shake the solution with 10 ml of chloroform for 1 min. Discard the organic phase. Wash the aqueous phase by shaking it for 30 sec with 10 ml of chloroform and discard the organic phase.

Transfer the aqueous phase to a small quartz dish and evaporate to fumes of sulphuric acid. To decompose residual organic matter, add 1 ml of 30% hydrogen peroxide and heat gently. Evaporate the solution until white fumes appear. Use the residue for the TTA-xylene extraction.

RESULTS AND DISCUSSION

Absorption curve

The absorption curves are shown in Fig. 1. The manganese-TTA complex does not show a absorption maximum in the analytically-useful wavelength range. Because the absorption of the reagent blank is great below 430 mμ, a wavelength of 440 or 450 mμ has been adopted for the determination of manganese.

Effect of sulphuric acid concentration

The effect of sulphuric acid concentration on the absorbance of the extract is shown in Fig. 2. A suitable sulphuric acid concentration is 0·25–0·75*M*.

Effect of sodium bromate concentration

As indicated in Fig. 3, the absorbance of the extract remains almost constant between 0·2 and 0·4*M*. Potassium bromate was not used because of its small solubility.

Effect of TTA concentration

A suitable TTA concentration is 0·3–0·5*M* (Fig. 4). In the present work, the concentration of 0·5*M* has been adopted.

Time of extraction

It is necessary to shake the system for 10–20 min (Fig. 5).

Stability of extract

The absorbance of the manganese complex and reagent blank solutions remains constant for at least 3 hr (Fig. 6). The experiments were carried out at room temperatures within a range of 14–21°.

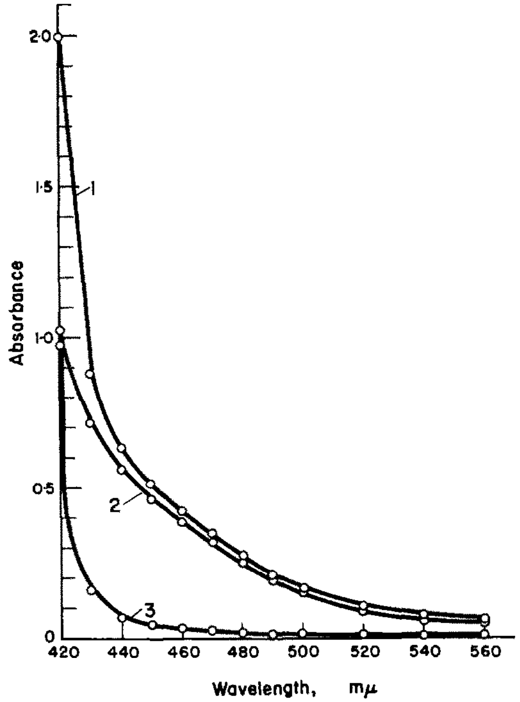

FIG. 1.—Absorption curves:

(1) 100 μg of manganese *vs.* xylene,
(2) 100 μg of manganese *vs.* reagent blank,
(3) Reagent blank *vs.* xylene.

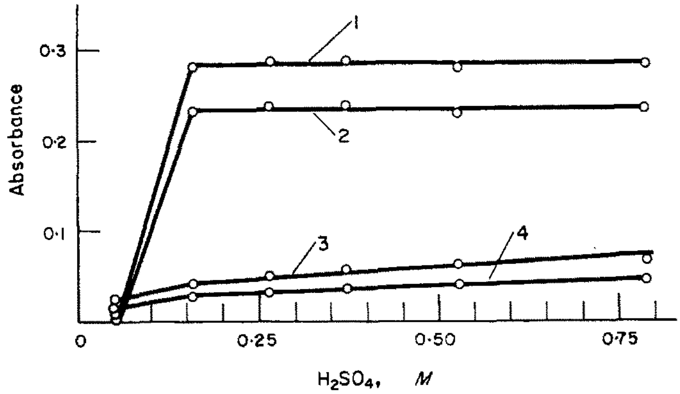

Fig. 2.—Effect of sulphuric acid concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

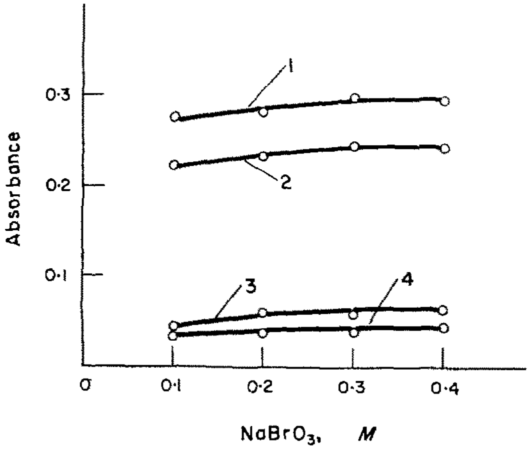

Fig. 3.—Effect of sodium bromate concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

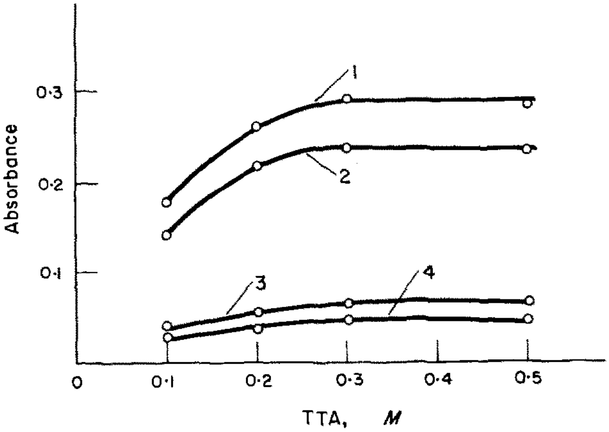

Fig. 4.—Effect of TTA concentration:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

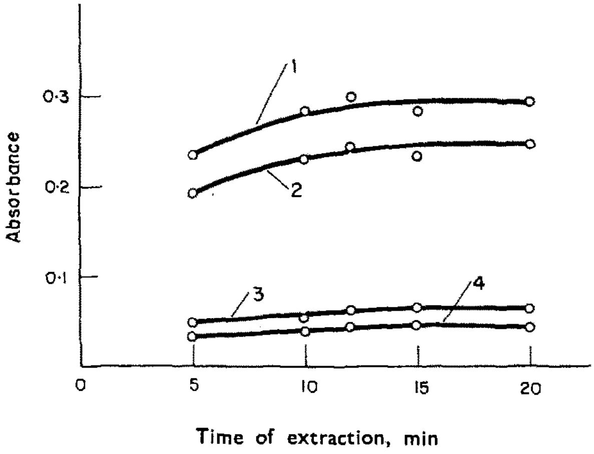

Fig. 5.—Time of extraction:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

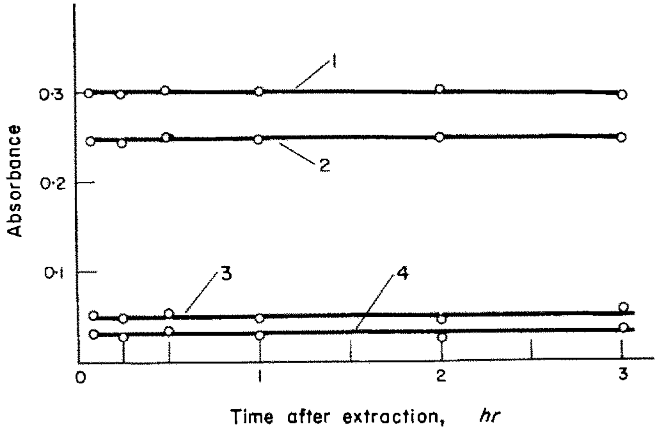

FIG. 6.—Stability of extract:

(1) 50 μg of manganese *vs.* reagent blank (440 mμ),
(2) 50 μg of manganese *vs.* reagent blank (450 mμ),
(3) Reagent blank *vs.* xylene (440 mμ),
(4) Reagent blank *vs.* xylene (450 mμ).

Calibration curve

The manganese-TTA system conforms to Beer's law with concentrations of up to 10 μg of manganese/ml of organic phase. Assuming that the extraction of manganese into the organic phase was complete, the apparent molar absorptivities were $3{\cdot}0 \times 10^3$ and $2{\cdot}5 \times 10^3$ at 440 and 450 mμ, respectively. In other words, for $\log I_0/I = 0{\cdot}001$, the sensitivities were 0·018 and 0·022 μg of manganese. cm^{-2} at 440 and 450 mμ, respectively. In this connection, it may be mentioned that the permanganate method has a sensitivity of 0·027 μg of manganese. cm^{-2} for $\log I_0/I = 0{\cdot}001$ at 522 mμ.[4]

Eight experiments with 50 μg of manganese gave an average absorbance of 0·297 and 0·245 at 440 and 450 mμ, respectively. The relative standard deviations were 1·7 and 1·3% at 440 and 450 mμ, respectively.

Nature of reaction

It has been reported that manganese(II) ion in a sulphuric acid solution is oxidised with bromate to the tripositive state.[5,6] Manganese(II) in 0·5*M* sulphuric acid does not give a coloured product with TTA. Presumably, the reaction product of TTA with manganese in the presence of bromate is manganese(III)-TTA complex. This point is being studied.

A single TTA extraction followed by a back-extraction with an equal volume (10 ml) of 7·5*M* nitric acid gave a recovery of 93% with 100 μg of manganese. The manganese was determined by the permanganate method using potassium metaperiodate as oxidising agent.[4]

Interference study

It was considered that the elements[1,2] that interfered with the photometric determination of cerium with TTA were likely to interfere with the determination of manganese. Table I summarises the results of the interference study. This study was

TABLE I.—INTERFERENCE STUDY

Addition		Mn found,[a] μg	
		440 mμ	450 mμ
Al^{III}	10 mg	52	52
As^{III}	0·10 mg	51	51
	1·0 mg	58	61
Bi^{III}	1·0 mg	50	51
	10 mg	50	51
Ca^{II}	10 mg	51	50
Cd^{II}	10 mg	49	49
Co^{II}	5·0 mg	51	51
	10 mg	51	51
Cr^{III}	10 mg	51	51
Cu^{II}	1·0 mg	52	51
	5·0 mg	58	58
Fe^{III}	10 μg	55	55
La^{III}	10 mg	51	51
Mg^{II}	10 mg	51	50
Mo^{VI}	0·10 mg	51	51
	1·0 mg	53	50
Ni^{II}	10 mg	51	51
Pb^{II}	1·0 mg[b]	52	52
Th^{IV}	5·0 mg	52	52
	10 mg	50	51
Ti^{IV}	0·10 mg	51	51
	1·0 mg	51, 50	50, 49
	5·0 mg	78	61
U^{VI}	10 mg	51	51
V^{V}	0·10 mg	51	51
	1·0 mg	60	61
W^{VI}	5·0 mg	50	50
	10 mg	50	50
Y^{III}	5·0 mg	50	50
	10 mg	51	51
Zn^{II}	10 mg	52	51
Zr^{IV}	10 mg	50	49
K_2SO_4	0·50 mmole	51	50
$(NH_4)_2SO_4$	0·50 mmole	54	54
	1·0 mmole	55	54
$NaClO_4$	0·50 mmole	48	48
	1·0 mmole	46	46
$NaNO_3$	1·0 mmole	49	49
Na_2SO_4	1·0 mmole	49	50
F(NaF used)	10 mg	50	50
Cl(NaCl used)	0·20 mg	51	50
	0·40 mg	44	44
	0·50 mg	37	37
P(KH_2PO_4 used)	10 mg	51	52
	20 mg	50	50

[a] 50·0 μg of manganese taken.
[b] $PbSO_4$ precipitates in the aqueous phase.

made by using 10 ml of aqueous solution that was 0·5*M* in sulphuric acid and 0·3*M* in sodium bromate and 10 ml of TTA in xylene.

Most of the metals used were in the forms of sulphate and nitrate. The oxidation state of metals in the table refers to that before addition of sodium bromate. Cerium, iron and chloride interfere seriously. The absorbance at 440 mμ of 50 μg of cerium is nearly the same as that of 60 μg of manganese. As a matter of fact, the optimum conditions for the determination of manganese are the same as those for cerium.[1] Chloride can be removed by fuming with sulphuric acid. If we take an error greater than ±2 μg of manganese as a limiting concentration of interference, 1 mg each of arsenic, molybdenum (at 440 mμ) and vanadium interfere. Five mg each of copper and titanium also interfere. Ammonium sulphate gives a slightly high result. In general, the present method is more selective and sensitive than the method[3] that is based on the extraction of manganese(II) with TTA at pH 6·7–8·0.

Cupferron-chloroform extraction

Iron(III), molybdenum, vanadium and some other metals are known to be extracted as cupferrates with chloroform from mineral acid solution. In the proposed procedure, the sulphuric acid concentration for the cupferron-chloroform extraction was chosen from a consideration of the sulphuric acid concentration suitable for the TTA-xylene extraction.

Results obtained in applying the proposed procedure are collected in Table II. Five determinations of 50 μg of manganese gave an average recovery of 100% and a relative standard deviation of 3·3% at 440 mμ. Iron(III), molybdenum, titanium and vanadium can be removed satisfactorily from 50 μg of manganese(II). Cerium(III) is not removed by the cupferron-chloroform extraction and remains quantitatively in the aqueous phase.[2]

TABLE II.—DETERMINATION OF MANGANESE WITH TTA AFTER CUPFERRON–CHLOROFORM EXTRACTION

Addition, *mg*	Mn found,[a] *μg*	
	440 mμ	450 mμ
None	22[b], 18[b], 19[b]	23[b], 18[b], 19[b]
None	52, 51, 48, 49, 49	52, 50, 47, 49, 49
Fe^{III} 10	52	52
Mo^{VI} 10	51	51
Ti^{IV} 10	53, 52, 51	53, 51, 51
V^{V} 2·0	51	50
10	49	49
Zr^{IV} 10	53, 51, 50	52, 50, 49
Fe^{III} 10, Mo 1·0, Ti 1·0, V 1·0, Zr 1·0	53, 51, 52	52, 51, 52

[a] 50·0 μg of manganese taken.
[b] 20·0 μg of manganese taken.

TABLE III.—DETERMINATION OF MANGANESE IN THE PRESENCE OF CERIUM

Taken, *μg*	Mn found, *μg*	
	440 mμ	450 mμ
Ce 20	2, 1	1, 1
Ce 50	3, 3	4, 3
Ce 100	3, 3	4, 4
Ce 50, Mn 50·0	54, 52, 54, 54	54, 52, 54, 54
Ce 100, Mn 50·0	54, 55, 53, 52, 55, 54	54, 54, 53, 52, 55, 55

Determination of manganese in presence of cerium

Cerium(III) is not separated from manganese by the cupferron-chloroform extraction. As reported previously,[2] when the TTA solution containing both cerium-(IV) and manganese is shaken with an aqueous solution that is $0{\cdot}1M$ in ammonium hydrogen fluoride and $0{\cdot}2M$ in nitric acid, cerium is selectively back-extracted.

Results obtained in applying the proposed procedure are shown in Table III. In the presence of 50–100 μg of cerium, 50 μg of manganese can be determined within an error of +10%.

Zusammenfassung—Eine neue spektralphotometrische Methode zur Bestimmung von Mikrogrammengen Mangan mit Thenoyltrifluoraceton (TTA) wird beschrieben. Nach Oxydation mit Natriumbromat wird (wahrscheinlich dreiwertiges) Mangan mit 0,5 m TTA in Xylol aus 1 n Schwefelsäure extrahiert. Die organische Phase wird bei 440 oder 450 mμ photometriert. Das Beersche Gesetz gilt bis 10 μg Mangan pro ml organischer Phase. Außer Cer, Eisen und Chlorid stören kleine Mengen vieler häufiger Elemente nicht. Eisen(III) kann durch Extraktion mit Cupferron in Chloroform und Cer durch Waschen des TTA-Extrakts mit Ammoniumhydrogenfluorid-Salpetersäurelösung entfernt werden.

Résumé—On décrit une nouvelle méthode spectrophotométrique de dosage du manganèse à l'échelle du microgramme, au moyen de thénoyltrifluoroacétone (TTA). Après oxydation au bromate de sodium, le manganèse (probablement trivalent) est extrait au moyen de TTA 0,5 M en xylène, à partir d'une solution 1 N en acide sulfurique. On mesure l'absorption de la phase organique à 440 ou 450 mμ. La loi de Beer est observée jusqu'à 10 μg de manganèse par ml de phase organique. A l'exception du cérium, du fer et des chlorures, de petites quantités de nombreux éléments communs n'interfèrent pas. Le fer (III) peut être éliminé par extraction au cupferron-chloroforme. Le cérium peut être éliminé par lavage de l'extrait TTA au moyen d'une solution fluorure acide d'ammonium-acide nitrique.

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SEPARATION AND POLAROGRAPHIC DETERMINATION OF CADMIUM IN STAINLESS STEEL

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Summary—A method has been developed for the determination of small amounts of cadmium in stainless steel. Cadmium and copper are initially separated from other elements with thioacetamide. After extraction of the copper with Neocuproïne in chloroform, cadmium is determined polarographically in an ammonium chloride–aqueous ammonia electrolyte. Over the range 0.001–0.01% of cadmium, results are accurate to within 10% of the amount present. As little as 0.0005% of cadmium may be determined, and the upper limit may be extended beyond 0.01% by using smaller samples or by aliquoting. This method may be applied to all commercial grades of stainless steel.

INTRODUCTION

CADMIUM-PLATED steel scrap and white metal may be inadvertently included in the charge of an electric furnace for the melting of stainless steel, so that cadmium may be present in the stainless steel in concentrations up to about 0·01%. Because small amounts of cadmium are detrimental to the hot-working properties of stainless steel, it is desirable to analyse for this element. Although cadmium had been previously determined in non-ferrous materials, such as zinc and aluminium, in this laboratory, no method was available for determining cadmium in steel. Therefore, the present investigation was initiated to provide standards for optical emission spectrographic analyses.

Hildebrand, Lundell, Bright and Hoffman[1] indicate that cadmium cannot be separated ordinarily except as the sulphide. In previous work in this laboratory, as little as 5 μg of cadmium were separated as the sulphide from several elements in non-ferrous materials.

The classical method of sulphide precipitation makes use of hydrogen sulphide, a noxious and toxic gas, as the precipitant. Within the last 30 years thioacetamide, a considerably less toxic chemical, has been substituted for hydrogen sulphide. According to Ivanov[2] and Flaschka and Jakobljevich,[3] thioacetamide can be used successfully for the precipitation of heavy metals. Although thioacetamide has been employed for the quantitative separation of cadmium from aluminium, molybdenum-nickel alloys and tungsten-nickel alloys,[4,5] no evidence was found in the literature that it had ever been used to separate cadmium from a steel matrix. This laboratory, therefore, investigated the use of thioacetamide to precipitate cadmium.

The determination of small concentrations of cadmium, after separation from the stainless-steel matrix, requires a sensitive technique, such as absorption spectrophotometry or polarography. The photometric determination of cadmium, as described by Sandell,[6] makes use of dithizone or di-β-naphthylthiocarbazone. Unfortunately, these photometric methods are laborious, require the use of highly toxic cyanide compounds, and are sometimes subject to error because of nickel interference.

Lingane[7] has investigated the polarographic characteristics of cadmium in various supporting electrolytes and has found that the greatest sensitivity for cadmium was obtained in an ammonium chloride–aqueous ammonia electrolyte. This electrolyte is also advantageous in that copper and nickel are the only elements common to stainless steel which exhibit half-wave potentials over the range of 0 to −1·0 V *versus* a saturated calomel electrode.

EXPERIMENTAL

Apparatus

Model XXI Sargent polarograph

Reagents

Reagent-grade chemicals are used throughout.

Citric acid: 25%w/v in water.

Formic acid mixture: Dissolve 250 g of ammonium sulphate in 300 ml of water. Add 200 ml of 90% formic acid and 30 ml of 15 M aqueous ammonia, then dilute to 1 l. with water. Store in a ground-glass stoppered bottle.

10%w/v *Thioacetamide reagent:* Prepare this solution in warm water as needed.

2% *Thioacetamide wash water:* To 500 ml of water add 4 ml of 90% formic acid and 10 ml of 10% thioacetamide reagent.

10% *Hydroxylamine hydrochloride solution*: Prepare this solution as needed.

2,9-*Dimethyl*-1,10-*phenanthroline* (*Neocuproïne*) *reagent:* This solution (0.1%w/v in 95% ethyl alcohol) should be refrigerated when not in use.

Hydrochloric acid polarographic solvent: Add 14 ml of 12M hydrochloric acid to 30 ml of water.

Ammonium chloride (1M)-*aqueous ammonia* (1M) *electrolyte:* Dissolve 53·5 g of ammonium chloride in 300 ml of water. Add 67 ml of 15M ammonia solutions and dilute to 1 l. Store in a ground-glass-stoppered bottle at 20°.

Standard cadmium solution: Dissolve exactly 0·1000 g of 99·9% cadmium in 10 ml of 1:1 nitric acid. Evaporate this solution to dryness. Add 5 ml of 12M hydrochloric acid and again evaporate to dryness. After cooling, digest the residue for 5 min in 200 ml of water containing 53·5 g of ammonium chloride. Cool again, add 67 ml of 15M ammonia solution, transfer to a 1-l. volumetric flask and dilute the mark with distilled water ($|1\text{ml}| \equiv 100$ μg of cadmium). Less concentrated standard cadmium solutions are made by dilution of appropriate aliquots of this stock solution with 1M ammonium chloride—1M aqueous ammonia electrolyte. Store in a ground-glass-stoppered bottle at about 20°.

Procedure

Transfer 1·0 g of sample to a 600-ml beaker, add 20 ml of 1:1 hydrochloric-nitric acid mixture and dissolve the sample at low heat. Add 20 ml of 12M perchloric acid, heat until dense fumes of perchloric acid are evolved, then carefully add 10 ml of 12M hydrochloric acid and heat to volatilise the chromium. Continue to heat the sample to fumes of perchloric acid, and make second and third additions of hydrochloric acid. Again heat the solution to dense fumes of perchloric acid and continue heating until less than 5 ml of perchloric acid remain in the beaker. Cool, then add 50 ml of water to dissolve the perchlorate salts. (If iron hydrolyses from solution, add 3 ml of 12M hydrochloric acid and heat until it redissolves, then add 2 ml of 12M perchloric acid and again take to fumes of perchloric acid.) Add 25 ml of 6% sulphurous acid. Heat to boiling and boil for 2 min. While boiling, add 0·5 g of hydrazine sulphate. After the latter has dissolved, remove the beaker from the hot plate and cool to room temperature. Adjust the pH to 2·0 ± 0·2 (pH meter) by carefully adding aqueous ammonia dropwise. Next, add 20 ml of 25% citric acid solution and adjust the pH to 6·0 ± 0·5 with aqueous ammonia. Add 25 ml of formic acid mixture. (A precipitate may form at this point in the procedure. It will redissolve on heating.) Dilute the sample to 300 ml and digest at low heat. Heat to boiling and add 20 ml of 10% thioacetamide reagent. Again heat to boiling, and repeat the addition of this reagent until 60 ml has been added. Digest at 90° for 1 hr. While still hot, filter the thioacetamide precipitate through a 12·5-cm Whatman No. 42 filter paper containing pulp. Wash the beaker and paper 10 times with thioacetamide wash water. Transfer the paper and precipitate to the beaker in which the precipitation was made, and add 15 ml of water, 30 ml of 16M nitric acid and 8 ml of 12M perchloric acid. Decompose the paper and precipitate by heating until dense fumes of perchloric acid are evolved. Remove the beaker from the hot plate, cool and add 100 ml of water. Add 10 ml of 10%

hydroxylamine hydrochloride solution and adjust the pH with aqueous ammonia until Congo Red paper changes from blue to red. Transfer to a 250-ml separatory funnel, and add 15 ml of Neocuproïne reagent. Shake, add 25 ml of chloroform and shake again for 30 sec. After separation of the phases, discard the organic phase. Repeat with a further 25 ml of chloroform. Make a second and third extraction with Neocuproïne and chloroform. Use one 10-ml portion of Neocuproïne and two 15-ml portions of chloroform in each of these extractions. After the final extraction, transfer the aqueous phase to the original 600-ml beaker. Add 5 ml of 12*M* hydrochloric acid and evaporate the solution to 50 ml to ensure the volatilisation of ethanol. (This precaution is necessary to prevent a violent reaction between nitric acid and hot ethanol.) Remove the beaker from the hot-plate, carefully add 30 ml of 16*M* nitric acid and heat until dense fumes of perchloric acid are evolved. Cool, add 10 ml of water and digest the solution at low heat for 5 min. Transfer the contents of the 600-ml beaker to a 150-ml beaker, rinsing the 600-ml beaker with a minimum of water. Carefully evaporate the contents of the 150-ml beaker to complete dryness at high heat. Cool, add 2 ml of hydrochloric acid polarographic solvent and digest at low heat until the residue in the beaker completely dissolves. Cool and adjust the solution to a pH of 9·6 ± 0·2 (pH meter and micro electrodes) with 1:1 aqueous ammonia (approximately 4 ml 1:1 is necessary). Carefully transfer the contents of the 150-ml beaker to a 10-ml volumetric flask. Rinse the beaker with a minimum of electrolyte. Dilute to the mark with electrolyte.

Pipette a 3-ml aliquot of the solution into a dry polarographic cell, record the polarogram for cadmium *versus* a mercury-pool electrode according to the method suggested by Meites,[8] and calculate the percentage of cadmium.

DISCUSSION

Separation of cadmium

Four elements present in stainless steel can interfere in obtaining accurate polarograms of cadmium: chromium, iron, copper and nickel. Because both chromium and iron form insoluble hydroxides in the ammonium chloride–ammonia electrolyte, they must be separated from the cadmium. The chromium was removed by volatilisation as chromyl chloride from fuming perchloric acid after dissolution of the sample, and the iron contamination of the sulphide precipitates was prevented by careful control of pH and repeated washing of the precipitates. Copper and nickel are soluble in the electrolyte and reducible at the dropping mercury electrode. It was found that a very small amount of nickel was carried along with the copper and cadmium sulphide precipitates. However, the half-wave potential of nickel, which occurred at −0·95 V, could be easily differentiated from the cadmium wave at −0·67 V. Copper exhibited a double wave with half-wave potentials of −0·25 V and −0·51 V. When present in the concentrations found in the stainless-steel matrices, it produced large polarographic waves which made the accurate determination of cadmium virtually impossible. Extreme compensation was required to obtain the cadmium wave on scale and a large residual current was produced. The copper interference was overcome by complexing the copper with Neocuproïne and extracting the complex with chloroform.

Bowersox and Swift[9] have established the conditions of pH and temperature necessary to precipitate cadmium quantitatively with thioacetamide from a solution containing no other element. In addition to these conditions, it was found necessary to reduce the iron(III) in the sample to iron(II) and also to reduce the small amount of chromium(VI), remaining after volatilisation to chromium(III), before the thioacetamide separation. Table I shows the effect of chemical reduction on the recovery of cadmium in 2 samples of stainless steel. The lack of precipitation of cadmium as a sulphide in those samples not reduced is probably caused by the consumption of thioacetamide in reducing iron(III) and chromium(VI). As can be seen in this table, the cadmium lost in the thioacetamide precipitation was recovered with hydrogen sulphide from the filtrates of the thioacetamide separation.

TABLE I.—EFFECT OF REDUCTION ON RECOVERY OF CADMIUM[a]

	Recovered, %	
	Thioacetamide separation	Subsequent H_2S separation
No reduction	0·0000 0·0000	0·0092 0·0098
With reduction	0·0098	0·0000

[a] Cadmium added to a solution of NBS 101e stainless steel to give 0·010%.

As indicated by Lundell and Hoffman,[10] copper precipitates together with cadmium during the hydrogen sulphide separation of these elements. Copper also accompanied cadmium during the thioacetamide separation of cadmium from stainless steel. Because copper interferes in the polarographic determination of cadmium, it became necessary to separate the copper from the cadmium after the sulphide precipitation.

Cadmium sulphide, after precipitation with hydrogen sulphide, is reportedly soluble in hot 1:2 hydrochloric acid.[11] After verification of this information, the solubility of copper sulphide (from a hydrogen sulphide precipitation) in the same solution was investigated. It was found that copper sulphide is only slightly soluble in hot 1:2 hydrochloric acid. This suggested a means of separating the cadmium from the bulk of the copper. However, as can be seen in Table II, when the cadmium sulphide recovered after the thioacetamide precipitation was treated with 1:2 hydrochloric acid, much of the cadmium remained in the residue. The cadmium sulphide precipitate from the thioacetamide separation was coarse and crystalline, and probably did not dissolve as rapidly as the cadmium sulphide precipitated with hydrogen sulphide. Thus, copper and cadmium sulphides precipitated with thioacetamide could not be easily separated by the preferential dissolution of cadmium sulphide with hydrochloric acid.

TABLE II.—RECOVERY OF CADMIUM BY ACID TREATMENT

	Recovered[a], %	
	In 1:2 HCl	In residue
Hydrogen sulphide	0·0090 0·0083	0·0009 0·0007
Thioacetamide	0·0042 0·0041	0·0051 Not determined

[a] Cadmium added to NBS 101e stainless steel to give 0·010%.

There are very few methods for quantitatively separating large amounts of copper from trace amounts of cadmium. Those available involve either precipitation or electrodeposition of the copper; they are lengthy, involved and laborious. They suffer from inaccuracy because of coprecipitation or codeposition of a portion of the cadmium. It was, therefore, decided to investigate a different approach to the problem.

Smith and McCurdy[12] have proposed Neocuproïne (2,9-dimethyl-1,10-phenanthroline) as a specific reagent for copper. Luke and Campbell[13] studied the reaction of 56 metals (including cadmium) with Neocuproïne and found that only copper would form a coloured compound which was extractable into chloroform. We investigated the possibility that cadmium might form a colourless compound which was extractable. Several solutions were prepared containing either copper or cadmium in amounts similar to those expected in the stainless steels. The copper was then extracted into chloroform as its Neocuproïne complex. The aqueous layer was evaporated to dryness, the residue was dissolved in the ammonium chloride—ammonia electrolyte and polarograms of suitable aliquots were recorded. The results of these polarograms are presented in Table III. It was found that copper was completely separated from the cadmium by the Neocuproïne-chloroform extraction method, because no diffusion current for copper could be detected. The recovery of cadmium from the aqueous layer of the extractions was within ±0·0002% of the amount present.

TABLE III.—CADMIUM RECOVERY FOLLOWING SEPARATION OF COPPER[a]

Cadmium, %		
Added	Recovered	Difference
0·0010	0·0012	+0·0002
0·0040	0·0038	−0·0002

[a] 0·40% of copper taken

Evaluation of procedure

The procedure was checked by adding various concentrations of cadmium to a National Bureau of Standards (NBS) stainless-steel sample. The polarographic results

TABLE IV.—RECOVERY OF CADMIUM FROM STAINLESS STEEL 18 Cr-9 Ni (NBS 101e)

Cadmium added, %	Cadmium recovered, %			
	Average	Minimum	Maximum	Difference
0·0005	0·0005	0·00047	0·00062	0·0000
0·0010	0·0010	0·00098	0·00011	0·0000
0·0050	0·0048	0·0046	0·0049	−0·0002
0·010	0·0093	0·0091	0·0097	−0·0007

TABLE V.—RECOVERY OF CADMIUM FROM VARIOUS STEELS

Stainless steel	NBS no.	Cadmium, %	
		Recovered[a]	Difference
18 Cr-9Ni	101e	0·0048	−0·0002
Nb-Ta stabilised	123b	0·0051	+0·0001
18Cr-10Ni-0·4Ti	121c	0·0047	−0·0003
18Cr-14Ni-3Mo	160A	0·0048	−0·0002

[a] 0·0050% of cadmium added.

in Table IV show that recovery was within ±10% of the amount present, except at the 0·0005% level where recovery was within ±13% of the amount present.

Table V shows that in spite of the presence of niobium, tantalum, molybdenum and titanium, the recovery of added amounts of cadmium from National Bureau of Standards steel samples was within 10% of the amount added.

Zusammenfassung—Eine Methode für die Bestimmung von kleinen Mengen Cadmium in tostfreiem Stahl wurde entwickelt. Dabei wurden Cadmium und Kupfer zuerst mit Thioacetamid von den anderen Elementen getrennt. Nach Extraktion von Kupfer mit Neocuproin in Chloroform wurde Cadmium polarographisch in einem Ammoniumchlorid-Ammoniak-Elektrolyten bestimmt. Zwischen 0,001 und 0,01% entsprachen die Cadmiumwerte auf etwa 10% genau den anwesenden Mengen. Bis herunter zu 0,0005% Cadmium wurden bestimmt, die obere Grenze wurde durch kleinere Proben oder Teilung der Proben über 0,01% hinaus ausgedehnt. Die Methode kann auf alle handelsüblichen rostfreien Stähle angewandt werden.

Résumé—On a élaboré une méthode pour le dosage de petites quantités de cadmium dans l'acier inoxydable. Dans cette technique, on sépare d'abord le cadmium et le cuivre des autres éléments par le thioacétamide. Après extraction du cuivre à la néocuproïne en chloroforme, on dose le cadmium par polarographie, dans un électrolyte chlorure d'ammonium ammoniaque. Entre 0,001 et 0,01 p. cent, les résultats en cadmium sont précis à 10% près. On a pu doser une quantité de cadmium n, excédant pas 0,0005%, et la limite supérieure a été étendue au-delà de 0,01% en utilisant un plus petit échantillon, ou en prélevant une partie aliquote. Cette méthode peut être appliquée à toutes les qualités commerciales d'acier inoxydable.

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PRELIMINARY COMMUNICATION

Purification of metal chelates by a zone-refining technique*

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ZONE-refining techniques have recently been adopted as a promising method of purifying various organic compounds.[1] This communication reports on the application of this technique to the purification of metal chelate compounds.

It is well known that certain types of metal chelate compound have definite melting points without decomposition. Most of such chelate compounds belong to the inner complex type, in which the positive charge of the metal ion is neutralised by the negative charge of the ligands, and the co-ordination number of the metal ion is completed by the ligand molecules. Typical examples of this class are the metal chelates of β-diketones or α-dioximes. We have examined the zone-refining technique for the purification of various inner complex chelates in the hope that the central metal ion could be purified by this process.

For example, tris(acetylacetonato)chromium-III (m.p. 214°) was subjected to zone refining. The crude material, which was synthesised from reagent-grade chemicals, was melted in a borosilicate glass tube (8 mm in diameter, 150 mm in length) which was sealed under nitrogen. The tube was processed for zone refining, with a heater temperature of approximately 220°, and with a downward rate of 3 cm/hr. After repeating the process, the samples from the top, middle and bottom portions of the column were subjected to emission spectrographic analysis. The results are shown in Table I.

TABLE I.—ZONE REFINING OF TRIS(ACETYLACETONATO)CHROMIUM-III

Exp. no.	No. of passes	Portion of column sampled	Elements detected*						
			Al	B	Ca	Fe	Mg	Na	Si
1	17	Top	x			x	x	x	
		Middle				x	x		x
		Bottom	x			x	x		x
2	26	Top				x			x
		Middle				x	x	x	x
		Bottom	x	x	x	x	x	x	x
3	36	Top							
		Middle				x			
		Bottom	x		x	x	x		x

* Emission spectrographic analysis were carried out using a Shimadzu QL-170 Littrow type spectrograph.

It is seen from the table that, as the number of passes increases, the purity of the top portion of the column improves progressively. It is also apparent that the impurities are concentrated in the lower part of the column. With 36 passes, no element other than chromium could be detected in the top portion of the column. From these results, it is evident that the central metal ion of the chelate compounds is purified by zone refining, and the results suggest that this technique could be a useful method of obtaining ultra-pure metals which cannot or which would be very difficult to obtain by the direct zone melting of the metals, because of their high melting points or of their ease

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* Contribution No. 68 from Department of Organic Synthesis, Kyushu University, Japan.

of oxidation during the process. It would also be of interest to investigate the physico-chemical properties of the ultra-pure metal chelates. Detailed investigations are in progress, and will be published elsewhere.

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Summary—Metal chelate compounds may be purified by a zone-refining technique. As an example, zone refining of tris(acetylacetonato)chromium-III is described. It has been proved that the central metal ion can be purified by this technique.

Zusammenfassung—Metallchelate lassen sich durch Zonenschmelzen reinigen. Als Beispiel wird die Reinigung von Tris(acetylacetonato)-chrom(III) beschrieben und gezeigt, daß das Zentralion auf diese Weise gereinigt werden kann.

Résumé—On purifie les chélates métalliques par la technique de raffinage par fusion de zone. A titre d'exemple, on décrit le raffinage par fusion de zone du tris (acétylacétonato)Cr^{III}, et on montre que l'ion métallique central peut être purifié par cette technique.

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SHORT COMMUNICATIONS

Separation of certain cations from mixtures of various cations on ion-exchange papers—IV*: arsenic, cobalt, magnesium, manganese, mercury, nickel or vanadium

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EARLIER parts of this series have reported the separation of silver or thallium;[1] antimony or arsenic;[2] and arsenic, barium, cadmium, tin, or zinc[3] from essentially all other ions by paper chromatography with complex-forming solvents on filter paper impregnated with either strongly-acidic cation-exchange resin or strongly-basic anion-exchange resin. Systems have now been found for other analytically useful separations.

EXPERIMENTAL

Standard procedures for the downward development of paper chromatograms in a commercially-available chamber were employed to test aqueous solutions of various selective reagents as developers. Details have been given in the papers cited above. Exploratory tests were performed by developing the following 26 representative ions individually with each reagent: Ag, Tl, Pb, Cu, Cd, Co, Ni, Hg^{I}, Hg^{II}, As^{III}, Fe^{III}, Sb^{III}, V^{V}, Bi, Sn^{IV}, Au^{III}, Pt^{IV}, Al, Ce^{III}, Ce^{IV}, Mg, Zn, Ba, Mn^{II}, Cr^{III} and U^{VI}. The method of preparation of each test solution at 0·050*M* was reported earlier.[4] The promising reagents were then tested with the following compatible mixture, to which were added the ions to be separated if necessary: Ag, Al, Ba, Cd, Ce^{IV}, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Tl and Zn. Four spray reagents, previously described,[1,2,5] served to detect all the ions listed above. These included 8-quinolinol followed by ammonia for Mn, Cr, Al, Ce, Mg, and Zn; potassium rhodizonate for Ba; potassium ferrocyanide for U; and ammonium sulphide followed by hydrochloric acid for the rest.

Some of the reagents tested were also used as background electrolytes in earlier electrochromatographic studies of these ions.[5,6] We consequently knew the sign of the charge of each ion, in each of these particular solutions, from the mode of migration of each ion. As shown earlier,[4] this did not help us to predict accurately which, if any, ion would be separated in the present paper-chromatographic studies.

RESULTS AND DISCUSSION

The separations obtained in various systems are summarised in Table I. The results given below are based upon at least four migrations of each ion in each system, with stated R_F values (measured to the front of solute zones) having a standard deviation of ±0·04 or less. The solvents were allowed to travel 30–35 cm past the origin in each case, which required about 2 hr with the cation-exchange paper and about 90 min with the anion-exchange paper, depending upon the form of the paper and the solvent used.

Arsenic was separated from all 25 other ions, and vanadium was separated from all except mercury^{I}, mercury^{II}, and antimony^{III} ions, by development with a solution of 0·010*M* sulphuric acid containing 1·0% of hydrogen peroxide, pH 2·5, on cation-exchange paper in the hydrogen form (Reeve Angel Grade SA-2, control A-7802-1,2). Arsenic migrated in a compact zone with the solvent front (R_F, 1·0), but vanadium (R_F, 0·36) formed a zone 5·4 cm in length, the tail of which was 6·2 cm from the origin. Arsenic and vanadium were separated by about 20 cm from each other. Except for antimony and the two forms of mercury, which formed diffuse zones extending from the origin and contaminated the vanadium, all other ions remained at or within 2·0 cm of the origin. Electrochromatographic studies[6] showed that vanadium, uranium and platinum were complexed by this solution to give anions. However, the latter two anionic zones had enough affinity to retain them at the origin of the cation-exchange paper. The fact that anions do not necessarily leave the origin on cation-exchange paper has been noted before.[2] Fritz and Abbink[7] found similarly that although titanium^{IV}

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* Part III: see reference 3.

TABLE I.—IONS SEPARATED FROM MULTICOMPONENT MIXTURES

	Ion separated	Interferences
1.	As	
	V	Hg^{I}, Hg^{II}, Sb
2.	As	V, Pt
	V	As, Pt, Al
3.	Mg	As, Ba, Co, Mn, Ni
4.	Ni	Co, Zn
5.	Hg^{I}	Al, V, Ag, Hg^{II}
	Hg^{II}	Al, V, Ag, Hg^{I}
6.	Mn	Ce^{III} (Mg and Ba lost)
7.	As	Hg^{I}, Hg^{II}, Al, Co
	Co	Hg^{I}, Hg^{II}, Al, As

also formed a negative complex in this solvent, it resisted elution and remained in a tight band at the top of a column of hydrogen-form cation-exchange resin. However, columns of resin and papers impregnated with the same resin do not always yield identical chromatographic results when the same substances are developed with the same solvent. This has been demonstrated before[4] and again in this system, because Fritz and Abbink[7] were able to separate mercury-II from vanadium on a column of resin by elution with this solvent.

Arsenic was separated from all 25 other ions except vanadium and platinum, and vanadium was separated from all 25 other ions except arsenic, platinum and aluminium by development with a solution of 0·0125*M* ammonia-triacetic acid (nitrilotriacetic acid) and 2·1*M* ammonia, pH 10·9, on SA-2 paper in the sodium form. Vanadium (R_F, 0·84) migrated in a narrow zone 4·0 cm in length, and arsenic (R_F, 0·86) gave a circular zone 2·0 cm in diameter. Platinum streaked from the origin to contaminate both arsenic and vanadium, and aluminium formed a similar, less diffuse zone which contaminated vanadium but which was separated by 1·0 cm from arsenic. None of the other ions were closer than 4·0 cm (cobalt) to either arsenic or vanadium. Antimony and the two forms of mercury, which were not separated from vanadium in the previous system, remained within 3·0 cm of the origin in this system; platinum and aluminium, which were not separated from vanadium in this system, were within 2·0 cm of the origin in the previous one. Therefore, vanadium can be separated from all other ions in one or other system. Electrochromatography proved that all ions except silver (which formed the ammonia complex) were negatively charged; again, many of them did not migrate at all on cation-exchange paper.

Magnesium was separated from all 25 other ions except arsenic, barium, cobalt, manganese and nickel by development with a solution of 0·10*M* ammonium thiosulphate and 0·10*M* ammonia, pH 9·5, on anion-exchange paper in the thiosulphate form (Reeve Angel Grade SB-2, control A-10297). Magnesium (R_F, 0·99) migrated in a fairly diffuse zone (11·0 cm in length), which was clearly separated from all ions except the five mentioned above. All of these except nickel streaked from the origin for almost the entire length of the paper. Except for these, zinc was the closest zone to magnesium, and it was separated by at least 12 cm.

Nickel was separated from all 25 other ions except cobalt and zinc by development with a solution of 0·10*M* ammonium thiosulphate, 0·0050*M* sodium hydroxide and 6·0*M* ammonia, pH 11·0, on SB-2 paper in the thiosulphate form. Cationic nickel was detected spread out along the solvent front (R_F, 1·0); cobalt streaked from the origin to within 1·0 cm of the solvent front, and zinc migrated (R_F, 1·0) in a zone 4·1 cm in length. Of the other ions, aluminium was the closest, being separated by 2·5 cm from nickel. Nickel was separated from zinc in the thiosulphate system mentioned zinc immediately above; in it, nickel migrated (R_F, 0·98) in a zone 9·5 cm in length, and was always within 7·0 cm of the origin. Cobalt and nickel were not separated in that system either, but were separated in the cyanide system described below. In a previous paper[8] the separation of zinc from all ions except vanadium was reported. In the present system, vanadium (R_F, 0·68) was separated from zinc by at least 5·0 cm.

The mercury zones were separated from all 24 other ions except aluminium, vanadium and silver by development with the same solvent as described immediately above on SA-2 paper in the ammonium form. The three interfering ions all streaked from the origin to contaminate the two forms of mercury, both of which migrated in an oblong zone 1·3 cm in length and 0·80 cm wide (R_F, 1·0). Of the others only platinum and arsenic were close to mercury, being separated by 4·0 and 1·0 cm, respectively.

Manganese was separated from 22 other ions by development with a solution of 0·11*M* hydrocyanic acid and 0·10*M* tetraethylammonium hydroxide, pH 9·7, on SB-2 paper in the chloride form. Manganese migrated with the solvent front (R_F, 1·0) in an oblong zone 2·4 cm in length and 1·3 cm wide which was contaminated only by cerium^{III}, which formed a diffuse zone extending from the origin almost the entire length of the paper. The closest of the rest of the zones were those of arsenic and thallium, both of which were separated from manganese by at least 2·5 cm. Because cyanide complexed many of the ions very strongly, it was necessary to spray the papers with hydrochloric acid and to allow them to stand for several hours before the usual detection tests (above) were successful. Magnesium and barium, which are not complexed strongly by cyanide, inexplicably could not be located in this system by the usual tests or by any reagent which we could find referred to in the literature. Their position relative to manganese is therefore indeterminate. Electrochromatography showed that manganese was among the many anions in this solvent; thallium was cationic, and arsenic was uncharged.

Arsenic and cobalt were separated from all 24 other ions except mercury^{I}, mercury^{II} and aluminium, but not from each other, by development with the same cyanide-hydroxide solvent on SA-2 paper in the sodium form. Anionic cobalt migrated in a compact zone 1·5 cm in length (R_F, 0·86), and uncharged arsenic migrated (R_F, 0·90) in a zone 2·4 cm in length. The mercury and aluminium zones (all anionic) streaked from the origin almost the entire length of the paper. The closest of the other zones, vanadium, was separated from arsenic and cobalt by 4·0 cm. It was possible to locate all ions in this system by using the preliminary acid spray described above.

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Summary—Conditions are described for separating one or two ions from multicomponent mixtures by development with complexing agents on filter paper impregnated with ion-exchange resin. The ions separated from complex mixtures are: As and V; Mg; Ni; $Hg^{I} + Hg^{II}$; Mn; As + Co.

Zusammenfassung—Es werden Arbeitsvorschriften zur Abtrennung verschiedener Ionen (As und V; Mg; Ni; $Hg^{I} + Hg^{II}$; Mn; As + Co) aus Gemischen vieler Ionen angegeben. Die Ionen werden auf mit Ionenaustauscherharz imprägniertem Papier durch komplexbildende Reagentien aufgetrennt.

Résumé—On décrit les conditions de séparation de certains ions (As et V; Mg; Ni; $Hg^{I} + Hg^{II}$; Mn; As + Co) de mélanges comportant de nombreux constituants, par développement au moyen d'agents complexants, sur un papier filtre imprégné de résine échangeuse d'ions.

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An investigation of fast neutron activation analysis for determination of oxygen in metals*

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UNTIL a few years ago the only method which could be used for the determination of oxygen in almost all metals and alloys, was vacuum fusion. In the vacuum-fusion analysis of certain materials problems have been encountered in complete extraction of the oxygen from the sample and in gettering of the released gas by the metal vapour in the furnace. Because of the difficulties involved in preparing absolute standard samples of oxygen in metals, none are available for procedure development work. In view of the above-mentioned potential problems in applying vacuum fusion to all metals and alloys, nuclear methods of analysis[1] were considered.

EXPERIMENTAL

Apparatus

A Texas Nuclear Corporation model 150 neutron generator was used for irradiation. The generator produces 14-MeV neutrons by the ^{3}H (d, n) ^{4}He reaction. The neutron flux was of the order of 1×10^8 neutrons.cm^{-2}.sec^{-1}.

The counting of the activated sample was carried out with a Radiation Instrument Development Laboratory 200 channel pulse-height analyser in conjunction with two 3″ × 3″ NaI(Tl) scintillation crystals.

The sample transfer system used for rapidly transporting the samples from the generator to the counting position was operated by compressed nitrogen. A ⅝ × 2¼″ rabbit was generally used. The total transfer time for the 40-ft system was about 3 sec.

Samples

In order to compare effectively the results obtained by vacuum fusion analysis and fast-neutron activation, it is necessary to use samples of known analytical history. The samples used in this study were selected because of the consistency of the results, which had been obtained by vacuum fusion in several different laboratories.

Sample preparation and encapsulation

All samples for vacuum fusion and activation analysis were prepared by abrading with a clean file, then degreasing with benzene followed by an acetone rinse. Those which were intended for activation analysis were sealed in either polyethylene or aluminium capsules which were purged with dry methane before sealing. The polyethylene vials were sealed thermally and the aluminium vials were sealed by the Magneform process. The removal of both air and moisture from the vials before sealing is necessary.

The standard sample was prepared from primary standard grade arsenic trioxide mixed with graphite and contained in a polyethylene capsule. The mixture contained 100 mg of oxygen and was prepared so that it completely filled the polyvial.

Procedure

The samples and standard were loaded into the pneumatic transfer device and transferred to the irradiation position at the neutron generator. The sample was irradiated for 0·4 min, then transferred to the counting position and counted for 0·4 min. The relative neutron flux reading was taken before each irradiation so that corrections could be made for the variation of neutron flux with time.

In the case of the polyvials, after irradiation and counting the vials were cut open, the samples removed, and the vials analysed several times in order to obtain the oxygen content of the vial. In the case of the aluminium vials, the analysis was carried out on each vial before encapsulation of the sample. Only one analysis was made for each aluminium vial because of the relatively low oxygen content.

* The activation-analysis portion of this work was conducted by the author in the laboratories of the General Atomic Division of General Dynamics Corp., San Diego, California, U.S.A.

Calculations

The spectrum of the gamma radiation obtained from the ^{16}N is shown in Fig. 1. The area above the dotted line is the 6–7 MEV gamma radiation. This energy range was covered by about 25 channels of the multi-channel analyser. The area above the dotted line is proportional to the ^{16}N and therefore to the oxygen content of the sample. The area under the curve above the dotted line is compared to that of the standard to compute the amount of oxygen present in the sample. The only correction made is a normalisation of the counts for the variation in neutron flux used for irradiation of the standard and the sample. No correction is made for the decay in the ^{16}N activity during transfer from the irradiation position to the counting position because this time is essentially the same for the standard and the sample. The variation of neutron flux with time is shown in Fig. 2 and some actual data and calculations are shown in Table I.

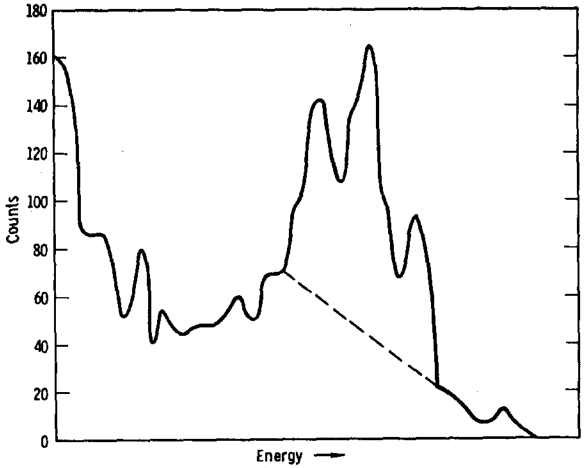

FIG. 1.—Gamma ray spectrum of ^{16}N from ^{16}O in iron.

TABLE I.—COUNTING RESULTS

Sample	Total counts	Net counts	Normalised counts	Oxygen, *mg*	Net oxygen, *mg*	Oxygen, *wt.* %
Fe	1749	998	1010	8·86[a]	7·76	0·106
Nb	593	374	378	3·31[a]	2·25	0·0125
Si-Fe	569	299	311	2·47[b]	1·37	0·0069
Mo	146	77	91	1·44[c]	1·27	0·0061
Al	16	16	14·5	0·227[c]	0·227	0·0008

[a] Sensitivity: 114 counts/mg of oxygen.
[b] Sensitivity: 126 counts/mg of oxygen.
[c] Sensitivity: 63 counts/mg of oxygen.

RESULTS AND DISCUSSION

Table II contains a comparison of results obtained on various metals by both vacuum fusion and fast neutron activation analysis. The majority of the values obtained by both methods are in good agreement. The values marked (a) were encapsulated in aluminium and the value marked (b) was obtained without using a capsule. It was a single piece of aluminium machined to the size of a capsule. All other samples were encapsulated in polyethylene vials.

The duplicate results shown in Table II were obtained on separate duplicate specimens, and not reactivation of a sample which had been previously analysed. It can be seen from Table I that the net counts for some samples is rather small and therefore the counting statistics are poor. The statistics could be improved by rerunning the sample several times. It can also be seen that the sensitivity for oxygen in aluminium or in samples contained in aluminium capsules is much less than that in the other metals investigated. This is because of interference from the aluminium in the lower energy portion of the ^{16}N spectrum. The interference is eliminated by using only the high energy portion of the curve.

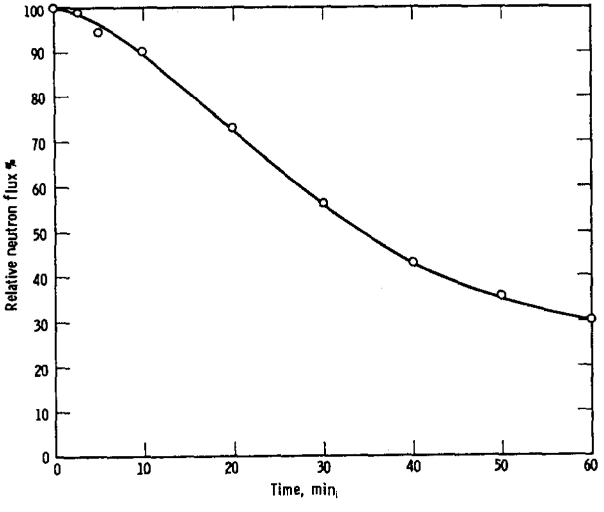

FIG. 2.—Variation of neutron flux with time.

TABLE II.—COMPARISON OF RESULTS

Sample composition	Oxygen, *wt.* %		Sample wt, *g* (activation analysis)
	Vacuum fusion	Activation analysis	
Fe	0·102	0·106	7
Fe	0·0165	0·0170	11
Nb	0·0152	0·0125	18
Nb base	0·0330	0·0298	24
Nb base	0·0183	0·0185	8
		0·0204	
Si-Fe	0·0023	0·0022	
		0·0023[a]	19
		0·0024	
Si-Fe	0·0070	0·0069	20
Mo	0·0067	0·0061[a]	20
Al	0·0009	0·0008[b]	27

[a] Aluminium capsules.
[b] No capsule.

In order to obtain good agreement between vacuum fusion and activation analysis, it is necessary to consider the possible sources of error in activation analysis and ways in which they can be eliminated or minimised. Because activation analysis is not absolute but a comparison between a standard and the unknown sample, the geometry of both counting and irradiation is extremely important. The use of the small neutron source makes this point even more important because of the relatively small neutron beam. The outside dimensions of both the standard and the unknown should be as close as possible to ensure similar irradiation and counting. It is not necessary that the density be the same, however, because almost all materials are transparent to fast neutrons and gamma rays.

When dealing with short half-life species, such as ^{16}N, it is essential that rapid transfer between neutron source and counter be effected. This can be accomplished by using a pneumatic transfer system. Most samples are, however, not of the proper shape or form to be transferred without encapsulation. Polyethylene vials are very convenient to use for this purpose; however, the oxygen and nitrogen content is usually very high and erratic. One series contained 1100 ± 150 μg of oxygen. If the value of each vial is determined separately and the oxygen value of the unknown corrected for the oxygen content of the polyvial, fairly good results can be obtained.

Other materials, such as aluminium and copper, which contain fairly low concentrations of oxygen and nitrogen, can also be used for encapsulation of the samples. Aluminium has been tried with good results, but problems exist in the sealing of the capsule. While the aluminium from which the capsules were fabricated contained about 8 ppm of oxygen, the finished capsules contained over 20 ppm. This value was not consistent between capsules and the increase was probably caused by the heat generated by the Magneforming operation which was used to seal the aluminium capsule. The use of aluminium capsules lowered the background by about a factor of 10 below that when polyvials were used. Further work on fabrication will undoubtedly lower the background of aluminium capsules by a factor of 2 or 3.

The oxygen content of the encapsulation material is not the only problem in encapsulation of samples, however. The volume of each capsule, if filled with air, contains about 2 mg of oxygen. Even though the sample occupies much of this volume, the oxygen content of the air occupying the capsule is significant and therefore must be removed. When polyvials are used this is done by purging with methane and sealing with a soldering iron. The problem is more complicated when aluminium capsules are used, because the capsule must be enclosed in a bag containing an inert atmosphere in order to have the top Magneformed on. Because the delay between sealing and irradiation can be considerable, the seal must be tight to prevent air leaks.

Obviously, the way to eliminate the problems of air contamination and capsule background is to use a transfer system in which encapsulation is unnecessary. For many materials transfer systems, both pneumatic and mechanical, can be devised which will have a negligible background.

From the data obtained in this study it appears that fast neutron activation analysis is a useful tool for the determination of oxygen in metals and compounds. While in some cases the large sample weight necessary may be a disadvantage, it is an advantage in material where an oxygen gradient exists across the specimen. The one technical advantage that fast neutron activation analysis has over vacuum fusion is that the result does not depend on recovery of the gas. Consequently, problems, such as gettering and incomplete reduction of oxides, are non-existent. Because of this, oxygen determination by activation analysis can be accomplished on materials that are a problem by vacuum fusion. Some of these are phosphorus, silicon carbide, gallium phosphide and various sulphides. The largest contribution of activation analysis to the determination of oxygen in metals is probably in the area of alloys and compounds which cannot be determined by vacuum fusion or other conventional methods.

While the combined activation and counting time for oxygen in metals is only 0·8 min, other variables tend to lengthen the actual analysis time. The surface preparation of the sample takes considerably more time for activation analysis than for vacuum fusion because of the longer time necessary to prepare the surface of the large samples properly and for the purging and encapsulation operation. While a degassing operation is unnecessary in activation analysis, accelerator maintainance time is significant. This is mainly because of deterioration of the target at an appreciable rate when the accelerator is operated at a high neutron flux. At present the life of targets operated at near full power is a matter of a few hours and the useful flux for oxygen analysis may be available for less than this because deterioration of the target is gradual.

CONCLUSION

It has been shown that fast neutron activation can give results comparable to those obtained by vacuum fusion for oxygen in metals. It is felt, however, that activation analysis should be used to compliment vacuum fusion in areas where difficulties are encountered with the vacuum fusion technique. Unfortunately, both methods have drawbacks and advantages in certain areas, and they should be used in the areas of their greatest strength.

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Summary—A comparison has been made between results obtained for the oxygen content of metals obtained by vacuum fusion and fast neutron activation over the range 0·0008–0·1% of oxygen. The metals investigated included iron, silicon-iron, aluminium, molybdenum, niobium and niobium-base alloys. The problems encountered in the use of activation analysis for oxygen are discussed and solutions to them suggested.

Zusammenfassung—Die Ergebnisse von Sauerstoffbestimmungen in Metallen durch Vakuumschmelze und durch Aktivierung mit schnellen Neutronen wurden im Bereich von 0,0008 bis 0,1% Sauerstoff verglichen. Die untersuchten Metalle waren Eisen, Ferrosilicium, Aluminium, Molybdän, Niob und Legierungen auf Niobbasis. Die bei der Sauerstoffbestimmung durch Aktivierungsanalyse auftretenden Probleme werden diskutiert und Vorschläge zu deren Lösung gemacht.

Résumé—On compare les résultats obtenus, pour la teneur en oxygène des métaux, par la fusion sous vide et par l'activation aux neutrons rapides, dans le domaine compris entre 0,0008 et 0,1% d'oxygène. Les métaux étudiés comprennent le fer, le ferrosilicium, l'aluminium, le molybdène, le niobium et les alliages à base de niobium. On discute des problèmes rencontrés dans l'emploi de l'analyse par activation pour l'oxygène, et on suggère des solutions à ces problèmes.

REFERENCE

[1] L. C. Bate, *Nucleonics*, 1963, **21**, 72.

Miniature magnetic stirring motor for use in teaching and analytical control laboratories

(*Received* 17 *April* 1964. *Accepted* 25 *May* 1964)

ELECTRICALLY powered magnetic stirring devices of many types are available. Although much used in research laboratories, they are too expensive for regular use by students. They are too large for convenience, they cannot be immersed in water baths, and they generate heat in operation. The stirring motor here described is free from these faults. The speed can be varied over a wide range, from slow to fast, and will remain constant at any predetermined level over a long period of use.

The parts of the motor are shown in Fig. 1. A magnet of Alnico, 45 × 20 × 8 mm, and weight 46 g, capable of lifting 150 g of iron on contact, is hermetically sealed into a plastic armature, 57 mm in diameter and 10 mm thick, with 24 driving prongs. The rotor bearings are of brass. When sealed into its plastic casing, which is 75 mm in diameter, and 20 mm thick, the assembly weighs 105 g in all.

The uses of this stirrer are illustrated in Figs. 2–6. It can be driven by water or compressed air, singly or with several units together.

Expensive Teflon-coated Alnico-cored stirring bars are not needed. A satisfactory stirring bar can be made as follows. A length of Pyrex tubing of 4-mm bore is sealed off at one end. While it is still hot, a 25-mm length cut from a carpenter's nail of slightly smaller diameter is heated just to redness and dropped into the tube. The tube is then drawn off just beyond the end of the piece of nail. For this operation, the tube can be held in forceps, or better, in a piece of spiral steel spring just small enough in diameter to grip the glass. The important thing is to heat the piece of iron before putting it into the tube; this makes it possible to achieve a closely fitting and well rounded seal.

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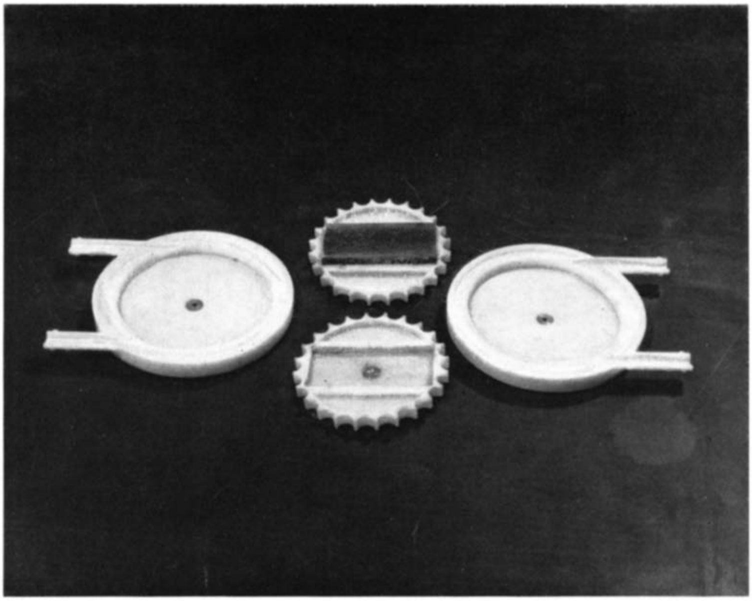

FIG. 1.—Integral parts of magnetic stirring motor.

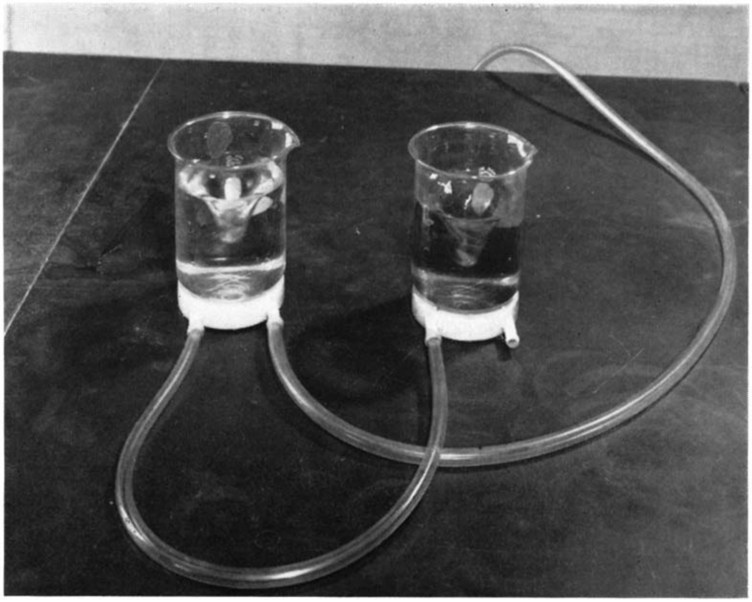

FIG. 2.—Tandem stirring operations with vacuum drive.

FIG. 3.—Stirrer operating whilst submerged in water bath.

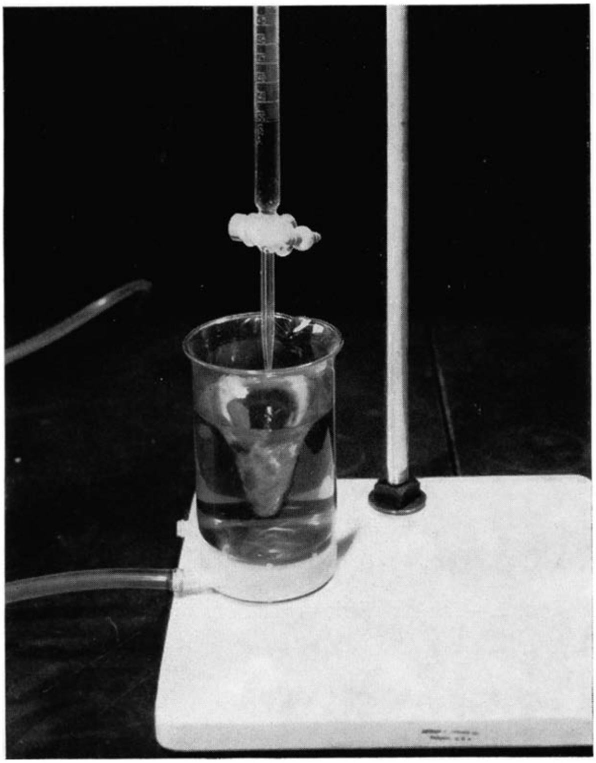

FIG. 4.—Beaker titration assembly.

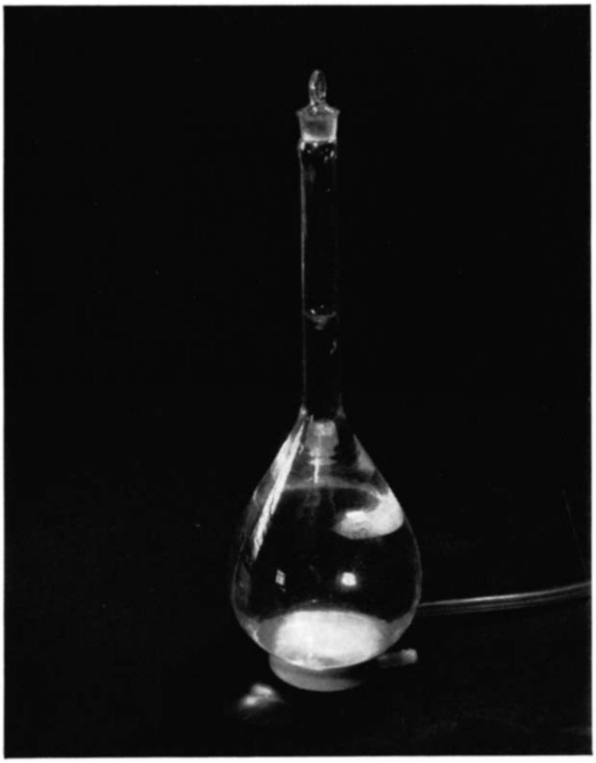

FIG. 5.—Stirring contents of 1000-ml flask. Note cone at surface of liquid.

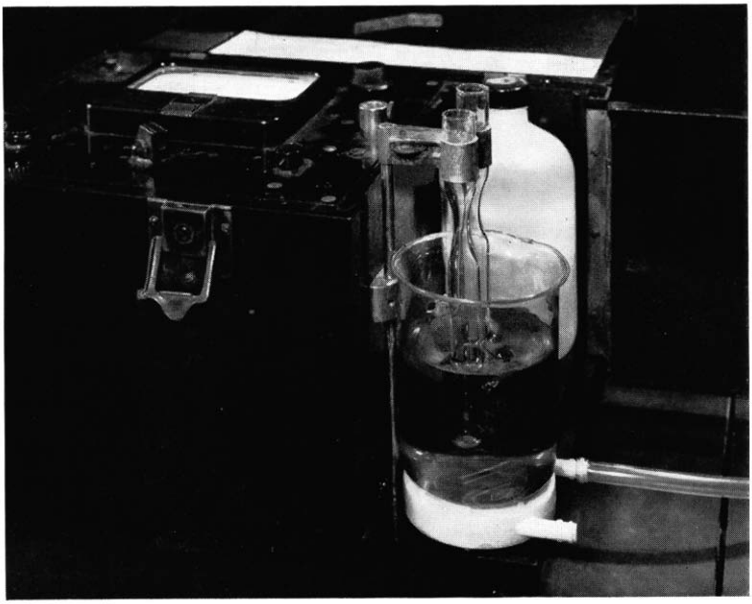

FIG. 6.—Stirring in conjunction with pH meter.

Summary—A magnetic stirrer is described which may be powered by water, air or vacuum, and which can be used for a variety of stirring operations, more satisfactorily than the electrically driven stirrers.

Zusammenfassung—Ein Magnetrührer wird beschrieben, der durch Wasser, Luft oder Vakuum angetrieben werden kann. Er eignet sich für viele Rühroperationen viel besser als elektrisch angetriebene Rührer.

Résumé—On décrit un agitateur magnétique qui peut être propulsé au moyen d'eau, d'air ou de vide, et que l'on peut utiliser pour diverses opérations d'agitation, de façon plus satisfaisante que les agitateurs mûs électriquement.

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DETERMINATION OF COBALT(II) IONS BY A DIFFERENTIAL SPECTROPHOTOMETRIC METHOD

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Summary—Cobalt(II) ions can be determined in the form of perchlorate by a differential spectrophotometric method, after evaporating the cobalt samples with perchloric acid to the production of perchloric acid fumes. From the absorption spectrum of cobalt(II) perchlorate the peak occurring at 19600 cm^{-1} (511 $m\mu$) is chosen for the determination. By the systematic investigation of optimum concentration limits it has been shown that if a solution containing 12 g/litre of cobalt is used as a reference, the concentration determination can be carried out with an error less than 1%, while the corresponding photometric error decreases to less than 0·1%. The effects of some foreign ions have been investigated; chromium, if present in the tervalent state, causes high positive errors. Other metal ions examined have no significant effect.

THE use of high-performance spectrophotometers permits of a desirable increase in the accuracy of analytical determinations. In particular, differential spectrophotometry promises the reduction of errors to such an extent that even ions which are present as main constituents in samples can be determined with adequate accuracy. Numerous differential spectrophotometric methods have already been described by various authors, among which determinations of copper,[1] nickel,[2] dichromate and permanganate,[3] titanium,[4] uranium,[5,6] vanadium[7] and phosphate[8] are the most widely used. The present investigation was to find the best experimental conditions for the determination of cobalt in the form of cobalt(II) perchlorate. From the point of view of differential spectrophotometric methods, the measurement of the optical densities of metal perchlorates are very suitable, partly because perchlorates generally do not form complexes which cause deviation from Beer's law, and partly because perchlorates can easily be prepared by simple evaporation with perchloric acid.

EXPERIMENTAL

Reagents

Cobalt(II) *perchlorate solution*, containing 50·00 mg/ml of cobalt, was prepared by dissolving 246·904 g of analytically pure cobalt(II) nitrate hexahydrate in water to which 350 ml of 60% perchloric acid were added, and cautiously evaporating the mixture to the appearance of white perchloric acid fumes. The solution was then diluted with water to exactly 1 litre. The cobalt content of the solution was checked by gravimetric methods.

This was used as a stock solution for the preparation of comparison standards. Because no marked effect on the optical densities was found if the concentration of perchloric acid was changed over a wide range, dilutions from the stock solution were simply made by water.

Apparatus

The absorption spectra of the metal perchlorates were obtained by a Unicam SP 700 spectrophotometer, equipped with a recorder presenting transmittance *vs.* wave numbers. One-cm silica cells were used, and spectra were recorded between 50×10^3 and 4×10^3 cm^{-1} wave numbers.

Optical densities were measured with a Hilger Uvispec spectrophotometer. Two 1-cm silica cells were used systematically, one always containing the reference solution, the other being the one to be measured.

RESULTS AND DISCUSSION

Absorption spectra

The transmittances of accurately prepared metal perchlorate solutions, containing 10 g of metal ion in 1 litre of solution (10 mg/ml), were measured against water. Fig. 1 shows the absorption spectrum of cobalt(II) perchlorate. The curve shows a characteristic maximum at 19600 cm^{-1} (511 mμ). This wavelength was used for the optical density measurements, where the specific absorbance of cobalt^{II} ions is $7{\cdot}9 \times 10^{-2}$ litre.g^{-1}.cm^{-1}. Similarly, the absorption spectra of the perchlorates of those metal ions which often occur with cobalt were checked carefully for interference.

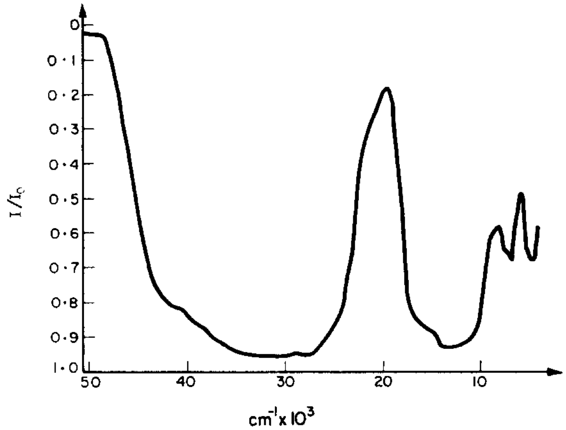

FIG. 1.—Absorption spectrum of cobalt(II) perchlorate (10 g of Co^{II}/litre)

The absorption spectra of the perchlorates of nickel(II), iron(II), copper(II) and chromium(III) are shown in Figs. 2, 3, 4 and 5 respectively.

By comparing these spectra it can be seen that the absorbances of nickel(II), iron(II) and copper(II) perchlorates at 19600 cm^{-1} are very low, and therefore there are no serious interferences to be expected in their presence. Chromium(III) perchlorate, however, shows marked absorption at this wavelength, and therefore a marked interference from chromium(III) is to be expected in determinations.

Optimum concentration limits

The determination of the optimum concentration limits was made by carrying out a series of sets of optical density measurements and calculating the corresponding percentage errors of the concentration determinations.[9] The region showing lowest errors was chosen as the most suitable one.

A set of solutions was prepared, containing 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 and 38 g of cobalt per litre. Five sets of experiments were made. As reference solutions water (concentration = 0) and cobalt(II) perchlorate solutions containing 6, 12, 18 and 24 g of cobalt per litre were chosen. Optical densities were measured in all cases six times (including refilling of the cells and readjustment of the instrument). The means of six readings are presented in Table I.

In each set the optical densities, when plotted against concentrations, yield linear curves. Using the method of least squares, the equations of the best linear curves fitting the experimental points were determined, together with the standard deviations of the intercept and the slope. These equations are summarised in Table II.

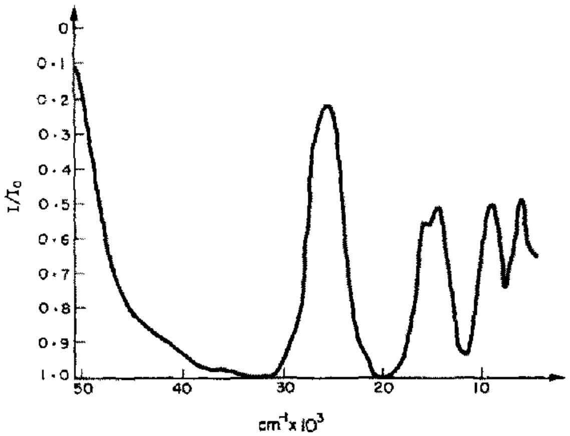

FIG. 2.—Absorption spectrum of nickel(II) perchlorate (10 g of Ni^{II}/litre)

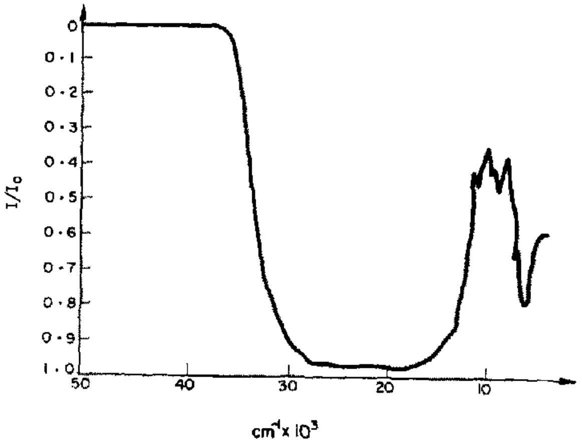

FIG. 3.—Absorption spectrum of iron(II) perchlorate (10 g of Fe^{II}/litre)

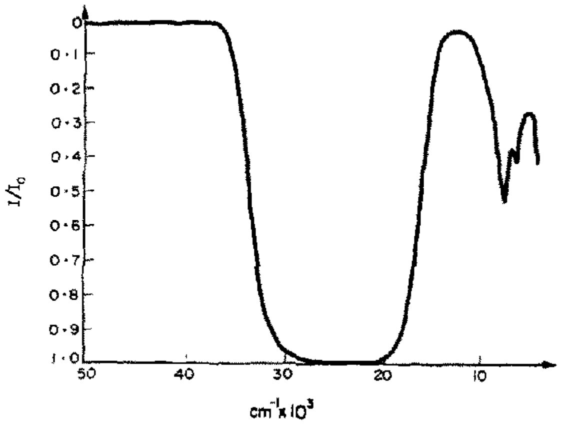

FIG. 4.—Absorption spectrum of copper(II) perchlorate (10 g of Cu^{II}/litre)

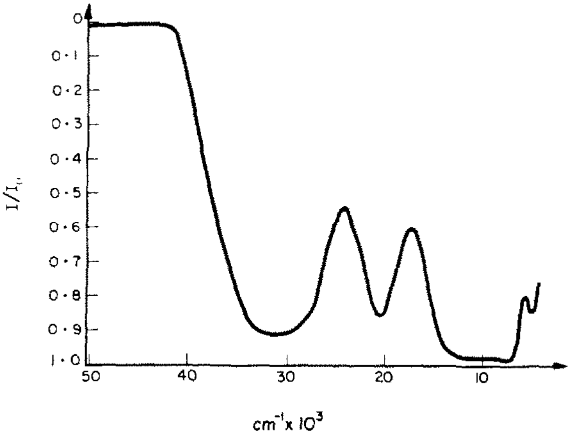

FIG. 5.—Absorption spectrum of chromium(III) perchlorate (1 g of Cr^{III}/litre)

TABLE I.—OPTICAL DENSITIES OF COBALT(II) PERCHLORATE SOLUTIONS

Concentration of cobalt, *g/litre*	Optical density measured against solutions having concentrations of cobalt, *g/litre*				
	0	6	12	18	24
0	0·0000				
2	0·168				
4	0·334				
6	0·506	0·0000			
8	0·674	0·1676			
10	0·816	0·3075			
12	1·045	0·5180	0·0000		
14	1·194	0·6825	0·1680		
16	1·372	0·8600	0·3393		
18	1·562	1·0440	0·4958	0·0000	
20	1·738		0·6720	0·1649	
22			0·8272	0·3244	
24			1·0030	0·4904	0·0000
26			1·1900	0·6865	0·1928
28			1·3625	0·8405	0·3537
30			1·5525	0·9604	0·5290
32					0·6778
34					0·8320
36					0·9835
38					1·1484

TABLE II.—CORRELATIONS BETWEEN CONCENTRATION AND OPTICAL DENSITY

Concentration of the reference solution, C_{ref}, *g/litre*	Best linear curve fitting the experimental points, E = ac + b	Standard deviation of	
		Intercept S_a	Slope S_a
0	0·0874 C + 0·0206	$\pm 1{\cdot}14 \times 10^{-2}$	$\pm 9{\cdot}20 \times 10^{-4}$
6	0·0873 C − 0·5362	$\pm 5{\cdot}01 \times 10^{-2}$	$\pm 3{\cdot}97 \times 10^{-3}$
12	0·0855 C − 11·0343	$\pm 8{\cdot}05 \times 10^{-3}$	$\pm 3{\cdot}7 \times 10^{-4}$
18	0·0820 C − 1·4736	$\pm 4{\cdot}39 \times 10^{-2}$	$\pm 1{\cdot}81 \times 10^{-3}$
24	0·0807 C − 1·9149	$\pm 3{\cdot}30 \times 10^{-2}$	$\pm 1{\cdot}10 \times 10^{-3}$

TABLE III.—ERRORS OF COBALT DETERMINATIONS BY DIFFERENTIAL SPECTROPHOTOMETRIC METHODS

Cobalt(II), *g/litre*	Photometric error, $\frac{S_E}{E - b} \times 100$, %	$\frac{S_b}{E - b} \times 100$, %	$\frac{S_a}{a}$, %	Total error, $\frac{S_c}{c} \times 100$, %
Measured against water ($C_{ref} = 0$)				
2	1·36	6·54	1·05	8·95
4	0·22	3·27		4·54
6	0·15	2·18		3·38
8	0	1·63		2·69
10	0·11	1·31		2·47
12	0·14	1·09		2·28
14	0·25	0·93		2·24
Measured against C_{ref} = 6 g of Co per litre of solution				
8	0·03	7·18	4·55	11·76
10	0·06	5·75		10·36
12	0·02	4·79		9·37
14	0·06	4·11		8·71
16	0·07	3·59		8·21
18	0·07	3·19		7·80
Measured against C_{ref} = 12 g of Co per litre of solution				
14	0·04	0·67	0·43	1·15
16	0·03	0·59		1·04
18	0·02	0·52		0·98
20	0·02	0·47		0·92
22	0·08	0·43		0·94
24	0·07	0·39		0·89
26	0·05	0·36		0·84
Measured against C_{ref} = 18 g of Co per litre of solution				
20	0·04	2·68	2·21	4·92
22	0·21	2·43		4·85
24	0·03	2·23		4·47
26	0·06	2·06		4·32
28	0·07	1·91		4·19
30	2·29	1·78		6·28
Measured against C_{ref} = 24 g of Co per litre of solution				
26	0·04	0·04	1·38	5·06
28	0·04	1·46		5·14
30	0·09	1·36		5·25
32	0·18	1·28		5·41
34	0·21	1·20		5·54
36	0·39	1·14		5·81
38	0·25	1·08		5·77

For all the sets of experiments the errors were then calculated, as described elsewhere.[9] It was there pointed out that the error of concentration determination by a differential spectrophotometric method depends on the measured optical density (*i.e.*, on the concentration itself) and can be expressed by the following equation:

$$\frac{S_C}{C} \times 100 = \frac{S_E}{E - b} \times 100 + \frac{S_b}{E - b} \times 100 + \frac{S_a}{a} \times 100.$$

Simplifications arising from the use of cells of 1 cm in length are included in this expression. Here S_b and S_a are the standard deviations of the intercept and slope, respectively, while the value S_E is the standard deviation of the optical density measurements. The value $\frac{S_E}{E - b} \times 100$ is the so-called photometric error; for the details of its calculation see the earlier paper.[9] The results of the error calculations are shown in Table III. The best results can be obtained using a solution containing 12 g of cobalt per litre as a reference. In this case the total error of the method is somewhat lower than 1%, while the "photometric error," *i.e.*, the coefficient of variation of the optical density measurement, is generally lower than 0·1%. The calibration curve is shown in Fig. 6.

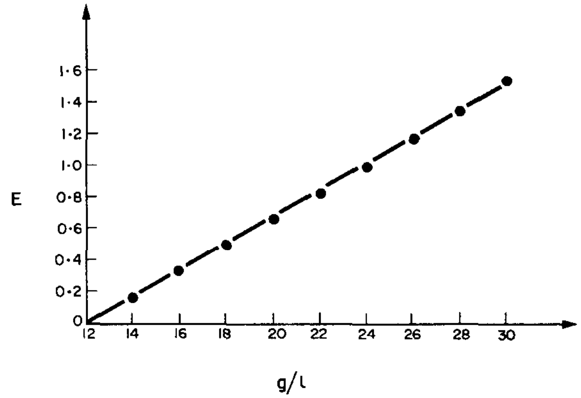

FIG. 6.—Calibration curve for cobalt determination ($E_{ref} = 0·975$)

Effect of foreign ions

Various metal ions (5, 10, 15 and 20 g per litre) were added to solutions containing 22 g of cobalt(II) per litre. The optical densities of the resulting solutions were measured against a reference solution containing 12 g per litre of cobalt.

The results of these measurements, together with the errors caused by the metal ions, are presented in Table IV. As may be seen from these results, the investigated metal ions reduce the optical density, causing about a 1% negative error in the concentration measurement. This excludes chromium which, as pointed out earlier, causes a very high positive error; this can be eliminated, however, by the oxidation of chromium to chromate. A further report will be given later on this, and on the differential spectrophotometric determination of chromium.

TABLE IV.—EFFECT OF FOREIGN ION

Ion	Concentration of foreign ion, *g/litre*	Optical density	Cobalt concentration, *g/litre*		Error caused by the ion	
			True value	Measured value	*g/litre*	%
Cr^{3+}	5	1·136	22·00	25·38	+3·38	+15·3
	10	1·518	22·00	20·84	+7·84	+35·6
	15	1·944	22·00	34·83	+12·83	+58·3
	20	2·245	22·00	38·35	+16·35	+74·3
Ni^{2+}	5	0·792	22·00	21·35	−0·65	−2·95
	10	0·820	22·00	21·68	−0·32	−1·45
	15	0·840	22·00	21·91	−0·09	−0·41
	20	0·820	22·00	21·68	−0·32	−1·45
Cu^{2+}	5	0·792	22·00	21·35	−0·65	−2·95
	10	0·776	22·00	21·17	−0·83	−3·77
	15	0·776	22·00	21·17	−0·83	−3·77
	20	0·814	22·00	21·61	−0·39	−1·77
Mn^{2+}	5	0·826	22·00	21·75	−0·25	−1·13
	10	0·831	22·00	21·81	−0·19	−0·86
	15	0·844	22·00	21·96	−0·04	−0·18
	20	0·835	22·00	21·85	−0·15	−0·68
Fe^{2+}	5	0·794	22·00	21·38	−0·62	−2·81
	10	0·824	22·00	21·73	−0·27	−1·22
	15	0·816	22·00	21·63	−0·37	−1·68
	20	0·828	22·00	21·77	−0·23	−1·04
Fe^{2+}	5	0·784	22·00	21·26	−0·74	−3·36
	10	0·823	22·00	21·71	−0·29	−1·31
	15	0·812	22·00	21·59	−0·41	−1·86
	20	0·832	22·00	21·82	−0·18	−0·81

Procedure

Dissolve a sample, containing about 1·5–2·5 g of cobalt in 50 ml of perchloric acid (1:3). If this cannot be done, dissolve the sample in any other way and evaporate the solution together with 50 ml of perchloric acid (1:3) until white perchloric acid fumes appear. Allow to cool, transfer the solution to a 100-ml volumetric flask, dilute with water to the mark, mix the solution well, and measure the optical density of the solution against a reference solution containing 12 g of cobalt per litre. Prepare a calibration graph with solutions containing 14–26 g of cobalt per litre. (The calibration solutions can be prepared as described under *Reagents*.) Chromium(III) causes high positive errors.

Zusammenfassung—Kobalt(II)-ionen können als Perchlorat mit einer spektralphotométrischen Differenzmethode bestimmt werden, wenn die Kobaltproben mit Überchlorsäure bis zum Erscheinen von Überchlorsäurenebeln eingedampft werden. Aus dem Absorptionsspektrum von Kobalt(II)-perchlorat wurde die Bande bei 19,600 cm^{-1} bzw. 511 mμ zur Bestimmung ausgewählt. Durch systematische Untersuchung der optimalen Konzentrationen ließ sich zeigen, daß die Konzentrationsbestimmung auf besser als 1% genau ausgeführt werden kann, wenn als Vergleichslösung eine Lösung mit 12 g Kobalt pro Liter verwendet wird. Der photometrische Fehler wird dabei kleiner als 0,1%. Der Einfluß einiger Fremdmetalle wurde untersucht; dreiwertiges Chrom gibt hohe Plusfehler. Andere untersuchte Metallionen haben keinen nennenswerten Einfluß.

Résumé—On peut doser les ions cobalt(II) par une méthode spectrophotométrique différentielle, à l'état de perchlorate, après évaporation des échantillons de cobalt avec de l'acide perchlorique, jusqu'à apparition de fumées de cet acide. Dans le spectre d'absorption du perchlorate

de cobalt(II), on a choisi, pour ce dosage, le pic situé à 19,600 cm^{-1} (511 millimicrons). Par l'étude systématique des limites de la concentration optimale, nous pouvons établir que, si l'on emploie une solution contenant 12 grammes de cobalt par litre comme référence, la détermination de la concentration peut être effectuée avec une erreur inférieure à 1%, cependant que l'erreur photométrique correspondante est inférieure à 0,1%. On a étudié l'influence de quelques mètaux ètrangers. Parmi ceux-ci le chrome, s'il est présent à l'état trivalent, est cause d'erreurs positives élevées. D'autres ions métalliques examinés n'ont pas d'effet significatif.

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THE DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, MANGANESE AND CALCIUM IN CEMENT BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—Various aspects of the determination of sodium, potassium, magnesium, manganese and calcium in cement by atomic-absorption spectrophotometry are described. For the determination of sodium, potassium and magnesium, both the calibration curve method and the addition method were found suitable because of the linear relationship between absorption and concentration. For the determination of manganese and calcium, the calibration curve method was found suitable. The calibration curves for sodium and potassium must be prepared to contain the same concentration of calcium as the analysed samples. The method is rapid, and no preliminary separations are necessary. The precision for the determination of sodium, potassium, magnesium and manganese is satisfactory, but is insufficient for calcium because of the large calcium content of cement.

INTRODUCTION

CURRENT methods for determining sodium, potassium, magnesium, manganese and calcium in cement include flame-emission techniques for sodium and potassium, titration with ethylenediaminetetra-acetic acid for magnesium and calcium, and a photometric technique for manganese. The phenomena of self and mutual interferences are observed in the flame-emission methods for alkalis.[1] Magnesium and manganese can also be determined by the flame-emission method. This method, however, is insufficiently sensitive.

The method of atomic-absorption spectrophotometry has been found suitable for use in routine analysis because of the marked freedom from interference, the high degree of accuracy and the simplicity of operation compared with other procedures. The aim of the work described in this paper was to examine the application of atomic-absorption spectrophotometry to the determination of sodium, potassium, magnesium, manganese and calcium in cement.

EXPERIMENTAL

Apparatus

The instrument used in this work was a Hitachi photoelectric spectrophotometer EPU-2, together with the Hitachi atomic-absorption attachment RA-1. Fig. 1 shows the optical system of the equipment. The electrical emission-compensation system was used to measure the intensity of the absorbed radiation without interference by emission from the vaporised sample.

The 7-cm fish tail burner, which could use an air-acetylene mixture, was water-cooled throughout the work. A sample solution was atomised into the spray chamber by an air stream. Acetylene was introduced directly into the burner, and mixed with the air from the spray chamber at the bottom of the burner.

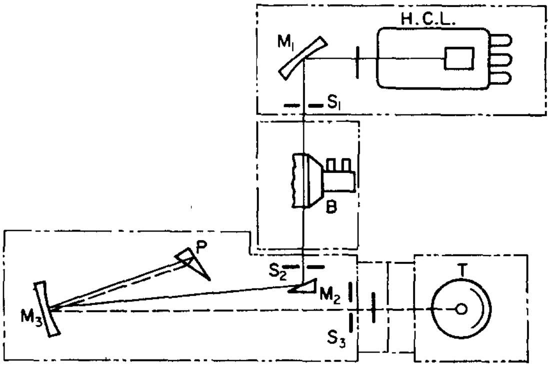

FIG. 1.—Optical system of Hitachi atomic absorption spectrophotometer.
H.C.L: Vapour discharge lamp or hollow-cathode lamp.
M_1, M_2, M_3: Mirrors.
S_1, S_2, S_3: Slits.
P: Prism.
T: Photomultiplier tube.

Operating conditions

The optimum conditions listed in Table I were established by preliminary work with solutions of pure sodium, potassium, magnesium, manganese and calcium.

Lamp current: The lowest possible lamp current was necessary for operating the magnesium or calcium cathode lamps. The magnesium hollow-cathode lamp (Mg-Al cathode) used in this work could not be operated with a current less than 30 mA because of the low light intensity of the lamp and poor sensitivity of the detector for low light intensity. The limit of detection of magnesium in the present method is 1 μg/ml. The effect of lamp current on magnesium absorption is shown in Fig. 2. However, the manganese lamp showed an increase of sensitivity with increase in lamp current (Table II).

Acetylene pressure: After the air pressure had been set at a constant value (1·4 Kg/cm^2), an examination was made of the effect on absorbance when the acetylene pressure was varied. The position of the passage of the beam from the hollow-cathode lamp through the flame was set at 6 mm above the burner top. The top of the inner cone was 4 mm above the burner top. No incandescence in the flame was observed at 0·32 Kg/cm^2 of acetylene. The top of the inner cone varied and the incandescence increased with increase of the acetylene pressure. The incandescence was visible in the whole of the flame at 0·46 Kg/cm^2 of acetylene. The results are summarised in Fig. 3. From these results it can be seen that an acetylene pressure from 0·32 to 0·46 Kg/cm^2 seems to have no effect on absorbance of sodium, magnesium and manganese. The absorbance of calcium varied,

TABLE I.—OPTIMUM CONDITIONS FOR DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, MANGANESE AND CALCIUM

Element	Light source	Lamp current, *m*A	Lines, *A*	Slit width, *mm*
Na	Sodium lamp (Toshiba)	—	5890	0·03
K	Potassium lamp (Hitachi)	—	7665	0·15
Mg	Hollow-cathode lamp (Mg-Al)*	30	2852	0·03
Mn	Hollow-cathode lamp (Mn-Cu)*	75	2798	0·15
Ca	Hollow-cathode lamp (Ca-Al)*	50	4225	0·035

* Hitachi hollow-cathode lamp.

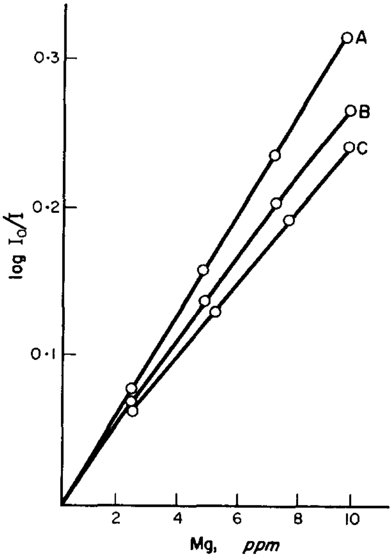

FIG. 2.—Effect of lamp current on magnesium absorption.
A: 30 mA.
B: 40 mA.
C: 50 mA.

and that of potassium varied slightly with variation in the acetylene pressure. The smallness of the region over which calcium atoms in the flame are abundant may be responsible for the variation of the absorbance with the variation of the height of the inner cone.

Slit width: Experiments were made at various slit widths. The slit widths shown in Table I were necessary to obtain satisfactory results. Because of the fluctuation of emission, the small slit width was adequate for compensating the emission from sodium. The increased absorption was obtained for manganese by opening the slit. Too wide a slit may result in unsatisfactory precision.

Relation between absorption and concentration of elements

Calibration curves were prepared for sodium, potassium, magnesium or manganese without calcium and containing calcium. The resulting curves are shown in Fig. 4. In the presence of calcium, depression of the sodium and potassium absorptions was observed. Therefore a calibration curve for the analysis of cement must be prepared by the addition of calcium. Magnesium absorption was not affected by the presence of 500 ppm of calcium. Larger amounts of calcium did affect the magnesium absorption. Sodium, potassium and magnesium can be determined by the addition method, because the curves indicate linearity, within the limits of experimental error, in the presence of calcium. Because slightly curved calibration curves were obtained for manganese and calcium,

TABLE II.—EFFECT OF LAMP CURRENT ON ABSORPTION FROM MANGANESE-COPPER HOLLOW-CATHODE LAMP

Lamp current, *m*A	Absorbance to manganese[a]
45	0·184
55	0·201
65	0·213
75	0·239
85	0·244
95	0·244

[a] 38 ppm.

the addition method was not useful for these elements in cement. The calibration curve for manganese could be prepared in the absence of calcium.

Reproducibility

Reproducibility was determined by repeatedly measuring the absorption of solutions containing sodium, potassium, magnesium, manganese or calcium. The coefficients of variation were 1·3% for a solution containing 5·8 ppm of sodium, 1·1% for a solution containing 23 ppm of potassium, 1·5% for a solution containing 7·4 ppm of magnesium, 2·3% for a solution containing 26 ppm of manganese and 1·2% for a solution containing 101 ppm of calcium.

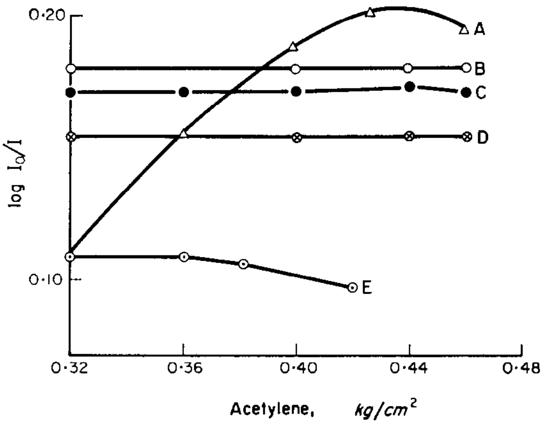

FIG. 3.—Effect of flame condition on the absorption of sodium, potassium, magnesium, manganese and calcium.

A: Calcium.
B: Sodium.
C: Manganese.
D: Magnesium.
E: Potassium.
(Air pressure kept constant at 1·4 Kg/cm^2.)

Interferences

A systematic investigation of interference effects was carried out, using various amounts of other elements. Apart from calcium, other elements, in the proportions normally found in cement, had no effect on the determination of sodium and potassium. The majority of elements did not interfere with the determination of manganese. Serious interference for magnesium in pure solution was observed in the presence of aluminium and silicon (Fig. 5). But these interference effects were not observed in the analysis of cement because of the suppression effect of calcium present in the sample on the aluminium (or silicon) interference. Phosphorus interference was observed in an air-propane flame, but not in an air-acetylene flame. Calcium absorption was interfered with in the presence of aluminium, silicon and phosphorus. The addition of large amounts of strontium was necessary to suppress the interference.

The solutions used for the analysis were about 0·24*M* in hydrochloric acid, and this was sufficient to give results lower by 20% than for solutions containing no free acid. Sulphuric or perchloric acid behaved in much the same way as hydrochloric acid.

Enhancement of absorption was obtained by the addition of acetic acid, alcohols and acetone to the solution. An increase in sensitivity of about 3-fold by the addition of 50% of propanol or about 5-fold by the addition of 50% of acetone was obtained, similar increases being obtained for the different elements.

Recommended procedure

Decompose 0·5 g of sample with 20 ml of hydrochloric acid (4*M*), heat and evaporate to dryness. Dissolve the residue in 5 ml of hydrochloric acid (4*M*) and filter through a filter paper into a 100-ml

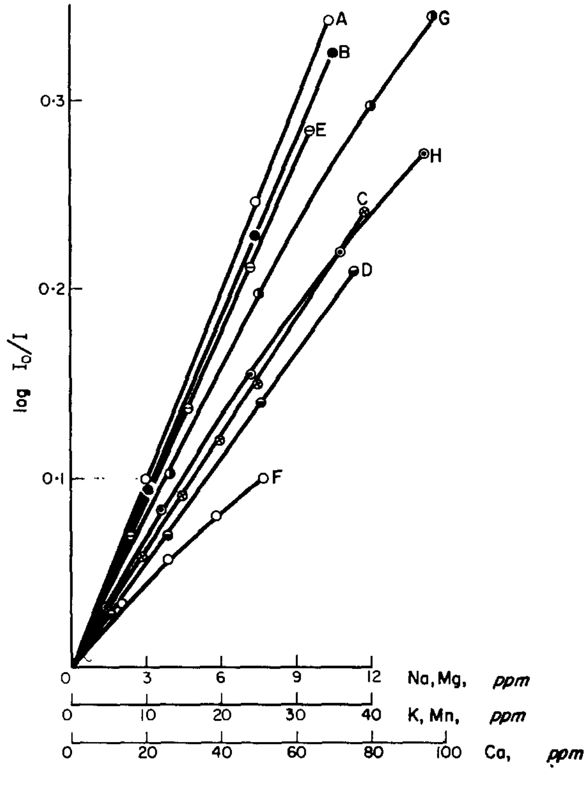

FIG. 4.—Typical calibration curves for sodium, potassium, magnesium, manganese and calcium.

A: Na without Ca.
B: Na containing 3350 ppm of Ca.
C: K without Ca
D: K containing 3350 ppm of Ca.
E: Mg without Ca and containing 503 ppm of Ca.
F: Mn without Ca and containing 3350 ppm of Ca.
G: Ca without Sr.
H: Ca containing 5000 ppm of Sr.

volumetric flask, washing with small volumes of hot water. Cool the filtrate and dilute to the mark with cold water.

Sodium: Take three 10-ml portions of the sample stock solution. Add 25 ml of solutions of sodium chloride containing 6, 12 and 18 ppm of sodium to these, and dilute each solution to 50 ml with water. Spray the solutions into the flame, and measure the absorbance. Plot the absorbance against the added amounts of sodium and read the amount of sodium in the original sample by extrapolating the linear relation curve of absorption *versus* concentration to zero absorbance.

Potassium: Take three 10-ml portions of the sample stock solution. Add 5 ml of solutions of potassium chloride containing 20, 40 and 60 ppm of potassium to these, and dilute each solution to 20 ml with water. Proceed as for sodium.

Magnesium: Take three 5-ml portions of the sample stock solution. Add 25 ml of solutions of magnesium chloride containing 4, 8 and 12 ppm of magnesium to these, and dilute each solution to 50 ml with water. Proceed as for sodium.

Manganese: Spray the sample stock solution into the flame and measure the absorbance. Obtain the manganese content of the sample by reference to a previously prepared calibration curve which was prepared from standard solutions containing the same concentration of acid as the sample solution.

Calcium: Take 5 ml of the sample stock solution. Add 50 ml of a solution of strontium chloride containing 25,000 ppm of strontium, and dilute to 250 ml with water. Proceed as for manganese.

Sodium, potassium and magnesium can also be determined using calibration curves as for manganese or calcium.

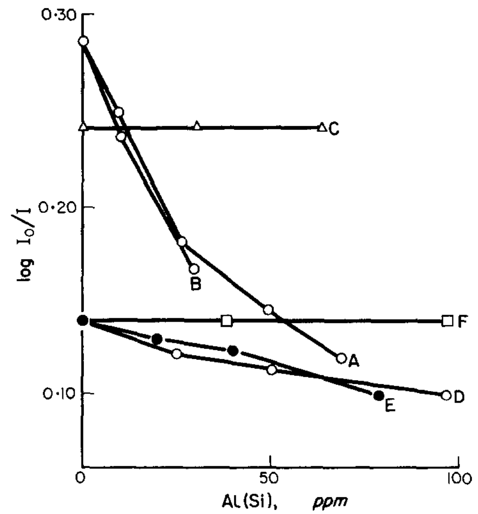

FIG. 5.—Effect of aluminium and silicon on the absorption of calcium and magnesium.

A: 76 ppm of Ca plus Al.
B: 76 ppm of Ca plus Si.
C: 76 ppm of Ca plus Al (or Si) plus 5000 ppm of Sr.
D: 4·8 ppm of Mg plus Al.
E: 4·8 ppm of Mg plus Si.
F: 4·8 ppm of Mg plus Al (or Si) plus 500 ppm of Ca.

RESULTS AND DISCUSSION

Two samples of cement were examined by the *Recommended procedure*. The results are shown in Table III.

Willis[2] has shown that the presence of sodium increases potassium absorption when using an air-coal gas flame. However, Malmstadt and Chambers[3] observed that a 20-fold excess of sodium did not interfere with potassium determination using an air-propane flame. The present authors also observed no interference of sodium on the determination of potassium.

Calcium lowered the slope of the calibration curves for sodium and potassium. The effect of calcium may be explained by assuming that the solid particles are only

TABLE III.—DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, MANGANESE AND CALCIUM IN CEMENT

Element determined	Sample I			Sample II		
	Atomic absorption		Other method,[a] %	Atomic absorption		Other method, %
	Addition method, %	Calibration curve method, %		Addition method, %	Calibration curve method, %	
Na	0·19, 0·20	0·19, 0·19	0·19	0·42, 0·41	0·40, 0·41	0·42
K	0·23, 0·23	0·25, 0·26	0·24	0·30, 0·29	0·32, 0·34	0·32
Mg	1·11, 1·13	1·11, 1·11	1·09	0·91, 0·93	0·91, 0·93	0·90
Mn	—	0·21, 0·21	0·20	—	0·028, 0·031	0·03
Ca	—	47·1, 46·4	46·08	—	45·3, 45·8	45·71

[a] Na and K: flame photometric; Mn: photometric; Ca and Mg: titrimetric.

partially evaporated and so liberate only a small proportion of the sodium atoms present. The magnitude of the effect of calcium depended on the atomiser. The use of a more efficient atomiser might suppress the effect of calcium. Rubeška *et al.*[4] have also discussed the effect of calcium on the sodium absorption.

Elwell and Gidley[5] described the marked effect of silicon on magnesium absorption using an air-coal gas flame. The present authors found no interference from silicon using an air-acetylene flame.

The addition method was found to be satisfactory for the analysis of cement for sodium, potassium and magnesium, because of the linear relationship between absorption and concentration. Results obtained by both addition and calibration curve methods, in the determination of sodium and magnesium in cement, are in good agreement; but results for potassium by the addition method are lower by 10% than those by the calibration curve method.

It was found, in agreement with David,[6] that interference from aluminium, silicon and phosphorus, in the determination of calcium, was suppressed by the addition of large amounts of strontium. The results for calcium would, however, be lacking in precision because of the large calcium content of cement.

Zusammenfassung—Verschiedene Gesichtspunkte bei der Bestimmung von Natrium, Kalium, Magnesium, Mangan und Calcium in Zement durch atomare Absorptionsspektralanalyse werden untersucht. Bei der Bestimmung von Natrium, Kalium und Magnesium wurden sowohl die Eichkurvenmethode als auch die Additionsmethode für geeignet befunden, da Absorption und Konzentration linear zusammenhängen. Zur Bestimmung von Mangan und Calcium ist die Eichkurvenmethode geeignet. Die Eichkurven für Natrium und Kalium mußten in Gegenwart der selben Calciumkonzentration wie in der Probe aufgenommen werden. Die Methode geht schnell und bedarf keiner vorausgehenden Trennung. Die Genauigkeit der Bestimmung von Natrium, Kalium, Magnesium und Mangan ist befriedigend, bei Calcium ist sie wegen des hohen Calciumgehaltes von Zement unzureichend.

Résumé—On décrit l'étude de divers aspects du dosage de sodium, potassium, magnésium, manganèse et calcium dans le ciment, au moyen de la spectrophotométrie d'absorption atomique. Pour le dosage de sodium, potassium et magnésium, les méthodes par courbe d'étalonnage et par addition sont toutes deux convenables, par suite de la relation linéaire entre l'absorption et la concentration. Pour le dosage de manganèse et calcium, la méthode par courbe d'étalonnage est convenable. Les courbes d'étalonnage pour le sodium et le potassium doivent être préparées en présence d'une concentration en calcium égale à celle des échantillons analysés. La méthode est rapide, et ne nécessite pas de séparations préliminaires. La précision est satisfaisante pour le dosage de sodium, potassium, magnésium et manganèse, mais elle est insuffisante pour le calcium par suite de la forte teneur du ciment en cet élément.

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CHELATING PROPERTIES OF THE CHELATING ION EXCHANGER DOWEX A-1*

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Summary—The properties and behaviour of the chelating ion exchanger Dowex A-1 have been studied when in contact with an aqueous solution containing metal ions complexed with aminocarboxylic ligands. The stability constants of the metal ion complexes with the resin have been determined as well as the structure of the complexes formed by the metal ions, the resin and the ligands in the solution. Dowex A-1 behaves as a solid complexing agent and forms stable 1:1 complexes with metal ions.

FUNDAMENTAL research carried out so far on Dowex A-1, a chelating ion exchanger, has dealt mainly with kinetics[1,2,3], equilibrium studies,[4] separation possibilities,[5] and the effects of the medium.[6]

In the present work an attempt is made to solve problems of a new kind, connected with the mechanism of binding metal ions to this resin and with the stability of the complexes formed. This raises a number of secondary problems, such as the structure of the resin, the ligands entering together with the metal ions, the definition of the order of affinity of the metals, the connection between the stability of the metal complexes in solution and their adsorbability, *etc.* Answers to these fundamental questions should further applied analytical research on Dowex A-1 and contribute towards an understanding of complexation mechanisms in general.

It is proposed to show how information on the structure of the complexes and their stability may be obtained with the help of simple equilibrium experiments in a solid-liquid system (the solid being Dowex A-1, the liquid being metal ions in aqueous solution bound to aminocarboxylic ligands) where chelation takes place in both phases, which are easily separable and analysable after equilibrium has been attained.

DISCUSSION

Structural considerations

Much information regarding the structure of Dowex A-1 is obtainable from elemental analysis of the sodium form of the resin. The composition of a homogeneous sample specimen of the sodium resin, when dried at 100°, is as follows:

C—52·91%
H— 6·26%
N— 3·50%
O—25·63%
Na—11·7%.

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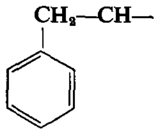
* Part of an M.Sc. thesis to be presented by Mrs. H. Loewenschuss to the Senate of the Technion.

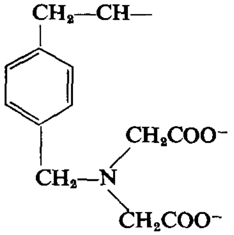
Dowex A-1 is a polymer composed of styrene-divinylbenzene rings, some of which are substituted by iminodiacetic acid (IDAA).

(a) *Calculation of number of substituted rings.* Assume that the resin is composed of two kinds of rings : A-rings, aromatic rings which have no functional group,



C_8H_8 (molecular weight 104)

and B-rings, aromatic rings substituted by IDAA.



$C_{13}H_{13}NO_4$ (molecular weight 247)

Because nitrogen is present only in the substituted rings, the number of B-rings may be calculated on the strength of the nitrogen content. The content of 3·5% of nitrogen means that each 1 g of resin contains 2·5 mmole of nitrogen or 2·5 mmole of B-rings.

One g of resin, therefore, contains 617 mg of B-rings (2·5 × 247 = 617 mg), but the balance does not give the number of A-rings, because in the substance dried at 100° water molecules are still bound as ligands to the metal ion. The required data will, however, be provided by the material balance of carbon atoms.

(b) *Carbon balance.* The carbon content being 52·91%, 1 g of resin contains 44 mmole of carbon, of which the B-rings have taken up 2·5 × 13 = 32·5 mmole of carbon. The balance (44 − 32·5 = 11·5 mmole of carbon) is available for A-rings. From this it may be inferred that of every 8 rings there are 5 substituted ones,* *i.e.*, not all rings are substituted. The chelating ligands in the resin are, therefore, well spaced, so that a metal ion is unlikely to be bound to two IDAA ligands from the resin.

(c) *Calculation of water content.*

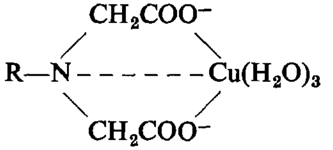
One g of resin contains 2·5 B-rings = 617 mg
1·45 A-rings = 150·8 mg
11·7% of Na = 117 mg
884·8 mg

* The basis of this inference is as follows. B-rings contain 13 carbon atoms, so that the amount taken up by them is 13 × 2·5 = 32·5 mmole of carbon. In the A-rings, on the other hand, there are only 8 carbon atoms and, because only 44 − 32·5 = 11·5 mmole are left, there can only be 11·5/8 = 1·45 A-rings. From this it is concluded that for every 8 rings in the resin there are 5 substituted ones.

giving a balance of 115 mg of water. The fact that water remains in the resin and does not evaporate at 100° is interesting in itself, because it proves the penetration of the ligands, together with the metal ions, from the solution into the resin matrix.

(d) *Oxygen balance.* Subtracting the proportion bound to water (10·2%) from the over-all percentage of oxygen (25·63%), for each mmole of nitrogen there are 4 mmole of oxygen, which corresponds to the structural considerations of the rings substituted by IDAA.

(e) *Structure of resin when containing copper.* Elemental analysis of the copper-containing resin produces results similar to the sodium-containing resin, so far as carbon, nitrogen, oxygen and hydrogen contents are concerned. The water balance shows that for each mmole of copper in the resin 3 molecules of water enter. This gives rise to the assumption that the structure of the complex formed by copper and Dowex A-1 is as follows



where R is the polymer matrix. Copper is thus seen to enter the resin in an octahedral configuration,[15] and it will be shown later that if the copper in the solution is bound to chelating ligands, it will also enter the resin with these ligands instead of with water.

Stoichiometry

In order to understand the stoichiometry of the reactions between the metal ions and Dowex A-1, measurements of the maximum capacity of the resin may be used. Experimentally, this is done by bringing a known weight of dry resin in contact with solutions of increasing concentration of the metal ion. Experiments were conducted with Cu^{2+}, Pb^{2+}, Fe^{3+} and Th^{4+} ions, and in all cases similar results were obtained, *viz.*, 2·4–2·5 mmole of metal ions/g of Dowex A-1. Because 1 g of resin contains 2·5 mmole of IDAA, it is found that metal ions are complexed by the resin in the stoichiometric ratio of 1:1, independent of valency. This is similar to the stoichiometry of the reactions of EDTA with metal ions in solution.

A marked difference in behaviour is seen to exist between IDAA in solution and in the resin matrix. In solution the metal ions combine with more than 1 molecule of IDAA, in accordance with their valency, while in the resin complexation is accomplished in a single step, from which it may be concluded that the complexes in the resin are more stable than those formed in solution.

Metal and ligand sorption

In a system consisting of a certain quantity of dry resin in contact with a solution containing a few mmole of metal ions bound to an excess of a tridentate ligand, such as IDAA, the relation between the concentration of ligands in solution and the resin's adsorptive capacity for metal ions must be established. Obviously, increasing the concentration of the ligand in the solution reduces the concentration of ions in the resin because of competing complexation. Experiments have shown two important facts:

(a) A definite quantitative relation exists between the stability constants of the metal ion complexes with the ligands in solution and their adsorbability on the resin.

(b) Stoichiometric penetration takes place of 1 IDAA molecule together with 1 metal ion.

The significant equilibria involved in this experimental system are as follows

In Solution

$$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML_2};\ k_2 = \frac{(\mathrm{ML_2})}{(\mathrm{ML})(\mathrm{L})} \tag{1}$$

In Resin Phase

$$\mathrm{ML} + \mathrm{R} \rightleftharpoons \mathrm{MLR};\ \mathrm{K_{MLR}} = \frac{(\mathrm{MLR})}{(\mathrm{ML})(\mathrm{R})} \tag{2}$$

Over-all Reaction

$$\mathrm{ML_2} + \mathrm{R} \rightleftharpoons \mathrm{MLR} + \mathrm{L};\ \mathrm{K_{over\text{-}all}} = \frac{(\mathrm{MLR})(\mathrm{L})}{(\mathrm{ML_2})(\mathrm{R})} = \frac{\mathrm{K_{MLR}}}{k_2} \tag{3}$$

or expressed logarithmically

$$\log(\mathrm{L}) = \log\frac{(\mathrm{ML_2})(\mathrm{R})}{(\mathrm{MLR})} + \log \mathrm{K_{over\text{-}all}} \tag{3a}$$

where L represents the polydentate ligand and R represents the polymer matrix.

The quantities appearing in equation (3a) are defined as follows:

(MLR) = The quantity of metal present in the resin after the system has reached equilibrium.

(L) = The quantity of uncomplexed ligand (the quantity of ligand introduced minus the quantity of ligand bound to the metal).

$(\mathrm{ML_2})$ = The quantity of metal complex remaining in solution after phase separation; this may be calculated by subtracting the quantity of metal bound to the resin from the total quantity of metal introduced into the system.

(R) = The quantity of resin not bound to the complexing metal ion; this may be calculated by subtracting the quantity of (MLR) from the maximum capacity of the resin.

The quantities in the brackets denote the concentrations of the various species. The concentrations of the constituents in the solution ($\mathrm{ML_2}$, ML and L) are expressed in mmole/100 ml, while those in the solid phase are in mmole of metal ions (which is equivalent to the number of mmole of chelating groups in the resin) (*cf*. Table I). $\mathrm{K_{over\text{-}all}}$ is an apparent constant. It is the quotient of the stability of the mixed complex in the resin phase divided by the stability of the complex in the solution. If the proposed mechanism is correct, the graphic correlation of log (L) *vs*. log $[(\mathrm{ML_2})(\mathrm{R})]/(\mathrm{MLR})$ should be a straight line of unit slope, the intersection of which with the x-axis gives $\mathrm{K_{over\text{-}all}}$; k_2 may be found from the literature, hence $\mathrm{K_{MLR}}$

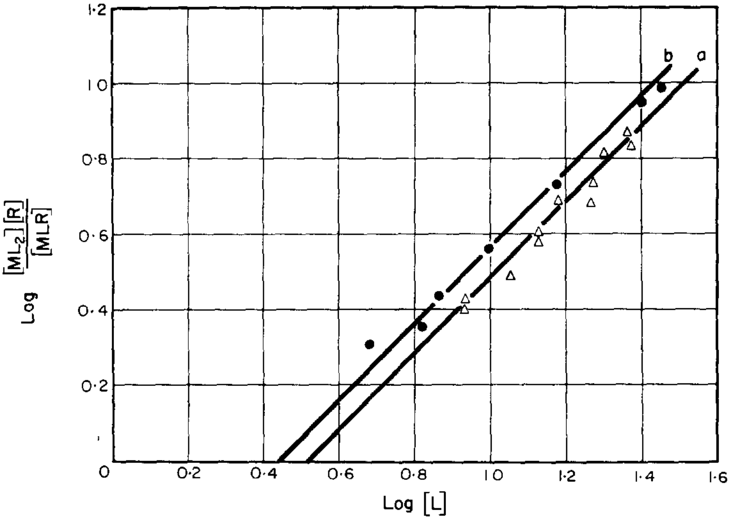


Fig. 1.—Graphical correlations from equilibrium measurements of:
(a) Cu^{2+} with IDAA in contact with 0·5-g portions of Dowex A-1.
(b) Ni^{2+} with IDAA in contact with 0·5-g portions of Dowex A-1.

may be determined. Fig. 1 shows that the results of the experiments with copper and nickel bound to IDAA confirm the above theoretical considerations.

Similar experiments were made by binding the copper ion to other ligands, such as glycine and glutamic acid. Here too, straight lines were obtained with a slope close to unity (Fig. 2). The slight deviations from unit slope are probably from neglecting the activity coefficients.

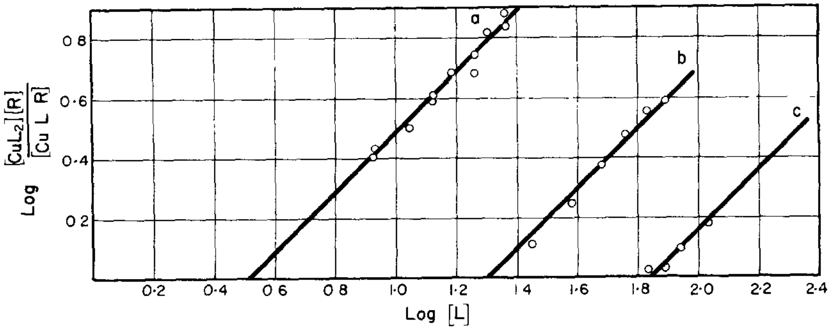
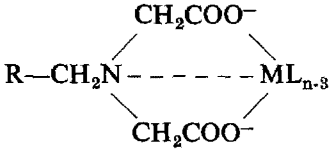


Fig. 2.—Equilibrium measurements of copper ions with various aminocarboxylic acid ligands [equation (3a)]:
(a) IDAA,
(b) glutamic acid,
(c) glycine.

Ligand sorption in cation exchangers was first described by Stokes and Walton[7] and its theory elaborated by Helfferich,[8,9] who made use of the phenomenon for ligand exchange and separations in columns containing metal ions bound to ion exchangers.

It can now be definitely concluded that the structure of the complex formed is



L denotes the additional ligand to which the metal is bound in the resin phase. It may consist of water molecules, an anion of the salt of the metal in the solution or an aminocarboxylic ligand, as was shown before. n is the co-ordination number of the metal.

*Determination of stability constants of metal ions with Dowex A-*1

So far the formation of mixed complexes consisting of metal ions, Dowex A-1 and bi- or tridentate ligands has been discussed. Now the order of affinity of the metals to the resin must be established.

When an aqueous solution containing several metal ions is passed through a column of Dowex A-1, the ions will enter the resin according to a certain order, which depends on the stability constants of the metals with the resin. In order to determine a constant of the type K_{MR}, the resin must be brought into contact with a solution containing metal ions bound to a large polydentate ligand, such as EDTA or the like, which, because of its bulky molecules and the stereospecificity of its complexes, will not enter the resin, as did IDAA or glycine. The result will be that the hydrated metal ion alone will enter the resin.

In this system two competing complexation reactions take place

$$M + Y \rightleftharpoons MY; \;\; K_{MY} = \frac{(MY)}{(M)\,(Y)} \tag{4}$$

$$M + R \rightleftharpoons MR; \;\; K_{MR} = \frac{(MR)}{(M)\,(R)} \tag{5}$$

$$MY + R \rightleftharpoons MR + Y; \;\; K_{\text{over-all}} = \frac{(MR)\,(Y)}{(MY)\,(R)} = \frac{K_{MR}}{K_{MY}} \tag{6}$$

$$\log (R) = \log \frac{(MR)\,(Y)}{(MY)} - \log K_{\text{over-all}} \tag{6a}$$

Y denotes the large polydentate ligand to which the metal ion in the solution is bound. In the present case the ligand selected was *N*-hydroxyethylenediaminetriacetic acid (HEDTA). R again denotes the polymer matrix.

Analogously to K_{MLR}, K_{MR} may be found by graphic correlation of log (R) *vs.* log [(MR) (Y)]/(MY). In Fig. 3 the constants for nickel and copper within the resin are determined experimentally. For these equilibrium measurements HEDTA was chosen because it binds these metal ions more strongly than Dowex A-1 (log $K_{NiY} = 17{\cdot}0$; log $K_{CuY} = 17{\cdot}4$) and gives convenient distribution ratios of the ions between the resin and the solution. The lines obtained in Fig. 3 are straight

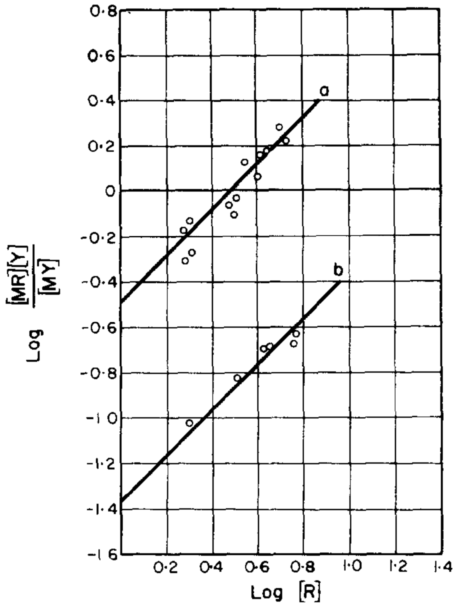


FIG. 3.—Graphical determination of stability constants [equation (6a)] of:
(a) Cu^{2+} with Dowex A-1,
(b) Ni^{2+} with Dowex A-1.

and of unit slope, which proves the correctness of the proposed mechanism [equations (4) and (5)] and also the fact that a ligand of the type HEDTA does not enter the resin. A further conclusion to be drawn is that Dowex A-1 behaves similarly to the complexation agents in the solution, and that its property to bind the metals to the solid phase makes it a convenient and effective means for the study of complexation mechanisms.

EXPERIMENTAL

Reagents

0·1*M* *Standard copper solution:* Prepared by dissolving 7·594 g of reagent-grade copper^{II} oxide in nitric acid (1 : 1), evaporating excess acid and making up to 1 litre.

0·1*M* *Standard nickel nitrate solution:* Prepared by dissolving 29·08 g of reagent grade $Ni(NO_3)_2{\cdot}6H_2O$ in distilled water and making up to 1 litre.

0·1*M* *Standard EDTA solution:* Prepared by dissolving 37·21 g of pure disodium dihydrogen ethylenediaminetetra-acetate dihydrate in distilled water and making up to 1 litre.

Complexing agents

Dowex A-1 chelating resin was prepared in the sodium form from the Dow Chemical Co. product and dried at 100°. Glycine, monosodium glutamate, iminodiacetic acid (IDAA) and *N*-hydroxyethylenediaminetriacetic acid (HEDTA) were used as analytical-grade solids.

Procedure for distribution measurements of cations from solutions containing complexing ligands (Figs. 1 *and* 2)

Weighed portions of the dried sodium form of the resin (exactly 500 mg) were placed into 250-ml beakers. To each beaker were added 100 ml of solution containing 1 mmole of copper or nickel ion and varying quantities of the complexing ligands (5–40 mmole). The pH of all solutions was adjusted to 8·5 to diminish the "pH effect" (the effect of the hydrogen ions on the stability of the complexes). The solutions were magnetically stirred for 2 hr in a water bath of 70° and for a further 2 hr at room temperature. Experience has shown that heating considerably speeds up the reaction. Without heating, equilibrium is reached after not less than 17–18 hr. After equilibrium the phases were separated at room temperature (23–27°) by means of filtration and the metal ions eluted from the resin with 6*M* nitric acid. Copper was determined polarographically with EDTA,[6] and nickel gravimetrically with dimethylglyoxime.

Knowing the general quantity of metal ions and ligand introduced into the system and the quantity of the metal ions adsorbed by the resin, all of the other quantities required for the construction of Figs. 1 and 2 may be calculated.

Procedure for determination of stability constants

The experimental set-up is identical with that described in the previous paragraph, with the exception that because log (R) appears in the abscissa of Fig. 3, different quantities of resin had to be weighed. Table I shows the concentrations of the different components with which the required data for line (a) of Fig. 3 were obtained.

TABLE I.—EQUILIBRIUM MEASUREMENTS FOR THE COPPER-HEDTA SYSTEM

No.	Cu^{2+} taken, *mmole*$_3$ 100 *ml*	HEDTA taken, *mmole*$_3$ 100 *ml*	Resin$_3$ *g*	pH	Cu^{2+} found in resin phase (Cu R), *mmole*	Uncomplexed HEDTA left in solution (Y), *mmole*	Cu-HEDTA found in solution (MY), *mmole*	Resin[a] left uncomplexed (R), *mmole*
1	0·500	1·000	1·000	10·6	0·250	0·750	0·250	2·150
2	0·500	1·000	1·250	10·7	0·265	0·765	0·235	2·735
3	1·000	1·000	1·500	10·3	0·591	0·591	0·409	3·009
4	1·000	1·000	2·000	10·2	0·678	0·678	0·322	4·122
5	1·000	2·000	1·000	10·3	0·334	1·334	0·666	2·066
6	1·000	2·000	2·000	10·6	0·500	1·500	0·500	4·300
7	1·000	2·000	2·500	10·2	0·600	1·600	0·400	5·400
8	1·500	3·000	1·500	10·1	0·452	1·952	1·048	3·148
9	1·500	3·000	2·000	9·9	0·543	2·043	0·957	4·257
10	1·500	3·000	2·500	10·0	0·641	2·141	0·859	5·359
11	1·500	3·500	1·000	10·1	0·292	2·292	1·208	2·108
12	1·500	3·500	1·500	10·0	0·408	2·408	1·092	3·192

[a] Calculated by subtracting (CuR) from the maximum capacity of the resin (2·4 mmole/g).

RESULTS

Table II summarises the numerical results obtained for the stability constants of the mixed metal-ligand-resin complexes and of the hydrated nickel and copper ions with Dowex A-1. For comparison, stability constants of these metals with the same ligands (IDAA, glycine, glutamic acid and HEDTA) in aqueous solutions, taken from the literature, are also quoted.

The constants for reactions of the type $ML + R \rightleftharpoons MLR$ were calculated from the intercepts with the x-axis in Figs. 1 and 2, utilising equation (3a).

The constants for reactions of the type $M + L + R \rightleftharpoons MLR$ were taken as the sum of two reactions

$$M + L \rightleftharpoons ML \text{ (from the literature)}$$

$$ML + R \rightleftharpoons MLR.$$

The constants for reactions of the type $M + R \rightleftharpoons MR$ were calculated from the intercepts with the y-axis in Fig. 3.

From the numerical results shown in Table II two important conclusions may be drawn:

(1) The stability constants of mixed complexes of the type MLR are higher than the sum of the stepwise complexation constants of the metals with the ligands in the solution. This was also proved for the mixed complexes in aqueous solution of the metal chelonates with ammonia and the hydroxyl and hydrogen ions, the stability of which is greater than that of the pure metal chelonates.[14]

(2) The stability constants of complexes of the type MR are lower than those of the corresponding metals with HEDTA, but higher than the sum of the stability

TABLE II.—STABILITY CONSTANTS OF COPPER AND NICKEL WITH SOME AMINOCARBOXYLIC LIGANDS

Reaction investigated	Stability constant (log K)	Reference
[a]Cu + IDAA ⇌ Cu—IDAA	10·55	10
[a]Cu − IDAA + IDAA ⇌ $\mathrm{Cu(IDAA)_2}$	5·65	10
Cu − IDAA + R ⇌ Cu(IDAA)R	6·17	
Cu + IDAA + R ⇌ Cu(IDAA)R	16·72	
[a]Cu + Glycine ⇌ Cu—Glycine	8·38	11
[a]Cu − Glycine + Glycine ⇌ $\mathrm{Cu(Glycine)_2}$	6·87	11
Cu − Glycine + R ⇌ Cu(Glycine)T	8·72	
Cu + Glycine + R ⇌ Cu(Glycine)R	17·10	
[a]Cu + Glutamate ⇌ Cu—(Glutamate)	7·85	12
[a]Cu − Glutamate + Glutamate ⇌ $\mathrm{Cu(Glutamate)_2}$	6·45	12
Cu − Glutamate + R ⇌ Cu(Glutamate)R	7·76	
Cu + Glutamate + R ⇌ Cu(Glutamate)R	15·61	
[a]Ni + IDAA ⇌ Ni—IDAA	8·21	10
[a]Ni − IDAA + IDAA ⇌ $\mathrm{Ni(IDAA)_2}$	6·35	10
Ni − IDAA + R ⇌ Ni(IDAA)R	6·79	
Ni + IDAA + R ⇌ Ni(IDAA)R	15·00	
[a]Cu + HEDTA ⇌ Cu—HEDTA	17·4	13
Cu + R ⇌ Cu—R	16·9	
[a]Ni + HEDTA ⇌ Ni—HEDTA	17·0	13
Ni + R ⇌ Ni—R	15·61	

[a] Numerical data taken from the literature.

constants of the metals with IDAA in aqueous solution. The reason for this is that in an aqueous solution binding to IDAA is accomplished in two steps, but in the resin in one step only.

CONCLUSION

In this work an attempt has been made to extend the general knowledge of chelating ion exchangers as regards their structure and to obtain information on the stability of the complexes formed between two transition metals and Dowex-A1. A connection has been shown to exist between complexation in solution and the adsorbability of the metal ions on the resin. The adsorption of ligands on the resin has been proved quantitatively.

The experimental results obtained in this work may be obtained by other experimental set-ups. Because the ligands used are of high molecular weight, data on ligand sorption may be inferred from measuring the increase in weight of the resin after adsorption. Another possibility is to use ligands labelled with carbon-14 and to measure their activity in the resin. Some tentative experiments were made in these two directions, but the method of graphic correlations appeared to be both the most accurate and the simplest.

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Zusammenfassung—Eigenschaften und Verhalten des chelatbildenden Ionenaustauschers Dowex A-1 wurden im Kontakt mit einer wäßrigen Lösung untersucht, die komplex an Aminocarbonsäuren gebundene Metallionen enthielt. Die Stabilitätskonstanten der Metallkomplexe des Harzes wurden bestimmt sowie die Struktur der Komplexe aus Metallionen, Harz und Liganden. Dowex A-1 verhält sich wie ein fester Komplexbildner und gibt mit Metallionen stabile 1:1-Komplexe.

Résumé—On a étudié les propriétés et le comportement de l'échangeur d'ions chélatant Dowex A-1, lorsqu'il est en contact avec une solution aqueuse contenant des ions métalliques fixés par coordination à des groupes aminocarboxyliques. On a déterminé les constantes de stabilité des complexes que donnent les ions métalliques avec la résine, ainsi que la structure des complexes formés par les ions métalliques, la résine et les agents coordinants dans la solution. La Dowex A-1 se comporte comme un agent complexant solide, et forme des complexes stables 1:1 avec les ions métalliques.

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A STUDY OF THE OXIDATION OF MANGANESE(II) AND CHROMIUM(III) IONS BY SILVER(II) OXIDE

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Summary—A study has been made of the oxidation of manganese(II) and chromium(III) solutions by silver(II) oxide in perchloric acid medium. Both the efficiency and the rate of the oxidation process were found to vary with the concentration of reductant, the amount of AgO added, the temperature, the acidity and the concentration of univalent silver ions in the solution. The inefficiency of the oxidation process can be attributed to the simultaneous formation of oxygen. The results are discussed in terms of a possible reaction mechanism, and the optimum conditions for oxidations using AgO are indicated.

INTRODUCTION

MOST titrimetric methods for the determination of manganese and chromium recommend pre-oxidation of these elements by ammonium persulphate in the presence of silver(I) ion as catalyst. The nature of the silver intermediate in these oxidations is not yet established. There is evidence to support both a bivalent and a tervalent species[1] and it has been suggested that the two higher valency silver species may be related through the equilibrium:

$$Ag^{3+} + Ag^{+} \rightleftharpoons 2Ag^{2+}.$$

The silver(II) ion in solution is a powerful oxidising agent and in the cold almost instantaneously oxidises manganous salts to permanganate[2] and chromic salts to chromate.[3] The bivalent silver ion is also reduced by water, yielding oxygen and silver(I) ion. The rate of reduction by water has been found to be dependent on the concentration and nature of the acid present.[4,5] Dissolution of silver(II) oxide in acids yields bivalent silver ions.[6]

The use of silver(II) oxide as an oxidimetric reagent for the determination of manganese, cerium and chromium has been examined by Lingane and Davis.[7] Procedures based on this reagent were found to be faster and more convenient than the classical procedures, and excellent results were obtained in determinations of manganese and chromium in aluminium and iron(II) alloys. Before this study, AgO had been used in microanalysis by Kimira and Murakim[8] for the determination of manganese and cerium, and by Tanaka[9,10] for the determination of chromium, manganese and vanadium.

These applications indicate the probable value of silver(II) oxide as an analytical reagent, but more fundamental information on oxidations by this reagent is required. This paper describes the results obtained in a study of the oxidation by silver(II) oxide of manganese(II) and chromium(III) salts in perchloric acid solution. Perchloric acid was chosen as the solvent medium to avoid complications, such as the tendency of chromium salts to form sulphato complexes in sulphuric acid solutions, and the tendency of argentic silver to form nitrate complexes in nitric acid solutions.[4]

EXPERIMENTAL

Reagents

The silver(II) oxide used was prepared according to the directions of Hammer and Kleinberg.[11] Standard manganese(II) solutions were prepared from May and Baker R-grade manganese sulphate. The solutions were standardised by oxidation to permanganate with potassium periodate, followed by spectrophotometric measurement of colour intensity.

Chromium(III) perchlorate solutions were prepared by dissolving freshly precipitated hydrated chromium(III) oxide in dilute perchloric acid solutions. The solutions were standardised colorimetrically after oxidation of the chromium by ammonium persulphate using silver ion catalyst. The excess acid present was determined by titration against standard borax solution.

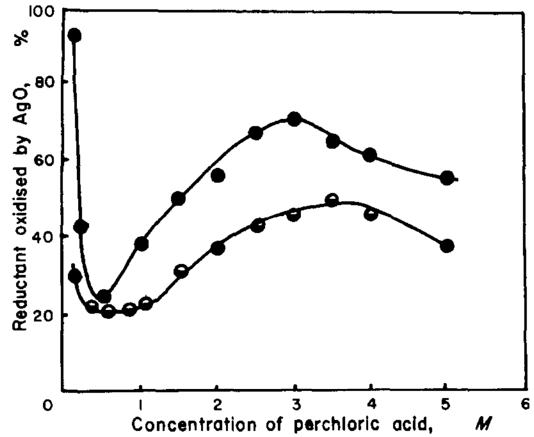

FIG. 1.—The effect of acidity on the amount of metal ion oxidised.
⊖—0·55 mg of Mn^{2+} treated with 0·021 g of AgO.
●—0·70 mg of Cr^{3+} treated with 0·032 g of AgO.

Perchloric acid solutions of differing concentrations were prepared by dilution of May and Baker 61% and 72% R-grade perchloric acid. The solutions were standardised against standard borax solution.

Apparatus

The apparatus used in the investigation was a water-jacketed reaction cell, fitted with a drain tap, and stirred by a magnetic stirrer. During the studies water was circulated around the cell from a constant temperature tank.

A Coleman Model 14 Spectrophotometer and a Unicam SP 500 Spectrophotometer were used for colorimetric measurements.

Procedure

For equilibrium studies, reaction mixtures were prepared containing varying amounts of reducing agent (0·004–0·050 mg/ml for manganese and 0·0075–0·048 mg/ml for chromium) and varying amounts of acid (0·1–5·5*M*).

Aliquots (25 ml) of these reaction mixtures were added to the thermostatted reaction cell and stirred to reach thermal equilibrium. Varying amounts of AgO (0·004–0·085 g for manganese and 0·007–0·145 g for chromium) were weighed into small plastic boats. These boats were placed on the surface of the solutions and were subsequently submerged by the stirring action. When the AgO had completely dissolved, the resulting solutions were run off into a receiving vessel and the intensity of colour was measured with a spectrophotometer. The intensity of the permanganate ion was measured at 545 mμ in the Coleman instrument and the dichromate ion was measured at 390 mμ using the Unicam SP 500 instrument. The concentrations of the oxidised products were determined from appropriate calibration graphs. The results of these studies are summarised in Figs. 1 and 2.

Varying amounts of silver(I) ion were added to a series of solutions containing a fixed amount of manganese(II) or chromium(III) salts in solutions 3·0–3·5*M* in respect of perchloric acid. The results obtained on adding a constant amount of AgO are summarised in Fig. 3.

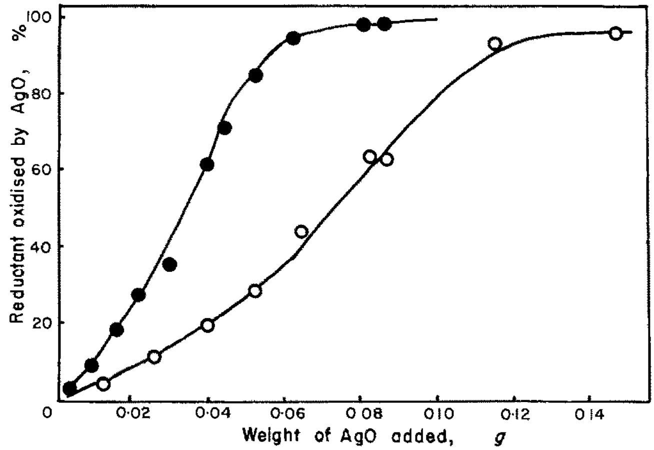

FIG. 2.—The effect of varying weights of silver(II) oxide on the percentage of metal salt oxidised.

●—0·85 mg of Mn^{2+} in 50 ml of 3·5M $HClO_4$; t = 25°; theoretical weight of AgO required for complete oxidation 0·010 g.

○—1·0 mg of Cr^{3+} in 50 ml of 3·0M $HClO_4$; t = 20°; theoretical weight of AgO required for complete oxidation 0·007 g.

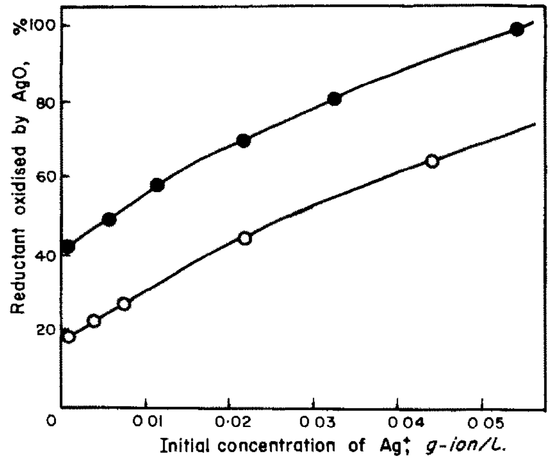

FIG. 3.—The effect of adding silver(I) ion on the percentage of metal salt oxidised.

○—0·5 mg of Mn^{2+} in 25 ml of 1M $HClO_4$ + 0·022 g of AgO; t = 25°.

●—0·7 mg of Cr^{3+} in 25 ml of 1M $HClO_4$ + 0·037 g of AgO; t = 20°.

Finally, oxidations were carried out at different temperatures and the effect of temperature is shown in Fig. 4.

Some studies of the rate of oxidation of the chromium salt at 5° were made, using solutions having acidities varying in concentration from 0·2M to 1·0M. A weighed amount of AgO was added to the solutions in the reaction cell and a sample was extracted from the cell after varying periods of time by means of a pipette fitted with a cotton wool plug to trap particles of unreacted solid. The absorbance of each sample extracted was measured at the appropriate wavelength, and the amount of metal ion oxidised was determined from the calibration graph. These kinetic results were recorded and subsequently treated as a pseudo first order reaction in order to yield the values of apparent rate constants listed in Table I.

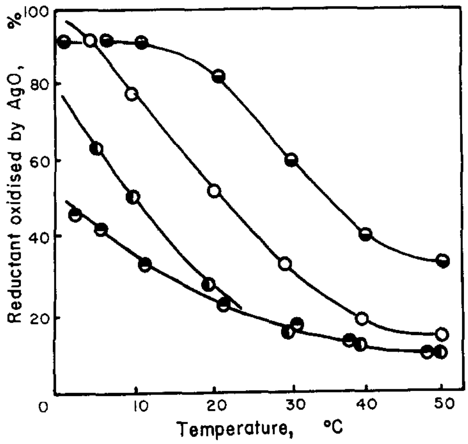

FIG. 4.—The effect of temperature on the percentage of metal salt oxidised.
◓—0·5 mg of Mn^{2+} in 25 ml of 3·5*M* $HClO_4$ + 0·015 g of AgO.
◒—0·5 mg of Mn^{2+} in 25 ml of 3·5*M* $HClO_4$ + 0·037 g of AgO.
◐—0·7 mg of Cr^{3+} in 25 ml of 3·0*M* $HClO_4$ + 0·022 g of AgO.
○—0·7 mg of Cr^{3+} in 25 ml of 3·0*M* $HClO_4$ + 0·030 g of AgO.

TABLE I.—RATE OF FORMATION OF CHROMATE ION
(Temperature, 5°)

AgO added, *g*	Concentration of Cr^{3+}, *g ion/litre* × 10^4	Concentration of $HClO_4$, *M*	Apparent rate constant, *k* × 10^3	Initial rate, $k_i \times 10^3$ *mg/sec*
0·060	5·44	0·209	2·26	4·38
0·060	5·44	0·413	7·27	8·31
0·060	5·44	1·047	24·0	44·8
0·060	5·44	1·516	33·2	72·4
0·060	2·63	0·40	7·72	7·03
0·060	7·93	0·40	5·90	8·42
0·060	10·6	0·40	7·52	10·9
0·045	5·44	0·40	8·13	7·29
0·090	5·44	0·40	4·54	11·1
0·110	5·44	0·40	4·29	14·5

RESULTS

Although, stoichiometrically, sufficient AgO was added to each solution to oxidise completely all the manganese or chromium present, complete oxidation of these species was only achieved in the presence of a large excess of reagent. To emphasise the effect, the results have been recorded in the form of percentage of the original manganese or chromium ion oxidised to permanganate or chromate.

The effect of acid concentration on the percentage conversion is shown in Fig. 1. Similar curves, displaced vertically, were obtained on adding different weights of AgO. Maximum conversion was obtained with solutions which were either 0·1–0·2*M* or 3·0–3·5*M* in respect of perchloric acid. In the former case, the rate of solution of solid was slow (5–15 min) as compared with seconds for the more concentrated solutions.

The effect of adding varying weights of AgO to a given solution is indicated by the typical results shown in Fig. 2. Total conversion was obtained if sufficient excess of oxidant was added. An interesting side effect was observed in manganese studies using sulphuric acid of equivalent strength. Where the Mn^{2+} was not fully oxidised to permanganate, there was a gradual fading of the initial purple colour, and the formation of a brown precipitate of MnO_2, indicating that the remaining Mn^{2+} in the presence of Ag^+ was reducing the oxidised species. This effect was not so marked using perchloric acid solutions.

For a given set of conditions, the percentage conversion was considerably increased by the addition of silver nitrate before oxidation, as shown by the results recorded in Fig. 3. The effect of an increase in temperature was to reduce the amount oxidised, as illustrated in Fig. 4.

In the kinetic studies, the oxidation of the chromium(III) ion approximated to a pseudo first order reaction if the ultimate amount of chromate formed was taken to represent the initial concentration of some species responsible for the formation of the chromate. On this basis, values for apparent rate constants under different conditions were calculated for comparison purposes, and these results are summarised in Table I. Initial rates of chromate formation for the varying conditions were estimated from the rate curves and these rates are shown in Table I also. The kinetic values are considered to be of limited accuracy, for it was necessary to separate the solid phase from the solution during collection of the sample, and because the time for complete reaction was only a matter of minutes, slight variations in the rate of sample collection through the filter introduced significant errors.

To obtain mathematical relationships between the results recorded in Table I, the varying sets of results were plotted against each other on log-log paper. In each case a linear relationship was obtained, and the slopes were measured to give the power dependence of the rate on the various factors. Combination of the results yielded the following expressions:

$$\text{Apparent rate constant } k = k_1 \,.\, [H^+]^{1.36} \,.\, \{AgO\}^{-0.77} \tag{1}$$

$$\text{Initial rate of formation } \left(\frac{dCrO_4}{dt}\right) k_i = k_2 \,.\, [H^+]^{1.48} \,.\, \{AgO\}^{0.74} \,.\, [Cr^{3+}]^{0.32} = k \,.\, (X)_i \tag{2}$$

where { } represents a measure of the amount of AgO added and X represents the unknown species considered to be the rate determining reactant in the pseudo first order reaction.

From equation (2) it may be suggested that

$$(X)_i = k_3 \,.\, [H^+]^{0.12} \,.\, \{AgO\}^{1.5} \,.\, [Cr^{3+}]^{0.32} \tag{3}$$

DISCUSSION

Calculations based on stoichiometric equations for the oxidation reactions indicated that only about 14% of the AgO added was used in oxidising manganese(II) to its higher valency state and only about 7% of the AgO added to the chromium solutions was responsible for chromate formation. These calculations show that most of the added AgO was reduced by some secondary process. Because the reaction mixtures effervesced greatly when the AgO was added, and solution of AgO in acid is known to liberate oxygen,[12] it can be accepted that the process responsible for the reduction of most of the added oxidant is the evolution of oxygen. Because this reaction predominates, any reduction in the rate of oxygen formation must increase the relative amount of manganese or chromium salt oxidised.

The reduction of Ag^{2+} by water to yield oxygen in perchloric acid solutions has been studied by Kirwin and co-workers.[5] The plot of apparent rate constant against acidity was found to yield a definite minimum at a perchloric acid concentration of $3{\cdot}0M$. This is the acid concentration at which oxidation of manganese and chromium salts was most efficient (Fig. 1). The rate of oxygen formation in perchloric acid solutions was found to be second order in respect of $[Ag^{2+}]$, inversely proportional to $[Ag^+][H^+]^2$ and related in a complex way to $[ClO_4^-]$. The increased yield of oxidised manganese and chromium salts observed on the addition of Ag^+ to the solutions (Fig. 3) can thus be attributed to the inhibition of the oxygen formation process. The effect of excess AgO (Fig. 2) may also be explained in part by the higher concentrations of Ag^+ formed on reduction of the excess oxidant.

The rate equation relating the evolution of oxygen to amount of AgO added is more complex than the equations obtained for solutions of silver(II) ion. Not only does dissolution of the solid in acid yield decreasing amounts of Ag^{2+}, but during the course of the reaction increasing amounts of the inhibiting species Ag^+ are formed. The mathematical expression obtained in a study of oxygen liberation on the addition of AgO to sulphuric acid solutions had the form[13]

$$dO_2/dt = K\,.\,[H^+]^{0.24}\,.\,\{AgO\}^{0.6} \tag{4}$$

The rate of oxygen formation became very slow at pH values approaching 3 and this would explain the marked increase in permanganate and chromate yields in solutions which were $0{\cdot}1$–$0{\cdot}2M$ in respect of perchloric acid. (Fig. 1).

An increase in temperature has a greater influence on the oxygen liberation process than on the other oxidation mechanisms. This is demonstrated by the effect of temperature on the amount of metal ion oxidised (Fig. 4).

The results recorded in Figs. 1–4 cannot be explained entirely on the basis of the influence of the various factors on the rate of oxygen formation, because, as indicated by equation (2), the rate of chromate formation is itself a complex function of at least three variables. The existence of the fractional terms indicates that the mechanism is complex and that each species may be involved in more than one reaction.

The oxidation of the chromium and manganese ions could occur in solution or on the surface of the solid. The production of chromate or permanganate in solution requires multiple collisions between higher valency silver ions and a hydrated chromium or manganese ion, and although this is feasible, reaction on the solid surface appears more probable. The initial rate of chromate formation was nearly linear in respect to the amount of solid added (Table I) for a given set of conditions, and this tends to support the idea of a surface reaction, because this relationship has been found to apply to heterogeneous reactions involving a species in solution and a solid catalyst.[14] A surface mechanism has previously been proposed to explain the oxidation of ammoniacal solutions by silver(II) oxide.[15]

Using the model of a heterogeneous reaction, the unknown species X can be considered to be an intermediate formed on the surface of the solid. From equation (3), the concentration of X is related to $[H^+]^{0.1}\,.\,\{AgO\}^{1.5}\,.\,[Cr^{3+}]^{0.3}$. The power in respect of Cr^{3+} can be explained in terms of an adsorption isotherm for this species on the surface of the solid; the small power term in respect of $[H^+]$ could arise from solution of Ag_2O residues on the surface or from suppression of hydrolysis of the chromium ion; and the fractional power in respect of AgO may merely reflect particle size variation in the solid. Because of the limited solubility of silver chromate, desorption of the oxidised product could be a rate-controlling step. Solution of the silver chromate would be retarded by univalent silver ions in solution and accelerated by protons. Such reactions are in agreement with the terms $[H^+]^{1.36} . \{AgO\}^{-0.77}$ found in the expression related to apparent rate constants [equation (1)].

CONCLUSIONS

Manganese and chromium salts can be quantitatively oxidised by the addition of excess silver(II) oxide, and the amount of excess required can be reduced greatly if the rate of the competing reaction, namely the liberation of oxygen, is reduced to a minimum.

The rate of oxygen liberation in nitric acid solutions is much slower than in sulphuric or perchloric acid,[4] hence the 2–5*M* nitric acid medium proposed by Lingane and Davis[7] is preferable on these grounds to the sulphuric acid solutions used by the earlier workers.[8–10] On the other hand, it is necessary to warm the nitric acid solutions to destroy excess reagent present as silver(II) nitrate complexes. It is also desirable to avoid the presence of nitric acid in oxidation-reduction titrations.

To use sulphuric or perchloric acid as the reaction medium requires alternative methods of retarding oxygen liberation. Methods available include lowering the temperature to a minimum, lowering the acidity, or adding univalent silver ion to the solution. Variation of the first two of these factors tends to increase the time required for oxidation, and therefore the preliminary addition of silver ion has much to recommend it. On the assumption that the reaction is a surface process, greater efficiency of oxidation should also result from smaller particle size for the AgO and more vigorous stirring.

It must be emphasised at this point that the efficiency of excess silver(II) oxide in oxidising manganous and chromic salts was clearly demonstrated by Lingane and Davis.[7] Because excess reagent can be destroyed by warming the solution, the method is preferable to that using sodium bismuthate, where excess has to be removed by filtration, and is preferable to the use of ammonium persulphate with silver ion as catalyst because in this case excess persulphate ion has to be destroyed by boiling.

The theoretical study described in this paper gives some information on the mechanism of the oxidation process and suggests ways in which the amount of silver(II) oxide required to give the desired excess can be reduced, but it should not deter workers from using the method of Lingane and Davis, who solved the problems described in this paper in a practical manner.

Zusammenfassung—Die Oxydation von Mangan(II)- und Chrom(III)-Lösungen durch Silber(II)-oxyd in überchlorsaurer Lösung wurde untersucht. Ausbeute und Geschwindigkeit der Oxydation ändern sich mit der Konzentration des Reduktionsmittels, der zugesetzten AgO-Menge, Temperatur, und Konzentration von Säure und einwertigen Silber in der Lösung. Schlechte Ausbeuten bei der Oxydation können der Bildung von Sauerstoff zugeschrieben werden.

Die Ergebnisse werden im Sinne eines möglichen Reaktionsmechanismus diskutiert und die besten Arbeitsbedingungen für Oxydationen mit AgO angegeben.

Résume—On a étudié l'oxydation de solutions de manganèse(II) et chrome(III) par l'oxyde d'argent(II) en milieu acide perchlorique. On a trouvé que l'efficacité, et la vitesse du processus d'oxydation, varient toutes deux avec la concentration du réducteur, la quantité d'AgO ajouté, la température, l'acidité, et la concentration en ions argent monovalent dans la solution. L'inefficacité du procédé d'oxydation peut être attribuée à la formation simultanée d'oxygène. On discute des résultats du point de vue mécanisme réactionnel possible, et indique les conditions optimales pour les oxydations utilisant AgO.

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SOME PROBLEMS IN THE ANALYSIS OF GASEOUS DECOMPOSITION PRODUCTS*

A CRITICAL EVALUATION

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Summary—Whether the analysis of effluent gases during thermal decompositions is used to elucidate the progress or the mechanism of the decompositions, or to characterise the specimen, certain problems must be dealt with. These problems, involving heating, the analysis of the products, and the compromises which must be made in simultaneous measurements, are discussed.

INTRODUCTION

THE analysis of effluent gases during thermal decompositions can be of great help in elucidating the progress or the mechanism of the decomposition. In some cases, too, the decomposition products may be used to characterise or identify the specimen. For whatever purpose the analysis is carried out, certain problems must be overcome. These problems relate to the heating, to the analysis of the products and to the compromises which must be made in simultaneous measurements.

HEATING OF SPECIMENS

The solid material being studied has been or can be heated in several ways, and for multiple-purpose studies as well as specifically for the analysis of the decomposition products. The most common of the multiple determinations would be simultaneous differential thermal analysis and effluence analysis; the effluence from a thermogravimetric analysis could also be analysed, but this will invariably be accompanied by considerable dilution. In any event, in such simultaneous determinations the heating programme and heating conditions are fairly rigidly prescribed by the requirements of the other technique. In those cases in which the sample is heated specifically for analysis of gaseous decomposition products, a fairly wide range of heating conditions can be and have been used. Examples could include slow heating of a rather massive sample to some fixed temperature or, at the other extreme, flash heating by use of a high-intensity source of visible and infrared radiation. A common technique, intermediate between these, is the practice of placing the sample on a heater (wire) or in a heater specially formed, then applying a predetermined voltage to the heater so that the specimen heats in an uncontrolled but approximately reproducible manner. In contrast to this latter, the specimen can be heated in some programmed manner, as would be typical in the simultaneous determinations.

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SIMULTANEOUS DETERMINATIONS

Let us use as a starting point the present author's work with some simultaneous determinations. This has been, of late, generally concerned with some form of thermal analysis, so that simultaneous differential thermal analysis and effluence analysis would have obvious benefits. In previously reported work,[1] the author has connected a dynamic-atmosphere differential thermal analyser to various devices for detecting gaseous products and/or establishing the nature of the products.

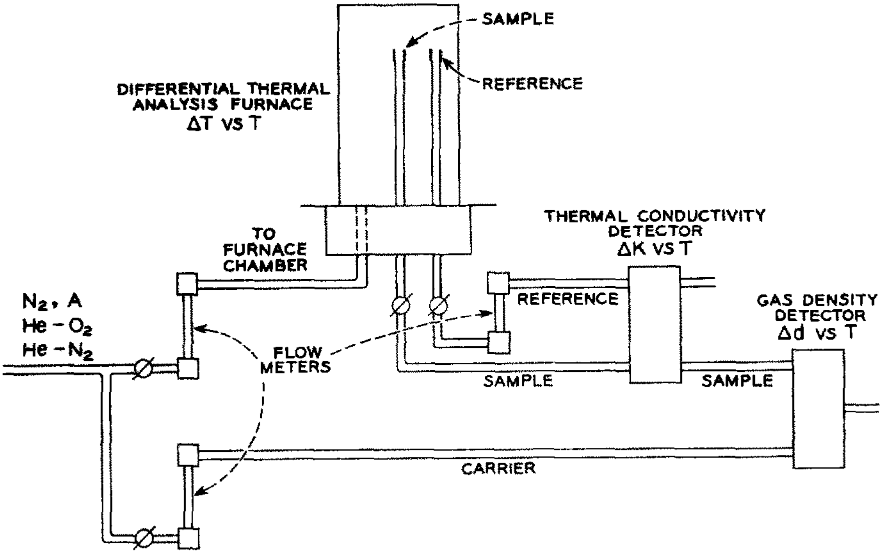

FIG. 1.—Combination differential thermal analysis and double effluence analysis. The transient changes in the sample stream are detected in chromatographic-type analysers.

One arrangement used is shown in Fig. 1. In this arrangement a gas is supplied to the furnace chamber under sufficient pressure to cause a reasonable flow—this flow varies with the type of experiment—downward through the sample and through the reference materials. The gas passing through the reference is used as the reference gas in the thermal conductivity detector, and the gas passing through the sample is compared with it. Any gaseous decomposition product whose thermal conductivity is different from that of the "chamber gas" will then produce in the thermal conductivity detector a different cooling effect from that produced by the pure chamber gas during the time that the product gas is passing through the thermal conductivity detector. The magnitude of the differential signal from the thermal conductivity detector is, at low concentrations, proportional to the quantity of the product gas passing through at the moment, so that integration of the area under a total deflection is a measure of the quantity of the gas evolved, provided that the nature of the gas is known. In this arrangement, the gas which has passed through the sample then goes into the gas density detector. The gas density detector has the advantage (over the thermal conductivity detector) that it is not only a quantitative measuring device, but is to some extent qualitative. It has a further advantage that the sensitivity of the detection can be adjusted by judicious selection of carrier gas, because the density or "apparent molecular weight" is the only property of importance in the measurement.

The gas density detector depends for its operation on the effect of minor changes of flow in the vertical column on the total flow in tubes connected to the top and bottom of a vertical column. Let us assume that in this device (Fig. 1) a steady-state flow of sample and carrier gases into their ports has been established so that we have a steady-state cooling of the detector elements. Now at some point upstream we inject a small quantity of a product gas, as we might in the normal course of a decomposition in differential thermal analysis. If this product gas is heavier than the carrier gas, the change in density, of course, will be an increase and, hence, the sample plus carrier gas will tend to flow downward to a greater extent than upward. This downward flow will decrease slightly the flow in the lower supply tube (Fig. 1 of ref. cited) and increase slightly the flow in the upper supply tube; this change in flow in the supply tubes produces a change in the cooling effect on the detector elements, an increase in the upper and a decrease on the lower. The differential flow at any moment is proportional to the difference in density of the sample plus carrier gas from that of the sample gas alone, permitting, of course, a quantitative measurement of the material passing through (assuming that it is a single gas). Note, however, that the density of the sample plus carrier gas is dependent not only on the quantity of sample but also on the nature of the sample; *i.e.*, that a gas which, pure, is only slightly heavier than the carrier gas will at a given level of concentration produce some fixed differential flow, but a gas substantially heavier than the carrier gas will at the same concentration produce a significantly greater differential flow. Because of this, qualitative as well as quantitative information can be obtained. If the sample gas is unknown, a second experiment with a carrier gas of different density will provide results for calculation of the real or apparent molecular weight of the sample. (If the sample is a mixture of gases, the apparent density will be dependent on their relative proportions and their relative densities in the pure state.) If the number of possibilities is quite limited, a simpler identification is possible by bracketing the density of the suspected gas in two runs; for example, if there is reason to believe that the specimen gives off oxygen when heated in an inert atmosphere, an experiment using nitrogen as the carrier gas will show that the sample is more dense, and a second experiment using argon will show that the sample gas is less dense; if necessary, direct comparison of the areas will show whether or not the apparent molecular weight of the gas is 32.

The present author has used this type of identification in several cases of which two may be cited. In some studies of cobalt oxalate hydrate the nature of the second step was not known with certainty. Most oxalates decompose in a non-oxidising atmosphere by loss of carbon monoxide to go to the corresponding carbonate. A cobalt oxalate resulting from the heating of the dihydrate decomposed *ca.* 400° to yield what appeared to be a finely divided metal. In closed-chamber differential thermal analysis experiments with air as the furnace atmosphere, this metal powder had, around the opening along the support tube, evidence of oxide formation. The question was resolved by differential density analysis using nitrogen as the carrier gas. If the cobalt oxalate decomposes directly to the metal, 2 moles of carbon dioxide are released and because 2 moles of water are also released the areas should be in direct relation to the density difference. The density difference between water and nitrogen, assuming ideal gas, *etc.*, is 28–18 or 10 g per mole; the difference between carbon dioxide and nitrogen would be 44–28 or 16 g per mole. The ratio of areas then should be 1·6 if the decomposition is directly to the metal. Within a few percent, attributable to experimental error, this is the result obtained. Note that in this experiment carbon monoxide, having a molecular weight of 28, would not have shown its presence at all, because its density is the same as that of nitrogen.

As part of the same work, nitrogen and argon were used to establish the evolution of oxygen during the decomposition of lanthanum oxalate hydrate. Some carbon had been found with the lanthanum oxide when the material was heated in an inert atmosphere. Above 700° a gas heavier than nitrogen, but lighter than argon, was evolved. In another experiment, reported therein but using oxygen as the dynamic gas, the arrangement shown in Fig. 1 was used to obtain simultaneous measurements of ΔT, Δd and ΔK as lanthanum oxalate hydrate was decomposed. The thermal conductivity measurements are not very useful, because carbon monoxide does not differ enough from oxygen. Carbon dioxide could be detected, but not with nearly the sensitivity obtainable in a helium or hydrogen stream.

Although these particular sets of curves were obtained during single runs with all measurements being made simultaneously, this is not by any means a necessary procedure. Separate experiments would be just as instructive, and possibly experimentally more convenient, so long as they were planned properly.

GAS CHROMATOGRAPHY

In many cases a more specific identification than described above may be needed, because at some stages in the decomposition more than one product may be given off. For such cases, the addition of gas chromatography is useful. Gas chromatography, as ordinarily practised, would be relatively ineffective; it would measure all the decomposition products up to the time of sampling. Specific identification of the product of a particular reaction requires that the sampling be made for that reaction alone; *i.e.*, any reaction products from previous decompositions should already have been removed from the site of sampling. This can be done readily by an arrangement such as that shown in Fig. 2. In this system a furnace like that shown in Fig. 1 is used to carry out the thermal decomposition. The carrier gas which passes through the sample, may, if desired, be passed through a thermal conductivity cell for a continuous and general survey of decomposition products, but, more important, it passes through a pair of sampling valves with, in some cases, an interposed water trap. These sampling valves operate at programmed intervals to withdraw samples of gas from the stream and pass them through chromatographic columns and detectors. The programming is done by trial and error. For the Fluoropak column, and separately for the split column flow, conditions were determined which gave adequate separation. An adjustable cam timer was then connected to the sampling valves so that during each revolution one sampling valve would open for 5 sec, then close. The oven temperature, the flow rates and the sampling times were chosen for each type of experiment specifically to permit rapid sampling. In effect, each sampling occurs soon after the last expected peak from the previous sampling.

The Fluoropak column, when used, permits all non-polar and not very polar materials to run through rapidly, but holds up the water long enough to give separation and permit measurement.

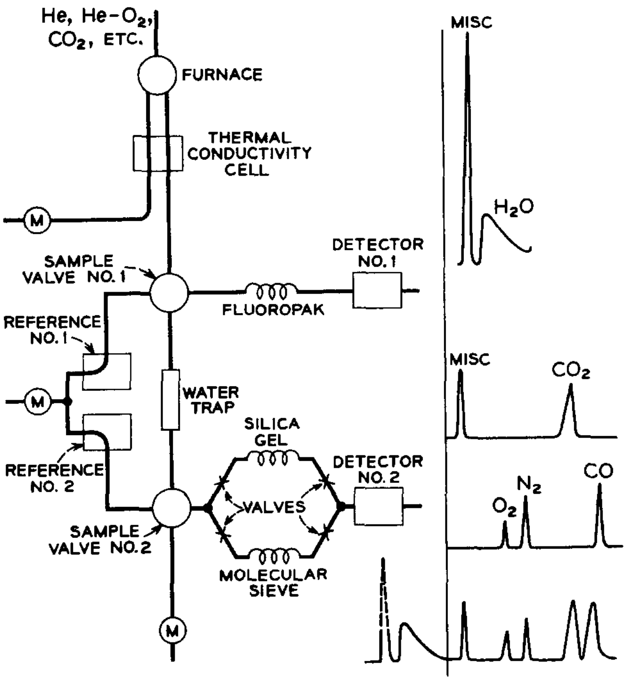

Fig. 2.—Gas train and switching for repetitive dual-sampling chromatography. Sample valve No. 1 transfers a 3-ml sample and No. 2 a 5-ml sample. Sampling interruptions have been deleted in copying (see Fig. 3.)

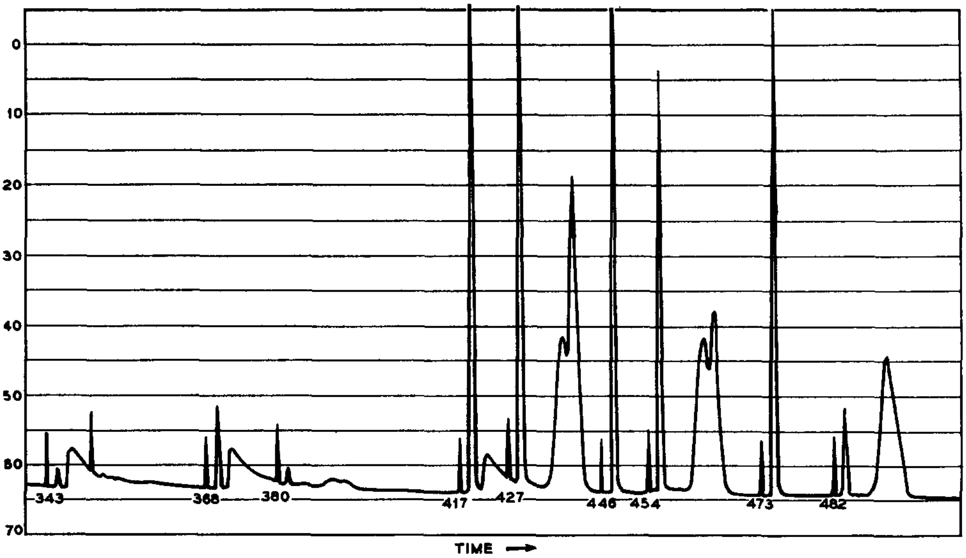

Fig. 3.—Chart section showing a number of sampling cycles and the temperature at which the sample was taken.

The temperature at the moment of sampling is measured and the reaction occurring at that temperature thus described. Alternate samplings, *e.g.*, 417° and 446°, are into the Fluoropak column; the others go through the split column.

The second sampling valve in turn withdraws a specimen from the stream and directs it through a split column to a second detector. This split column has silica gel in the one side and a molecular sieve in the other; the silica gel holds up the carbon dioxide but passes the other permanent gases through rapidly, and the molecular sieve separates the permanent gases. Proper adjustment of the relative flows permits appearance of the carbon dioxide conveniently in the interval of time between the appearance of nitrogen and of carbon monoxide from the molecular sieve. The chromatogram results from the presence of all the gases, but is shown at the right for each column and at the bottom for a complete cycle. Fig. 3 shows a chart section with a number of cycles, the appearance and disappearance of peaks reflecting the beginning and subsidence of reactions as the specimen material is heated.

Examination of several cycles of the chromatographic analysis permits, then, the following of a reaction or, more important, a series of reactions by the relative heights or areas of peaks. Fig. 4 shows such a series. The left-hand analyses are solely for water; those to their immediate right are the associated samplings for the permanent gases and those at the far right a subsequent series of analyses for the permanent gases. No water appeared in the later analyses for water so these are not shown. Note that even in the water analysis an indication of the increasing concentration of other gases was apparent from the growth of the peak just before the rather broad water peak. Similarly, even though the carbon dioxide and carbon monoxide peaks run together at high concentrations, the sharp peak shortly after the sampling, resulting from the permanent gases other than carbon dioxide passing rapidly through the silica gel column, gives an indication of the concentration of carbon monoxide even when the peak is almost obscured by the carbon dioxide. At the higher temperatures, carbon dioxide evolution ceases and carbon monoxide is the only product detected.

The results from one run are tabulated in Fig. 5 along with the differential thermal analysis and differential conductivity curves. The water is given off over a rather wide range, and the peaks are poorly defined in this dynamic atmosphere of helium; then the decomposition of oxalate occurs very sharply, and the interrupted peak on the thermal-conductivity curve can be related to the more or less continual evolution of carbon dioxide coupled with the quickly-terminated evolution of carbon monoxide. The new appearance of carbon monoxide at higher temperatures is also apparent. The high drift in the differential thermal analysis signal is a result of sintering of the specimen and consequent change in the heat transfer from the side to the centre of the specimen. One might conclude from these particular curves that ΔK is a more sensitive measurement than ΔT, and in some cases this could be justified. Consider, however, that this particular experiment used a helium atmosphere and the thermal conductivity change is at a maximum; a dynamic atmosphere of helium would seldom be picked for differential thermal analysis (*vide infra*). Further, differential thermal analysis detects changes of state which the thermal conductivity of the gas stream obviously cannot reflect.

Some of the earlier exploratory work combining chromatography with differential thermal analysis shows the hazard of vitiating results from one of the techniques. Fig. 6 shows some differential thermal analysis curves for an ocean sediment specimen obtained with air and with helium as dynamic atmospheres. While the analysis in helium was being performed, a technician took chromatographic samples by manual operation of a sampling valve at regular intervals.[2] There is no difficulty in following the appearance of carbon monoxide and the appearance and virtual disappearance of carbon dioxide in the decomposition products, but there is significant difficulty in finding any thermal effects in the helium run to which to relate the gas evolution.

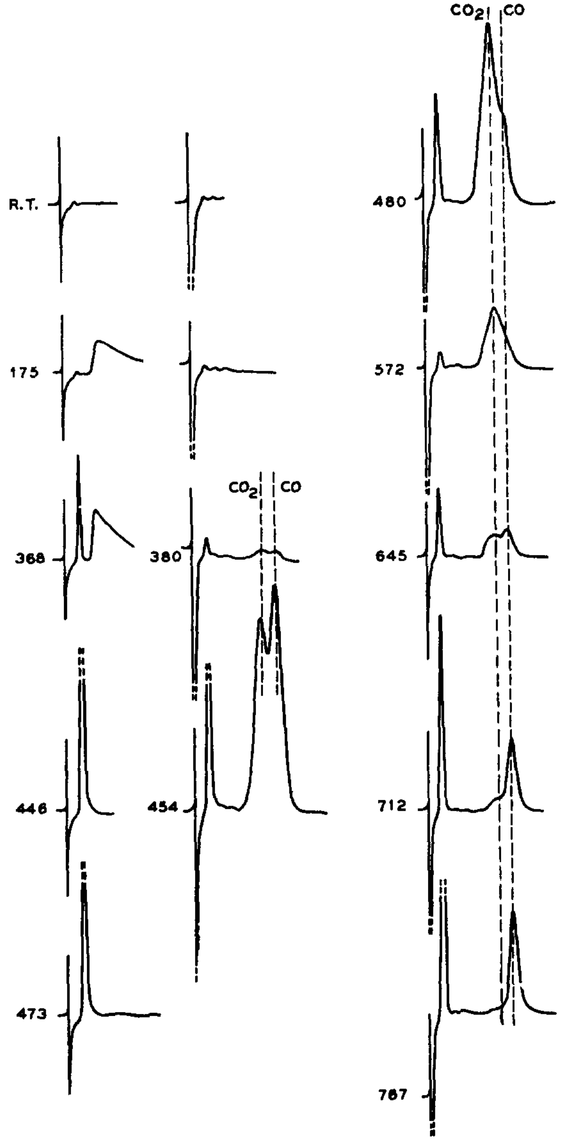

Fig. 4.—Reproduction of several chromatographic analyses from the chart of which Fig. 3 showed a part. The temperatures of sampling are indicated. The appearance and disappearance of specific products can be followed easily.

One may not conclude that combinations of techniques will necessarily be useful. Simultaneous determinations are of benefit only under those conditions in which neither technique is greatly compromised. The planning of separate experiments for each technique will often be more fruitful.

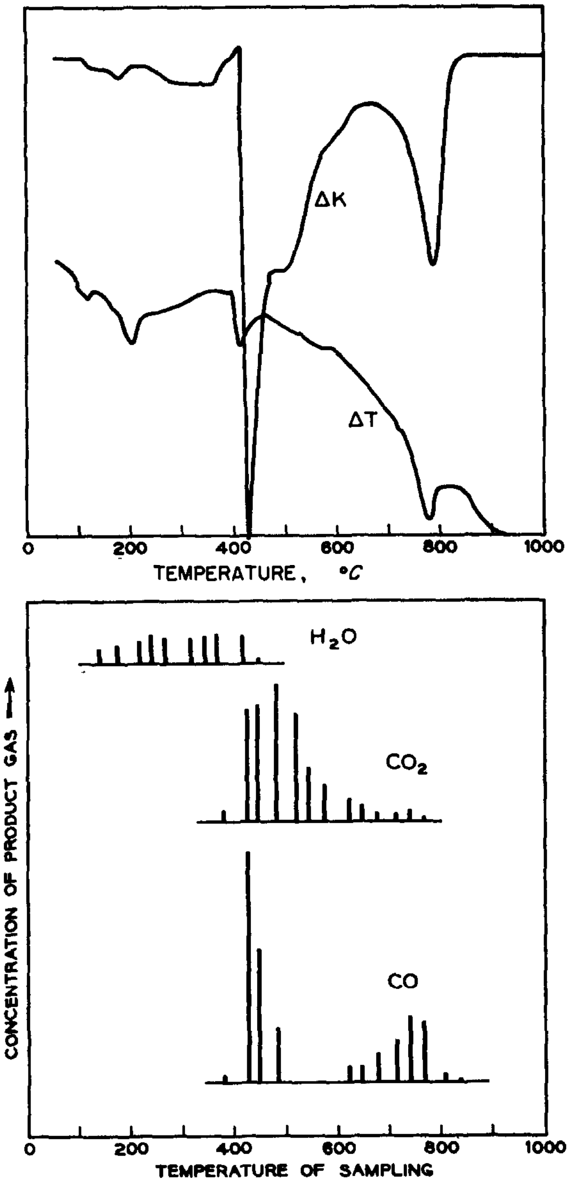

FIG. 5.—Tabulated chromatographic peak heights related to the simultaneously-obtained differential thermal analysis and thermal conductivity analysis of the effluent stream.

The sudden appearance of carbon monoxide and dioxide is indicated also by the plots. The curves, however, give no hint of the relative amounts of CO_2 and CO.

CRITIQUE

With all the problems of simultaneous analysis, and the distinct probability that separate experiments could be better or more instructive, the simultaneous-determinations technique is generally superior to point-by-point sampling for the same types of analyses. Let us consider the technique devised by Murphy, Hill and Schacher[3] in which a differential thermal analysis was performed of poly(vinyl chloride) in an evacuated vessel which had connections also to some previously evacuated sampling tubes for mass spectrometry. The object is, of course, to determine the identity of the gaseous products coming off at various stages of the heating, but consider the required procedure. One must first make a trial run in order to establish the temperatures which may be of interest. After selecting the sampling temperatures a re-run must be made with operator monitoring in order that the selected samples may be taken at the proper time; and finally, the gaseous samples taken must be conveyed to the other instrument, in this case a mass spectrometer, and analysed individually. All of this is perfectly possible, and may be justified on the basis of the need for information about a particular sample; but there immediately arises the problem of the need for an operator to make a judgment on probably inadequate results. That is, on a specimen with which the operator is not familiar, a single thermogram is seldom sufficient to establish the identity of a given reaction.

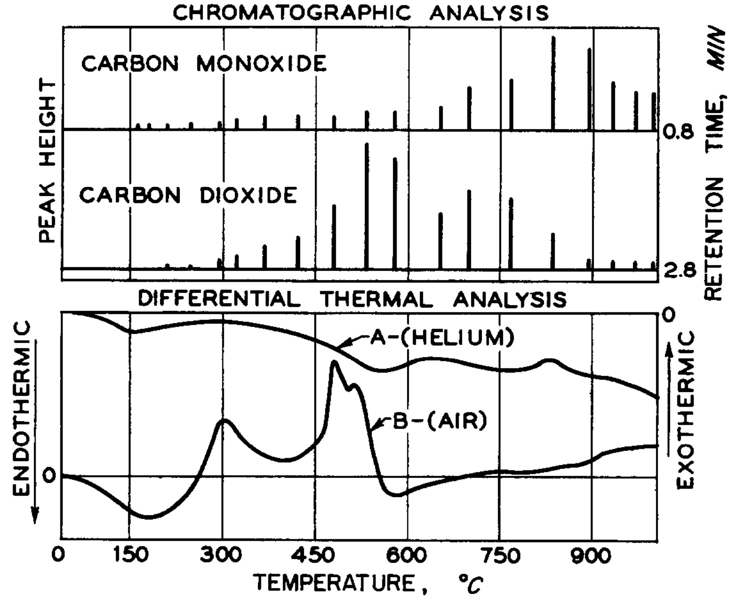

FIG. 6.—Differential thermal analyses of an ocean sediment related to the effluence analysis. The appearance and disappearance of the gases can be related to the peaks of curve *A*, but curve *B* bears no appreciable resemblance because the reactions are quite different.

In this technique the choice of sampling points is obviously extremely important, yet the example shown by Murphy *et al.*, involves what is apparently an error in choice. They sampled at 300 and 400°, the lower temperature being at the peak of an endothermic reaction and the higher temperature at what they describe as a flat exotherm. They found, as they expected, hydrogen chloride evolved at 300°; and we may infer that they had expected similar evolution at 400° for they reported that no hydrogen chloride was evolved, without specifying the presence or absence of any other material. The absence of any material evolved in the 400° region should not be a surprise; that region is almost certainly not an exotherm or caused by any reaction at all. It is far more likely a simple change in base line resulting from the change in thermal properties of the specimen. The important point here is not that their information needs re-interpretation, but that such an error is easily possible with point-by-point sampling techniques.

Let us now consider an arrangement in which the gas given off by a heated specimen is swept by a carrier gas into a thermal conductivity detector. In the arrangement described by Ayres and Bens,[4] the sample cells are test-tubes set in a metal block. A differential thermal analysis is performed on the specimen, and the plot from the thermal conductivity cell is related to the differential thermal analysis plot. The carrier gas passes through a preheater and then flows over the sample and reference specimens and thence into the detector cell; note that the gas does not pass *through* the specimen, so the atmosphere surrounding the particles will vary depending on the nature of the product gas and the depth of the particle within the total specimen. The upper layers are continually exposed to an atmosphere of essentially pure helium, but, during a decomposition, the helium will be displaced by the product gas and, especially near the bottom, the particle will experience an enrichment of the product gas concentration.

The effect of the enrichment within the bulk of the specimen will vary, depending on the nature of the sample. Reactions having any appreciable semblance of reversibility will be spread over a range of temperatures because of the atmospheric effect, but yet not to the same extent as would be the case in the absence of a moving atmosphere, because we can consider any product gas to be diffusing outward into a zero level concentration above the specimen. For a reversible reaction, then, this technique will yield differential thermal analysis curves intermediate between those obtained in static atmospheres and those in dynamic atmospheres, as cited previously. The effluent gas analysis will closely parallel the differential thermal analysis curve. Irreversible decompositions, such as the perchlorate decomposition and many organic decompositions, will be virtually unaffected by any movement of the atmosphere, because these reactions proceed rapidly when the decomposition temperature is reached, regardless of the ambient atmosphere. The detection of the effluent gas can be expected to agree less well than in the case of the reversible reactions, because a tailing off is essentially certain to follow a rapid exothermic reaction; in addition to the effect from burst of gaseous products spewed into the carrier stream, these products displace the carrier gas from the nooks and crannies within the specimen, and some reasonable interval of time will be required for this material to diffuse out of the specimen and into the gas stream. In reversible reactions, under this type of condition, there is very probably a diminution in the rate of formation of the product gases as their concentration increases and, towards the bottom of the sample vessel, material which has not reacted may yet exist after the peak temperature difference has passed. The return to the base line will be slow because of this continuing reaction, and during the same period these last portions of product gases will be diffusing out of the specimen and into the gas stream in ever-decreasing quantities; the effect in the gas detector is, then, rather similar to the differential thermal analysis peak.

Let us examine the results by Ayres and Bens using ammonium perchlorate, first reviewing the reactions of ammonium perchlorate under a small variety of conditions. Differential thermal analysis curves in various atmospheres were obtained by Stone;[5] in an ammonia atmosphere the entire decomposition occurs at one temperature, because the presence of the ammonia represses the initial decomposition. In any other gas a preliminary decomposition occurs which is slightly pressure-dependent. The final decomposition temperature remains the same. Note that this initial decomposition is not a *necessary* prelude to the exothermic decomposition. The evidence so far suggests that in the absence of ammonia this initial decomposition comprises the loss of all or part of the ammonia. We might predict either a double salt remaining at this stage or, if all the ammonia is lost, that the perchloric acid vapour pressure has not yet reached 1 atmosphere.

In vacuum the final decomposition is not exothermic at all. We may infer that the ammonium perchlorate decomposition products from the initial reaction volatilise and the material is swept out before decomposition.

In any case, the curve obtained by Ayres and Bens in helium would correspond to the third of Stone's curves, *i.e.*, the one obtained in nitrogen at 1 atmosphere. The difference in the nature of the flowing or dynamic gas between the two experiments is of no consequence, so long as the gas does not enter into any sort of reaction with the specimen. The drawn-out initial decomposition, and the tailing off of the gas evolution after the final decomposition, can be attributed to the manner of passing the gas across the sample as explained above.

Less volatile products will cause a rather different trouble, but the problem is apparently purely physical, and could be corrected by redesign of the apparatus. Ayres and Bens also show decomposition curves for nitroglycerine and a propellant. Note that at the upper extremes in temperature an evolution of gas appears to take place with no evidence of a thermal effect. This is more likely caused by the condensation of a decomposition residue in a cooler part of the glassware and subsequent vaporisation of the residue as the heating continues and that part of the glassware reaches a sufficiently high temperature.

Ayres and Bens called attention to the possible troubles from condensation; the present author's contribution is the delineation of events within the sample.

Another use of simultaneous differential thermal analysis and a form of effluence analysis was of a very special kind. Bussière and others[6] constructed an apparatus in which they could simultaneously perform differential thermal analysis, thermogravimetric analysis, and a measure of the emanation from radioactive thoron. Their work is based on the absorption of radioactive thoron along the interfaces between crystallites. The sample used was thorium oxalate hydrate. The radioactive decay of thorium produces thoron, (also radioactive), part of which escapes and part of which is trapped in the interfaces or interstices and, at best, moves slowly to the particle surface. When, however, the material undergoes a change of state, the disruption of the crystals permits more ready escape of the thoron from amongst the crystallites.

Bussière *et al.* passed a gas stream across their specimen and into a detector in which the radioactivity of this gas stream (from the thoron) was measured. Their results are not easily interpreted at first sight. The first dehydration is unambiguous; each of the measurements demonstrates an effect which we can accept as decomposition to the dehydrate, as stated by Bussière and others. The second weight loss and accompanying endotherm are clear enough, but there is no corresponding event in the emanation measurement. Further, in the final decomposition, not only does the thermogravimetric curve indicate a single, smooth-wave loss while the differential thermal analysis curve shows a pair of reactions, but the emanation curve even shows a decrease rather than the predicted increase.

The two-step final endotherm shown by the differential thermal analysis could be the decomposition of the oxalate, first to the carbonate, and subsequently to the oxide. On moderately large specimens, and with no *useful* atmosphere control, these two decompositions will (or at least can) overlap enough to give a single thermogravimetric weight loss. The present author will not attempt to explain the slow rise in the emanation between about 120 to 250°. The decrease in the region of 300° may possibly be the result of dilution; the evolution of the other gases may become such a significant part of the total gas flow that the flow through the counter is increased, and the quantity of thoron present in the counter at any moment consequently decreased. As the rapid evolution diminishes, the increased concentration is again apparent. The method is interesting, and may be particularly useful in special cases. As a general technique, it suffers from the disadvantages that it does not provide a complete and unambiguous response to events in the specimen and, further, it requires the presence of thorium or some other radioactive material producing a radioactive gas with a short half-life.

DETERMINATION ONLY OF GASEOUS PRODUCTS

Let us now consider some experiments in which the gathering of information was confined to study of the gaseous products of decompositions. These range from systems in which only the event is of interest to systems in which the products are measured quite specifically, both qualitatively and quantitatively. One of the former type is that of Rogers and others[7] in which the specimen was pyrolysed in a stream of helium. The organic vapours from the pyrolysis chamber are oxidised to water and carbon dioxide in the combustion tube, to avoid condensation as well as to enhance sensitivity. (The conversion of a molecule of some fairly complex organic material to many molecules of carbon dioxide and water will quite naturally enhance the signal obtained in passing through the thermal conductivity cell.) The pyrolysis block is heated by commercial cartridge heaters through a temperature programme. The results obtained from the thermal conductivity measurements are simple indications of decompositions without identification, except, in some cases, by the temperature at which the decomposition occurs. It has the advantage over the Ayres and Bens apparatus that the conversion to carbon dioxide and water rids the system of easily condensable materials which might later vaporise and give a false signal.

These simple indications of decompositions are useful principally in establishing temperatures of decomposition, but with known products the technique can also be used as a quantitative measure with the same confidence as gas chromatography, because the same type of detector is used. The user must know the product gases specifically, or at least know that the same material containing the same proportions of carbon and hydrogen will come off from each sample tested. If this knowledge is not available with certainty, more detailed analyses may be in order. It is necessary only to substitute a technique for analysis instead of, or as well as, detection of the gaseous products. There is no reason why programming of the temperature is not still possible. The most generally useful technique for analysis of these effluent gases is gas chromatography; in the reported work seen by the present author, these sample materials have been vaporised into the carrier gas stream, and carried immediately into the chromatographic column.

QUALITATIVE IDENTIFICATION OF DECOMPOSITION PRODUCTS

In general, direct injection of the decomposition product gases into the chromatograph is done by rapidly heating the material in the gas stream, the means of heating being usually the sample container as well. Experimenters principally interested in the chromatographic analysis can very easily overlook the importance of the manner of heating and, indeed, this is a common occurrence. The specimens are heated rapidly, so that the product gases appear in the chromatograph as a single pulse of gases; identification of the gases given off at intermediate temperatures is not attempted.

The transfer of heat from the heater wire to the sample material is a source of variation and error with specimens of appreciable thickness. Jennings and Dimick[8] avoided the heat transfer problem by evaporating the specimen on the heater wire (using aqueous phosphoric acid to supply hydrogen and oxygen for the decomposition reaction). They examined the effect of temperatures from 550 to 1100°, finding that for thymine there was no appreciable difference in the pyrolysis pattern, *i.e.*, the identities and relative quantities of products. The first composite peak in their Fig. 2 is likely to be permanent gases. These results show their reproducibility on repetition of the experiment as indicated in their table. This is not the sort of reproducibility one would expect from an ordinary chromatographic analysis, so that the deviation of irreproducibility must be related to the pyrolysis technique. The non-linearity in Jennings and Dimick's calibration values may still possibly be a heat transfer problem; the thin specimens with good exposure to the atmosphere may partly volatilise without decomposition, but the thicker specimens, being heated from the inside, may be subject only to the same absolute quantity of vaporisation, and hence a smaller percentage effect. The probability that the thicker specimens reach higher temperatures locally may also lead to some variation in the relative quantities of the several products, even though the identities of the products remain the same. Note that Jennings and Dimick were able to distinguish quite clearly between positional isomers; cytosine and isocytosine showed quite different proportions of products under similar pyrolysis conditions.

Quite different heating conditions were used by Strassburger, Brauer, Tryon and Forziati;[9] these authors used a much lower temperature pyrolysis in their studies of methyl methacrylate copolymers. They heated their pyrolysis coil to about 450° with 10–15 mg of specimen contained therein. At that temperature, and in the absence of oxygen or of hydrogen, a relatively non-volatile residue is formed. The reactions causing the formation of the residue also introduce distinct non-linearities into the calibration for quantitative measurements so that, for example, the sample weight-to-peak area ratio varies by a factor of 2 in the methyl methacrylate–ethylene dimethacrylate copolymer.

DEPENDENCE OF PRODUCTS ON CONDITIONS

Although some of the authors cited indicate that the pyrolysis products are the same over a wide range of pyrolysis conditions, to assume this happy circumstance for any given material to be studied would be exceedingly optimistic. A thin layer of material in contact with a heating element or other form of hot surface, at a temperature approximating the ultimate decomposition temperature of the material, may transmit heat rapidly enough to permit the entire film to decompose at essentially the same time, and more or less at the same temperature. The material in contact with the heated surface does not necessarily rise in temperature greatly above the surface of the film. If this heated surface were several hundred degrees, say, above the ultimate decomposition temperature, rapid decomposition of the inner portion of the film could change the conditions of heat transfer substantially. With very thin specimens the problem will arise only in the extreme cases, because the heating of the surface is not instantaneous; the heat capacity of the wire itself will cause some delay in reaching the final temperature, permitting a similar smooth rise by the specimen material.

If a thick sample is placed in contact with a heating element, and the heating element is supplied with a sudden application of an electric circuit, the relatively low thermal conductivity of the typical organic specimen will permit the establishment of a high (and not necessarily continuous) temperature gradient through the specimen. The over-all effect will depend on the nature of the sample-holding system; if the material has been deposited on a wire or other surface by evaporation of a solvent, so that there is a continuous layer on the heating surface, the material next to the heating surface may well be heated slowly enough to permit low temperature decomposition products to form; but these decomposition products cannot escape and will consequently be subject to further decomposition. If particles are laid upon the heating surface, the portion of the surface initially in contact may be heated slowly enough to undergo a low temperature decomposition, but the new layers of material subsequently touching the heated surface are coming in contact with a hotter and hotter surface, bringing about the possibility of a different decomposition mechanism.

The change in products obtained with change of pyrolysis conditions has been demonstrated by Martin and Ramstad,[10] who used flash pyrolysis to decompose cellulose in the sample chamber of a two-stage column. They separated the permanent gases on a gas-solid absorption column, using polypropylene glycol. The specimen was heated by flash photolysis; *i.e.*, intense radiation from a flash tube or arc source was directed on the specimen for a short length of time, the temperature reached depending both on the intensity and the time of exposure. They induced momentary temperatures in the sample in excess of 600°, with intense radiation of a millisecond duration, and compared the results with a slower pyrolysis in the 250–350° range, induced by less-intense radiation lasting for several seconds. The decomposition products are carried into the polypropylene glycol column, where the permanent gases are impeded only slightly. These are led from the glycol column into the activated charcoal column where the gases are separated, the columns being uncoupled immediately after passage of the permanent gases from stage 1 into stage 2. The slow pyrolysis produces only carbon monoxide and carbon dioxide among the permanent gases, but the flash pyrolysis produces significant quantities of the lighter hydrocarbons. The principal feature of the partition column curves is the greatly diminished amount of water relative to the other components in the flash pyrolysis. Although it is the major component, two of the other peaks at least surpass it in height. Note, too, that the magnitude of the carbon monoxide peak in the flash pyrolysis is more than ten times as high as the carbon dioxide peak, but in the slow pyrolysis it is somewhat smaller. Explanation of these variations would require further knowledge of the system, but a safe general conclusion can be stated: variations in the rate of heating of an organic specimen may cause different products or different relative quantities of products.

OTHER POSSIBILITIES

Now let us consider some of the extensions of effluence analysis. First of all let us consider changes in the carrier gas, made with the intention of encouraging or inhibiting some particular reaction. The use of helium-oxygen and helium-nitrogen mixtures has already been discussed in relation to determining the steps of an inorganic reaction. In this case, the helium-oxygen mixture permitted the oxidation of carbon monoxide, but the absence of oxygen brought about decomposition without oxidation. Similarly, small quantities of oxygen in the carrier gas stream would permit oxidation or partial oxidation of the specimen; or the presence of hydrogen might permit saturation of organic carbon chains. This is not being recommended as a general technique, but as a modification of procedure which might yield useful information. Repetitive sampling into the column in the manner practised by the present author (*vide supra*) would yield successive lots of decomposition products as the temperature was increased. Decompositions of specimens can be carried out directly in the sampling locations of analytical instruments other than chromatographs or chromatographic type of detectors, and similarly the decompositions can be programmed either step-wise or continuously. Two types of analyser are of particular promise, optical and mass spectrometers. Decomposition into, say, an infrared absorption spectrometer sample tube would be of particular interest if a particular compound or functional group were being monitored. Fairly high resolution would be required to obtain unambiguous results. There is the advantage, however, that the appearance of the product could be followed during the entire decomposition and if the decomposition is programmed some measure of the temperatures of appearance of various products may be obtained.

Of the mass spectrometers, the time-of-flight spectrometer would be of special interest because of the high frequency of repetitive sampling possible. Decomposition in a chamber connected to the spectrometer by an appropriate orifice would make possible the gathering of kinetic information on decompositions.

Relating the events recorded by these various techniques needs to be done with great care. Bussière *et al.*[6] compared curves obtained by their simultaneous determinations (*vide supra*) to those obtained on other (apparently single-purpose) apparatus. Bussière *et al.* conclude that it is preferable to make all the measurements simultaneously in order to obtain agreement in the interpretation of a given reaction. This is a fairly common attitude. The present author has contended[11]—and still contends—that unless the results from each technique have some real significance, attempts to relate them are seldom rewarding even when apparently successful. The agreement that is almost unavoidable in simultaneous determinations can give the observer an entirely unwarranted confidence in whatever he chooses the curves to mean. Further discussion of simultaneous determinations is presented in a forthcoming monograph.[12]

Zusammenfassung—Die Analyse der bei thermischen Zersetzungen entwickelten Gase kann dazu dienen, das Fortschreiten oder den Mechanismus der Zersetzungen zu verfolgen oder die zersetzte Probe zu charakterisieren. In jedem Fall müssen bestimmte Probleme berücksichtigt werden. Diese Probleme werden diskutiert, darunter das Vorgehen bei der Aufheizung, die Analyse der Produkte und die Kompromisse, die bei Simultanmessungen geschlossen werden müssen.

Résumé—Que l'analyse des gaz qui se dégagent lors de décompositions thermiques soit utilisée pour élucider le développement ou le mécanisme des décompositions, ou pour caractériser l'échantillon, on doit traiter de certains problèmes. On discute de ces problèmes, comprenant le chauffage, l'analyse des produits, et les compromis auxquels on doit avoir recours lors de mesures simultanées.

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QUENCHOFLUOROMETRIC ANALYSIS FOR FLUORANTHENIC HYDROCARBONS IN THE PRESENCE OF OTHER TYPES OF AROMATIC HYDROCARBON

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Summary—In this first paper of a series, a new analytical tool is introduced for the analysis of fluorescent molecules—quenchofluorescence analysis. This field of research will have far-reaching ramifications in organic trace analysis. Analytical use is made of the quenching effect in spectrophotofluorometry. Compounds such as anthracene, phenanthrene, pyrene, benz(*a*)anthracene, benzo(*a*)pyrene, perylene, *etc.*, have been found to be non-fluorescent in nitromethane solution, but hydrocarbons containing the fluoranthenic ring are fluorescent. Use has been made of this phenomenon in characterising fluoranthene and benzo(*k*) fluoranthene in airborne particulates, following column chromatography. The phenomenon has also been used in thin-layer chromatography, directly on the plate.

FLUORESCENCE quenching is a serious problem in the analysis for polynuclear aromatic hydrocarbons in airborne particulates, especially with fairly high solution concentrations of either the compound being analysed or the impurities. Primarily because of this difficulty it was believed that quenching could be a useful analytical tool. With a proper reagent it should be possible to quench part of the fluorescence excitation or emission spectra or all the fluorescence excitation and emission spectra of a molecule. In the former case the quenching could result from the direct absorption of the exciting light by the quencher; in the latter case it could result from the same phenomenon or from formation of a non-fluorescent molecule, or from both. The new molecule could be a complex or a newly formed derivative.

As a first approximation, nitro derivatives, many of which are well-known complexing agents, were selected for investigation for the following reasons. Alcoholic solutions of rhodamine B are quenched to some extent by the addition of nitrobenzene.[1] Aqueous solutions of rhodamine B are completely quenched by picric acid.[2] Complex formation is believed to cause this phenomenon. Acetone solutions of chrysene are quenched by picric acid and many other nitro compounds.[2]

Benzo(*a*)pyrene and six other polynuclear aromatic hydrocarbons have been shown to be nonfluorescent in solutions of nitromethane or nitrobenzene.[3] Of compounds of this type tetranitromethane was the most potent quencher. The fluorescence of 1 μg of benzo(*a*)pyrene in 10 ml of petroleum ether was completely inhibited by 200 μg of tetranitromethane.[3]

It is reported that in the presence of bromine, under carefully controlled conditions, the fluorescence of benzo(*a*)pyrene disappears but that of benzo(*k*)fluoranthene is unaffected.[4] By this procedure, for which details are not given, benzo(*k*)fluoranthene and benzo(*a*)pyrene were satisfactorily estimated in synthetic mixtures containing equivalent amounts of these two chemicals, perylene, and benzo(*e*)pyrene. The pure spectrum of benzo(*k*)fluoranthene could not be obtained from this mixture.

The selective use of the quenching phenomenon in the analysis for one component in a mixture has been studied in only a few isolated cases, and even in those cases the implications of the general use of quenching to increase greatly the selectivity of many fluorometric methods have not, as yet, been grasped. A thorough study is needed, because quenching reagents can greatly increase the selectivity and usefulness of spectrophotofluorometric and spectrophotophosphorometric analysis for many types of aromatic compound. It is predicted that this type of analysis will have a very wide range of application in organic analysis. It is suggested that these procedures be called *quenchofluorometric* and *quenchophosphorometric* analysis.

In the work reported in this paper, fluoranthenic hydrocarbons are characterised and determined in the presence of other types of polynuclear aromatic hydrocarbon. In subsequent papers, other types of quenchofluorometric procedures with a very high order of selectivity will be introduced.

Fluoranthenic hydrocarbons such as benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, and indeno(1,3,3-*cd*)pyrene have been reported to be carcinogenic to mice.[5]

EXPERIMENTAL

Reagents and apparatus

Nitromethane was obtained from Matheson, Coleman, and Bell, Cincinnati, Ohio, and distilled before use. Alumina adsorbent was obtained from Brinkman Instruments, Inc., Great Neck, L.I., New York.

All chromatographic plates were examined for fluorescence colours in a Chromato-Vue cabinet (Kensington Scientific Corp., Berkeley, California) under a 3660-Å light source.

The following settings were used with the Aminco-Bowman spectrophotofluorometer: sensitivity 50, meter multiplier 0·01 (whenever possible), slit arrangement No. 2, and phototube RCA type 1 P 21.

Thin-layer chromatographic procedures

A. Plates were prepared and developed by procedures analogous to those described previously.[6] Where mixtures of an alkane and nitroalkane were used as developing solvents, the plate was read under the ultraviolet light as soon as it was taken out of the tank, and was then read again after it had dried (about 15–30 min).

B. *Nitromethane test for non-quenchable compounds, such as fluoranthenes*, etc. After thin-layer chromatography the line of development is treated with small bursts of nitromethane fumes, or with microdrops of the liquid. This can be done with a throwaway pipette fitted with a squeeze bulb. Any change or loss in fluorescence colour is noted.

RESULTS

Spectrophotofluorometry

In previous work the fluorescence spectra of a large variety of hydrocarbons were obtained in pentane and sulphuric acid.[7] One of the main variables in the spectra of these different hydrocarbons was their broad range of intensities. With nitromethane as the solvent most of these hydrocarbons become non-fluorescent, thus greatly increasing the selectivity of the fluorometric procedure. Thus, all non-fluoranthenic hydrocarbons are non-fluorescent in nitromethane (Table I). It must be emphasised that although all the hydrocarbons in Tables I and II are fluorescent in pentane or chloroform solution, only the fluoranthenic hydrocarbons are fluorescent in nitromethane solution.

TABLE I.—COMPOUNDS WHOSE FLUORESCENCE IS QUENCHED IN NITROMETHANE SOLUTION

Acenaphthylene
Phenanthrene
Anthracene
9-Bromoanthracene
Benz(*a*)anthracene
11-*H*-Benzo(*a*)fluorene
11-*H*-Benzo(*b*)fluorene
7-*H*-Benzo(*c*)fluorene
Benzo(*c*)phenanthrene
Chrysene
4-*H*-Cyclopenta(*def*)phenanthrene
Naphthacene
Pyrene
1-Bromopyrene
1-Methylpyrene
Triphenylene
Benzo(*b*)chrysene
Benzo(*a*)pyrene
Benzo(*e*)pyrene
Perylene
Dibenz(*ac*)anthracene
Dibenz(*ah*)anthracene
Dibenz(*aj*)anthracene
Picene
Anthanthrene
Benzo(*ghi*)perylene
Naphtho(2,1,8-*qr*)naphthacene
Dibenzo(*ae*)pyrene
Dibenzo(*gp*)chrysene
Dibenzo(*brst*)pentaphene

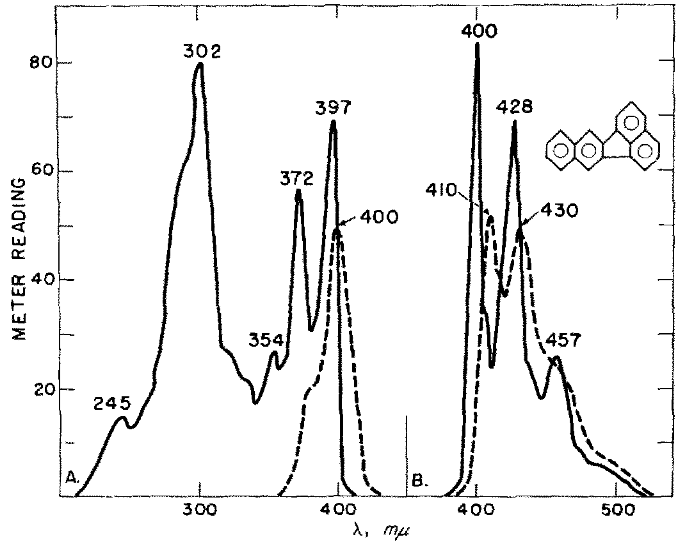


FIG. 1.—Fluorescence spectra of benzo(*k*) fluoranthene.
A. Excitation spectra: at emission λ 400 mμ, MM = 0·01 and 10^{-6} *M* in pentane (———) and at emission λ 430 mμ, MM = 0·03 and 10^{-5} *M* in nitromethane (– – –).
B. Emission spectra: at excitation λ 302 mμ, MM = 0·01 and 10^{-6} *M* in pentane (———) and at excitation λ 400 mμ, MM = 0·03 and 10^{-5} *M* in nitromethane (– – – –).

Although these latter hydrocarbons are fluorescent in nitromethane solution, their short-wavelength excitation spectral bands have been quenched (Table II). This latter effect may result from direct absorption of the short-wavelength light by the quencher. The striking effect of nitromethane on the fluorescence spectrum of benzo(*k*)fluoranthene as compared to the spectrum in pentane is shown in Fig. 1. The intensities of all bands have been decreased. The partial quenching of the short-wavelength excitation bands, which probably results to some extent from the internal filter effect of the solvent, merits further investigation. The emission spectral bands, which are present in chloroform or pentane, are present in nitromethane also, although their intensity has been decreased.

TABLE II.—FLUORESCENCE SPECTRA OF FLUORANTHENIC HYDROCARBONS IN NITROMETHANE

Compound	Det. limit, *ng/0·1 ml*	Molar concn.	Emission spectra[a]		Excitation spectra[b]	
			EM. λ, *mμ*	*MM.T*	Exc. λ, *mμ*	*MM.T*
Fluoranthene[cf]	340	10^{-4}	460	0·65	380	0·68
Benzo(*b*)fluoranthene[c]	400	10^{-4}	*400*	0·45	378	0·67
			440			
			450	0·69	*390*	0·40
				0·63		
Benzo(*k*)fluoranthene[df]	13	10^{-5}	409	2·0	*384*	0·9
			430	2·0	400	2·0
			458	0·9		
Benzo(*ghi*)fluoranthene[cf]	250	10^{-4}	420	1·1	395	1·3
			445	1·4	*410*	0·6
			472	0·9		
			500	0·4		
Indeno(1,2,3-*cd*)pyrene[cg]	14	10^{-5}	480	2·0	385	2·5
			500	2·4	408	2·4
					415	2·2
					440	0·8
Indeno(3,2-j)acenaphtho-(1,2-*k*)fluoranthene[df]	7	10^{-6}	474	0·55	390	0·7
			500	0·62	*400*	0·6
					430	0·3
Diacenaphtho(1,2-*j*: 1′,2′-*l*) fluoranthene[eg]	5	10^{-7}	474	0·11	395	0·11
			500	0·12	*405*	0·10
					430	0·05
Acenaphtho(1,2-*b*)quinoxaline[gh]	750	10^{-4}	494	0·27	397	0·27
Acenaphtho(1,2-*b*)benzo(*f*)-quinoxaline[gi]	60	10^{-5}	468	0·45	399	0·48
Acenaphtho(1,2-*b*)benzo(*g*)-quinoxaline[cg]	70	10^{-5}	500	0·42	399	0·42
					403	0·40
Diacenaphtho(1,2-*b*: 1′,2′-*d*)-thiophene[dg]	100	10^{-5}	472	0·34	394	0·41
			501	0·41	*409*	0·38

[a] Instrument set at most intense excitation wavelength maximum. Values *in italics* are shoulders.

[b] Instrument set at most intense emission wavelength maximum. Values *in italics* are shoulders.

[c] Band intensities in nitromethane-trifluoroacetic acid (99: 1, v: v) decreased one-half to one-third.

[d] Same intensities in acid solution.

[e] Intensity doubled in acid solution.

[f] Band intensities in nitromethane-triethylamine (99: 1, v: v) decreased one-half to one-sixth.

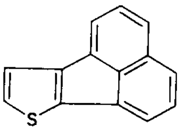
[g] Same intensity in alkaline solution.

[h] In nitromethane-trifluoroacetic acid (99: 1, v: v) at $2 \times 10^{-5}M$: excitation λ max. 400, MM.T 0·67 and emission λ max. 515, MM.T 0·67.

[i] In nitromethane-trifluoroacetic acid (99: 1, v: v) at $10^{-6}M$: excitation λ max. 423, 450 and MM.T 0·64, 0·70, respectively and emission λ max. 507.

A tentative explanation for the complete quenching of the non-fluoranthenic hydrocarbons is that these compounds form a non-fluorescent π-complex in the excited state. In line with this hypothesis is the fact that naphtho(2,1,8-*qr*)naphthacene is fluorescent in chloroform and non-fluorescent in nitromethane, but its absorption spectra in chloroform and nitromethane are essentially identical from 600 to 370 mμ (the cut-off point for nitromethane). Consequently a complex is not present in the ground state, but could be present in the excited state (all concentrations were $10^{-5}M$). This hypothesis is being investigated.

Every hydrocarbon so far investigated that is fluorescent in nitromethane solution has a fluoranthenic ring as part of its structure. Even the heterocyclic hydrocarbons appear to follow the same rule. The quinoxaline derivatives have 1 ring in the fluoranthenic part of the molecule with *para*-nitrogen atoms. In spite of these nitrogens, the compounds act like the other fluoranthenic derivatives. In the thiophene compound a true fluoranthenic ring is not present. A sulphur analogue, which is iso-π-electronic to fluoranthene, is present, however, *e.g.*,



Consequently, it appears that a fluoranthene-type ring in a molecule is necessary for a polycyclic aromatic hydrocarbon to be fluorescent in nitromethane. Exceptions to this rule are being sought.

APPLICATION

Characterisation following column chromatography

Following the column-chromatographic fractionation of organic airborne particulates, some of the fluoranthenic compounds can be readily characterised in the various fractions. When the fluorescence spectrum is obtained in nitromethane solution, the interfering aromatic hydrocarbons are eliminated. For example, the interfering spectra of all the other components in the pyrene fraction are eliminated and the fluorescence spectrum of fluoranthene is obtained (Fig. 2).

In the same way, the pure excitation and emission spectra of benzo(*k*)fluoranthene can be obtained from a nitromethane solution of the benzpyrene fraction of organic airborne particulates (Fig. 3). Thus, with a single spectral run in nitromethane, benzo(*k*)fluoranthene can be readily characterised in the benzpyrene fraction.

Characterisation following thin-layer chromatography

The use of nitromethane following a thin-layer chromatographic separation of the benzene-soluble fraction of airborne particulates is shown in Fig. 4c. The fluorescence colours obtained for a dry chromatogram following development are seen in Fig. 4b. Treatment with trifluoroacetic acid fumes gives the chromatogram as shown in Fig. 4a. The brilliant emerald green and pink fluorescent spots (marked 1 and 2) have been found in many of the benzene-soluble fractions of urban airborne

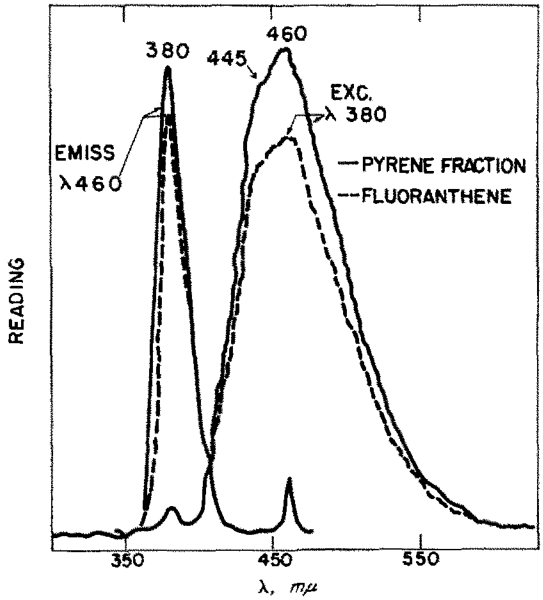


FIG. 2.—Fluorescence spectra of the pyrene fraction of airborne particulates (———) and fluoranthene (- - - - -), both in nitromethane.

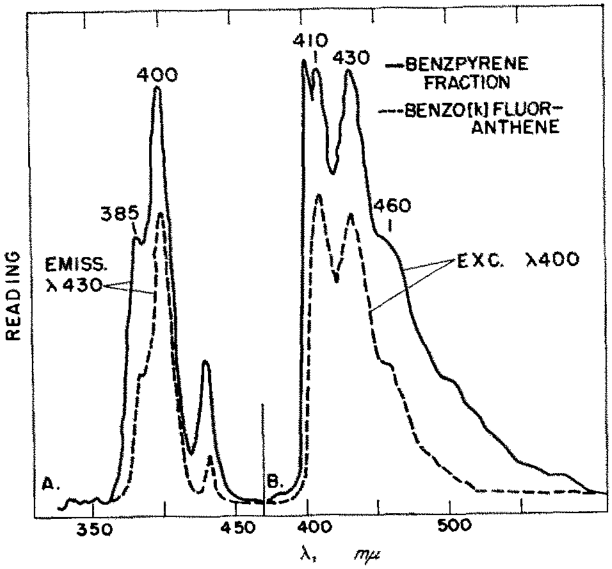


FIG. 3.—Fluorescence spectra of the benzpyrene fraction of airborne particulates (———) and benzo(*k*)fluoranthene (- - - -), both in nitromethane.

A. Excitation spectra.
B. Emission spectra.

particulates that have been examined. They serve the function of markers, in that their R_f values denote the relative activity of the alumina or the moving power of the solvent system. Treatment of the original chromatogram with nitromethane quenches the fluorescence of most of the spots, and in addition brings out new spots at 3 and the solvent front. This technique should prove useful in the eventual characterisation of the many unknown aromatic compounds in airborne particulates and other complicated mixtures. When a benzene-soluble fraction is separated on a thin layer of alumina with pentane-2-nitropropane (19 : 1, v : v), the final results differ drastically (Fig. 5a) from the pentane-ether chromatogram (Fig. 4). As the figure shows, hydrocarbons such as benzo(*a*)pyrene are invisible, while benzo(*k*)fluoranthene fluoresces with a brilliant blue colour. On standing, the fluorescence colours of most of the spots change, and new spots appear (Fig. 5b). Thus, evaporation of the nitropropane causes the compounds that are non-fluorescent in nitropropane to become fluorescent. This phenomenon is demonstrated by the benzo(*a*)pyrene spot, which is not seen in Fig. 5a, but which is shown fluorescent in Fig. 5b. Thus, these two different procedures both dependent on the quenching effect of a nitroalkane, can be used in thin-layer chromatography. In addition, either of these procedures can be followed by the treatment with trifluoroacetic acid fumes.

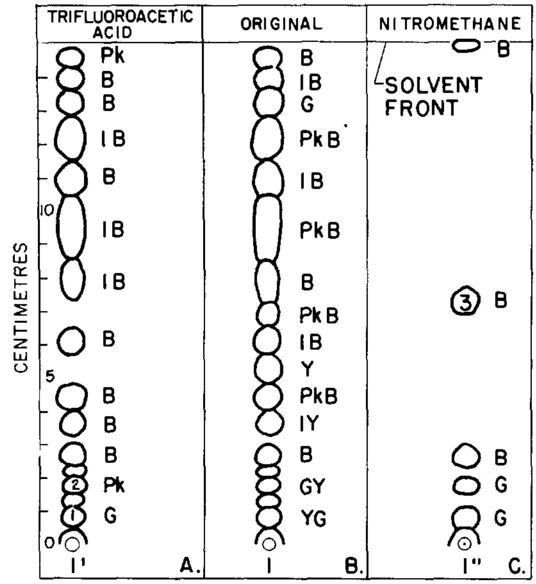


FIG. 4.—Alumina thin-layer chromatogram of a benzene-soluble fraction of airborne particulates.
A. Original treated with trifluoroacetic acid fumes.
B. After development with pentane-10% ether.
C. Original treated with nitromethane fumes.

Determination of fluoranthenes

Beer's law type relations were found to hold for fluoranthene in nitromethane from 2 to 25 μg/ml and for benzo(*k*)fluoranthene from 0·2 to 2·5 μg/ml. Fluoranthene could be readily determined in a synthetic mixture of equal amounts of pyrene, fluoranthene, chrysene, and benzo(*a*)anthracene. Similarly, benzo(*k*)fluoranthene could be readily determined in a synthetic mixture of equal amounts of benzo(*a*)pyrene benzo(*e*)pyrene, perylene and benzo(*k*)fluoranthene. The pure excitation and emission spectra of fluoranthene and benzo(*k*)fluoranthene are obtained from these synthetic mixtures. The procedure involved dissolution of the mixture in nitromethane and then reading of the meter multiplier × transmittance (MM.T) values at the most intense excitation and emission wavelength maxima of fluoranthene or benzo(*k*)fluoranthene. When this procedure was applied to the pyrene fraction obtained after column chromatography of a sample of urban airborne particulates, the values obtained for fluoranthene were 2·5 times those obtained by the ultraviolet absorption base-line method of measurement.[9,10] Similarly, high values were obtained for benzo(*k*)fluoranthene. Because fractions obtained after the fluoranthene fraction, and just before and after the benzpyrene fraction, were fluorescent in nitromethane solution, it was concluded that either additional fluoranthenic compounds or some other types of unquenched compound were present. The procedure is therefore of value for characterisation but cannot be used for the determination of individual fluoranthenic compounds until better separation is achieved and more information is obtained on any other types of compound that fluoresce in nitromethane solution.

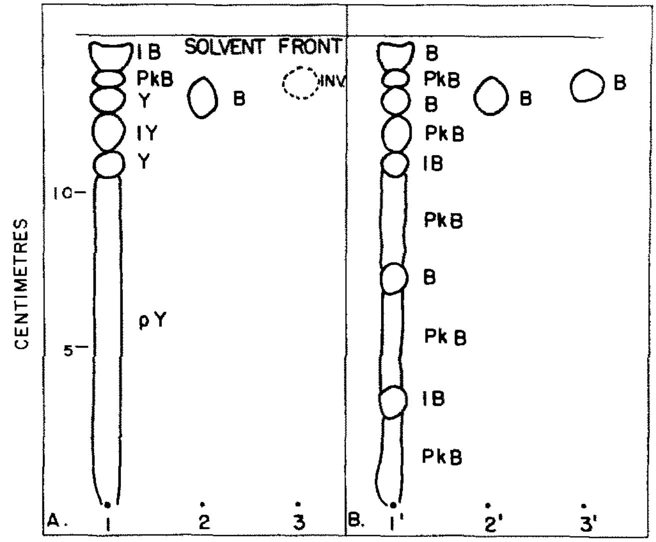


FIG. 5.—Alumina thin-layer chromatogram of (1) benzene-soluble fraction of airborne particulates, (2) benzo(*k*)fluoranthene and (3) benzo(*a*)pyrene.
A. Immediately after development with pentane—5 % 2-nitropropane.
B. After plate has dried about 30 min.

CONCLUSION

A simple technique is introduced that facilitates the characterisation of fluoranthenic compounds following chromatography. The method is based on the non-fluorescence of non-fluoranthenic hydrocarbons and the fluorescence of fluoranthenic hydrocarbons in nitromethane solution. By this technique the two types of compound can be differentiated on a thin-layer plate or in solution.

Zusammenfassung—In dieser Arbeit, die die erste einer Reihe weiterer Arbeiten sein soll, wird eine neue Art der Analyse fluoreszierender Moleküle eingeführt: die Fluoreszenz-Löschungs-Analyse. Diese Methode wird in der organischen Spurenanalyse einen weit verzweigten Anwendungsbereich finden. Es wird dabei analytischer Gebrauch von dem Effekt der Fluoreszenzlöschung gemacht. Verbindungen wie Anthracen, Phenanthren, Pyren, Benz(*a*)anthracen, Benzo(*a*)pyren, Perylen usw. fluoreszieren in Nitromethanlösung nicht, während Kohlenwasserstoffe mit Fluoranthenring fluoreszieren. Diese Erscheinung wurde dazu ausgenutzt, Fluoranthen und Benzo(*k*) fluoranthen in Schwebeteilchen aus der Luft nach vorhergegengener Säulenchromatographie zu identifizieren. Die Erscheinung wurde auch bei der Dünnschichtchromatographie direkt auf der Platte ausgenutzt.

Résumé—Dans ce premier mémoire d'une série, on présente une nouvelle méthode analytique pour l'analyse des molécules fluorescentes: l'analyse par extinction de fluorescence. Ce domaine de recherches aura des ramifications lointaines dans l'analyse organique de traces. On utilise analytiquement l'effet d'extinction en spectrophotofluorimétrie. On a trouvé que des composés tels que l'anthracène, le phénanthrène, le pyrène, le benzo(*a*)anthracène, le benzo(*a*)pyrène, le pérylène, etc. ne sont pas fluorescents en solution dans le nitrométhane, cependant que des hydrocarbures contenant le noyau fluoranthénique sont fluorescents. On a utilisé ce phénomène en caractérisant le fluoranthène et le benzo(*k*)fluoranthène dans les particules en suspension dans l'air, après chromatographie sur colonne. Le phénomène a été également utilisé en chromatographie sur couches minces, directement sur la plaque.

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SOME RATHER UNUSUAL CHEMICAL ANALYSES

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Summary—Some rather unusual chemical analyses are described. A typical example is the determination of a few μg of one element in a sample composed essentially of the elements listed in the periodic table. This somewhat bizarre sample is a solution containing 10 mg each of about seventy different elements.

INTRODUCTION

FOR the past few years, the authors and their colleagues have been concerned with developing methods for the determination of trace elements in beryllium and beryllium oxide.[1-7] Although these methods were developed primarily for application to a beryllium matrix, they were intended to have much wider usage.

It is the authors' opinion that the determination of a trace amount of an element in a matrix is rarely difficult because of the particular matrix. The real difficulty is the presence in the matrix of unknown amounts of other elements which can interfere with the method to be used. A check of the analytical literature will immediately reveal that few indeed are the methods which have been investigated comprehensively. Rarely does one know which elements of all those in the periodic table interfere, and in what amounts. Consequently, the analyst must frequently use a method whose limitations are unknown, and must apply it to a sample which might contain a number of interfering elements. Therefore, we attempted to develop, within certain limitations, specific methods of analysis. Although many tests of these methods have been made, the most critical test made is the one here described.

When measuring the effect of other elements in an analytical procedure, it is common practice to test the effect of each individual element on the determination of the constituent, in this case a trace element. However, "other elements" do not occur individually in a sample, but rather in an assorted collection of kinds and amounts. Furthermore, if there are n elements to be included in the investigation, there would be 2^n-1 combinations to be tested. This assumes that all elements would be at the same concentration level. Because the latter situation is never true, one can easily see that there is an infinite number of combinations to test. In order to make a meaningful test of the effect of other elements, it is necessary to simplify this situation. The method chosen was to measure the effect, if any, of all elements added simultaneously at one concentration level—10 mg.

The effect of 71 elements was tested (72 minus the element being determined): aluminium, antimony(III), arsenic(III), barium, beryllium, bismuth, boron, bromine (as bromide), cadmium, calcium, cerium(IV), caesium, chlorine (as chloride), chromium(III), cobalt, copper, dysprosium, erbium, europium, fluorine (as fluoride), gadolinium, gallium, germanium(IV), gold, hafnium, holmium, indium, iodine (as iodide), iridium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese(II), mercury(II), molybdenum(VI), neodymium, nickel, niobium, palladium, phosphorus (as phosphate), platinum, potassium, praseodymium, rhenium(VII), rhodium, rubidium, samarium, scandium, selenium, silicon (as silicate), silver, sodium, strontium, sulphur (as sulphate), tantalum, tellurium(IV), terbium, thallium(I), thorium, thulium, tin(II), titanium, tungsten, uranium(VI), vanadium(V), ytterbium, yttrium, zinc and zirconium. It should be noted that two valence states of an element were used for several of the tests.

All of the above elements were added (in the valence state indicated) in every test, except where noted.

The technique used to make the test was as follows. Fifty mg of each of the elements (in solution) were added to a beaker, together with the appropriate amounts of acid(s) and complexing agent, if any. If precipitation or hydrolysis occurred, the solution was filtered and the precipitate was analysed to determine what amounts of what elements were not being included in the test. This analysis is given under *Analysis of Residue*. The filtrate was then diluted to a convenient volume and divided into 5 equal parts. One part was used to make an estimate of the amount of the element being determined which was present as a trace in the elements added. Two parts, labelled B1 and B2, were carried through the procedure as blanks. In order to confirm the fact that the absorbance of the blank was caused by the element being determined, the coloured solution was analysed spectrographically. Although this measurement may not be very accurate, it is sufficiently so to confirm the fact that the absorbance measured was actually caused by the element being determined. This spectrographic analysis is listed under *Element found, spectrographic*.

The other two parts of the solution, labelled S1 and S2, were "spiked" with an appropriate amount of the element being determined and analysed by the method developed for this particular element.

EXPERIMENTAL* AND RESULTS

Determination of iron[1]

Eight hundred ml of a solution were obtained containing the elements whose effect was to be investigated. Titanium was added as Ti^{III}. Silicon was not added because of its tendency to form an emulsion during extraction. Tellurium, gallium, and uranium were not added because of their known interference effect. The solution, $6M$ with respect to hydrochloric acid, containing 5 g of citric acid and sufficient bromine to oxidise the iron, was divided as described and treated as follows.

Six extractions were made with 25 ml of $0{\cdot}01M$ tri-n-octylphosphine oxide (TOPO) in cyclohexane. The combined extracts were shaken with 35 ml, 35 ml and 10 ml of $3M$ sulphuric acid (iron reverted to the aqueous phase). The sulphuric acid phase was washed 10 times with 25-ml portions of $0{\cdot}1M$ TOPO in chloroform and the organic phases were discarded. Sixty ml of hydrochloric acid were added, and the iron was extracted with 10 ml of $0{\cdot}01M$ TOPO in cyclohexane. A 1-ml aliquot was transferred to a 25-ml volumetric flask containing 15 ml of isopropyl alcohol and sufficient hydroquinone for reduction of the iron. After addition of 1,10-phenanthroline, iron was determined as the iron(II)-phenanthroline complex. The results are shown in Table I.

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* Because of the number of methods discussed, the reader is referred to the original publications for greater detail concerning reagents, procedures, *etc.*

The results indicate that accurate results will be obtained using this method if:

(1) the amount of silicon is reduced to a level at which it will not cause emulsification when the TOPO extraction is made;

(2) sufficient initial extractions are made to remove iron;

(3) the 1,10-phenanthroline complex solution is clear when the final absorbance measurement is made;

and (4) gallium, tellurium and uranium are below the level indicated in the published report.

TABLE I.—TEST OF IRON METHOD

Soln.	Iron, μg Added	Iron, μg Found	Recovery %	Iron found (spectrographic) μg
B1	—	66·2	—	90
B2	—	71·7	—	—
S1	103·5	170	98	—
S2	103·5	171	98	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 4 mg of Hf, 2 mg of Ta, and 1·5 mg of Zr.

Determination of copper[2]

Twelve hundred ml of a solution were obtained containing the elements whose effect was to be investigated. Iron was added as both Fe^{II} and Fe^{III} (50 mg of each), manganese as both Mn^{II} and Mn^{VII} (50 mg of each), and titanium as both Ti^{III} and Ti^{IV} (50 mg of each). Chromium and hafnium were not added. The solution, which contained 25 g of citric acid, 25 ml of hydrochloric acid, 50 ml of sulphuric acid and 5 g of hydroxylamine hydrochloride (to reduce the copper), was neutralised to a pH of 5·0, and divided as described.

Copper was determined by extraction of the neocuproïne complex using the method described[2] except that the extraction was made with 25 ml of 4-methyl-2-pentanone, and the absorbance was measured using 2-cm cells. The results are shown in Table II under B1 and S1. When the extracts were diluted in a volumetric flask (because of the varying solubility of 4-methyl-2-pentanone in the aqueous phase) the results were somewhat better, as shown by B2 and S2 in Table II.

TABLE II.—TEST OF COPPER METHOD

Soln.	Copper, μg Added	Copper, μg Found	Recovery %	Copper found (spectrographic) μg
B1	—	14·6	—	15
S1	60·9	72·2	95	—
B2	—	16·5	—	15
S2	60·9	77·4	100	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 4 mg of Au, 4 mg of Pt, 4 mg of Sr, 1·6 mg of Rh, and 1·6 mg of Pb.

When the same experiment was performed in the presence of 10 mg each of Cr^{III}, Cr^{VI} and Hf, only 90% recovery of the added copper was obtained, in agreement with the published report (*loc. cit.*).

Determination of molybdenum[3]

In addition to the elements whose effect was to be investigated, the solutions to be analysed contained the proper amounts of tartaric acid, hydrochloric acid and sulphuric acid. Barium, gold, and silver were not added because of the tendency of the large amount of precipitate to clog the separatory funnel. Palladium, platinum, rhenium, selenium and tellurium were not added because of their known interference effect. Molybdenum was extracted as the thiocyanate complex with 4-methyl-2-pentanone. The results are shown in Table III.

TABLE III.—TEST OF MOLYBDENUM METHOD

Soln.	Molybdenum, μg Added	Molybdenum, μg Found	Recovery, %	Molybdenum found (spectrographic) μg
B1	—	5·6	—	5
B2	—	5·6	—	5
S1	75	78·7	97	—
S2	75	78·7	97	—

Determination of cobalt[4]

In addition to the elements whose effect was to be investigated, the solutions to be analysed contained the proper amounts of hydrochloric acid, sulphuric acid and citric acid. Iron was added as both Fe^{II} and Fe^{III} (50 mg of each), and titanium as Ti^{III} and Ti^{IV} (50 mg of each). Chromium and manganese were not added in order to omit an ion-exchange step.

After adjustment of the pH to 4·0, the solutions were washed several times with acetylacetone. Sodium thiocyanate was added and cobalt was extracted as the thiocyanate complex with acetylacetone. The results are shown in Table IV.

TABLE IV.—TEST OF COBALT METHOD

Soln.	Cobalt, μg Added	Cobalt, μg Found	Recovery, %	Cobalt found (spectrographic) μg
B1	—	5	—	4
B2	—	5	—	4
S1	106	108	97	—
S2	106	108	97	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 10 mg of Ag, 1·6 mg of Sr, 1·2 mg of Zr, 0·8 mg of Pd, and 0·8 mg of Rh.

Determination of cadmium[5]*

In addition to the elements whose effect was to be investigated, the solution contained the proper amounts of hydrochloric, sulphuric and citric acids. Iron was added as Fe^{III}, and titanium as Ti^{III}. Cadmium was precipitated from an ammoniacal citrate solution with benzotriazole using nickel as a collector. After treatment of the precipitate with nitric and perchloric acids, a 10% hydrochloric acid solution of the residue was passed through an anion-exchange column. Cadmium, retained by the resin and subsequently eluted with 3*M* nitric acid, was finally determined by extraction from a strongly alkaline medium with a chloroform solution of dithizone. The results are shown in Table V.

TABLE V.—TEST OF CADMIUM METHOD

Soln.	Cadmium, μg Added	Cadmium, μg Found	Recovery, %	Cadmium found (spectrographic) μg
B1	—	1·1	—	1
B2	—	1·3	—	—
S1	3	4·2	100	—
S2	5	6·0	96	—

Determination of niobium and tantalum[6]*

In addition to the elements to be investigated, the solution contained the proper amounts of sulphuric acid and hydrochloric acid. Titanium was not added. Niobium and tantalum were precipitated with cupferron using zirconium as a collector. After ignition of the precipitate and fusion with sodium bisulphate, the fused mass was dissolved in 25% hydrochloric acid-20% hydrofluoric acid and added to an anion-exchange column. Niobium and tantalum were eluted from the column separately, and again precipitated with cupferron as before. After fusion and dissolution of the precipitates, niobium was determined as the hydroquinone complex and tantalum as the pyrogallol complex. The results are shown in Tables VIA and VIB.

* Test made at Ledoux and Company by S. Kallmann *et al.*

TABLE VIA.—TEST OF NIOBIUM METHOD

Soln.	Niobium, μg Added	Niobium, μg Found	Recovery, %	Niobium found (spectrographic) μg
B1	—	142	—	—
B2	—	153	—	130
S1	700	805	94	—
S2	1400	1490	96	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ba, 10 mg of Ag, 10 mg of Sr, 10 mg of P, 2 mg of Au, 1·5 mg of Pd, 0·5 mg of Zr, 0·5 mg of Hf, and 0·5 mg of Pb.

Niobium and tantalum were determined in the same solution; consequently, the *Analysis of residue* in Table VIA applies to Table VIB also. When titanium was added with the rest of the elements, the results were high and erratic. Titanium was not completely removed from the ion-exchange column, despite the fact that it does not interfere with the determination of niobium and tantalum when it (titanium) is added by itself. This is the first indication of a "synergistic effect" in any of the methods thus far.

TABLE VIB.—TEST OF TANTALUM METHOD

Soln.	Tantalum, μg Added	Tantalum, μg Found	Recovery, %	Tantalum found (spectrographic) μg
B1	—	43	—	—
B2	—	47	—	[a]
S1	819	877	102	—
S2	1638	1708	102	—

[a] Not detected spectrographically.

Determination of nickel[7]

In addition to the elements to be investigated, the solution contained the proper amounts of sulphuric acid, hydrochloric acid, and tartaric acid. Titanium was added both as Ti^{III} and Ti^{IV} (50 mg of each), and chromium was added both as Cr^{III} and Cr^{VI} (50 mg of each). Nickel was precipitated from an ammoniacal citrate solution with benzotriazole using cadmium as a collector. After treatment of the precipitate with nitric and perchloric acids, the residue was dissolved in a mixture of hydrochloric acid and isopropyl alcohol, and an anion-exchange separation was performed. Nickel was finally determined as the aqueous dimethylglyoxime complex. The results are shown in Table VII.

TABLE VII.—TEST OF NICKEL METHOD

Soln.	Nickel, μg Added	Nickel, μg Found	Recovery, %	Nickel found (spectrographic) μg
B1	—	68·0	—	55
B2	—	68·3	—	54
S1	100	167·5	99	—
S2	100	166·5	98	—

Analysis of residue (on the basis of 10 mg added): 10 mg of Ag, 10 mg of Au, 7·5 mg of Ba, 2·5 mg of In, 0·5 mg of Sr, and 2 mg of rare earths.

DISCUSSION

At one time it was hoped that the analyst's shelf would some day consist of a reagent specific for the determination of each element. Today, this idea seems to be somewhat naïve, although it may yet come to pass. However, the analyses presented here seem to indicate that specific methods can be developed. Furthermore, it is very evident that these methods are practical; *i.e.*, they can be applied to a wide variety of samples. The application of these methods will be the subject of a forthcoming paper.

It should be of interest at this time to repeat (but not in their original order) some of the remarks made by Lundell.[8]

> . . . there is an increasing tendency to devote more and more time to determinations which deal with the final act of a chemical analysis, and less time to chemical analysis itself—in other words, to consider chemical analysis as dealing with one or two variables instead of the dozen or more that are often involved . . . . Of course, there is good reason for confining analytical discussions to determinations which involve one or two variables. A system containing ten to twenty diverse components can hardly be handled on a strictly scientific basis, and any handling of it requires actual experience in analysis . . . . Methods of the type described (methods dealing with one or two variables) are about as helpful to the analyst as the method for catching a bird which the old folk used to recommend to children—namely to sprinkle salt on its tail. To do that one obviously must have the bird in hand, and in that case there is no need for the salt . . . . There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone, for nature and man both frown on celibacy. Methods of determination must therefore be judged by their "selectiveness." It is in this respect that most methods are weak and that improvements must come . . . . Because of their lack of selectivity, methods for the chemical analysis of things as they are do not stay put. Therein lies the danger of standard methods of analysis. As soon as the other group members creep in—for example, through changes in manufacture—the method must be changed.

These remarks, made over thirty years ago, are still appropriate today, with, we think, but one exception. It has been our endeavour to develop standard methods of analysis (which, of course, can be replaced or improved as new advances are made). The results of this paper indicate that specific methods can be developed, and the forthcoming paper will indicate the wide applicability of such methods.

In conclusion, it is the authors' opinion that these analyses are unique in the field of chemical analysis and should arouse the interest and thoughtful speculation of today's Lundells.

Acknowledgement.—The authors gratefully acknowledge those individuals who assisted in the development of these methods. The authors are greatly indebted to Dr. Louis Gordon who suggested this particular test.

Zusammenfassung—Enige ziemlich ungewöhnliche chemische Analysen werden beschrieben. Ein typisches Beispiel ist die Bestimmung weniger Mikrogramme eines Elements in einer Probe, die fast alle Elemente des periodischen Systems enthält. Es handelt sich um eine Lösung, die je 10 mg von etwa 70 verschiedenen Elementen enthält.

Résumé—On décrit quelques analyses chimiques un peu inhabituelles. Un exemple typique en est le dosage de quelques microgrammes d'un élément dans un échantillon essentiellement composé des éléments figurant dans le tableau périodique. Cet échantillon quelque peu bizarre est une solution contenant 10 mg de chacun d'environ soixante-dix éléments différents.

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STUDIES OF THE FIRE ASSAY FOR PLATINUM METALS BY LEAD COLLECTION

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Summary—A fire-assay procedure for determining platinum, palladium, rhodium or iridium in the nitric acid parting solution from a lead button is described. Palladium is the only metal which is completely attacked by the parting solution; traces of platinum and rhodium are also dissolved. The presence of copper in the lead button has been found to encourage the dissolution of both platinum and iridium in the nitric acid parting solution; rhodium remains unaffected. Ion-exchange and precipitation procedures for separating palladium from lead are also included. Efforts have been made to identify the source of iridium loss which is a characteristic of classical fire assay collections.

FUNDAMENTALLY, there are two stages to the classical fire assay collection of the noble metals. The initial stage involves the accumulation by lead of the noble metals from the fusion flux prepared to provide the lead *in situ*. The result is a lead alloy containing the noble metals, called a button or regulus. The second stage involves the removal of lead from the button by volatilisation of litharge and its absorption by a cupel to form, finally, a silver alloy. A variation of this approach is a cupellation to accomplish the so-called dry assay, which is made in the absence of added silver. Traditionally, the formation of the silver alloy is followed by a series of wet separations whose character depends upon the composition of the silver collecting medium.

In recent years, the efficiency of the recovery by the silver alloy has been examined critically. In the case of iridium, it has become evident that a loss may result from mechanical processes, partly because iridium appears as intrusions on the surface of the silver bead.[1] The same phenomenon is observed with rhodium and ruthenium, except that with the latter two metals the loss is relatively small. In any case, with these three metals, there is always a considerable risk of loss except when the metals are present in microgram quantities. In the case of osmium the cupellation process can result in a complete disintegration of the silver bead, sometimes explosively. Undoubtedly this is caused by the expulsion of the readily formed volatile octavalent oxide formed with the oxygen, which is significantly soluble in silver at cupellation temperatures. On the other hand, gold, platinum and palladium silver beads can be produced and the noble metals subsequently separated by wet methods with accuracy and simplicity. In addition to the probability of cupellation losses of the more insoluble platinum metals, the subsequent wet treatments involved in separations and determinations of these metals require a high order of analytical skill.

Thus, while one must acknowledge the superiority of the cupellation process for the more common noble metals, one may hope for a more efficient method for the determination of osmium, ruthenium, iridium and rhodium immediately following a collection by lead. Recent researches with these four metals have provided evidence that the lead collection stage of the assay provides for a complete recovery of osmium and ruthenium.[2] Proof for this has been obtained by the use of perchloric acid, as a parting acid for the lead button, and simultaneously as an oxidant to form the octavalent oxides of both osmium and ruthenium. Information has also been provided to indicate a satisfactory recovery of rhodium.[3]

Because of the deficiencies of recovery of the more insoluble noble metals by cupellation to form the silver bead, and the inherent problems associated with their wet treatment, and because the lead alloy has proved to be an effective collector for the noble metals with the possible exception of iridium, it seemed profitable to examine the possibility of a wet analysis of the button, thus obviating the necessity of a cupellation.

Any effort to provide ultimately a complete wet procedure for the determination of noble metals in lead-assay buttons required first a preliminary examination of the composition of the nitric acid parting solution. The few recorded procedures for the analysis of the lead button, none of which is either proved or recorded in detail, were based on the assumption that of the noble metals, palladium was the only metal simultaneously attacked by the nitric acid parting solution. The restricted classical procedure involves the precipitation and filtration of lead sulphate, and the removal of adsorbed palladium by dissolution in ammonium acetate and reprecipitation as the sulphate. Undoubtedly, it is this cumbersome and inaccurate method which has discouraged attempts to provide complete and accurate procedures for the analysis of the lead button.

A direct lead-fusion method for the analysis of platinum-iridium alloys was developed by Gilchrist.[4] By this method the button was parted with nitric acid, and the residue was treated with *aqua regia;* iridium in the residue was determined gravimetrically. The results obtained suggest that iridium is not attacked by the parting acid used, and the small observed loss is probably the result of a slight dissolution of iridium in *aqua regia*. However, the lead button obtained by normal assay procedures differs from that obtained by Gilchrist in that appreciable amounts of copper and other base metals are often present. The influence of copper and other base metals on the dissolution of platinum metals by the nitric acid parting solution has not been recorded, although it is known that traces of copper will encourage the dissolution of precipitated platinum when the latter is leached with nitric acid.

Various techniques were applied by the present authors to determine the platinum metals content of the nitric acid solution used to part the button. The selective precipitation and ion-exchange methods described below proved of limited value. Although acceptable separations and determinations of the palladium in the parting acid could be made in the presence of other platinum metals, the techniques proved cumbersome and inaccurate. However, it seemed reasonable that an evaporation of the lead-nitric acid parting solution and a subsequent roasting to form litharge, together with the addition of flour and the usual fluxing constituents, followed by a fire assay would prove to be an applicable technique.

The fire-assay treatment described below was applied to nitric acid parting solutions derived from the dissolution of lead buttons. Initial determinations with buttons containing palladium, platinum, rhodium and iridium indicated that the parting acid contained high proportions of palladium and traces of rhodium and platinum. In the case of iridium, dissolution occurred only when copper was present in the button. Evidence was also obtained to indicate that the presence of copper in the lead button encouraged the dissolution of platinum. Because copper is a natural associate of the platinum metals, and frequently appears in small amounts in lead-assay buttons, it was necessary to determine its influence on the codissolution of the platinum metals. Methods described below allowed for the determination of each of the four platinum metals in a nitric acid parting solution. In the event that the amounts of platinum, rhodium and iridium in the parting acid are not considered significant, and a palladium separation only is required, the precipitation and ion-exchange procedures described below may also be applied.

EXPERIMENTAL

Standard solutions

Platinum: Pure platinum sponge was dissolved by *aqua regia*, and the nitric oxides were removed by repeated evaporation with hydrochloric acid. The platinum content was determined gravimetrically by thiophenol. The solution contained 1·011 mg of platinum per ml.

Palladium: Palladium chloride was dissolved in water with the addition of a little hydrochloric acid. Precipitation by the sodium salt of dimethylglyoxime yielded 0·994 mg of palladium per ml.

Rhodium: Sodium rhodium chloride was dissolved in water and standardised gravimetrically by 2-thiobarbituric acid. The solution contained 0·958 mg of rhodium per ml.

Iridium: Ammonium chloro-iridate was dissolved in water and standardised gravimetrically by 2-mercaptobenzthiazole. The solution contained 1·042 mg of iridium per ml.

The chemicals used were all of C.P. reagent grade.

Apparatus

Assay crucibles, 30-g, were supplied by A. P. Green Fire Brick Co. Ltd., Canada. The furnace used was a Williams and Wilson, 25 cycle-15 kV-amp. Globar type. For colorimetric measurements a Beckmann model B spectrophotometer was used with 10-mm glass cells.

Procedure

The following three fusion mixtures were used:

A

Litharge	125·3 g
Sodium carbonate	30·0 g
Silica	21·7 g
Flour	1·0 g

B

Litharge	124·2 g
Copper oxide	1·5 g
Sodium carbonate	30·0 g
Silica	21·9 g
Flour	1·0 g

C

Litharge	122·5 g
Copper oxide	3·0 g
Sodium carbonate	30·0 g
Silica	22·7 g
Flour	1·0 g

In each case three buttons and one blank button were prepared.

About two-thirds of the fusion mixture was transferred to a porcelain dish previously lined with an 8-in.^{2} Cellophane sheet. A small depression was made at the centre of the dish, and the mixture was salted with 5·0 ml of the standard solution (1·0 ml in the case of platinum). The mixture was dried overnight in an air oven at 70°, then 10 g of fusion mixture were carefully transferred to a 30-g assay crucible previously lined with an 8-in.^{2} Cellophane sheet. The remaining fusion mixture was added to the material in the crucible.

The crucible was transferred to the furnace at a temperature of about 1150°. The temperature was raised to 1225° over a period of 35–40 min, at which time the fusion was considered to be complete. The fused mixture was then transferred to a conical iron mould, from which a clean lead button was obtained on cooling.

Assay of the slag: The slag was crushed, pulverised to a fineness of 45-mesh and mixed with 27 g of litharge, 3 g of flour and 20 mg of silver powder. The mixture was transferred to the original assay crucible and assayed. The lead button obtained was cupelled to the silver bead, which was treated in the same manner as that obtained from the assay of the parting solution, except in the case of palladium.

Parting of the button: The button was treated with nitric acid (1:2 in case of palladium and 1:4 for other metals) and parted on a hot water bath. Subsequent to the dissolution of the button, 100 ml of water were added and the residue was allowed to settle. The latter was filtered, washed and treated as described below for the individual metals.

Treatment of the parting solution: The parting solution, including the washings, was evaporated to dryness on a hot water bath and the dried material was transferred to an assay crucible. The beaker in which the evaporation was made was washed with dilute nitric acid, and the washings were evaporated to dryness. This residue was also added to the assay crucible, and the mixture was heated for 1·5 hr in an electric furnace maintained at 750°, by which time the decomposition of lead nitrate to lead oxide was complete. The crucible was cooled, and the lead oxide was removed and weighed. Accepting this weight of the lead oxide as the weight of the sample, the required quantity of a monosilicate flux of the type $2Na_2O.SiO_2$ was prepared and mixed with the lead oxide. It has been found that a monosilicate flux of this type can be used effectively for collecting platinum and palladium along with traces of rhodium and iridium.[5]

The following typical flux composition was used: weight of lead oxide obtained = 30·1 g; sodium carbonate = 30·1 g; silica = 14·0 g; litharge = 27·0 g; flour = 3·0 g; silver = 20 mg.

The fusion mixture was transferred to the same assay crucible used for the conversion of lead nitrate to lead oxide, and was heated at 1150° for 35–40 min. The cleaned lead button was cupelled at 1000° to obtain a silver bead. The bead method was used here because it was expected, and later proved, that, of the platinum metals, only palladium would be present in appreciable proportion; platinum, rhodium and iridium would be present only in microgram quantities, in which case the silver bead method, as described earlier, could be applied successfully. The bead was parted with 1:2 nitric acid, and the residue was filtered, washed and ignited. The ignited residue in the case of platinum and palladium was dissolved in *aqua regia*, and in the case of rhodium and iridium by chlorination in the presence of sodium chloride. Silver was precipitated as chloride from the filtrate obtained after dissolving the silver bead; any adsorbed platinum metal was removed by dissolving the precipitate in aqueous ammonia and reprecipitating the silver chloride. The solutions were mixed, and the platinum metals were determined either gravimetrically or colorimetrically as described below.

TABLE I. RECOVERY OF PLATINUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, *g*	Platinum in residue from parting acid, *mg*	Platinum in parting solution, *mg*	Platinum found in slag, *mg*	Total platinum recovered, *mg*	Platinum added, *mg*	Recovery, %
A	27·6	0·918	0·034	0·003	0·955	1·011	94·6
	29·8	0·944	0·031	0·003	0·978	1·011	96·5
	28·0	0·939	0·029	0·008	0·976	1·011	96·5
B	30·0	0·815	0·153	0·004	0·972	1·011	96·2
	30·2	0·801	0·156	0·005	0·962	1·011	95·2
	25·7	0·806	0·150	0·005	0·961	1·011	95·1

Fire-assay recovery of platinum, palladium, rhodium and iridium

Lead buttons were obtained after the fusion of the fluxes A, B and C, previously salted with standard solutions of the platinum metals, and were parted with nitric acid as described above.

Platinum: The parting residue containing platinum was ignited at 600° and dissolved in *aqua regia*. The oxides of nitrogen were removed by repeated evaporation with hydrochloric acid in the presence of 4 drops of 2% sodium chloride solution. Platinum was determined colorimetrically by stannous chloride reagent.

The parting solution was assayed as described above, and platinum was determined in the silver beads colorimetrically.

In the absence of base metals, Hoffman and Beamish[6] used a nitre method, and reported a recovery of 97·3% of platinum.

Palladium: After treatment of the parting residue with *aqua regia* and then with hydrochloric acid, palladium was determined colorimetrically by *p*-nitrosodiphenylamine.

The palladium in the silver bead obtained from the parting solution was determined gravimetrically by the sodium salt of dimethylglyoxime, but in the silver bead obtained from the slag palladium was determined colorimetrically as above.

TABLE II. RECOVERY OF PALLADIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, *g*	Palladium in residue from parting acid, *mg*	Palladium in parting solution, *mg*	Palladium found in slag, *mg*	Total palladium recovered, *mg*	Palladium added, *mg*	Recovery, %
A	31·5	0·009	4·75	0·124	4·883	4·97	98·2
	30·0	0·009	4·75	0·110	4·869	4·97	98·0
	30·8	0·008	4·67	0·109	4·787	4·97	96·3
B	29·2	0·007	4·69	0·132	4·829	4·97	97·2
	27·4	0·007	4·69	0·138	4·835	4·97	97·3
	28·4	0·007	4·77	0·129	4·906	4·97	98·7

With a fusion mixture of the same silicate degree, but carrying out the analysis by a different method, Fraser and Beamish[7] reported an average recovery of 97·4% of palladium in the absence of added base metals.

Rhodium: The residue obtained after parting a lead button as described for platinum was ignited at 850° for 20 min, cooled, hydrogenated for 15 min, and then chlorinated at 600° for 8 hr in the presence of about 50 mg of sodium chloride. Rhodium was determined gravimetrically by 2-thiobarbituric acid.

Rhodium in the silver beads obtained from the parting solution and the slag was brought into a soluble form by chlorination as described above and then determined colorimetrically by stannous bromide.

TABLE III. RECOVERY OF RHODIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, *g*	Rhodium in residue from parting acid, *mg*	Rhodium from parting solution, *mg*	Rhodium found in slag, *mg*	Total rhodium recovered, *mg*	Rhodium added, *mg*	Recovery, %
A	31·2	3·32	0·820	0·010	4·150	4·79	86·6
	30·7	3·33	0·836	0·025	4·191	4·79	87·5
	32·6	3·57	0·740	0·015	4·325	4·79	90·3
B	27·4	3·96	0·579	0·031	4·570	4·79	95·4
	30·2	3·61	0·885	0·008	4·503	4·79	94·0
	29·9	3·78	0·754	0·019	4·553	4·79	95·1

In the absence of base metals, Allen and Beamish[3] have reported an average recovery of 96% of rhodium from the synthetic lead-rhodium buttons.

Iridium: The residue obtained from the parting acid in the case of iridium-lead buttons was ignited at 650° for 45 min, cooled, hydrogenated for 1 hr, and then chlorinated for 8 hr as in the case of rhodium. Iridium was obtained in soluble form and was determined gravimetrically by 2-mercaptobenzthiazole.

The lead button obtained from the parting solution was not cupelled directly, but was treated as in the case of the original button. This variation was introduced because, as noted earlier, cupellation losses of iridium are significant if the lead button contains a large amount of iridium. The parting solution obtained after parting this second button was subjected to a treatment similar to that in the case of platinum, palladium or rhodium, *e.g.*, the lead button was cupelled and then the iridium in the silver bead was determined colorimetrically by stannous bromide.

Barefoot and Beamish,[8] working with acidic fluxes, reported an average recovery of iridium of the order of 99%. Presumably the percentage recovery in the present instance is low because of the more basic fluxes used; these fluxes were used here because of their greater efficiency for platinum metals in general. With a mono-silicate flux, Barefoot and Beamish[8] found a recovery of 96% of iridium with a 0·5-mg sample of iridium.

Influence of copper on the dissolution of platinum metals in nitric acid

As stated above the lead buttons obtained from a fusion of ores from the natural deposits of the platinum metals frequently carry traces of copper. It was observed in preliminary experiments that the presence of copper in the lead button affects the distribution of the platinum metals between the parting acid and the acid insoluble. Other researches on platinum, palladium, rhodium and iridium clearly indicate that the total recovery of these precious metals by lead fire-assay collection is affected by the presence of copper in the flux or in the lead button.[3,6–8] In order to determine the influence of copper on the extent of dissolution of the platinum metals, lead buttons were prepared to contain various amounts of copper. These were parted with nitric acid, and the quantity of the platinum metal in the parting solution was determined by the procedure described above. The results are recorded in Table V.

TABLE IV. RECOVERY OF IRIDIUM BY LEAD FIRE ASSAY

Flux no.	Weight of button, *g*	Iridium in residue from parting acid, *mg*	Iridium from parting solution, *mg*	Iridium found in slag, *mg*	Total iridium recovered, *mg*	Iridium added, *mg*	Recovery, %
A	29·4	4·98	nil	nil	4·98	5·21	95·6
	28·9	4·97	nil	nil	4·97	5·21	95·4
	31·1	4·97	nil	nil	4·97	5·21	95·4
B	28·5	3·39	1·15	nil	4·54	5·21	87·2
	28·7	3·47	1·00	nil	4·47	5·21	85·8
	30·2	4·28	0·249	nil	4·529	5·21	86·9
C	27·9	2·61	1·14	nil	3·75	5·21	72·0
	28·6	2·81	1·43	nil	4·24	5·21	81·4
	29·9	2·35	1·36	nil	3·71	5·21	71·2

TABLE V. INFLUENCE OF COPPER ON THE DISSOLUTION OF PLATINUM, PALLADIUM, RHODIUM AND IRIDIUM IN NITRIC ACID

Amount of copper in button, *g*	Average quantity of noble metal found in the parting solution			
	Platinum, *mg*	Palladium, *mg*	Rhodium, *mg*	Iridium, *mg*
nil	0·031	4·72	0·799	nil
0·35	0·153	4·68	0·739	0·800
0·68				1·310

The above results indicate that the amount of platinum and iridium in the parting solution increases with an increase of copper in the button. In preliminary experiments, it was observed also that if 5 mg of iridium are collected in pure copper, and the button is parted with nitric acid, the dissolution of iridium is practically complete.

Losses of iridium in a fire assay

It may be noted from the above results that the recovery of iridium by the lead-collection method may be adversely affected by the presence of copper in the slag. Barefoot and Beamish reported that the recovery of iridium is low in the presence of both nickel and copper. Iron may, however, be tolerated. Although the sources of the loss of iridium have not been determined, it has been assumed that the losses occur to the slag or to the pot wall.

Losses to the slag

Barefoot and Beamish[8] observed that after the initial fusion the recovery by lead from the slag was not efficient, even after a number of re-assays. However, a spectrographic examination of the monosilicate and basic slags failed to show the presence of iridium.

In the present investigation an attempt was made to determine the losses to the slag by neutron activation. The procedure employed was as follows.

Representative samples (about 60 mg each) of the ground slag were wrapped in aluminium foil and subjected to neutron bombardment. After the activation was complete, the hot samples were left for 2–3 weeks to allow the decay of radioactive sodium. The samples were transferred to plastic containers, the intensities were measured in the different energy channels, and were compared with those of the blank slag salted with known amounts of iridium (about 0·1 μg). No significant amount of iridium was found to be present in the slag.

Losses to the pot wall

For the fusion of the pot wall, a basic flux is required, *i.e.*, a ratio of acid oxygen to basic oxygen of the order of 0·5. The 30-g assay crucible, in which the fire-assay collection for iridium was carried out by using flux (B) or (C), was crushed and pulverised to a fineness of 45-mesh and mixed with the following flux:

Weight of pot wall taken = 60 g
Sodium carbonate = 60 g
Calcium oxide = 37·5 g
Silica = 12·5 g
Borax = 12·5 g
Litharge = 154·0 g
Flour = 4·3 g
Silver = 20 mg

The assay was made at 1200° for 1·5–2 hr, producing a clear and homogeneous slag. The lead buttons were cupelled to obtain silver beads, which were subsequently analysed for iridium colorimetrically by the stannous bromide method.

No detectable amount of iridium was recovered from the pot wall.

A standard solution containing 1·04 mg of iridium was added to the inside walls of a new 30-g assay crucible, the crucible was then dried overnight in an air oven and subjected to the same treatment as above; the weight of iridium recovered was 0·177 mg.

It would seem that the fusion process results in some incorporation of iridium with the pot wall. Because assay pots are essentially silicates, a basic flux is required for a suitable fusion. Fluxes of this type are ineffective for the quantitative collection of iridium.[8] In any case, the sources of loss of iridium during a fire assay have not yet been determined, although by process of elimination it is not unlikely that some inclusion with the pot wall does occur.

Separation and determination of palladium in the presence of lead

By the above assay procedure evidence was obtained to indicate the presence of large amounts of palladium and only traces of platinum and rhodium in the nitric acid parting solution. In general assay practice, and particularly in those instances where assay results are obtained for the purpose of indicating the commercial value of a natural deposit, the content of platinum, palladium and gold is of primary importance, and the small traces of platinum present in the parting solution are of relatively little significance. In these instances an effective method of isolating the palladium in the parting acid is useful. Efforts were made to provide a procedure which would avoid the necessity of the cumbersome lead sulphate separation.

Ion exchange

Recently, ion-exchange procedures for the isolation of platinum metals from large amounts of base metals, such as iron, copper and nickel, have been reported.[5] The methods involve the conversion of the six platinum metals to stable anionic halides and the base metals to a cationic form. Although this method could not be applied directly to lead buttons, because of the insolubility of lead halides, it seemed probable that a cation exchanger could be used to remove lead selectively from the nitric acid parting solution. This approach was investigated by the following procedure.

The lead button, containing only palladium, was parted with 1:2 nitric acid, and the resulting solution was treated with a filtered solution containing 0·5 g of the disodium salt of 1,2-diaminocyclohexanetetra-acetic acid in 15–20 ml of water. The pH was adjusted to 0·5–1·0 by sodium hydroxide, and the solution was heated on a hot plate for 15–20 min to complex the palladium. After cooling, the solution was passed through a cation-exchange column containing 50 W × 8 cation-exchange resin sufficient in quantity to adsorb approximately 30 g of lead. To remove the palladium, 3 litres of $1M$ nitric acid were passed through the column slowly. Lead remained adsorbed, and was stripped by passing 3 litres of $3M$ nitric acid through the column.

The palladium solution was evaporated almost to dryness and then transferred to a small beaker. The palladium complex was decomposed by treating with fuming nitric acid and hydrogen peroxide alternately. Finally, the palladium was dissolved by hydrochloric acid and determined gravimetrically by the sodium salt of dimethylglyoxime. The results are recorded in Table VI.

TABLE VI. SEPARATION OF PALLADIUM FROM LEAD BY ION EXCHANGE

Palladium added, *mg*	Palladium found, *mg*	Error, *mg*
9·94	9·85	0·09
9·94	9·86	0·08
4·97	4·87	0·10

Separation of the palladium from lead by precipitation

Beamish and coworkers[9] have reported the separation of palladium from large quantities of the lead by precipitating the former with salicylaldoxime after the removal of nitric acid by evaporation of the parting solution. In the present investigation, an attempt was made to separate palladium without a prior evaporation. Preliminary experiments indicated that ascorbic acid could be employed successfully for the gravimetric determination of palladium in an acetic acid medium, and that the large quantities of nitrates did not interfere. The following procedure was applied successfully for the separation of palladium from the parting acid.

Following the dissolution of the lead button by nitric acid, sodium hydroxide was added to neutralise the solution as indicated by the appearance of a permanent precipitate, acetic acid was added to dissolve the precipitate and the resulting solution was warmed. After addition of 0·5 g of ascorbic acid, the solution was heated for a few minutes, and the precipitate was allowed to settle. The precipitate was filtered, and the residue was washed thoroughly to remove all of the lead salts. The residue was dried, ignited at 600°, dissolved by *aqua regia*, and finally treated with hydrochloric acid containing a little sodium chloride. Palladium was determined gravimetrically by the sodium salt of dimethylglyoxime. The results are listed in Table VII.

TABLE VII. SEPARATION OF PALLADIUM FROM LEAD BY PRECIPITATION

Palladium added, *mg*	Palladium found, *mg*	Error, *mg*
9·94	9·81	0·13
9·94	9·84	0·10
9·94	9·90	0·04

DISCUSSION

Irrespective of the lack of an integrated procedure for the determination of the seven noble metals in a lead button, there is value in a simple wet method for the determination of platinum, palladium, rhodium and iridium in lead buttons. By far the larger proportion of the world's supply of platinum metals is derived from deposits in which platinum and palladium predominate, with a minor proportion of the more insoluble platinum metals. The fire-assay procedure described above allows an acceptably quantitative recovery of the four metals from a lead button without the cumbersome removal of lead as the sulphate, required by the classical procedure.

One may hope for an extension of the above procedure to include consecutive determinations of osmium and ruthenium. Although these metals are collected quantitatively by lead, the only existing method for their subsequent determination involves parting with perchloric acid, followed by simultaneous isolation of both osmium and ruthenium as tetroxides. Unfortunately, there is no established procedure recorded for a nitric acid parting of the lead button and the subsequent distillation of the octavalent oxides. It would seem reasonable that the osmium in the nitric parting solution could be oxidised to remove osmium quantitatively and selectively. However, the presence of the large amounts of lead in the parting solution may well vitiate this separation as a quantitative procedure. Furthermore, no procedure has been developed for the subsequent removal of ruthenium in a lead nitrate-nitric acid parting medium. With the accomplishment of these separations a most useful assay procedure would be available.

Acknowledgement—The authors wish to acknowledge the help rendered by Professor R. E. Jervis of the Department of Chemical Engineering of the University of Toronto in the neutron-activation analysis.

Zusammenfassung—Eine Schmelzmethode wird beschrieben, bei der Platin, Palladium, Rhodium oder Iridium in der salpetersauren Scheidelösung aus dem Bleiregulus bestimmt werden. Palladium ist das einzige Metall, das von der Scheidelösung völlig gelöst wird; Spuren von Platin und Rhodium werden mit gelöst. Die Anwesenheit von Kupfer im Bleiregulus begünstigt die Auflösung von Platin und Iridium in der Scheidelösung; Rhodium wird nicht angegriffen. Auch Ionenaustausch- und Fällungsmethoden zur Palladium-Platin-Trennung werden berücksichtigt. Es wurde versucht, die Ursache der Iridiumverluste zu ergründen, die für die klassischen Schmelzproben charakteristisch sind.

Résumé—On décrit une méthode de fusion plombeuse pour doser le platine, le palladium le rhodium ou l'iridium dans la solution nitrique de séparation obtenue à partir du bouton de plomb. Le palladium est le seul métal complètement attaqué par la solution de séparation; on dissout aussi des traces de platine et de rhodium. On a trouvé que la présence de cuivre dans le bouton de plomb favourise la dissolution du platine et de l'iridium dans la solution nitrique de séparation; le rhodium reste inattaqué. On décrit également les techniques d'échange d'ions et de précipitation pour séparer le palladium du plomb. On a fait des essais en vue d'identifier la source de la perte en iridium, qui est une caractéristique des méthodes de dosage par fusion plombeuse.

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SHORT COMMUNICATIONS

A new class of adsorption indicators

(*Received* 13 *January* 1964. *Accepted* 20 *March* 1964)

FAJANS[1] first suggested the use of certain luminescent dyestuffs as adsorption indicators in argentimetry. Their action is based on the disappearance of luminescence from solution at the equivalence point. This is brought about by adsorption of the dyestuff because of a change in the surface charge of the precipitate. Reversal of the charge of the precipitate causes desorption of the dyestuff and reappearance of luminescence.[2]

During investigations on the luminescence of cyanine dyes,[3] the experiment of using some of them as adsorption indicators was carried out. For this purpose the cyanometric method[4] was chosen; this can be used for the rapid determination of silver in light-sensitive precipitates of silver halides. As indicator a few drops of a saturated methanolic solution of a dyestuff were used. It was found that some of the dyestuffs were adsorbed on a precipitate of silver iodide and showed a strong fluorescence when excited with an ultraviolet lamp. This was observed with 1,1-dimethylbenzoxacyanine iodide (I), 1,1-dimethylbenzthiacyanine iodide (II) and many other oxacyanines and thiacyanines, prepared by the method of Fischer and Hamer.[5]

When using dyestuff (I) in the titration with 0·002*N* silver nitrate solution, the addition of 1 drop (0·05 ml) of titrant in excess causes the precipitation of silver iodide and the appearance of fluorescence. Titration can therefore be carried out in very dilute solution. If the titration is continued past the end-point, the intensity of fluorescence decreases as the silver iodide precipitate increases. This shows that the indicator is adsorbed on the initial precipitate and the light is scattered by the silver iodide subsequently precipitated. The addition of an excess of cyanide solution causes dissolution of the precipitate of silver iodide and disappearance of the fluorescence. After further addition of silver ions the fluorescence reappears instantly as silver iodide is again precipitated.

The fluorescence appears rapidly at the beginning of the precipitation, increases for a few sec, then remains constant. At low concentration of indicator the fluorescence is bluish-white, but with increasing indicator concentration there is a change towards green. Before the precipitation of silver iodide, the system (excited with an ultraviolet lamp) shows a violet fluorescence.

In the determination of silver in light-sensitive precipitates of silver halides in industrial laboratories, cases are sometimes encountered in which coloured or sparingly soluble compounds are also present. An accurate end-point cannot then be detected because the reprecipitated silver halide is obscured. In the presence of a fluorescent adsorption indicator, however, an accurate determination becomes possible.

The fluorescence from the adsorbed dyestuff (I) is quite selective. Precipitation of silver bromide in the presence of this indicator gives a green fluorescence, weaker than that with precipitates of silver iodide. In the case of silver chloride the precipitate shows only a trace of fluorescence.

Dyestuff (II) acts very slowly as a fluorescent indicator, apparently because of its low solubility in the system under investigation. Addition of a saturated methanolic solution of the dyestuff to an aqueous medium brings about partial precipitation of the solid dyestuff, showing a pink fluorescence. If silver iodide is precipitated in this system the pink fluorescence slowly changes to an intense yellow-green. This points to a change in form of the precipitated dyestuff to a more stable state of aggregation in the adsorbed form.

On filtering off silver iodide precipitated in the presence of dyestuff (I), it showed a strong fluorescence. The fluorescent emission curve obtained (Fig. 1) leads to the conclusion that there is a luminescence of the second type,[6] which is to be attributed to the polymeric form of the dyestuff. Such polymers are often formed in systems of monomethinecyanine dyestuffs containing water[7] and they are recognised by the Jelley adsorption band.[8]

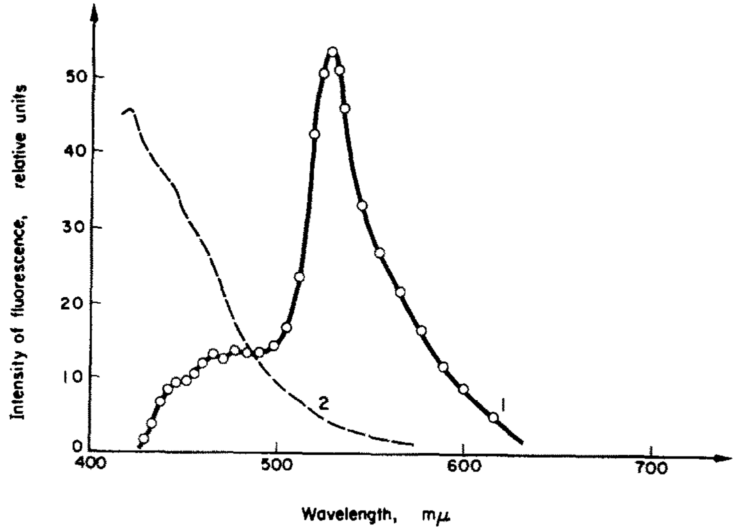

FIG. 1.—Fluorescent emission curves:
1—silver iodide precipitated in presence of dyestuff (I) (polymeric form),
2—filter paper stained with dyestuff (I) (monomeric form).

It is very interesting that cyanine dyestuffs fluoresce on silver iodide particles, *i.e.*, on a carrier which is known to absorb very easily the excitation energy of the dyestuff adsorbed on its surface. A more detailed account of the above investigations will be published in due course.

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Summary—Oxacyanine and thiacyanine dyes have been found to act as fluorescent adsorption indicators in the cyanometric titration of silver halides.

Zusammenfassung—Oxacyanin- und Thiacyaninfarbstoffe wirken als fluoreszierende Adsorptionsindikatoren bei der cyanometrischen Titration von Silberhalogeniden.

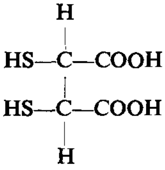
Résumé—On a trouvé que les colorants de l'oxacyanine et de la thiacyanine se comportent comme indicateurs d'adsorption fluorescents dans le dosage cyanométrique des halogénures d'argent.

Use of masking agents in chelatometric titrations—IV:* Dimercaptosuccinic acid†

(*Received* 6 *May* 1964. *Accepted* 7 *July* 1964)

In continuation of our investigations on the use of mercaptans as masking agents in chelatometric titrations, the properties of dimercaptosuccinic acid (DMS) have now been investigated. Although the antimony complex of DMS has been used as a chemotherapeutic agent for certain tropical diseases, the only paper which has discussed the chelating behaviour of DMS is that of Agren and Schwarzenbach, who investigated the chelation with zinc.[1]

DMS is a tetradentate ligand having two carboxylic acid and two mercapto groups:



$$\begin{array}{c} H \\ | \\ HS-C-COOH \\ | \\ HS-C-COOH \\ | \\ H \end{array}$$

However, all of these functional groups cannot co-ordinate with the same metal ion. As might be expected, most DMS-metal chelates are soluble in water. Although the co-ordinating groups of DMS are the same as those of thioglycolic acid or β-mercaptopropionic acid, differences in the number of co-ordinating groups and their steric arrangement will lead to a different selectivity of masking in EDTA titrations.

EXPERIMENTAL

Reagents

Dimercaptosuccinic acid (DMS):‡ This was synthesised from acetylenedicarboxylic acid and thioacetic acid according to the procedure of Gerecke, Friedheim and Brossi.[2] As is clear from the structure of DMS, four modifications (d, l, racemic and meso) are possible. However, only two of these (racemic and meso) have so far been known. The reported melting points for the pure isomers are 210–1° (meso form) and 127–8° (racemic form). The material used in this experiment has a melting point of 195–7° and is believed to consist mostly of meso form.

DMS is a white crystalline solid which is rather unstable and easily oxidised in the air. It has no objectionable odour. In the present experiments, a $0.1M$ methanolic solution of the disodium salt of DMS was employed. The methanolic solution can be stored for more than a month, if it is kept in a refrigerator in a sealed bottle. If it is used frequently in the laboratory, however, the solution should be prepared each week.

Buffer solutions: A standard composition of aqueous ammonia and ammonium chloride was used for pH 10 and hexamethylenetetramine for pH 6.

Indicator solutions: Eriochrome Black T (0.5% in methanol with an addition of hydroxylamine hydrochloride) and Xylenol Orange (0.1% aqueous) were used.

Solutions of cations and EDTA were prepared in $0.01M$ concentration from reagent-grade chemicals, and their strengths determined against primary standard metallic zinc.

Preliminary investigation

In order to estimate the selectivity of masking by DMS, the following experiments were carried out:

One ml of a $0.01M$ cation solution was diluted to 50 ml, and to this were added 1 ml of DMS solution and 1 ml of buffer solution. Tests were also carried out in the presence of Xylenol Orange or Eriochrome Black T indicator both with and without the addition of DMS. The resulting colours of the solutions were compared.

As pointed out in a previous paper,[3] this test does not always suggest the possibility of masking in the EDTA titration of certain metals. However, it can be a useful guide in the screening test of masking agents. The results are shown in Table I.

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* Part III: *Talanta*, 1963, **10**, 1195.

† Contribution No. 50 from Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Japan.

‡ Now available from Dôjindô and Co., Kumamoto, Japan, in reagent-grade form.

Table I

	With Xylenol Orange at pH 6				With Eriochrome Black T at pH 10			
Metal ion	(1)	(2)	(3)	Masking against XO	(1)	(2)	(3)	Masking against Erio T
Al	colourless	red	red	no	colourless	violet	violet	no
Ca	colourless	—	—	—	colourless	red-violet	red violet	no
Cd	colourless	yellow	red	yes	colourless	blue	violet	yes
Co	brown	ND	red-violet	?	yellow-brown	green	violet	yes
Cu^{2+}	yellow	yellow	red	yes	yellow	blue-green	violet	yes
Fe^{3+}	red-brown	ND	red	?	red	ND	violet	?
Hg^{2+}	colourless	yellow	red	yes	colourless	blue-violet	violet	no
Mg	colourless	—	—	—	colourless	red	red	no
Mn^{2+}	colourless	violet	violet	no	brown	green	violet	yes
Ni	green	ND	violet	?	dark green	green	violet	yes
Pb	colourless	yellow	violet	yes (not quantitative)	colourless	blue	red	yes
Zn	colourless	red	red	no	colourless	blue	red	(not quantitative)

(1) Colour reaction observed after adding buffer and DMS to the metal ion solution.
(2) Colour reaction observed after adding indicator to the solution in (1).
(3) Colour reaction observed after adding buffer and indicator to the metal ion solution.
ND: Coloration of metal-DMS complex so intense that no distinct colour of indicator can be observed.

Titration of zinc in presence of cadmium or copper(II)

To a mixture of 10 ml of a 0.01*M* solution of zinc and 1–5 ml of a 0.01*M* solution of cadmium or 2–6 ml of a 0.01*M* solution of copper(II), 2–4 ml of DMS solution, about 100 mg of hexamethylenetetramine and a few drops of Xylenol Orange indicator solution were added. After diluting to 100 ml, the solution was titrated with 0.01*M* EDTA solution.

Titration of magnesium in presence of various bivalent cations

A similar procedure to that for the titration of zinc was followed, except that the pH was adjusted to 10 with 3 ml of ammoniacal buffer solution and Eriochrome Black T indicator was used as indicator.

The results of the titrations are summarised in Tables II and III.

Table II.—Titration of zinc at pH 6

Zn taken, *mg*	Metal present, *mg*	0.1*M* DMS added, *ml*	Zn found, *mg*	Error, *mg*
	Cd			
6.67	1.12	2	6.73	+0.06
6.67	2.24	4	6.75	+0.08
6.67	3.36	4	6.85	+0.18
6.67	5.60	4	6.78	+0.11
	Cu			
6.67	1.27	2	6.58	−0.09
6.67	3.18	3	6.51	−0.16
	Hg			
6.70	10.0	[a]	6.68	−0.02
6.70	20.0	[a]	6.67	−0.03

[a] A large excess of DMS tends to give a negative error. DMS solution should be added dropwise until the disappearance of the white precipitation which first forms.

TABLE III.—TITRATION OF MAGNESIUM AT pH 10

Mg taken, *mg*	Metal present, *mg*	0.1*M* DMS added, *ml*	Mg found, *mg*	Error, *mg*
	Pb			
2.44	10.36	7	2.44	0
2.44	20.72	12	2.46	+0.02
	Cu			
2.44	0.64	1	2.40	−0.04
2.44	1.27	2	2.40	−0.04
2.44	3.18	4	2.39	−0.05
2.44	6.35	5	2.37	−0.07
	Ni			
2.44	0.59	2	2.41	−0.03
	Co			
2.44	0.59	1	2.41	−0.03
2.44	1.18	2	2.41	−0.03
2.44	1.77	3	2.40	−0.04
	Cd			
2.44	11.24	15	2.42	−0.02

RESULTS AND DISCUSSION

Use of DMS at pH 6

Zinc can be titrated selectively in the presence of cadmium, if the amount of the latter does not exceed that of the zinc. Increasing positive errors are noted with an increasing amount of cadmium. These errors may be caused by indistinct colour change near the end-point, because the pure yellow colour is only observed slightly after the equivalence point. As to the selective titration of zinc in the presence of cadmium, Přibil has proposed a method in which a selective replacement reaction of cadmium-EDTA complex with diethyldithiocarbamate is utilised.[4] The present method is simpler and can be readily adapted to practical applications.

Copper can also be masked up to one half of the amount of zinc. In this case, however, the titration errors tend to be negative, and the reason may be that the yellow coloration of the copper-DMS complex tends to give an earlier end-point with Xylenol Orange. From Table I it seems that lead can also be masked with DMS. However, the complex is insufficiently stable to be masked against EDTA titration.

Iron(III), cobalt and nickel form coloured complexes with DMS in this pH region, and their colours are so intense that no distinct end-point colour change can be observed.

Use of DMS at pH 10

Lead, copper(II), nickel, cobalt and cadmium can be masked in the presence of the alkaline earth metals. Because lead and cadmium form colourless complexes with DMS, even large amounts of them can be masked efficiently. Copper(II) forms a yellow complex at pH 10, and negative errors are noted because of the earlier end-point. Although from Table I zinc can be masked against the indicator, the zinc-DMS complex is insufficiently stable to be masked against EDTA. Nickel and cobalt form dark green and brown complexes, respectively, and they must not be present in large amount. Iron(III) forms a dark red complex even in the presence of triethanolamine and must, therefore, be absent when DMS is employed as a masking agent.

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Summary—Dimercaptosuccinic acid has been examined as a masking agent in EDTA titrations. At pH 6 it is possible to determine zinc in the presence of cadmium, copper(II) and mercury(II). At pH 10 most bivalent cations except for the alkaline earth metals can be masked.

Zusammenfassung—Der Gebrauch von Dimercaptobernsteinsäure als Maskierungsmittel bei EDTA-Titrationen wurde studiert. Mit diesem Reagens kann Zink bei pH 6 neben Cadmium, Kupfer(II) und Quecksilber(II) bestimmt werden. Bei pH 10 können außer Erdalkalien die meisten zweiwertigen Kationen mit diesem Reagens maskiert werden.

Résumé—On a étudié l'acide dimercaptosuccinique en tant qu'agent de dissimulation dans les dosages à l'EDTA. En utilisant ce réactif à pH 6, on peut doser le zinc en présence de cadmium, cuivre(II) et mercure(II). A pH 10, la majeure partie des cations divalents, à l'exception des ions alcalino-terreux, peut être dissimulée par ce réactif.

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A specific method for the determination of trace amounts of titanium

(*Received* 18 *May* 1964. *Accepted* 29 *July* 1964)

While attempting to devise a method for the simultaneous determination of titanium and zirconium,[1] a specific method for determining trace amounts of the former element has been developed. Titanium is precipitated from a hydrochloric-sulphuric acid medium with cupferron using zirconium as a collector. A hydrochloric-hydrofluoric acid solution, containing the titanium and other elements precipitated quantitatively or partly with cupferron, is passed through a column containing Dowex-1 × 8 anion-exchange resin.[2,3] Niobium and tantalum are retained by the resin. Titanium and the remaining elements pass unadsorbed into the eluate, from which titanium is again precipitated with cupferron. Titanium is separated from tungsten and molybdenum by precipitation with sodium hydroxide using iron as a collector. The determination is completed colorimetrically after extraction of the titanium-thiocyanate complex with a solution of tri-n-octylphosphine oxide in cyclohexane.[4] The method is accurate to within $\pm 5\%$ (relative) or $\pm 0{\cdot}75\ \mu g$ of titanium, whichever is greater.

EXPERIMENTAL

Reagents

Hydrofluoric acid, 29*M*

Hydrochloric acid, 1·2*M* and 12*M*

Sulphuric acid, 3·6*M*, 6*M* and 18*M*

25% *Hydrochloric acid*-20% *hydrofluoric acid*

Filter paper, Whatman No. 40, 5·5 cm and 12·5 cm. Filter paper has been found to be the major cause of high blanks. If Whatman papers are unavailable, the papers to be used should be analysed for titanium before application of the procedure.

Filter paper pulp. Cut Whatman 40 filter paper into small (1 cm × 1 cm) pieces and shake vigorously with hot water in a stoppered Erlenmeyer flask.

Zirconium sulphate solution, 1 mg of zirconium/ml

Iron(III) chloride solution, 10 mg of iron/ml

Cupferron solution, 6% (w/v), freshly prepared

Summary—Dimercaptosuccinic acid has been examined as a masking agent in EDTA titrations. At pH 6 it is possible to determine zinc in the presence of cadmium, copper(II) and mercury(II). At pH 10 most bivalent cations except for the alkaline earth metals can be masked.

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EXPERIMENTAL

Reagents

Hydrofluoric acid, 29*M*

Hydrochloric acid, 1·2*M* and 12*M*

Sulphuric acid, 3·6*M*, 6*M* and 18*M*

25% *Hydrochloric acid*-20% *hydrofluoric acid*

Filter paper, Whatman No. 40, 5·5 cm and 12·5 cm. Filter paper has been found to be the major cause of high blanks. If Whatman papers are unavailable, the papers to be used should be analysed for titanium before application of the procedure.

Filter paper pulp. Cut Whatman 40 filter paper into small (1 cm × 1 cm) pieces and shake vigorously with hot water in a stoppered Erlenmeyer flask.

Zirconium sulphate solution, 1 mg of zirconium/ml

Iron(III) chloride solution, 10 mg of iron/ml

Cupferron solution, 6% (w/v), freshly prepared

Cupferron wash solution. Add 10 ml of 6% cupferron solution to 500 ml of 1·2*M* hydrochloric acid. Prepare just before use.

Sodium bisulphate

Anion-exchange resin. Dowex 1 × 8, 100-200 mesh resin obtained from Bio-Rad Laboratories.

Sodium hydroxide, 1% and 40% solutions

Citric acid

Thioglycolic (mercaptoacetic) acid, 98% solution

Ammonium thiocyanate

Tri-n-octylphosphine oxide (TOPO), 0·01*M* in cyclohexane

Standard titanium solution. Prepare a standard titanium solution containing 5 μg of titanium/ml in 6*M* sulphuric acid.

Procedure

Dissolve the sample, preferably containing a minimum of 15 μg of titanium, and obtain it in 150 ml of solution containing 10 ml of hydrochloric acid and 25 ml of sulphuric acid. Add 10 ml of zirconium sulphate solution and 0·5 g of filter paper pulp. Cool the sample solution, the 6% cupferron solution and the cupferron wash solution to 10–15°. Add 15 ml of cupferron solution, or sufficient to obtain complete precipitation, and filter. (It is very convenient to filter through a 6·3-cm i.d. Büchner funnel using suction. A piece of 5·5-cm filter paper is first placed in the bottom of the funnel, then a piece of 12·5-cm paper is pushed down into the funnel using a 150-ml beaker. Finally, with the suction on, the paper is wetted with water.) Wash the precipitate 10 times with the cupferron wash solution. Transfer the precipitate to a platinum crucible and ignite. Fuse the residue in about 2 g of sodium bisulphate. Dissolve the melt in a polyethylene beaker with 50 ml of 25% hydrochloric-20% hydrofluoric acid, warming gently. Pass 50 ml of the hydrochloric-hydrofluoric acid solution through the anion-exchange column (12 cm × 1 cm i.d., containing 8 cm of anion-exchange resin) and discard the eluate. Pass the sample solution through the column and wash with 50 ml of the same elutrient, collecting the eluate in a platinum dish. Add 5 ml of sulphuric acid and heat to fumes of sulphuric acid. Transfer the solution to a 250-ml beaker and dilute to about 100 ml with water. Cool, add 5 ml of 12*M* hydrochloric acid, 0·5 g of filter paper pulp and 15 ml of 6% cupferron solution. Filter as described and wash the precipitate 5 times with the cupferron wash solution.

Ignite the precipitate in a platinum dish or crucible, cool and dissolve the residue with 10 ml of hydrofluoric acid. Add 2 ml of sulphuric acid and evaporate to fumes of sulphuric acid. Cool, add 15 ml of water and warm to dissolve the salts. Add 1 ml of the iron(III) chloride solution and transfer the solution to a 50 ml centrifuge tube containing 20 ml of 40% sodium hydroxide. Mix, cool and centrifuge. Decant the supernatant solution, add 30 ml of 1% sodium hydroxide, mix, centrifuge and again discard the solution. Add 15 ml of 6*M* sulphuric acid to dissolve the basic salts and transfer with 6*M* sulphuric acid to a 125-ml separatory funnel. (If the sample is known to contain more that 15 μg of titanium, transfer the solution to a volumetric flask, dilute with 6*M* sulphuric acid, and use an aliquot containing 15 μg of titanium.)

Add sufficient 6*M* sulphuric acid to the separatory funnel to obtain a volume of about 35 ml. Add 1 g of citric acid, 1 ml of thioglycolic acid and 3 g of ammonium thiocyanate. Stopper the funnel and shake for 30 sec to dissolve the salts. Add exactly 15 ml of 0·01*M* TOPO solution, stopper the funnel and shake for 5 min.* Allow the layers to separate, and draw off and discard the aqueous layer. Wash the organic phase for 1 min with 35 ml of 6*M* sulphuric acid. Discard the acid wash. Draw the organic phase into a 15-ml glass-stoppered centrifuge tube and centrifuge the extract for 1 min. Measure the absorbance of the extract in a 1-cm cell at 429 mμ using cyclohexane in the reference cell. (At this wavelength, the molar absorptivity of the complex is about 43,000, indicating an absorbance of about 0·9 for 1 μg of titanium/ml in 1-cm cells. The extracted complex is stable, within experimental error, for at least 24 hr. The absorbance is a linear function of concentration, at least from 0 to 1 μg of titanium/ml, and obeys Lambert's law when 1-, 2,- and 5-cm cells are used.) Determine the titanium concentration by reference to a standard curve obtained by carrying known amounts of titanium in 6*M* sulphuric acid through the extraction steps. (It is, of course, desirable that one determine both a reagent blank and a recovery figure for the entire procedure.)

No interference was caused by the presence of 10-mg amounts of Al, $\mathrm{Sb^{III}}$, $\mathrm{As^{III}}$, Ba, Be, Bi, B, Br (as $\mathrm{Br^-}$), Cd, Ca, $\mathrm{Ce^{IV}}$, Cs, $\mathrm{Cr^{III}}$ Co, $\mathrm{Cu^{II}}$, Dy, Er, Eu, F (as $\mathrm{F^-}$), Gd, Ga, Ge, Au, Hf, Ho, In, I (as $\mathrm{I^-}$), Ir, $\mathrm{Fe^{III}}$, La, Pb, Li, Lu, Mg, $\mathrm{Mn^{II}}$, $\mathrm{Hg^{II}}$, Mo, Nd, Ni, Nb, N (as $\mathrm{NO_3^-}$), $\mathrm{Pd^{IV}}$, P (as $\mathrm{PO_4^{3-}}$), $\mathrm{Pt^{IV}}$, K, Pr, Re, Rh, Rb, Sm, Sc, $\mathrm{Se^{IV}}$, Si, Ag, Na, Sr, Ta, $\mathrm{Te^{IV}}$, Tb, $\mathrm{Tl^{I}}$, Th, Tm, $\mathrm{Sn^{IV}}$, W, $\mathrm{U^{VI}}$, $\mathrm{V^{V}}$, Yb, Y, Zn or Zr.

---

* The extraction of titanium is discussed in considerably more detail in reference 1.

Procedure modifications

(1) If niobium and tantalum are known to be absent in interfering amounts,[1] the ion-exchange step may be omitted. After the initial precipitation of titanium, ignite the precipitate and fuse the residue in a minimum amount of sodium or potassium bisulphate. Dissolve the fused mass with 15 ml of $3{\cdot}6M$ sulphuric acid, add 1 ml of iron(III) chloride solution and transfer to a 50-ml centrifuge tube containing 20 ml of 40% sodium hydroxide. Continue with the procedure as described.

(2) If tungsten and molybdenum are known to be absent in interfering amounts,[1] the sodium hydroxide precipitation step may be omitted. Dissolve the first cupferron precipitate, after ignition, with the hydrochloric-hydrofluoric acid solution and perform the ion-exchange separation as described. Add 2 ml of sulphuric acid to the eluate and evaporate to fumes of sulphuric acid. Continue with the extraction of titanium as described.

(3) If niobium, tantalum, molybdenum and tungsten are all absent, both the ion-exchange and sodium hydroxide precipitation steps can be omitted. The precipitate can be ignited, treated with hydrofluoric and sulphuric acids, evaporated to fumes of sulphuric acid, and extracted. If barium, tin and antimony are also absent, the precipitate can be destroyed by treatment with nitric and perchloric acids as described in reference 1.

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Summary—A method is presented which is specific for the determination of trace amounts of titanium. Titanium is precipitated with cupferron using zirconium as a collector. Further separation from interfering elements is made by anion exchange and precipitation with sodium hydroxide using iron as a collector. The determination is completed colorimetrically after extraction of the titanium-thiocyanate complex with a solution of tri-n-octylphosphine oxide in cyclohexane. The method is accurate to within ±5% (relative) or $\pm 0{\cdot}75$ μg of titanium, whichever is greater.

Zusammenfassung—Eine spezifische Methode zur Bestimmung von Titanspuren wird angegeben. Titan wird auf Zirkontrager mit Cupferron gefallt. Durch Anionenaustausch und Fallung mit Natriumhydroxyd auf Eisentrager werden weitere störende Elemente abgetrennt. Bestimmt wird Titan durch Extraktion seines Rhodanidkomplexes mit Tri-n-octylphosphinoxyd in Cyclohexan. Die Methode ist auf ±5% (relativ) oder bestenfalls ±0,75 μg genau.

Résumé—On présente une méthode de dosage spécifique du titane a l'état de traces. On précipitite le titane au cupferron en utilisant le zirconium comme agent collecteur. On procède ensuite à une séparation des éléments interférants par échange anionique, et précipitation a la soude, en utilisant le fer comme agent collecteur. On effectue le dosage par extraction du complexe thiocyanique du titane au moyen d'une solution d'oxyde de tri-n-octylphosphine en cyclohexane. La précision de la méthode est ±5% en valeur relative ou ±0,75 μg de titane. On prend la plus grande des deux erreurs.

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Response rates of cation-sensitive glass electrodes

(*Received* 30 *May* 1964. *Accepted* 7 *July* 1964)

THE response-rate characteristics of cation-sensitive glass electrodes ultimately determine the applicability of such electrodes to dynamic concentration measurements in continuous analysis or kinetic studies. Several authors[1,2] have noted the apparently sluggish response of cation-sensitive glass electrodes to rapid concentration changes in aqueous solution; in a previous paper,[3] we also reported response times of the order of several minutes for the Beckman 78137 V experimental electrode. In the light of modern evidence[4] on the nature of the potential-determining mechanism of both pH-type and cation-sensitive glass electrodes, it seems likely that the slow response of the latter results from poor construction characteristics and pretreatment, rather than from any inherent slow steps in the response mechanism. Because considerable technical advances in the manufacture of cation-sensitive glass electrodes have been achieved since our previous report, the response characteristics of the newest commercially available electrode were re-examined to test this hypothesis.

EXPERIMENTAL

Measurements were carried out in stirred solution, using the new Beckman 39137 cationic glass electrode. Potentials (*versus* Beckman 39170 fibre-junction calomel reference electrode) were determined with a Beckman Model 76 expanded-scale pH meter; the electrode response was timed with a stopwatch. The inherent deflection time of the pH meter was found to be 0·8 ± 0·1 sec per 100 mv on the expanded scale.

Electrode-response measurements were carried out by two procedures, employing (1) a dipping and (2) a dilution method. In all cases, the glass electrode was preconditioned by a 24-hr soaking in the appropriate reference solution. Experiments were performed at room temperature because changes in ambient temperature were negligible during the times involved.

Dipping procedure: Immerse the glass-calomel electrode pair in the stirred reference solution and measure the equilibrium potential. Transfer the glass electrode to the test solution containing the metal ion in a concentration greater than, smaller than, or equal to that of the reference solution.

TABLE I.—RESPONSE OF CATION-SENSITIVE GLASS ELECTRODE TO CONCENTRATION CHANGES

(1) Dipping experiments

Metal ion	Solution concentrations, *moles/litre*	Response times, *sec*
K^+(KCl)	Reference Test Reference	
	0·5 $\xrightarrow{t}$ 0·5	1·6
	0·1 $\xrightarrow{t}$ 0·1	1·5
	0·5 $\longrightarrow$ 1·0 $\xrightarrow{t}$ 0·5	1·6
	0·5 $\longrightarrow$ 0·0 $\xrightarrow{t}$ 0·5	2·5
	0·1 $\longrightarrow$ 1·0 $\xrightarrow{t}$ 0·1	3·1
	0·1 $\longrightarrow$ 0·05 $\xrightarrow{t}$ 01	2·3
	0·1 $\longrightarrow$ 0·0 $\xrightarrow{t}$ 0·1	2·6
Na^+(NaCl)	1·0 $\xrightarrow{t}$ 1·0	1·6
	0·1 $\xrightarrow{t}$ 0·1	1·6
	1·0 $\longrightarrow$ 0·1 $\xrightarrow{t}$ 1·0	2·4
	1·0 $\longrightarrow$ 0·0 $\xrightarrow{t}$ 1·0	2·5
	0·1 $\longrightarrow$ 1·0 $\xrightarrow{t}$ 0·1	3·1
	0·1 $\longrightarrow$ 0·0 $\xrightarrow{t}$ 0·1	2·3

(2) Dilution experiments

Metal ion	Solution concentrations, *moles/litre*	Response times, *sec*
K^+(KCl)	1·0 $\xrightarrow{t}$ 0·5	2·9
	1·0 $\xrightarrow{t}$ 0·5	3·9
	0·1 $\xrightarrow{t}$ 0·05	3·1

After 30 sec return the glass electrode to the reference solution and measure the time, *t*, required for the indicated potential to return to within ±0·5 mv of the equilibrium value.

Dilution procedure: With the glass-calomel electrode pair in the stirred reference solution and at equilibrium, rapidly add an equal volume of distilled water to the cell and measure the time, *t*, required for the indicated potential to come within ±0·5 mv of the expected value (determined by prior equilibrium measurements in solutions of appropriate concentration).

RESULTS AND DISCUSSION

The results of the dipping and dilution experiments are given in the Table I. The reported response times are, in each case, the mean of at least 4 measurements, and have an experimental uncertainty of about 0·2 sec. In the dilution experiments, an added uncertainty may result from the difficulty of effectively mixing two solutions of appreciable volume (50 ml) within a fraction of a second.

The response rates determined are considerably faster than those observed with the earlier types of cation-sensitive electrodes, and approach the response limitations of the usual potentiometric measurement systems. As expected, electrode recovery times increase as the ionic environment is changed more and more drastically, but response times are compatible with the requirements of continuous analyses or kinetic studies where concentrations may change rapidly over moderate ranges. The results suggest that first-order reactions with rate constants as large as 0·4 sec^{-1} could be effectively monitored using the cation-sensitive glass electrode.

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Summary—A re-evaluation of the response of cation-sensitive glass electrodes to rapid concentration changes indicates typical response times in the 1·5–4·0 sec range and suggests that such electrodes might be used for continuous analyses or for reaction rate studies.

Zusammenfassung—Eine Neubestimmung des Ansprechens kationenempfindlicher Glaselektroden auf schnelle Konzentrationsänderungen zeigt typische Ansprechzeiten in der Gegend um 1,5–4,0 Sekunden. Demnach bieten sich solche Elektroden zu kontinuierlichen Analysen oder zur Untersuchung von Reaktionsgeschwindigkeiten an.

Résumé—Une nouvelle évaluation de la réponse des électrodes de verre catio-sensibles aux variations rapides de concentration montre des temps de réponse caractéristiques entre 1,5 et 4 secondes, et suggère que de telles électrodes peuvent être employées pour des analyses en continu ou des études de vitesse de réaction.

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Talanta, 1964, Vol. 11, pp. 1469 to 1470. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

The international nature of *Talanta*

SIR,

The ever increasing amount of scientific research has resulted in a constant rise in the number of journals available for its publication. One of the newer journals is *Talanta*, and on its cover is printed "An International Journal of Analytical Chemistry". It would be interesting to know if this declaration is really justified. Is it possible for you to provide data concerning the numbers of papers from different countries which have been published in *Talanta*?

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5 *June* 1964

Dear Dr. PŘIBIL,

I hope that you will find the information for which you have asked in the Table overleaf.

CECIL L. WILSON (Editor-in-Chief)

CONTRIBUTIONS* TO THE FIRST 10 VOLUMES† OF TALANTA

Country	Volume										Contributions per country
	1	2	3	4	5	6	7	8	9	10	
	Contributions										
Australia	—	—	—	—	—	—	—	—	—	1	1
Austria	—	1	1	—	—	—	1	2	4	6	15
Belgium	1	3	1	—	—	—	—	3	3	2	13
Brazil	3	1	—	1	—	—	—	—	2	—	7
Bulgaria	—	—	—	—	—	—	—	—	2	1	3
Canada	1	2	3	3	2	3	1	1	2	6	24
Czechoslovakia	3	2	5	3	6	—	—	19	12	24	74
Finland	—	—	—	—	—	—	—	1	—	1	2
France	—	—	—	—	2	—	—	4	1	1	8
German Democratic Republic	—	1	—	—	—	—	—	—	1	1	3
German Federal Republic	—	1	1	—	—	—	—	1	—	—	3
Hungary	8	4	8	4	3	—	3	6	3	33	72
India	3	1	—	3	2	—	2	9	7	12	39
Ireland	—	—	—	—	—	—	—	—	1	—	1
Israel	1	—	—	—	2	—	1	2	1	4	11
Italy	—	—	—	—	1	—	—	1	1	—	3
Japan	3	2	5	4	5	—	—	3	9	8	39
Netherlands	—	—	—	—	—	—	—	1	1	2	4
Pakistan	—	—	—	—	—	—	—	—	—	1	1
Poland	—	3	—	1	2	—	1	1	2	4	14
Portugal	—	—	—	—	—	—	—	2	—	—	2
Rumania	—	—	—	—	1	—	3	1	—	1	6
South Africa	—	—	—	—	—	—	—	—	1	—	1
Spain	1	—	—	—	—	—	—	1	—	1	3
Sweden	—	—	2	4	—	—	—	1	—	1	8
Turkey	—	—	—	—	—	—	—	—	1	1	2
United Kingdom	15	16	15	9	7	—	3	28	51	30	174
U.S.A.	15	34	20	15	17	39	27	40	43	59	309
U.S.S.R.	—	—	—	—	—	—	—	6	6	1	13
Yugoslavia	—	—	—	—	—	—	—	1	—	—	1
Contributions per volume	54	71	61	47	50	42	42	134	154	201	856
Countries per volume	11	13	10	10	12	2	9	22	21	23	
Pages per volume	416	404	378	298	294	276	322	916	1076	1306	

* These include preliminary communications, short communications and letters.

† Monthly publication began with Volume 8.

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INFLUENCE OF FOAM TEMPERATURES IN BOILING SOLUTIONS ON EBULLIOMETRIC MEASUREMENTS

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Summary—The foam, in a boiling solution, is concentrated by the transport of adsorbed solute on the bubble surfaces. The excess of boiling temperature in the foam over that in the bulk can be predicted by a mass transport equation involving the total bubble surface produced in unit time. The surface tension variation was measured in terms of the average bubble diameters in the foam at each concentration. If d and c are the bubble diameters and bulk concentration, respectively, the excess of boiling temperature is given by

$$\delta T = \left\{ B \begin{pmatrix} \mathrm{d}d/\mathrm{d}c \\ c \to 0 \end{pmatrix} + a\, \mathrm{d}d/\mathrm{d}c \right\} \left(\frac{1}{d_0} - \frac{1}{d} \right)$$

where d_0 is the bubble diameter in the pure solvent and B is a constant. This is an equation relating excess concentration in the foam with rate of change of surface tension and the area of bubble surface. Direct measurements of the difference between bulk and foam concentrations indicate a linear relation between them. The assumption that the solutes associate in the surface provides a theoretical basis for the above equation, and for the apparent departure of the adsorption from the Gibbs' equation.

A NUMBER of authors have reported that extrapolations of ebulliometric measurements do not always pass through the origin of the temperature axis.[1–3] Smith[1] suggested that adsorption of solute on the bubble surfaces and its concentration in the foam would account for the positive deviations he observed with solutions of polythene. He measured the foam concentrations and found an excess over that in the bulk. Dimbatt and Stross[4] suggested that there was a similar explanation for the increase in 'boiling noise' they observed with polymer solutions.

The present author arrived at similar conclusions following measurements of boiling temperature elevations in ethanolic solutions of triglycerides.[5] The plots of elevation *versus* concentration were decidedly non-linear (see Fig. 1, for example). These curves in ethanol are complicated by association of the solutes. However, all are inflected and, although exhibiting a subsequent curvature, have some concentration range in which the elevations are appreciably greater than is predicted by theory. When ethanolysis was induced by the addition of ethoxide,[5] the ethyl esters which were formed produced elevations which could be calculated by the Beckmann equation from the weight of triglyceride added, indicating that the ethyl esters were behaving normally under the same conditions. Similarly inflected curves were observed in ether, cyclohexane, carbon tetrachloride and acetone (Figs. 2 and 5). Other solutes were found, to varying extents, to behave in the same manner, although the deviations were in the main not large (Fig. 3).

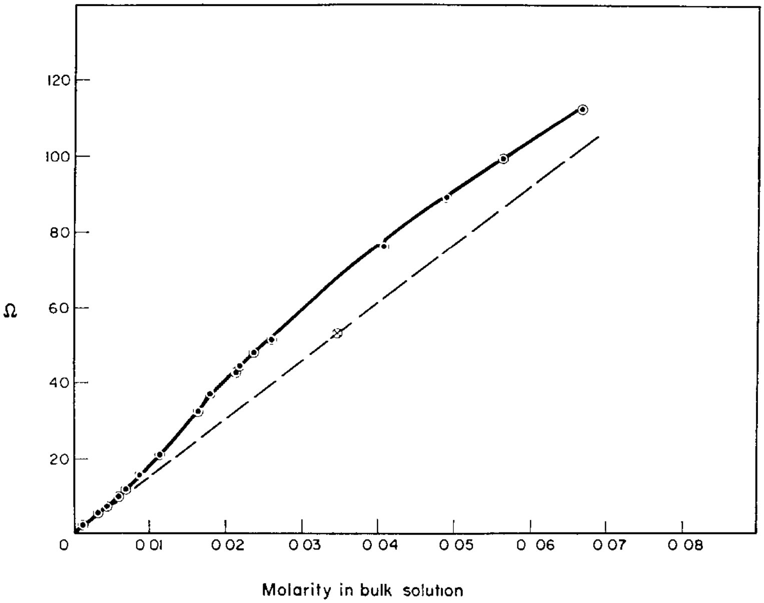

FIG. 1.—Glyceryl tripalmitate elevations in ethanol:

—— curve found in practice,

– – – line predicted by theory,

⊗ ¼-elevation after adding sodium ethoxide.

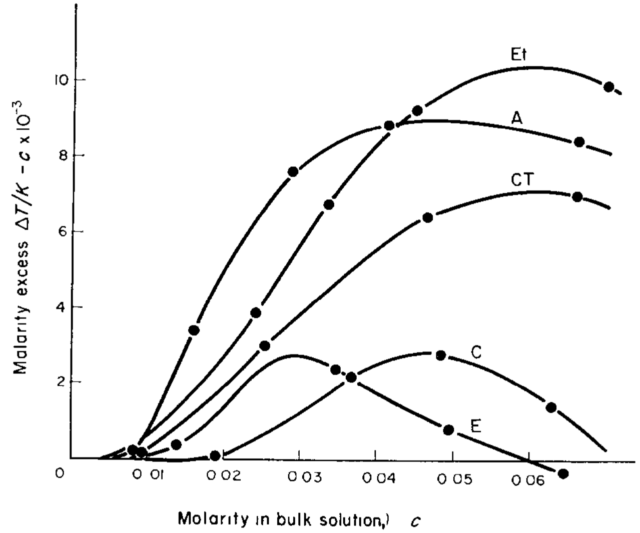

FIG. 2.—Equivalent molar excess elevations for glyceryl tribenzoate in different solvents:

Et = ethanol, CT = carbon tetrachloride,
A = acetone, C = cyclohexane, E = ether.

It was noticed that the magnitude of the excess elevation was related to the concentration at which foaming began. Also, in general, the higher the molecular weight of the solute the greater was the discrepancy. Preliminary attempts were made to measure the surface tension changes by the maximum bubble pressure method. These gave indications that the discrepancies were a function of the initial rate of change of surface tension with concentration. Measurements of the average bubble diameters with a cathetometer indicated that these were proportional to the bubble pressure measurements. In any given solvent the bubble diameters tended to almost the same minimum for all solutes, and the curves extrapolated back to the same diameter for the pure solvent (Fig. 6). These observations were sufficient to demonstrate that the excess elevations produced by different solutes were independent of the bubble diameters but bore some relation to their rate of change with concentration.

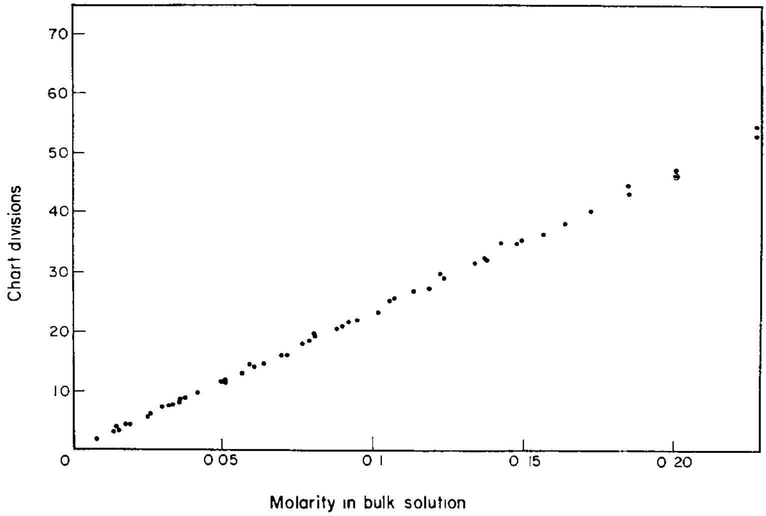

FIG. 3.—Elevations in pure acetone with the following solutes: benzophenone, benzoyl acetone, *o*-bromonitrobenzene, naphthalene, tri-n-butylphosphate, triacetone dialcohol.

The decision was taken to employ acetone as solvent for a number of solutes with widely differing foaming capacities. Acetone was chosen because it was known to have little tendency to encourage association and to lead to curves with a long linear region after the inflection.[3] Boiling temperature measurements were made of solutions in pure acetone and in acetone containing 1% of polydiethylene adipate (molecular weight *ca.* 3000: hereafter referred to as PDA). The latter foamed freely with a bubble diameter of 2·3 mm. It was expected that the additive would keep the surface tension constant for all but the most surface active solutes. The bubble diameters at each concentration were measured on high speed photographs.

DISCUSSION AND THEORETICAL TREATMENT OF EXPERIMENTAL RESULTS

The experiments in acetone confirmed the qualitative relationships noted above. With three exceptions, the curves of boiling temperature elevation (ΔT) *versus* concentration (c) could be divided into three sections. ΔT approached the theoretical line closely at the lowest concentrations; this was followed by an intermediate region in which the curve was inflected upwards, and finally by a linear section approximately parallel to, but displaced above the theoretical line (Fig. 5). For many of the solutes the inflection was small enough to have been ignored for practical purposes, or ascribed to experimental error.

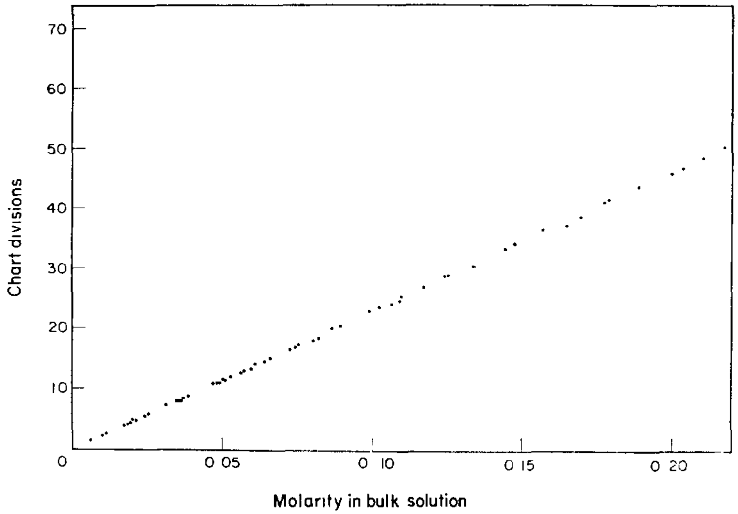

FIG. 4.—Elevations in acetone plus 1 % of PDA with the following solutes: benzophenone, benzoyl acetone, *o*-bromonitrobenzene, naphthalene, tri-n-butylphosphate, triacetone dialcohol, aspirin, glyceryl tribenzoate.

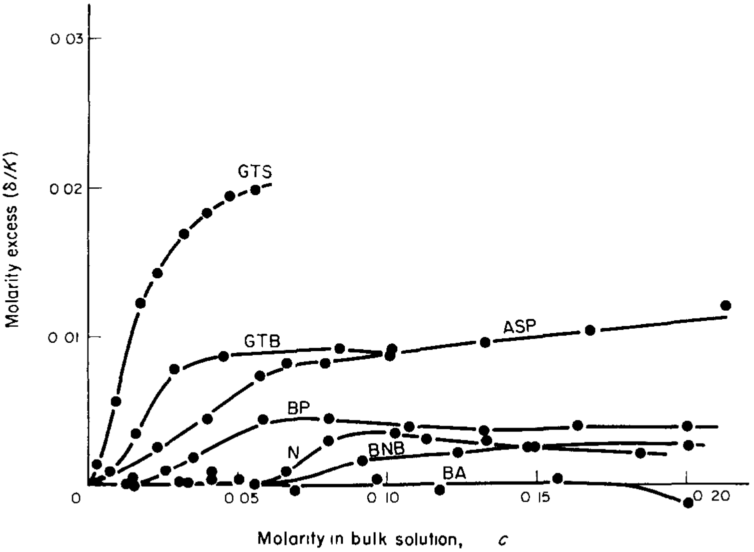

Fig. 5.—Excess elevations in pure acetone:
GTS = glyceryl tristearate, BP = benzophenone, GTB = glyceryl tribenzoate,
N = naphthalene, ASP = aspirin, BNB = *o*-bromonitrobenzene,
BA = benzoyl acetone.

All of the solutes foamed in sufficiently concentrated solution and *d*, the bubble diameter, tended to a limiting value. The curves of *d* against *c* could be extrapolated back to the zero of the concentration axis and giving the same limiting value at infinite dilution (Fig. 6). The bubbles of vapour rising to the surface of the liquid were produced on a small area of tungsten wire projecting into the base of the ebulliometer.[3] Presumably, they were generated at a constant number of asperities on the tungsten surface. The wire may be regarded as a group of minute orifices

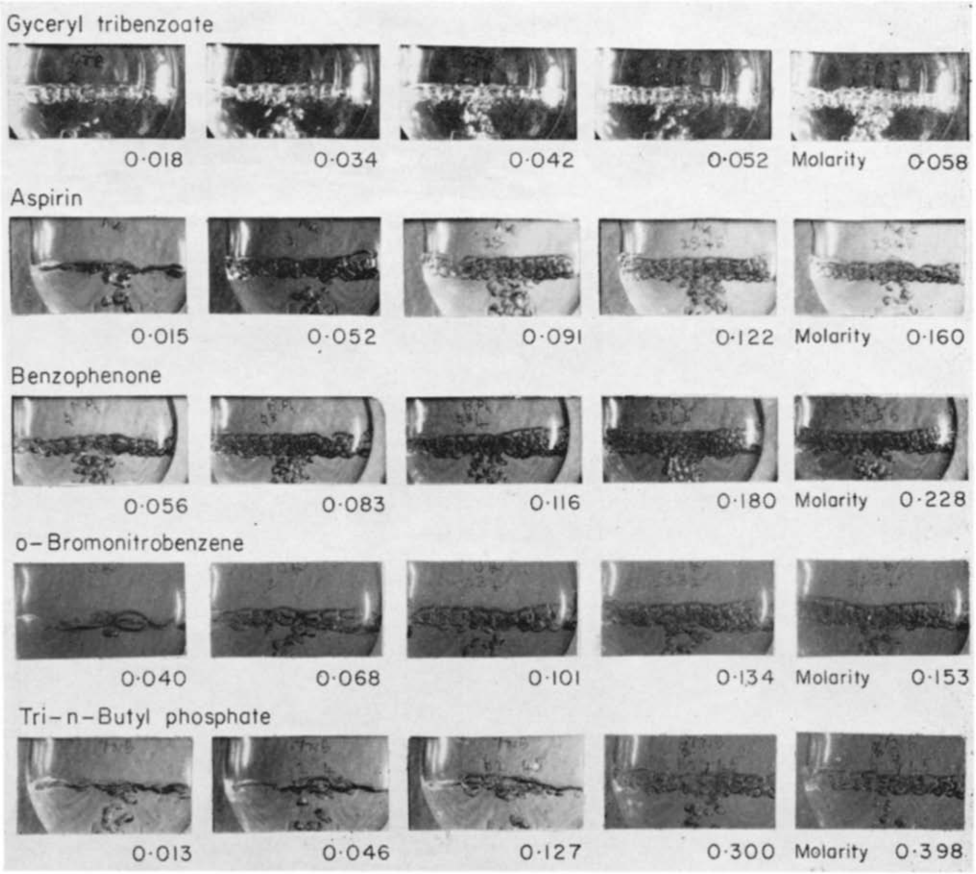

FIG. 6*a*.—Photographs of the bubbling in boiling acetone produced by various solutes at different concentrations.

through which vapour was pumped into the liquid. The heat input, which was maintained constant throughout the series of experiments, generated a constant volume of vapour in unit time (at atmospheric pressure). Bubbles detached themselves from the wire when they had achieved sufficient buoyancy. Thus, they all enclosed a similar volume of superheated vapour. The pressure within the bubbles when they left the wire was, however, governed by the surface tension of the solution. As they rose and attained equilibrium with the surrounding solution, their diameters in the short-lived foam on the surface became proportional to the surface tension.

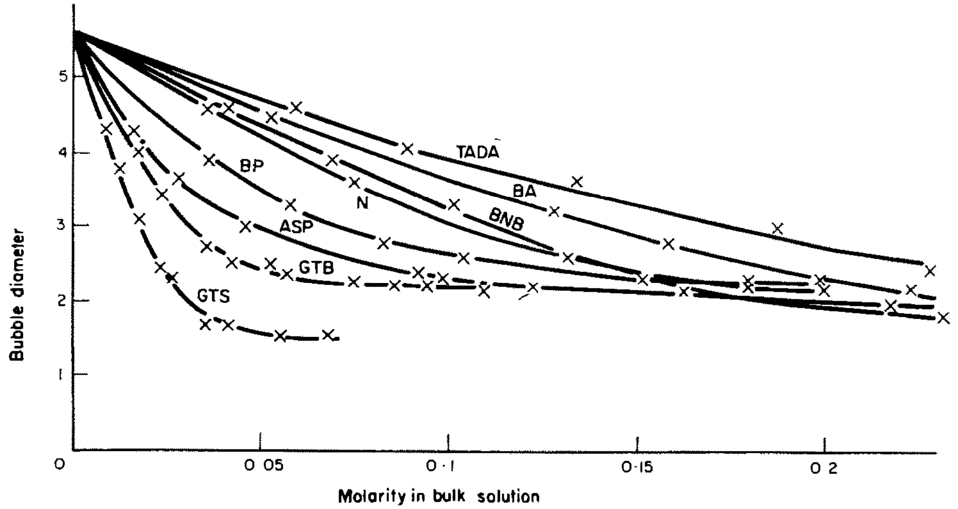

FIG. 6.—Bubble diameters in pure acetone:

TADA = triacetone dialcohol,
BA = benzoyl acetone,
BNB = *o*-bromonitrobenzene,
N = naphthalene,

BP = benzophenone,
ASP = aspirin,
GTB = glyceryl tribenzoate,
GTS = glyceryl tristearate.

Calculations. If V is the volume of vapour brought to the surface by the bubbles in unit time and n the number of bubbles containing this volume, then

$$V = \tfrac{1}{6} n\pi d^3$$

and the total surface of these bubbles is

$$S = n\pi d^2,$$

so that

$$6V/d = S.$$

The total surface transported through the solution changes with concentration from $6V/d_0$ at $c = 0$ to $6V/d$ at concentration c. Thus, the increase in the amount of solute transported on the bubble surfaces will be

$$\Delta S\mathrm{f}(c) = B(1/d - 1/d_0)\mathrm{f}(c) \qquad (1)$$

where $\mathrm{f}(c)$ is equal to the concentration of adsorbed solute per unit area of the bubble surface. $\mathrm{f}(c)$ was found to be constant beyond the inflection in the curves and

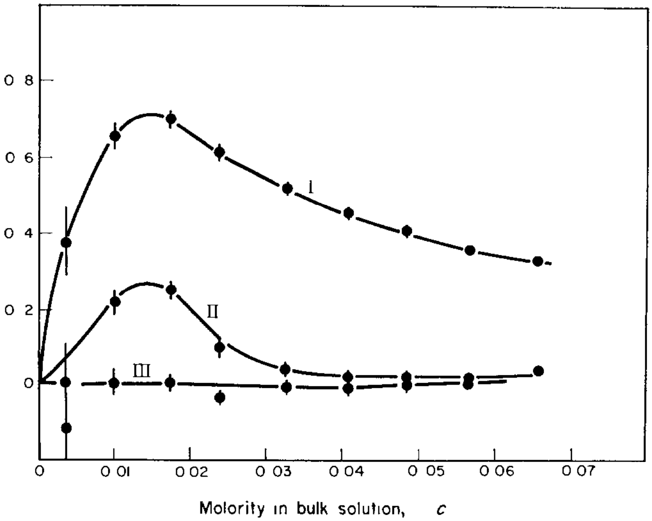

FIG. 7.—Glyceryl tristearate in pure acetone:

I. $\frac{\delta T}{Kc}$; II. $\frac{\delta T - 0\cdot08\left(\mathrm{d}d/\mathrm{d}c\right)_{c\to 0}\left(\frac{1}{d}-\frac{1}{d_0}\right)}{Kc}$;

III. $\frac{\delta T - \left\{0\cdot08\left(\mathrm{d}d/\mathrm{d}c\right)_{c\to 0} + 0\cdot05\ \mathrm{d}d/\mathrm{d}c\right\}\left(\frac{1}{d}-\frac{1_0}{d}\right)}{Kc}$

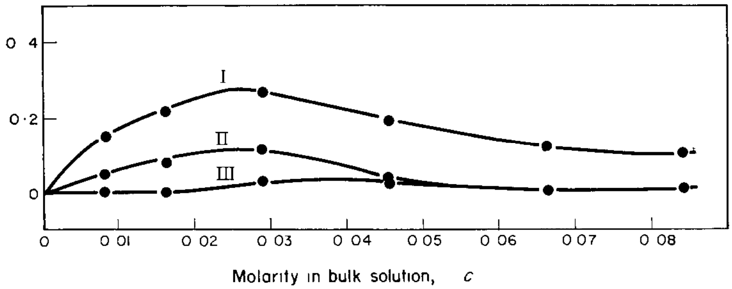

FIG. 8.—Glyceryl tribenzoate in pure acetone:

I. $\frac{\delta T}{Kc}$; II. $\frac{\delta T - 0\cdot08\left(\mathrm{d}d/\mathrm{d}c\right)_{c\to 0}\left(\frac{1}{d}-\frac{1}{d_0}\right)}{Kc}$

III. $\frac{\delta T - \left\{0\cdot08\left(\mathrm{d}d/\mathrm{d}c\right)_{c\to 0} + 0\cdot05\ \mathrm{d}d/\mathrm{d}c\right\}\left(\frac{1}{d}-\frac{1}{d_0}\right)}{Kc}$

proportional to $\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}$. When the constant B was put equal to 0·08, the final linear section of the curve was corrected to within the experimental error by deducting

$$0{\cdot}08\ \mathrm{d}d/\mathrm{d}c(1/d - 1/d_0) \qquad (2)$$

from the observed ΔT.

In the concentration range which included the inflection, the relative errors in ΔT pass through a maximum, and for glyceryl tristearate, glyceryl tribenzoate and aspirin, a maximum remained after applying the above correction (Figs. 7–9). In these graphs $(\Delta T - Kc)/Kc$ is plotted against c, where K is the ebulliometric constant, so that Kc is the theoretically expected elevation. Small errors in ΔT are accentuated at low concentration in these plots, and they illustrate the magnitude of the errors in molecular weight determinations that can result from the phenomena under discussion.

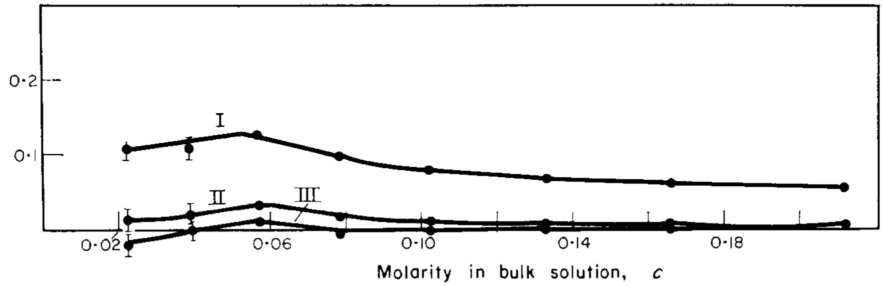

FIG. 9.—Aspirin in pure acetone:

$$\text{I.}\quad \frac{\delta T}{Kc}; \qquad \text{II.}\quad \frac{\delta T - 0{\cdot}08\left(\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}\right)\left(\frac{1}{d}-\frac{1}{d_0}\right)}{Kc};$$

$$\text{III.}\quad \frac{\delta T - \left\{0{\cdot}08\left(\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}\right) + 0{\cdot}05\mathrm{d}d/\mathrm{d}c\right\}\left(\frac{1}{d}-\frac{1}{d_0}\right)}{Kc}.$$

The fact that the excess elevation, $\delta T = \Delta T - Kc$, is almost constant and proportional to $\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}$ after the inflection, suggests that in the linear region adsorption was taking place onto aggregates or thick layers of adsorbed solute in the surface. According to Gibbs' equation:[6]

$$c_s - c_b = (c_b/RT)\,\mathrm{d}\gamma/\mathrm{d}c$$

where c_s is the concentration in the surface and c_b that in the bulk; γ, the surface tension, is proportional to d. It would appear from the above that the appropriate value of c_b to employ in the equation is that of the aggregates in the bulk solution which, if not zero, is at least always very small. Although the Gibbs' equation only strictly applies to equilibrium conditions, the adsorption here is assumed to be proportional to that at equilibrium.

Until thick layers supervene there will be areas of free solvent-vapour interface available for the adsorption of single molecules of solute, the surface becoming completely covered at concentrations beyond the inflection. Hence, a physical interpretation of the decrease of $\mathrm{d}\gamma/\mathrm{d}c$ with c in this region may be that in these cases

$\mathrm{d}\gamma/\mathrm{d}c$ is proportional to the free solvent surface available for the adsorption of solute. If S_f is the available solvent-vapour interface at each concentration, then the rate at which solute monomers enter the surface will be proportional to cS_f and also to $\mathrm{d}\gamma/\mathrm{d}c$. Hence

$$c_s - c_b\,(\text{monomers}) = bcS_f = \alpha\,\mathrm{d}\gamma/\mathrm{d}c = a\,\mathrm{d}d/\mathrm{d}c \tag{3}$$

where b, a and α are constants of proportionality. Combination with equation (2) and writing δT for the excess elevation gives

$$\delta T\,(= \Delta T - Kc) = \left\{B\left(\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}\right) + \mathrm{a}\,\mathrm{d}d/\mathrm{d}c\right\}\left\{\frac{1}{d_0} - \frac{1}{d}\right\} \tag{4}$$

The right-hand side of this equation is plotted against δT in Fig. 10, the constant B having the value 0·08 and $a = 0{\cdot}05$ when d is in cm and c in moles per litre. The excess elevations observed with glyceryl tristearate, glyceryl tribenzoate, aspirin, naphthalene, benzophenone and *o*-nitrobromobenzene were all predicted by this equation. The coefficient of correlation between the corrections and errors plotted in Fig. 10 is 0·975. In Fig. 11, δT is plotted against c for the above six solutes and for comparison the corrected points are plotted on the same figure; the standard deviation of the residual error was ±0·002°.

Of the other solutes examined, δT was within the experimental error (±0·001°) for benzoyl acetone and tri-n-butylphosphate up to 0·2*M*. The latter solute produced no persistent bubbles in this concentration range.

Triacetone dialcohol exhibited no inflection of the ΔT *versus* c curve, but the slope was 1% greater than theory predicted and this error was only partially corrected by equation (4). There was no error in the presence of PDA (see below), which implied that it was caused by adsorption. δT for this solute was approximately proportional to $c\Delta S\,\mathrm{d}d/\mathrm{d}c$, in agreement with the Gibbs' equation.

The curve of d *versus* s for *p*-dichlorobenzene was very shallow so that negligible adsorption would be expected, and the close agreement between the boiling point curves in pure acetone and in the presence of PDA supported this view. The molecular weight found was 153, instead of 147, and it appeared that the solute was associating. However, when the molecular weight in ether, acetone and ethanol are compared (see Table II), it is seen that they increase with the boiling point of the solvent rather than bearing any relation with its polarity. It is the author's opinion that the discrepancies arise from the volatility of this solute.

Boiling temperatures in acetone containing PDA

The curves in 1% PDA solutions generally included the origin to within the experimental error (Fig. 4). No point in the ΔT *versus* c curve was more than 0·002° displaced from a straight line up to a concentration of 0·1*M*, except for the solutes glyceryl tristearate and tribenzoate. These latter still gave rise to a reduced maximum in $\Delta T/Kc$ at the same concentration as in pure acetone.

An interesting result was observed when tri-n-butylphosphate was examined in this solution. The curve was linear and intercepted the origin, but the slope was 6% too high. The solute, which did not produce foam, in pure acetone, was adsorbed by the surface in the presence of PDA (Fig. 12).

A further series of measurements was carried out on six natural triglycerides in

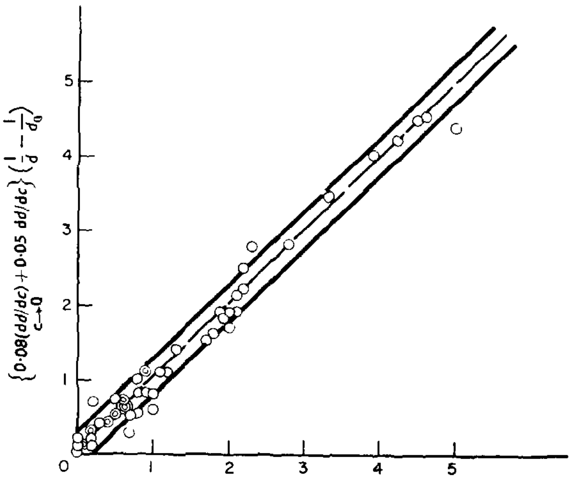

FIG. 10.—Error *versus* correction for acetone solutions of the following solutes: benzophenone, *o*-bromonitrobenzene, naphthalene, aspirin, glyceryl tribenzoate, glyceryl tristearate.

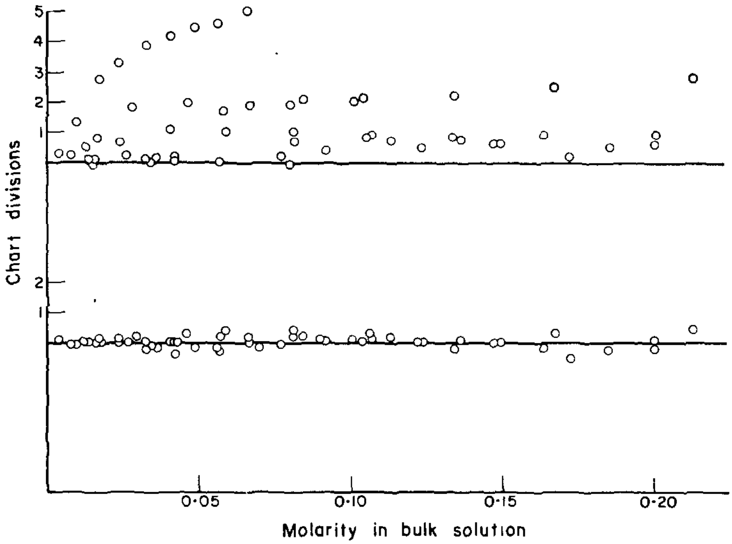

FIG. 11.—$\Delta T - K_c$ uncorrected (upper figure) and $\Delta T - (K_c + \text{correction})$ (lower figure) with the following solutes: benzophenone, *o*-bromonitrobenzene, naphthalene, aspirin, glyceryl tribenzoate, glyceryl tristearate.

acetone containing 2% of PDA. At this concentration the PDA completely suppressed the inflection and good agreement was obtained between the average molecular weights, calculated from the saponification equivalents and acid values, and those derived by ebulliometry (Table I).

It may be concluded that when the surface is saturated by an additive (preferably of high molecular weight), the phenomena observed in the pure solvent are suppressed.

Other solvents. The general occurrence of the errors from adsorption in the foam affects the choice of a suitable solvent for each class of solute. It may be impossible

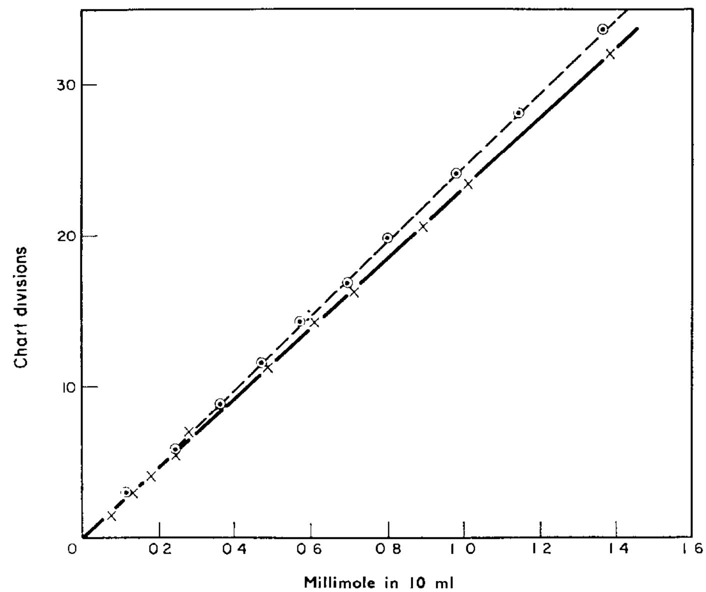

Fig. 12.—Elevations for tri-n-butyl phosphate:
×—in 10 ml of acetone, ○—in 10 ml of acetone containing 1% of PDA.
The full line is the one predicted by theory.

to reconcile the requirements of good solubility, absence of association and low adsorption. There is danger in extrapolating from the behaviour of low molecular weight materials; these can be measured at low weight concentrations. Surface phenomena are generally proportional to weight rather than molar concentration.

The ebulliometric constant, of benzene for example, apparently varies with the molecular weight when measurements are made on triglycerides. Taking *K* for naphthalene as unity, it is altered to 1·41 for diethylene glycol distearate (molecular weight 620) and to 1·50 for cacao butter (851). The ‘constant’ for diethylene glycol distearate was in good agreement with that obtained for palm kernel oil (679) and extracoa (678), while that found for cacao butter agreed with the remaining fats in Table II, which have molecular weights of the same order. No doubt both association and adsorption contributed to these results, but they indicate the caution to be exercised in drawing conclusions from ebulliometric measurements.

Table 1—Molecular weights of triglycerides in acetone plus 2% of PDA (molecular weight *ca.* 3000). The calculated weights were obtained from the saponification equivalents and corrected for free acidity

	Molecular weight	
	Calculated	Found
Cacao butter	851	845
Illipe butter	830	845
Hardened palm kernel oil	679	674
Coberine	867	854
Cacao shell butter	879	864
Extracoa	678	680

TABLE II.—THIS IS A LIST OF OBSERVED OVER EXPECTED ELEVATIONS ($\Delta T/Kc$) FOR 56 SOLVENT-SOLUTE PAIRS. FOR EACH PAIR THE VALUE OF $\Delta T/Kc$ IS GIVEN AT 0·05*M* AND FROM THE GRADIENT OF THE LINEAR PART OF THE CURVE. WHERE THERE IS NO FIGURE FOR THE ELEVATION AT 0·05*M*, THE OBSERVATION OF THE ZERO INCLUDED A SUPERHEATING ERROR. AN ASTERISK IN THE GRADIENT COLUMN INDICATES THAT THERE WAS EVIDENCE OF ASSOCIATION OF THE SOLUTE. VALUES GREATER THAN 1 INDICATE THAT THE OBSERVED MOLECULAR WEIGHT WAS TOO LOW AND *vice versa*

Solute	Acetone		Acetone + 1% of PDA		Ethanol		Ether		Carbon tetrachloride	
Aspirin	1·035	1·000	0·995	1·016	—	—	—	—	—	—
Benzidine	—	1·003	—	—	—	—	—	—	—	—
Benzophenone	1·087	0·988	0·966	0·972	—	—	—	—	—	—
Benzoic acid	—	1·010	—	—	—	—	—	—	—	—
Benzoyl acetone	0·995	0·987	0·995	0·994	—	—	—	—	—	—
o-Bromonitrobenzene	0·983	1·005	1·005	1·010	1·088	1·000	1·040	0·962*	0·963	0·990
Coumarin	—	1·002	—	—	—	—	—	—	—	—
p-Dichlorobenzene	0·966	0·923	0·952	0·931	0·955	0·754	0·938	0·938	—	—
Diethyleneglycoldistearate	—	—	—	—	1·200	1·030	—	—	—	—
m-Dinitrobenzene	—	1·001	—	—	—	—	—	—	1·010	1·005
Dioctylmalate	1·049	1·006	—	—	—	—	—	—	—	—
Diphenyloxide	—	—	—	—	—	—	0·977	0·960	—	—
Ethylbenzoate	—	—	—	—	—	—	1·003	1·000	—	—
Glycerylmonostearate	—	—	—	—	1·022	0·975	—	—	—	—
Glyceryltribenzoate	1·190	1·030	1·002	0·994	1·110	1·007	1·042	0·889*	1·002	0·915*
Glyceryltri-n-butyrate	1·060	0·964	—	—	—	—	—	—	—	—
Glyceryltripalmitate	—	—	—	—	1·242	—*	1·175	1·120*	1·156	1·342
Glyceryltriricinoleate	—	1·048	0·997	1·009	1·332	1·062*	—	—	—	—
Glyceryltristearate	1·345	1·130	1·154	1·020	1·291	—*	1·250	—*	—	—
Methyricinoleate	—	1·023	—	—	—	—	—	—	—	—
Naphthalene	1·008	1·008	0·988	0·992	0·993	1·000	0·993	1·000	1·011	1·026
Phenylbenzoate	—	—	—	—	1·016	1·041	0·963	0·918*	—	—
Phenylsalicylate	—	0·992	—	—	—	—	—	—	—	—
Triacetonedialcohol	1·011	1·010	1·009	1·004	—	—	—	—	—	—
p-Toluenesulphonamide	—	—	—	—	1·024	1·013	—	—	—	—
Tri-n-butylphosphate	1·007	1·000	1·043	1·038	—	—	0·967	1·010	—	—
Averages	1·072	1·012	1·010	0·998	1·119	1·014	1·034	0·978	1·028	1·058

TABLE III.—MOLECULAR WEIGHTS IN ETHER.
THE CORRECTED MOLECULAR WEIGHTS WERE OBTAINED BY DEDUCTING $3\left(\mathrm{d}d/\mathrm{d}c\right)_{c\to 0}$
FROM THE ELEVATION (IN Ω) AT 0·05M

	$\mathrm{d}d/\mathrm{d}c_{c\to 0}$,	Molecular weight		
	cm. litre mole^{-1}	Expected	Observed	Corrected
Glyceryl tripalmitate	17·0	807	694	795
Glyceryl tribenzoate	8·0	404	378	408
o-Bromonitrobenzene	5·3	202	194	201

Very similar results were obtained when measurements were made of the molecular weights of a number of polydiethylene adipates. The constant in ethanol was approximately 1·25 that found for naphthalene,[5] despite a long linear region displaced only 0·008° above the origin. In acetone 'K' was found to be very nearly proportional to the square root of the molecular weight of these esters as determined by end-group assay.

Values of $\mathrm{d}d/\mathrm{d}c_{c\to 0}$ were measured in ether for *o*-bromonitrobenzene, tripalmitin and glyceryl tribenzoate employing a cathetometer. These measurements were not as precise as those obtainable by photography and could not be extended reliably to the smaller bubbles, which formed more than one layer on the surface. The initial rate of change was found to be approximately proportional to the maximum error, *i.e.*, $\delta T_{\max} = B\,\mathrm{d}d/\mathrm{d}c_{c\to 0}$, and when this correction was applied to the molecular weights at 0·05M the weights were in good agreement with the expected values (Table III).

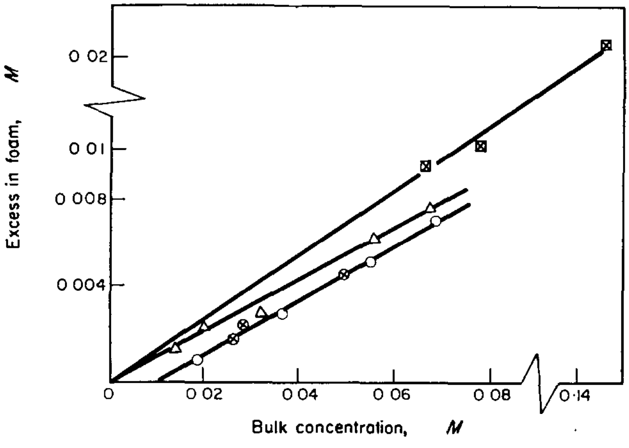

FIG. 13.—Direct measurements of foam concentration in acetone solution:
⊠—aspirin, △—glyceryl tristearate, ⊗—glyceryl tribenzoate, ○—glyceryl tripalmitate.

Maximum bubble pressure measurements in ethanol gave a more direct determination of $\mathrm{d}\gamma/\mathrm{d}c_{c\to 0}$. These measurements too, could not be extended to higher concentrations in the boiling solvent. Errors arising from adsorption of the solute on the inside of the capillary, variations in density of the solution and alterations of the mean depth of the liquid with increased foaming, became serious in all but the most dilute solutions. It was not possible to extrapolate from solutions below the boiling temperature because of the lower solubility of the solutes. Comparison of solutions of tristearin, tripalmitin and glyceryl tribenzoate showed that $\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}$ was closely proportional to $\underset{c\to 0}{\mathrm{d}\gamma/\mathrm{d}c}$. Association of the solutes precluded any attempt to correlate these figures with $\underset{\max}{\delta T}$.

Direct measurement of difference in concentration of foam and bulk

Gubbins has made measurements of foam concentrations using a specially designed flask.[9] He found that the solutes glyceryl tribenzoate, glyceryl tristearate, glyceryl tripalmitate and aspirin were all concentrated in the foam. The excess was found to increase with concentration throughout the range investigated. This result supports the view that these solutes are associated in the surface. On (Fig. 13) is plotted the relative excess against concentration for the four compounds. Because the flask was much larger and a different heating rate was applied these results cannot be compared directly with those reported above.

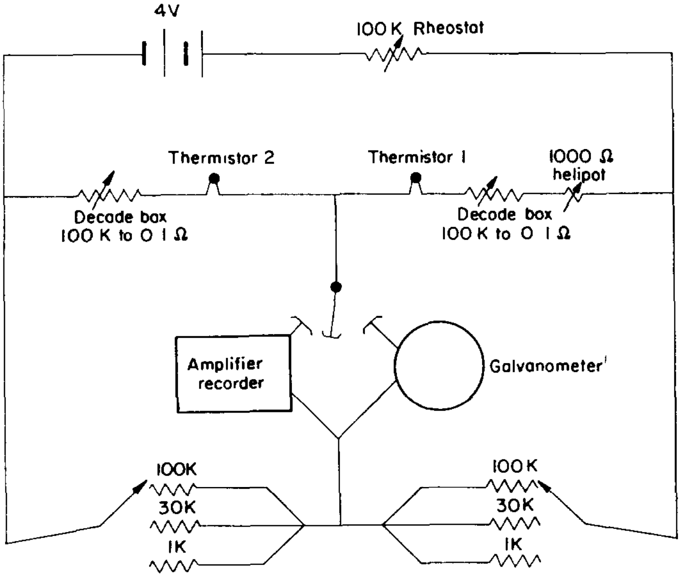

FIG. 14.—Ebulliometer circuit diagram.

CONCLUSION

It is commonly assumed that measurements which depend upon the colligative properties of solutions provide the most accurate results at the greatest dilutions. In particular, it has been the general belief that, provided the temperature changes could be assessed with sufficient accuracy, the most accurate result would be achieved at very low concentrations. This view presupposes that the only source of error, apart from superheating, is a simple departure from ideality. The work presented here indicates that the most accurate measurements of molecular weight are to be made at some intermediate concentration. The normal practice of finding the slope of the linear region of the ΔT *versus* c curve, although the line may not intercept the origin, is shown to have a theoretical as well as a pragmatic justification.

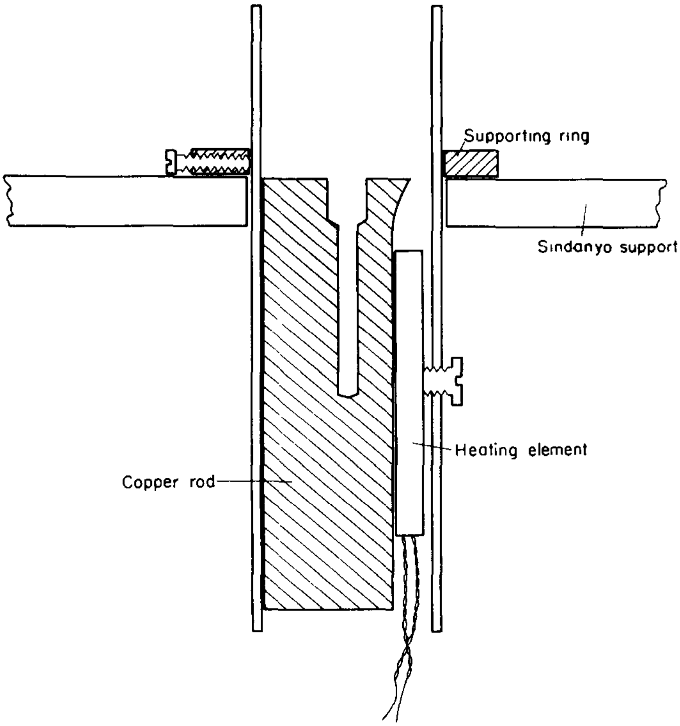

FIG. 15.—Section through heating block.

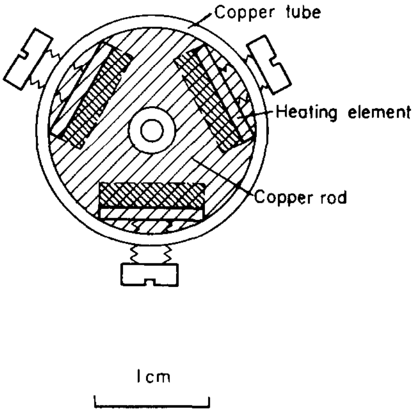

FIG. 15a.—Upper face of heating block.

EXPERIMENTAL

Measuring circuit

The elevations were measured in a commercially available ebulliometer of the author's design which has been described elsewhere.[3] A second ebulliometer, containing a 2% solution of PDA in acetone, was employed to compensate for barometric changes.[8] The thermistors from both cells were connected in opposite arms of a Wheatstone bridge circuit (Fig. 14).

The circuit was such that the total resistance of the thermistor can be kept constant by adding resistances in series. A precision decade box was used for this purpose, having six decades and a total range of 0·1 Ω to 111,111 Ω. Thus, changes in the thermistor resistance could be measured without altering the bridge ratios or affecting the sensitivity of the detecting instrument.

The 100-KΩ rheostat in series with the accumulators was set so that the current through the thermistors was about 0·2 mA. The out-of-balance current from the bridge was amplified and recorded on a Honeywell-Brown recording amplifier, and the sensitivity was such that 1 division on the recording chart (2·8 mm) corresponded fairly closely to an 0·01° change in the thermistor resistance. The sensitivity, in Ω per division, was tested frequently by switching 100 Ω into decade box 1.

In this series of experiments all of the elevations were measured in terms of chart divisions or resistance, so that it was not necessary to have an exact temperature calibration for the thermistor.

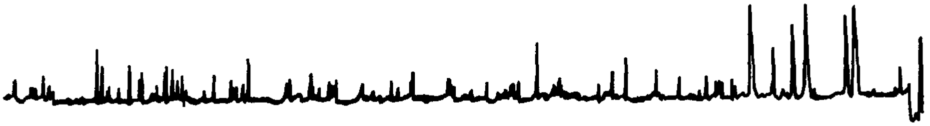

FIG. 16.—Trace of temperature *versus* time for boiling pure acetone.

Heating system (Fig. 15)

This was designed to provide good control over the boiling rate. Three 25-w miniature soldering iron elements were clamped into three grooves milled symmetrically round a 0·75-inch copper rod. The milling was continued, with decreasing depth towards the top, so that the upper face presented the appearance of Fig. 15*a*. The rod and elements were assembled inside the copper retaining tube. The device thus provided three channels up which hot air passed to flow round the ebulliometer, reducing heat losses from the main body of the flask. The tungsten wire projecting from the flask fitted into the hole in the top of the copper rod.

TABLE IV

	K, *divs./mole* × 10^{-1} . *litre*$^{-1}$	No. of observations
0·03–0·06M pure acetone	23·16 ± 0·15	11
0·03–0·06M acetone + PDA	23·20 ± 0·2	10
Gradients in pure acetone	23·24 ± 0·4	9
Gradients in acetone + PDA	23·02 ± 0·35	9

Boiling temperature of pure solvent

Fig. 16 is a facsimile of a record of the boiling temperature *versus* time for pure acetone. It is seen to have a constant baseline onto which a number of sharp peaks are superimposed. The peaks arise from splashes of superheated solvent reaching the thermistor, and if the detector were overdamped the average reading would have been too high. The boiling temperature zero was determined by taking the average of the minima in the baseline over the last inch of the chart (which ran at 300 sec per inch) before the first addition of solute. These minima varied by 0·1 division about their mean. The peaks were always reduced in the presence of solute, and for most solutes were completely absent at a low concentration.

Calculation of ebulliometer constant

For the five solutes naphthalene, triacetone dialcohol, benzoyl acetone, *o*-bromonitrobenzene and tri-n-butylphosphate, either no inflection was observed or it occurred at concentrations >0·06M. K was therefore taken as the average, for the above solutes, of $\frac{M\Delta T}{w}$ (where M is the molecular weight) between 0·03 and 0·06M, in pure acetone. A similar average was calculated for the PDA solutions, and from the gradients in both the presence of PDA and beyond the inflections in pure acetone. These averages are set out in Table IV.

The gradients of all solutes except *p*-dichlorobenzene were included in the average.

It was decided to accept 23·2 ± 0·2 as K. For the above five solutes the standard deviations of the temperature measurement of a single observation was ±0·1 chart division up to 0·05M. There was no reason to expect that this source of experimental uncertainty was greater at higher elevations.

Measurement of bubble diameters

The bubble ebulliometer is drawn full scale in (Fig. 17). It is a flattened version of the standard ebulliometer, with a similar pump, but no thermistor cavity. The pump tube ends 3 mm below the surface when the cell contains 10 ml of solvent.

The photographs were taken with a 35-mm single lens reflex camera fitted with extension tubes to provide unit magnification on the negative. Illumination was provided by a half-charged electronic flash unit (output *ca.* 20 joules), with a flash duration of 10^{-3} sec. The camera aperture was set at f22 and the cell illuminated at right-angles to the camera line-of-sight, with the flash 16 inch away. This was found to be the most efficient arrangement for delineating the bubble contours. There was little attenuation of the light across the cell.

Three techniques for obtaining the average bubble diameters were examined: (a) Outlining a magnified image of all of the bubbles in a photograph on mm graph paper and finding the total area A, then $d = \sqrt{\frac{A}{n}} \left(\text{not } \sqrt{\frac{4}{\pi}\frac{A}{n}}\text{, because the bubbles distort in contact with each other}\right)$. (b) Outlining a number of individual bubbles, measuring the longest and shortest diameters of each bubble and finally taking the average. (c) Measuring the average radius of curvature of the upper surfaces of the top layer of bubbles from the outlines of 10-fold magnified images.

There was no significant difference between the three methods, which generally agreed among themselves to within 0·2 mm. (a) was the preferred method, (c) being particularly tedious and time-consuming.

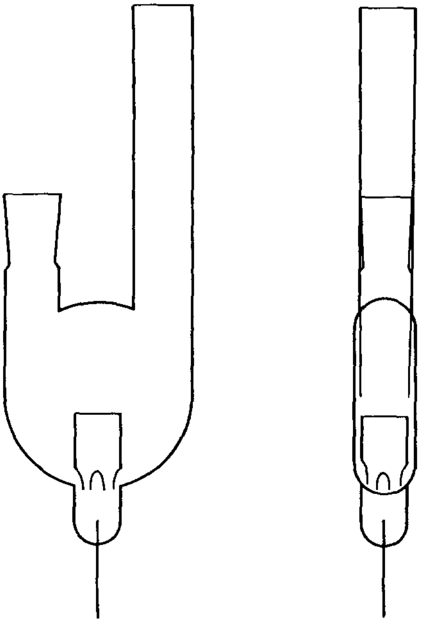

FIG. 17.—Bubble cell front view (left), side view (right).

Purification of materials

All of the solutes were purified by repeated recrystallisation from the solvent in which the measurements were to be made. This procedure could not be applied to tri-n-butylphosphate which was reprecipitated thrice from acetone by adding water. It was finally dissolved in acetone, the solution dried with Hi-Drite* and the acetone evaporated under reduced pressure. These procedures were adopted to ensure, so far as possible, that the only volatile impurity was the ebullioscopic solvent.

The glyceryl tristearate was free from acidity and had a saponification equivalent of 296, corresponding to a molecular weight of 888 (pure tristearin would be 891).

The acetone was purified by shaking first with a 30% solution of sodium hydroxide, then adding a 1% solution of silver nitrate and shaking further.[7] The acetone, now free from aldehyde, was redistilled, rejecting the first and last 25%. This distillate was dried over Hi-Drite and redistilled.

A granule of Hi-Drite (about 0·25 g) was introduced into the ebulliometer with the solvent in order to maintain a very low and constant moisture content.

---

* Hi-Drite Ltd., 17 New Bond Street, London, England.

Acknowledgements—I would like to thank many of my colleagues who have patiently borne with me in numerous discussions, and in particular those who have read this paper in preparation and offered much useful and constructive criticism. My thanks are also due for the project work of M. Gubbins and G. M. Pierce, who were responsible for the data in Fig. 13 and Table I, respectively.

Zusammenfassung—Der Schaum einer siedenden Lösung wird durch Transport adsorbierten gelösten Stoffes in die Blasenoberflächen konzentriert. Die Differenz der Siedetemperaturen von Schaum und Hauptmenge kann durch eine Massentransportgleichung berechnet werden, in der die pro Zeiteinheit gebildete Blasenoberfläche vorkommt. Als Maß für die Änderung der Oberflächenspannung wurde der mittlere Blasendurchmesser bei der jeweiligen Konzentration genommen. Sind d und c Blasendurchmesser und Konzentration der Hauptmerge und die Differenz der Siedetemperaturen von Schaum und Hauptmerge δT, dann ist

$$\delta T = \left\{B\left(\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}\right) + a\,\mathrm{d}d/\mathrm{d}c\right\}\left(\frac{1}{d_0}-\frac{1}{d}\right)$$

hier ist d_0 der Blasendurchmesser im reinen Lösungsmittel und B eine Konstante. Diese Gleichung setzt den Konzentrationsüberschuß im Schaum mit der Änderung der Oberflächenspannung und der Blasenoberfläche in Beziehung. Direkte Messungen der Konzentrationsdifferenz zwischen Hauptmenge und Schaum weisen auf einem linearen Zusammenang hin. Die Annahme, daß sich die gelösten Moleküle an der Oberfläche anreichern, liefert eine theoretische Grundlage für obige Gleichung und für die offenbare Abweichung der Adsorption von der Gibbsschen Gleichung.

Résumé—Dans une solution en ébullition, la mousse est plus concentrée, par le transport du corps dissous adsorbé sur les surfaces des bulles. L'élévation de la température d'ébullition de la mousse par rapport à celle de la masse du liquide peut être prévue par une équation de transport de masse mettant en jeu la surface totale des bulles produites dans l'unité de temps. La variation de tension superficielle a été mesurée en fonction du diamètre moyen des bulles dans la mousse à chaque concentration. Si d et c sont respectivement le diamètre des bulles et la concentration de la masse du liquide, l'élévation de la température d'ébulliton de la mousse par rapport à celle de la masse du liquide est donnée par

$$\delta T = \left\{B\left(\underset{c\to 0}{\mathrm{d}d/\mathrm{d}c}\right) + a\,\mathrm{d}d/\mathrm{d}c\right\}\left(\frac{1}{d_0}-\frac{1}{d}\right)$$

où d_0 est diamètre en solvant pur et B une constante. C'est une équation reliant l'excès de concentration dans la mousse à la vitesse de variation de la tension superficielle et à l'aire de la surface des bulles. Des mesures directes de la différence entre les concentrations de la masse du liquide et de la mousse montrent entre elles une relation linéaire. L'hypothèse selon laquelle le corps dissous s'associe sur la surface apporte une base théorique à l'équation ci-dessus, et au fait que l'adsorption s'écarte apparement de l'équation de Gibbs.

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AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT—IV*

TITRATION OF HYDRAZINE AND ISONICOTINIC ACID HYDRAZIDE AT ROOM TEMPERATURE

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Summary—The suitability of ammonium hexanitratocerate (IV) as an oxidimetric reagent for the determination of hydrazine and isonicotinic acid hydrazide has been investigated. Conditions for a rapid titration at room temperature both with a potentiometric and visual end-point have been developed. Under the conditions prescribed the combined nitrogen in both hydrazine and isonicotinic acid hydrazide is stoichiometrically liberated as gaseous nitrogen, unlike other cerimetric methods currently available.

BENRATH and Ruland[1] studied the reaction of hydrazine with an excess of cerium(IV) sulphate in a sulphuric acid medium and reported a yield of 11·22% of nitrogen and 12·88% of ammonia. However, the following stoichiometric reaction

$$N_2H_5^+ + Ce^{4+} \rightarrow 0{\cdot}5N_2 + NH_4^+ + Ce^{3+} + H^+ \tag{1}$$

requires 10·77% of nitrogen and 13·09% of ammonia to be formed. From a consideration of these results and in view of the relatively low speed of the reaction, Benrath and Ruland concluded that hydrazine cannot be determined by direct titration with cerium(IV) sulphate.

Recently, Krishna Rao, Subramanyam and Gopala Rao[2] reported that the electrometric titration of hydrazine with cerium(IV) sulphate is possible at 50–60° using manganese(II) salt as catalyst. They stated that the experimental values for hydrazine agree with the theoretical after they are multiplied by a factor of 0·985, assuming that the reaction proceeds according to equation (1).

Jílek and Brandštetr[3] have carried out a direct titration of hydrazine at 80–90° in 4·5*M* sulphuric acid or 3·75*M* hydrochloric acid in the presence of potassium bromide with cerium(IV) sulphate and either a visual end-point (using the azo dyes Victoria Rubin and Naphthol Blue Black 10B as irreversible indicators) or a potentiometric end-point. Under these conditions the results are about 0·8% lower than the theoretical as evident from their original paper, assuming the reaction to proceed according to the equation

$$N_2H_5^+ + 4Ce^{4+} \rightarrow N_2 + 4Ce^{3+} + 5H^+$$

Bapat and Sharma[4] titrated hydrazine with cerium(IV) sulphate *via* bromide to an amperometric "dead-stop" end-point in a 2·5–3·0*M* hydrochloric acid medium containing 2–3 g of potassium bromide/100 ml, at room temperature, and reported stoichiometric results. In titrations of hydrazine sulphate with cerium(IV) sulphate

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* Part III: *Talanta*, 1964, **11**, 955.

under the conditions prescribed by Bapat and Sharma with a potentiometric "dead stop" end-point or with a conventional potentiometric end-point, we obtained results which were about 2% lower than the theoretical. Evidently, the presence of bromide alters the course of the reaction from equation (1) to equation (2). It is interesting that the bromate method of Kurtenacker and Wagner[5] also involves the oxidation of hydrazine completely to nitrogen. The bromate method is stated to be the best available titrimetric procedure for standardisation of hydrazine solutions, and we have confirmed its accuracy using analytical reagent grade hydrazine sulphate. In a recent review on the use of hydrazine and its derivatives as reductometric reagents, Berka, Vulterin and Zýka[6] stated that "the reaction between cerium(IV) and hydrazine is not quantitative and depends upon the nature of the medium."

In view of the consistently low results obtained by us during the titration of hydrazine sulphate with cerium(IV) sulphate under the conditions prescribed either by Bapat and Sharma or by Jílek and Brandštetr, we have investigated the cause of the low results. This has been traced to the presence of sulphate ion introduced through the cerium(IV) sulphate solution and that arising from hydrazine sulphate; the exact effect of the sulphate has not been elucidated. To eliminate sulphate ion completely from the system we have worked with ammonium-hexanitratocerate(IV) in place of cerium(IV) sulphate and hydrazine dihydrochloride in place of hydrazine sulphate. It has been found that a rapid and accurate titration of hydrazine can be made in a hydrochloric acid medium with a solution of ammonium hexanitratocerate(IV) at room temperature, using potassium bromide as catalyst, either to a potentiometric end-point or to a visual end-point with α-naphthoflavone or *p*-ethoxychrysoïdine as internal indicator.

The details of our investigation are presented in this paper.

EXPERIMENTAL

Reagents

0·1M Ammonium hexanitratocerate(IV) solution. Prepared and standardised according to the procedure described in Part I[7] of this series.

0·025M Hydrazine dihydrochloride solution. The sample employed in this investigation was supplied by E. Merck, Darmstadt, Germany. It was twice recrystallised from aqueous alcohol (50% v/v) and dried at 110°. The melting point of the product was 198° as against a value of 198–199° reported in the literature,[8] thus confirming the purity of the recrystallised material. An approximately 0·025*M* aqueous solution of this material was prepared and standardised according to the bromate method of Kurtenacker and Wagner.[5]

0.025*M Isonicotinic acid hydrazide* (*isoniazid*) *solution.* Prepared from a sample, labelled "U.S.P." and supplied by Albert David (Private) Limited, Calcutta, India, by recrystallising twice from water. The 0·025*M* solution was standardised against potassium dichromate by the method recommended by Vulterin and Zýka.[9]

0·2% *Ethanolic solution of α-naphthoflavone.* Prepared from an E. Merck "guaranteed reagent" quality sample.

0·1 % *Aqueous solution of* p-*ethoxychrysoïdine.* Prepared by dissolving *p*-ethoxychrysoïdine hydrochloride supplied by E. Merck in doubly-distilled water.

Concentrated hydrochloric acid. Analytical reagent grade material (sp. gr. 1·18), supplied by Basynth Chemicals (Private) Ltd., Calcutta, India, was used.

All other reagents employed were of guaranteed reagent quality.

Apparatus

The potentiometric titration assembly employed in this investigation consists of a Junior potentiometer (W. G. Pye & Co., England), a taut suspension galvanometer (Cambridge Instrument Co., England), a saturated calomel electrode as reference electrode and a bright platinum rod (*ca.* 0·2 mm diameter) as an indicator electrode. The salt bridge consists of an inverted "U" tube with porous plate ends filled with a saturated solution of potassium chloride.

Potentiometric Titration of Hydrazine

The reaction between hydrazine sulphate and cerium(IV) sulphate was found to be very slow at room temperature in a 0·5*M* sulphuric acid medium as evidenced by the slow disappearance of the yellow colour of the cerate ion. During the early stages of the titration, when a drop of cerium(IV) sulphate is added to 50 ml of a solution of 0·1*M* hydrazine sulphate in 0·5*M* sulphuric acid, it takes about 3 min for the yellow colour to disappear and about 10 min towards the close of the titration. If the 0·5*M* sulphuric acid is replaced by 1·0*M* hydrochloric acid the time required for the disappearance of the yellow colour of the cerate ion is about 1–2 min in the early stages and 5 min towards the end. We have, therefore, avoided even the small concentration of sulphate ion introduced by cerium(IV) sulphate and hydrazine sulphate by using ammonium hexanitratocerate(IV) in place of cerium(IV) sulphate and hydrazine dihydrochloride in place of hydrazine sulphate. Even under these conditions the reaction was observed to be somewhat slow as the basis of a quick titration. Increasing the concentration of hydrochloric acid or the temperature did not bring about any improvement. Hence, we attempted the use of potassium bromide as a catalyst.

Effect of varying the concentration of potassium bromide

5·0 ml of hydrazine dihydrochloride solution (0·03140*M*) in a 150-ml Pyrex beaker were acidified with 5 ml of concentrated hydrochloric acid and varying volumes of 4*M* potassium bromide solution were added, followed by dilution to 60 ml. The reaction mixture was then titrated potentiometrically, using the assembly described above, with a solution of ammonium hexanitratocerate(IV) (0·1178*M*). The time taken for the disappearance of the yellow colour of the cerate ion or the time taken for the attainment of stable potentials after the addition of each portion of cerate solution was found to decrease with increasing concentration of potassium bromide. For example, the time taken for the attainment of stable potentials is about 40 sec and 25 sec when the concentration of potassium bromide is 0·1*M* and 0·5*M*, respectively.

Moreover, when the titration of hydrazine dihydrochloride is carried out in a 1·0*M* hydrochloric acid medium, titres lower than the theoretical are obtained when the over-all bromide concentration is lower than 0·5*M*. The results also show that the experimental titre increases as the over-all concentration of potassium bromide is increased from 0·1 to 0·5*M*, reaching the theoretical value within the limits 0·5 to 2·0*M*. The titre shows a slight decrease when the over-all concentration of potassium bromide is increased above 2·0*M*.

Effect of varying the hydrochloric acid concentration

A number of titrations have been carried out varying the concentration of hydrochloric acid but maintaining the concentration of potassium bromide constant at 1·0*M*. When the concentration of hydrochloric acid lies between 1·0 and 3·0*M*, the potentials attain stable values in about 30 sec after the addition of each portion of cerate solution, except near the equivalence point when about 1 min is necessary.

As the concentration of hydrochloric acid is decreased below 1·0*M* the time required for attainment of stable potentials increases and the titre is also less than the theoretical value (5.26 ml), being 5·14 ml and 5·20 ml in 0·10*M* and 0·25*M* acid. When the concentration of hydrochloric acid is 4·0*M* the experimental titre again becomes lower than the theoretical.

An accurate and satisfactory potentiometric titration of hydrazine dihydrochloride with ammonium hexanitratocerate(IV) at room temperature is, therefore, only possible in a 1·0–3·0*M* hydrochloric acid medium containing potassium bromide at an over-all concentration of 0·5 to 2·0*M*.

Recommended procedure

From 2·5 to 10 ml of about 0·025*M* hydrazine dihydrochloride solution (8–27·5 mg of the salt) are taken in a 150-ml Pyrex beaker and treated with 5 ml of concentrated hydrochloric acid and 15 ml of 4*M* potassium bromide solution. The mixture is then diluted with water to 60 ml and titrated potentiometrically with 0·1*M* ammonium hexanitratocerate(IV) solution. The potentials are measured 1 min after the addition of each portion of the cerate solution. The break in potential at the equivalence point is 140–170 mV/0·04 ml of 0·1*M* cerate solution. A typical E–V curve is given in Fig. 1.

Titrations of more dilute solutions of hydrazine dihydrochloride (0·0025*M*) have been carried out with about 0·01*M* cerate solution and the break in potential remains unaltered. Typical results, presented in Table I, show that the method now proposed gives values for the assay of hydrazine in agreement with those obtained by the bromate method.[5] The average error is about 0·2%(relative), assuming the bromate results to be exact.

Potentiometric Titration of Isonicotinic Acid Hydrazide

A survey of the existing literature has shown that so far cerium(IV) salts have not been employed for the direct titrimetric determination of isonicotinic acid hydrazide either at room temperature or at elevated temperatures. Vulterin and Zýka[9] state that the reaction between isonicotinic acid hydrazide and cerium(IV) depends to a large measure on the pH of the solution, but under no conditions does reaction proceed stoichiometrically. We have now found that isonicotinic acid hydrazide can be rapidly titrated to a potentiometric end-point with ammonium hexanitratocerate(IV) at room temperature under the same conditions as recommended above for hydrazine. Fig. 2 is a representative E-V curve of such titrations. The reaction may be represented by the equation:

$$C_6H_4NCONHNH_2 + 4Ce^{4+} + H_2O \rightarrow 4Ce^{3+} + C_5H_4NCOOH + N_2 + 4H^+$$

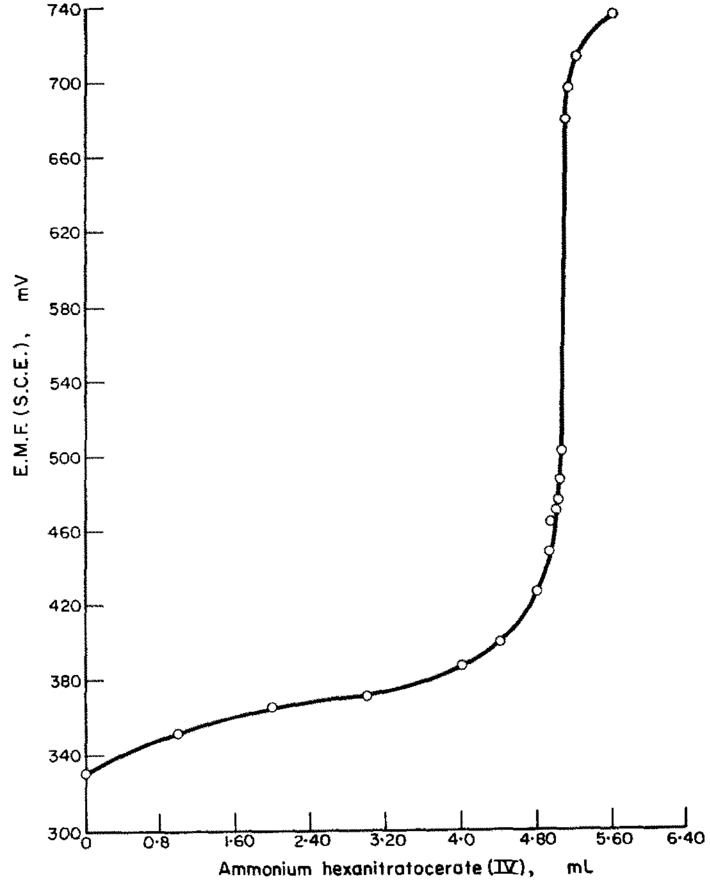

Fig. 1.—Potentiometric titration of hydrazine dihydrochloride (16·33 mg) with ammonium hexanitratocerate(IV).

Typical results on the assay of isonicotinic acid hydrazide are given in Table II, which show that the average error is 0·3%(relative), assuming the values obtained by the dichromate method to be exact.

Visual Titration of Hydrazine and Isonicotinic Acid Hydrazide

Having established conditions for a rapid potentiometric titration of hydrazine and isonicotinic acid hydrazide with ammonium hexanitratocerate(IV) at room temperature, we have attempted the use of visual indicators in these titrations with a view to providing a simple and rapid method for routine analysis. The use of the azo dyes Methyl Orange, Naphthol Blue Black 10B and Brilliant Ponceau 5R, both at room temperature and at elevated temperatures, has been investigated. In titrations at room temperature these dyes give a premature end-point, being irreversibly destroyed by the cerate solution. At higher temperatures (70–90°) Methyl Orange and Naphthol Blue Black can function as indicators provided the dye is added repeatedly, but this technique requires an appreciable indicator correction. Obviously, a procedure requiring high temperatures and repeated addition

TABLE I—ASSAY OF HYDRAZINE DIHYDROCHLORIDE

Hydrazine dihydrochloride, *mg*	
Bromate method[5]	Proposed cerimetric method
0·7896	0·7898
1·740	1·733
2·659	2·659
6·918	6·877
13·17	13·18
19·78	19·80
25·87	25·92
27·52	27·51

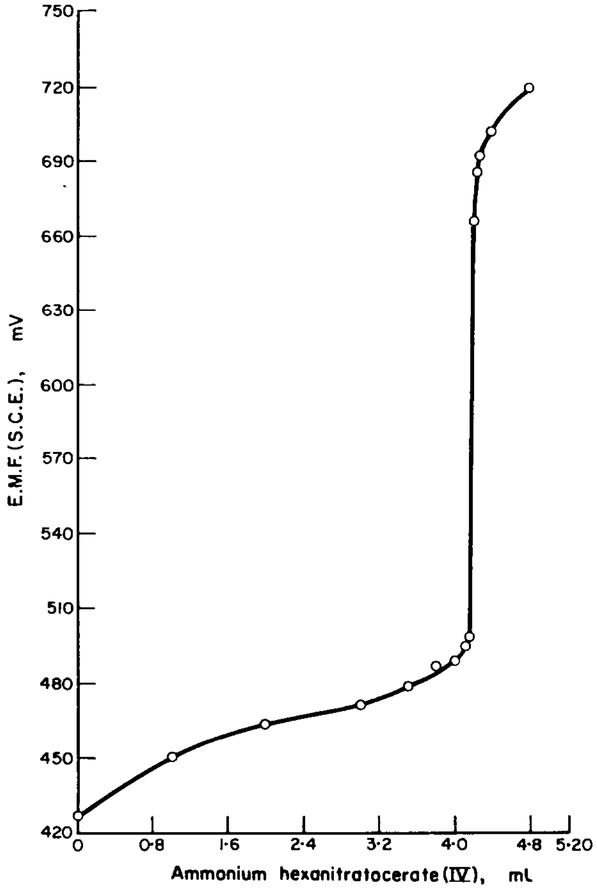

FIG. 2—Potentiometric titration of isonicotinic acid hydrazide (16·87 mg) with ammonium hexanitratocerate(IV).

TABLE II—ASSAY OF ISONICOTINIC ACID HYDRAZIDE

Isonicotinic acid hydrazide, *mg*	
Dichromate method[9]	Proposed cerimetric method
1·104	1·108
4·832	4·848
9·664	9·696
19·60	19·66
24·98	25·15
28·24	28·24
32·03	32·09

of indicator is inconvenient. Moreover, the indicator undergoes oxidation irreversibly. However, α-naphthoflavone and *p*-ethoxychrysoïdine give an excellent indication of the end-point in titrations of 0·025*M* solutions of hydrazine and isonicotinic acid hydrazide with 0·1*M* solutions of ammonium hexanitratocerate(IV) at room temperature in a medium containing an over-all concentration of 1·0*M* hydrochloric acid and 0·5–2·0*M* potassium bromide. In titrations of 0·0025*M* solutions of hydrazine and isonicotinic acid hydrazide with a 0·01*M* solution of cerate, *p*-ethoxychrysoïdine fails to give a sharp indication of the end-point, although α-naphthoflavone still works satisfactorily.

Laszlovsky[10] has already reported the use of both of these indicators in the titration of hydrazine and isonicotinic acid hydrazide with potassium bromate in the presence of potassium bromide. *p*-Ethoxychrysoïdine has been used as an indicator by Wojahn[11] for the bromometric determination of isonicotinic acid hydrazide and by Schulek and Burger[12] for the titrimetric determination of hydrazine and its derivatives with bromine monochloride.

Domleo[13] used the same indicator for the titrimetric determination of isonicotinic acid hydrazide with 0·05*M* potassium iodate in about 7·2*M* hydrochloric acid at room temperature, the indicator being added after the addition of 90% of the iodate solution. Thereafter, the titration is continued slowly. When the indicator colour changes from scarlet to orange, the iodate was added drop by drop at an interval of 30 sec for each drop until the liquid turns from orange to yellow. A blank determination is also carried out.

Recommended procedure with α-naphthoflavone as indicator

To a test solution, containing 0·8–25 mg of hydrazine dihydrochloride or 1·1–32 mg of isonicotinic acid hydrazide, taken in a 100-ml Erlenmeyer flask, 5 ml of concentrated hydrochloric acid and 15 ml of 4*M* potassium bromide solution are added and the mixture diluted to 60 ml. 0·2 ml of 0·1% ethanolic α-naphthoflavone is then added to the mixture, which assumes, on shaking, a pale greenish-yellow opalescence. On titrating the mixture with a 0·1*M* or 0·01*M* ammonium hexanitratocerate-(IV) solution, the indicator coagulates as a greenish-yellow compound. After the equivalence point it turns orange-red on the addition of a slight excess (0·02 ml) of the cerate solution. The indicator is reversible. Under these conditions the indicator correction is 0·02 ml of 0·1*M* ammonium hexanitratocerate(IV) solution, which has to be subtracted from the total titre. Some typical results of determinations of hydrazine and isonicotinic acid hydrazide carried out in this way are presented in Table III, which indicate that the average error of such determinations is about 0·25%(relative) in the case of hydrazine and 0·45%(relative) in the case of isonicotinic acid hydrazide.

When the contents of the titration flask are stirred by shaking by hand, the coagulated indicator distributes itself throughout the titration mixture. If a magnetic paddle is used for stirring, however, the coagulated indicator collects on a small area of the surface. As the cerate solution is added this floating patch of the greenish-yellow compound momentarily assumes an orange-red colour, but soon reverts to the greenish-yellow hue. This change of colour continues until the equivalence point is reached, then, with a slight excess of the cerate solution, the floating patch assumes an orange-red colour which is stable for over 12 hr.

Recommended procedure with p*-ethoxychrysoïdine as indicator*

To the test solution, containing 7–25 mg of hydrazine dihydrochloride or 8·4–32 mg of isonicotinic acid hydrazide, taken in a 100-ml Erlenmeyer flask, 5 ml of concentrated hydrochloric acid and 15 ml of 4*M* potassium bromide solution are added and the mixture diluted to 60 ml. When 0·1 ml of 0·1% aqueous *p*-ethoxychrysoïdine is added to the mixture, it imparts a yellow colour to it. On the addition of 0·1*M* ammonium hexanitratocerate(IV) solution, the colour changes to a light orange-red, which remains so throughout the titration until the end-point is reached when it changes to a pale yellow.

As the colour transition is somewhat slow, it is necessary to wait for about 15 sec at the end-point. Under these conditions the indicator correction is 0·04 ml of 0·1*M* cerate solution, which has to be subtracted from the total titre. Some typical results are presented in Table IV: the error averages 0·15 %(relative) in the case of hydrazine and 0·2 %(relative) in the case of isonicotinic acid hydrazide.

Blank experiments have shown that in the absence of potassium bromide the indicator is irreversibly oxidised to a pale yellow compound on the addition of the first few drops of the cerate solution. Evidently, bromide greatly accelerates the reaction between the intermediate orange-red oxidation product of the dye and the reductant.

TABLE III.—TITRIMETRIC DETERMINATION OF HYDRAZINE AND ISONICOTINIC ACID HYDRAZIDE USING VISUAL INDICATOR

α-Naphthoflavone				*p*-Ethoxychrysoïdine			
Hydrazine dihydrochloride, *mg*		Isonicotinic acid hydrazine, *mg*		Hydrazine dihydrochloride, *mg*		Isonicotinic acid hydrazine, *mg*	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
0·8432	0·8392	1·104	1·102	7·003	7·017	8·374	8·409
1·740	1·736	4·768	4·802	12·71	12·72	9·664	9·696
5·714	5·714	8·371	8·409	17·22	17·20	15·78	15·79
14·42	14·40	14·61	14·55	19·82	19·79	18·48	18·50
22·26	22·20	22·11	22·15	22·98	22·93	21·85	21·83
25·20	25·11	31·16	30·95	25·31	25·34	32·46	32·48

Removal of sulphate interference

Because of the interference of sulphate the new methods are inapplicable to the direct assay of hydrazine sulphate, a commonly encountered form of hydrazine. Hydrazine sulphate can be converted to the chloride by treating a hot aqueous solution of the former, containing dilute hydrochloric acid, with an excess of barium chloride and filtering off the precipitated barium sulphate.

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Zusammenfassung—Die Eignung von Ammoniumhexanitratocerat (IV) als oxydimetrisches Reagens bei der Bestimmung von Hydrazin und Isonicotinsäurehydrazid wurde untersucht. Die Bedingungen für eine schnelle Titration bei Zimmertemperatur, sowohl mit potentiometrischer als auch mit visueller Endpunktsanzeige, wurden ermittelt. Unter den angegebenen Bedingungen wird der Hydrazinstickstoff in Hydrazin und in Isoniazid stöchiometrisch als gasförmiger Stickstoff freigesetzt, im Unterschied zu den bisher üblichen Ceratverfahren.

Résumé—On a étudié la valeur de l'hexanitratocérate (IV) d'ammonium en tant que réactif oxydimétrique pour le dosage de l'hydrazine et de l'hydrazide de l'acide isonicotinique. On a mis au point les conditions d'un dosage rapide à température ambiante, avec détection potentiométrique ou visuelle du point de virage. Dans les conditions décrites, l'azote combiné, tant de l'hydrazine que de l'isoniazide, est libéré stoechiométriquement à l'état d'azote gazeux, contrairement à ce qui a lieu avec les autres méthodes cériques cériques couramment utilisées.

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DETERMINATION OF TITANIUM, TANTALUM AND NIOBIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—A method of precipitation from homogeneous solution has been developed for the gravimetric determination of titanium, by thermal decomposition of soluble peroxytitanate from either an alkaline or a slightly nitric acid medium. Recoveries are better than 99·6%. Coprecipitation of tungsten and manganese are reduced to a considerable extent. Furthermore, tantalum and niobium can be precipitated with highly satisfactory recoveries from a homogeneous nitric acid-hydrogen peroxide solution. Coprecipitation of titanium is investigated and corrections for coprecipitation calculated. The earth acids can also be precipitated from a homogeneous ammonia-hydrogen peroxide solution, the coprecipitation of tungsten being almost negligible. A study of the coprecipitation process of tungsten on tantalum and niobium shows that the distribution coefficients follow a linear pattern on both carriers. The method has been tested on a number of synthetic mixtures of the oxides, corrections for incomplete precipitation and coprecipitation being applied on the basis of the experimental values.

INTRODUCTION

THE gravimetric determination of titanium, tantalum and niobium in highly alloyed steels or in minerals and ores has always presented a rather difficult problem. The separation of the earth acids from tungsten and titanium requires particular attention because they tend to follow niobium and tantalum throughout the normal course of the analysis and appear in the final mixed oxide residue. The best method for separating the earth acids from large amounts of tungsten is probably Bedford's magnesia process.[1] However, Leliaert[2] recently showed that the precipitation of niobium is incomplete and that tungsten is coprecipitated to a considerable extent. The earth acids can be separated from titanium by Schoeller's classical separation,[3] in which the oxalates are decomposed with calcium chloride in the presence of sodium salicylate and the earth acids precipitated as salicylate complexes together with calcium oxalate. The titanium-salicylate complex is soluble, but it coprecipitates. As already shown in a previous paper,[4] tungsten can be successfully determined by precipitation from a homogeneous nitric acid-hydrogen peroxide solution. The same procedure is readily adaptable to the determination of titanium and the earth acids.[9] Radioactive tracer techniques were used to develop the proposed method.

EXPERIMENTAL

Radio-isotopes

Tantalum. ^{182}Ta, β, γ-emitter, half-life ± 111 day, produced by irradiation of tantalum pentoxide in the BR1 reactor.

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* This work is part of the research sponsored by "Het Interuniversitair Instituut voor Kernwetenschappen".

Niobium. ^{95}Nb, β,γ-emitter, half-life ± 35·5 day, obtained from The Radiochemical Centre, Amersham, England.

Tungsten. ^{187}W, β,γ-emitter, half-life 24 hr, produced by irradiation of tungsten trioxide in the BR-1 reactor.

Manganese. ^{54}Mn, γ-emitter, half-life 324 day, obtained from The Radiochemical Centre, Amersham, England.

Apparatus

Counting techniques. Integral γ-counting was used for each isotope using a well-type NaI(Tl) detector.

Spectrophotometer. Beckman D.U. or D.K.-1 spectrophotometer with 1·000-cm Corex cuvettes.

Precipitation of Titanium from Homogeneous Solution

Fuse the dioxide with potassium bisulphate and extract the cold melt with a hot 3% solution of hydrogen peroxide to give a clear solution of the soluble peroxytitanate. Adding potassium hydroxide and dilute aqueous ammonia to bring the solution to pH 8. Heat the solution at 70° for 6 hr, after which the precipitation is complete. During the heating, the excess of hydrogen peroxide and the peroxytitanate are decomposed, causing a precipitation of metatitanic acid from a homogeneous solution.

The homogeneous precipitation can also be realised from a slightly acid medium. Preliminary experiments on the precipitation of tungsten and titanium showed that optimum results were obtained in a nitric acid medium, the solution being acidified to pH 2·5. The decomposition in an acid medium proceeds slowly, heating for 6 hr at 85° being required for complete precipitation.

In all experiments the amount of titanium left in solution was determined spectrophotometrically as the peroxide. The results are summarised in Table I.

TABLE I.—COMPLETENESS OF THE TITANIUM PRECIPITATION

Titanium taken, *mg Ti/60 ml*	Titanium left in solution, %[a]	
	NH_4OH-H_2O_2	HNO_3-H_2O_2(pH 2·5)
120·3	0·06	0·05
90·2	0·08	0·20
60·3	0·14	0·37
30·4	0·16	0·02
15·1	0·27	0·11
9·0^5	—	0·10

[a] Average of 2 experiments.

From Table I precipitation of titanium from homogeneous solution gives highly satisfactory titanium recoveries from both ammoniacal and slightly acid media. At all titanium concentrations investigated, the recovery is better than 99·6%.

Coprecipitation of tungsten and manganese

It is well known that tungstate coprecipitates with metatitanic acid. The precipitation of titanium from a homogeneous slightly alkaline medium offers the possibility of considerably reducing this coprecipitation. The coprecipitation of tungsten was investigated for tungsten/titanium ratios varying from 0·1 to 10. The absolute amount of titanium precipitated varied between 100 mg for small ratios and 35 mg for large ratios. Before melting the oxides of titanium and tungsten a known activity (*ca.* 1 × 10^6 cpm) of ^{187}W tracer was added. The percentage of tungsten coprecipitated was found by counting the activity of the precipitate. The results are summarised in Table II.

TABLE II.—COPRECIPITATION OF TUNGSTEN WITH TITANIUM DURING PRECIPITATION FROM AMMONIACAL PEROXIDE SOLUTION

W/Ti ratio	W coprecipitated, %	Error on Ti, %
0·103	0·86	0·066
0·256	0·63	0·12^1
0·51	0·30	0·11^5
1·02	0·19	0·14^8
2·55	0·23	0·44^3
5·1	0·20	0·77^0
10·2	0·26	2·0^0

At all tungsten/titanium ratios investigated less than 1% of the tungsten is coprecipitated.

The precipitation of titanium from a homogeneous nitric acid-hydrogen peroxide medium allows a separation of titanium from hydroxides insoluble in alkaline medium. Manganese, for instance, often interferes with the determination of titanium. This coprecipitation was studied for manganese/titanium ratios varying from 1 to 20. The absolute amount of titanium precipitated was varied from 35 to 10 mg. The amount of manganese coprecipitated was computed from ^{54}Mn tracer experiments. The results, summarised in Table III, show that the coprecipitation is reduced to a considerable extent. A twenty-fold excess of manganese causes an error of only 4% on the titanium determination.

TABLE III.—COPRECIPITATION OF MANGANESE WITH TITANIUM (PRECIPITATION FROM HNO_3-H_2O_2, pH 2·5)

Mn/Ti ratio	Mn coprecipitated, %	Error on Ti, %
1·16^5	1·30	1·3^8
2·33	0·93^6	1·8^8
4·78	0·51^1	2·0^6
7·83	0·34^8	2·3^5
11·22	0·32^0	3·0^8
15·14	0·22^2	2·9^0
19·94	0·23^0	3·9^5

Precipitation of Tantalum and Niobium from Homogeneous Nitric Acid-Hydrogen Peroxide

Fuse the pentoxides with potassium bisulphate and treat the cold melt by heating with a 3% solution of hydrogen peroxide. Neutralise with potassium hydroxide to give a clear solution of soluble peroxytantalates and niobates. Add nitric acid and heat to decompose the excess of hydrogen peroxide and the peroxyacids. The earth acids are precipitated homogeneously.

Preliminary experiments showed that in 5*M* nitric acid optimum results were obtained. A heating period of 10 hr at 70° was required before the decomposition was complete. In the presence of small amounts of selenous acid as a catalyst, quantitative precipitation took place after 5 hr at 85°.

In all experiments the amount left in solution was computed from tracer experiments. The tracer solutions were prepared with the same experimental conditions as the earth acid stock solutions. The results for the tantalum and niobium precipitations are summarised in Table IV.

It can be seen from Table IV that precipitation from homogeneous solution

TABLE IV.—COMPLETENESS OF THE TANTALUM AND NIOBIUM PRECIPITATIONS FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Tantalum taken, *mg/60 ml*	Ta left in solution, %^{a}	Niobium taken, *mg/60 ml*	Nb left in solution, %^{a}	Niobium + tantalum taken, *mg/60 ml*	Nb left in solution, %^{a}
100·3	0·14	107·5	0·50	107·5 + 75	0·36
85·0	0·18	75·2^{5}	0·77	84·1 + 75	0·39
69·8	0·27	53·7^{5}	0·88	58·8^{3} + 75	0·48
41·1	0·28	43·0	1·1	43·0 + 50	0·85
29·1	0·26	32·2^{5}	0·63	32·2^{5} + 50	0·57
17·4	0·34	21·5	2·1	21·5 + 50	0·74
8·4	0·38	10·7^{5}	2·5	12·6^{2} + 50	0·60
5·0	0·35	4·3	8·1	4·3 + 50	1·38

[a] Average of 2 experiments.

gives highly satisfactory tantalum recoveries (better than 99·6%) even at low concentrations. For niobium it is somewhat less satisfactory, although in the presence of tantalum the recoveries of niobium are usually better than 99%.

Coprecipitation of titanium

The precipitation from a homogeneous nitric acid-hydrogen peroxide medium allows a separation of the earth acids from titanium over a considerable concentration range. The coprecipitation of titanium was investigated for titanium/tantalum or niobium ratios varying from 0·008 to 8. The absolute amount of earth acids precipitated varied between 120 mg for small ratios and 15 mg for larger ratios. The amount of titanium coprecipitated was determined spectrophotometrically or gravimetrically. The results are given in Tables V and VI. The induced error is plotted in Fig. 1.

From Tables V and VI it appears that coprecipitation errors are quite low, although far from negligible in the case of large titanium/tantalum or niobium ratios. For small ratios a correction for the titanium coprecipitation can easily be made, because the values are highly reproducible.

TABLE V.—COPRECIPITATION OF TITANIUM WITH TANTALUM FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Spectrophotometric determination			Gravimetric determination		
Ti/Ta ratio	Ti coprecipitated, %	Error on Ta, %	Ti/Ta ratio	Ti coprecipitated, %	Error on Ta, %
0·00804	47·^{6}	0·52			
0·0117	37·^{1}	0·59			
0·0237	35·^{1}	1·1^{3}			
0·0373	37·^{9}	1·9^{3}			
0·0568	24·^{3}	1·8^{8}			
0·0862	20·^{0}	2·3^{5}	0·0875	26·^{8}	3·2
0·175	14·^{2}	3·3^{9}	0·137	21·^{5}	4·0^{2}
0·335	8·2	3·7^{5}	0·434	11·^{0}	6·5^{2}
0·609	7·1	5·9^{1}	0·635	8·9^{7}	7·7^{8}
1·02	4·7	6·5^{5}	1·03	7·4^{8}	10·^{5}
2·10	2·6	7·4^{6}	1·99	3·2^{5}	8·8^{3}
3·02	1·9	7·8^{4}	3·16	2·2^{3}	9·6^{2}
7·29	0·8^{4}	8·3^{6}	9·01	0·8^{1}	10·0

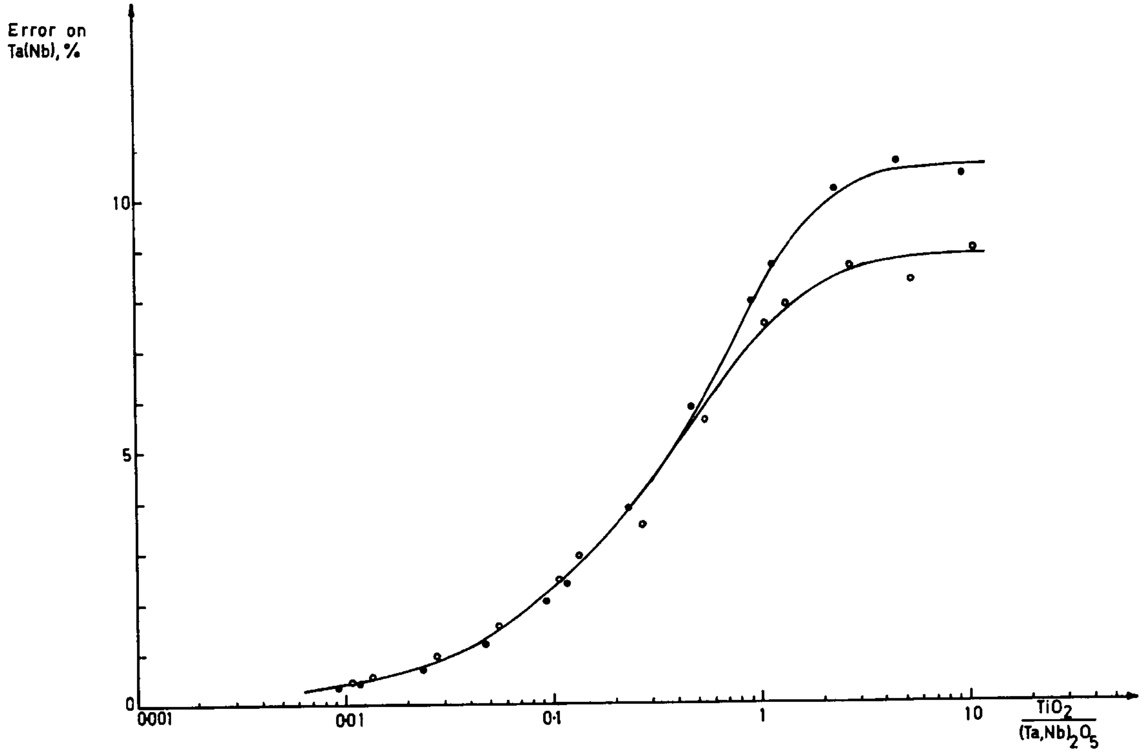

FIG. 1.—Titanium coprecipitation with tantalum and niobium:

● niobium precipitate,
○ tantalum precipitate.

TABLE VI.—COPRECIPITATION OF TITANIUM WITH NIOBIUM FROM NITRIC ACID-HYDROGEN PEROXIDE SOLUTION

Spectrophotometric determination			Gravimetric determination		
Ti/Nb ratio	Ti coprecipitated, %	Error on Nb, %	Ti/Nb ratio	Ti coprecipitated, %	Error on Nb, %
0·00868	38·^{8}	0·39			
0·0155	29·^{4}	0·53			
0·0224	26·^{5}	0·69			
0·0370	23·^{6}	1·0^{2}	0·0858	19·^{8}	1·9^{8}
0·0667	20·^{1}	1·5^{6}	0·171	15·^{7}	3·1^{5}
0·0925	26·^{9}	2·9^{0}	0·306	13·^{2}	4·7
0·170	19·^{7}	3·9^{0}	0·502	11·^{3}	6·6
0·301	17·^{8}	6·2^{5}	0·907	7·9^{1}	8·4
0·503	13·^{3}	7·8^{0}	1·51	5·2^{5}	9·2
0·863	8·9^{7}	9·0	3·05	3·8^{2}	13·^{6}
1·51	7·4^{2}	13·^{1}	3·66	2·8^{5}	12·^{2}
3·57	2·8^{8}	12·^{0}	4·85	1·7^{0}	9·6
4·97	1·8^{2}	10·^{5}	8·26	1·3^{5}	13·^{0}

Precipitation of Tantalum and Niobium from a Homogeneous Solution of NH_4OH-H_2O_2

Tantalum and niobium can also be precipitated from a homogeneous ammonical hydrogen peroxide solution, giving a separation of the earth acids from tungsten.

Leach the potassium bisulphate melt with hydrogen peroxide and neutralise with potassium hydroxide, carefully adjusting the pH to 7·5–8 with dilute aqueous ammonia. Heat solutions containing from 100 to 10 mg of tantalum or niobium for 20 hr at 85°, to decompose the soluble peroxytantalates and niobates. In the presence of selenous acid the heating period can be reduced to 8 hr. The decomposition causes a homogeneous precipitation of tantalum and niobium.

The completeness of the precipitations was examined by adding a known amount of ^{182}Ta or ^{95}Nb tracer and measuring the activity of the filtrate. The results are summarised in Table VII, which shows that at least 99.2% of the tantalum and niobium is precipitated.

TABLE VII.—COMPLETENESS OF THE TANTALUM AND NIOBIUM PRECIPITATIONS FROM HOMOGENEOUS SOLUTION OF AMMONIACAL HYDROGEN PEROXIDE

Tantalum taken, *mg/60 ml*	Ta left in solution, %^{a}	Niobium taken, *mg/60 ml*	Nb left in solution, %^{a}
100·1	0·08	100·2	0·15
70·2	0·13	80·2	0·12
60·6	0·14	65·2	0·33
48·5	0·17	50·1	0·74
28·7	0·50	40·1	0·41
24·0	0·62	25·0^{5}	0·80
14·9	0·67	10·0^{2}	0·71

[a] Average of 2 experiments.

Coprecipitation of tungsten

It might be expected that precipitation of the earth acids from a slightly alkaline medium would reduce the coprecipitation of tungsten on tantalum and niobium.

The coprecipitation of tungsten was investigated for tungsten/tantalum ratios varying from 0·01 to 10. The absolute amount of earth acids precipitated varied between 140 mg for small ratios and 20 mg for larger ratios. In all experiments the amount of tungsten coprecipitated was determined by measuring the ^{187}W activity of the filtrate or the precipitate. The results are presented in Table VIII.

TABLE VIII.—COPRECIPITATION OF TUNGSTEN WITH TANTALUM AND NIOBIUM DURING PRECIPITATION FROM HOMOGENEOUS AMMONIACAL HYDROGEN PEROXIDE

W/Ta ratio	W coprecipitated, %	Error on Ta, %	W/Nb ratio	W coprecipitated, %	Error on Nb, %
0·013	76·8	1·03	0·0116	73·9	0·76
0·0173	36·3	0·65	0·0169	59·0	0·88
0·0455	24·5	1·15	0·0445	33·4	1·31
0·0655	20·5	1·39	0·0640	16·4	0·92
0·101	8·5	0·74	0·101	10·7^{5}	0·96
0·134	5·3	0·73	0·135	8·0^{1}	0·95
0·402	2·1	0·87	0·405	3·1^{7}	1·13
0·580	0·84	0·50	0·604	1·9^{4}	1·03
0·963	0·67	0·67	1·00	0·73	0·64
1·93	0·64	1·27	1·95	0·56	0·96
5·00	0·52	2·6^{8}	4·97	0·33^{5}	1·4^{7}
10·00	0·27	2·7^{9}	10·0	0·22^{5}	2·0^{0}

Table VIII indicates that only small amounts of tungsten are coprecipitated with tantalum and niobium. The induced error is quite small even for large tungsten/earth acid ratios. When this small correction is made for the tungsten coprecipitation, a single precipitation is sufficient for a direct gravimetric determination of the earth acids.

Analysis of Synthetic Mixtures

An analysis of a mixture of the oxides of titanium, tungsten, tantalum or niobium is possible. Precipitation from nitric acid-hydrogen peroxide separates tungsten, tantalum and niobium from titanium, whereas from an ammoniacal hydrogen peroxide solution titanium, tantalum and niobium are precipitated, tungsten being kept in solution. In the filtrates titanium and tungsten are determined by precipitations from alkaline or acid solution. The sum of the earth acids is computed twice by difference.

This procedure was tested with synthetic mixtures containing known amounts of titanium, tungsten and tantalum. The values obtained were corrected for incomplete recoveries and coprecipitation of tungsten or titanium. The corrections were computed on the basis of the experimental values described above. The results are summarised in Tables IX and X.

From Tables IX and X it appears that the results are in good agreement with the expected values, the errors being within 1 %, except for some tungsten determinations. The larger errors in these cases are obviously caused by the fact that only small amounts of tungsten were determined.

Determination of distribution coefficients

It is well known that in coprecipitation phenomena three types of distribution occur between the solid and liquid phase. If x and y represent the respective amounts

TABLE IX.—DETERMINATION OF TITANIUM AND TANTALUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION[a]

Taken				Found			
WO_3, *mg*	$TiO_2 + Ta_2O_5$, *mg*	$\frac{WO_3}{TiO_2 + Ta_2O_5}$ ratio	$\frac{TiO_2}{Ta_2O_5}$ ratio	WO_3, *mg*	Error, %	$TiO_2 + Ta_2O_5$, *mg*	Error, %
27·9^{3}	209·4	0·13	1·2	28·01	+0·28	211·40	+0·96
73·1^{3}	156·7	0·47	1·1	72·15	−1·3^{5}	155·38[b]	−0·84
96·8^{8}	100·4	0·96	1·0	96·25	−0·66	100·85[b]	+0·45
9·8^{4}	155·3	0·063	0·50	10·08	+2·4	154·72	−0·31
10·7^{6}	118·4	0·091	0·16	11·37	+2·7	116·63	−1·5

[a] Titanium and tantalum precipitated from ammoniacal hydrogen peroxide, and tungsten from acid in hydrogen peroxide.

[b] Precipitation in presence of selenous acid.

TABLE X.—DETERMINATION OF TUNGSTEN, TANTALUM AND TITANIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION[a]

Taken				Found			
TiO_2, *mg*	$WO_3 + Ta_2O_5$, *mg*	$\frac{TiO_2}{WO_3 + Ta_2O_5}$ ratio	$\frac{WO_3}{Ta_2O_5}$ ratio	TiO_2, *mg*	Error, %	$WO_3 + Ta_2O_5$, *mg*	Error, %
55·3^{5}	150·1	0·37	2·0	55·75	+0·72	149·55[b]	−0·37
77·6^{2}	149·7	0·52	0·94	78·25	+0·81	149·75[b]	+0·03
111·2^{9}	128·6	0·88	0·30	112·35	+0·95	129·85	+0·98
14·0^{1}	114·3	0·12	0·12	13·90	−0·79	115·50	+1·05
52·2^{0}	114·8^{5}	0·45	0·11	52·50	+0·58	115·80	+0·83

[a] Tungsten and tantalum precipitated from acidic hydrogen peroxide solution, and titanium from ammoniacal hydrogen peroxide solution.

[b] Precipitation in presence of selenous acid.

separated and a and b the initial concentrations of coprecipitant and carrier, the three distribution laws are:

homogeneous distribution law[5]

$$\frac{x}{a - x} = \mathrm{D}\frac{y}{b - y} \tag{1}$$

logarithmic distribution law[6]

$$\ln\frac{a}{a - x} = \lambda \ln\frac{b}{b - y} \tag{2}$$

proportional distribution law[7]

$$\frac{x}{y} = \mathrm{K}\frac{a}{b} \tag{3}$$

From previous work[4] it was known that the distribution of molybdenum and vanadium on tungstic acid follows the proportional distribution law. In the present work the distribution of tungsten on tantalum and niobium, from a homogeneous ammoniacal hydrogen peroxide solution, was investigated. Tracer techniques offer a relatively simple means of determining the distribution coefficients.[4] The amounts

TABLE XI.—COPRECIPITATION OF TUNGSTEN WITH TANTALUM

Ta pptd., %	W copptd., %	Distribution coefficients		
		D	λ	K
$1{\cdot}5^{3}$	$1{\cdot}2^{6}$	$0{\cdot}82^{1}$	$0{\cdot}82^{3}$	$0{\cdot}82^{4}$
$7{\cdot}9^{5}$	$5{\cdot}6^{0}$	$0{\cdot}68^{7}$	$0{\cdot}69^{0}$	$0{\cdot}70^{4}$
$35{\cdot}3^{2}$	$30{\cdot}1^{5}$	$0{\cdot}79^{1}$	$0{\cdot}80^{6}$	$0{\cdot}85^{4}$
$70{\cdot}5^{0}$	$57{\cdot}0^{2}$	$0{\cdot}55^{6}$	$0{\cdot}70^{5}$	$0{\cdot}80^{9}$
$90{\cdot}9^{3}$	$84{\cdot}4^{0}$	$0{\cdot}54^{3}$	$0{\cdot}77^{5}$	$0{\cdot}93^{3}$
$99{\cdot}5^{8}$	$97{\cdot}7^{8}$	$0{\cdot}063^{6}$	$0{\cdot}50^{7}$	$0{\cdot}94^{2}$
				$\bar{K} = 0{\cdot}84^{4} \pm 0{\cdot}03^{6}$

TABLE XII.—COPRECIPITATION OF TUNGSTEN WITH NIOBIUM

Nb pptd., %	W copptd., %	Distribution coefficients		
		D	λ	K
$9{\cdot}8^{4}$	$4{\cdot}0^{1}$	$0{\cdot}38^{3}$	$0{\cdot}39^{4}$	$0{\cdot}40^{7}$
$37{\cdot}4^{5}$	$12{\cdot}2^{4}$	$0{\cdot}23^{9}$	$0{\cdot}26^{0}$	$0{\cdot}32^{7}$
$61{\cdot}6^{2}$	$26{\cdot}2^{5}$	$0{\cdot}22^{2}$	$0{\cdot}31^{8}$	$0{\cdot}42^{7}$
$70{\cdot}7^{2}$	$24{\cdot}7^{8}$	$0{\cdot}13^{6}$	$0{\cdot}23^{1}$	$0{\cdot}35^{0}$
$85{\cdot}2^{6}$	$29{\cdot}9^{3}$	$0{\cdot}074$	$0{\cdot}18^{6}$	$0{\cdot}35^{1}$
$91{\cdot}0^{8}$	$34{\cdot}5^{6}$	$0{\cdot}052$	$0{\cdot}17^{5}$	$0{\cdot}37^{9}$
$92{\cdot}5^{4}$	$35{\cdot}0^{1}$	$0{\cdot}043$	$0{\cdot}14^{7}$	$0{\cdot}37^{8}$
$97{\cdot}3^{7}$	$36{\cdot}6^{0}$	$0{\cdot}016$	$0{\cdot}12^{5}$	$0{\cdot}37^{6}$
$97{\cdot}8^{3}$	$35{\cdot}2^{4}$	$0{\cdot}012$	$0{\cdot}11^{3}$	$0{\cdot}36^{0}$
				$\bar{K} = 0{\cdot}37^{2} \pm 0{\cdot}008^{0}$

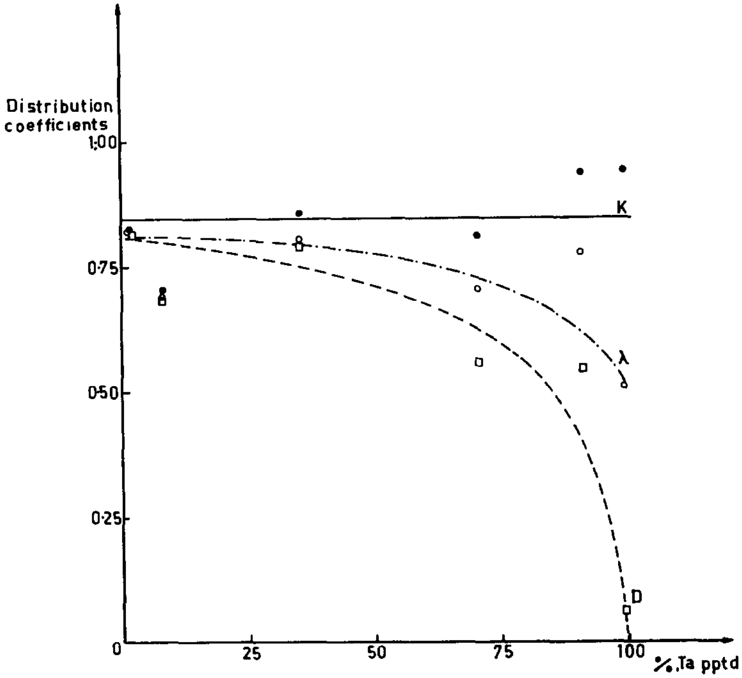

FIG. 2.—Distribution of tungsten on tantalum:

□ - - - - - D,
○ - · · · - · λ,
● ——— K.

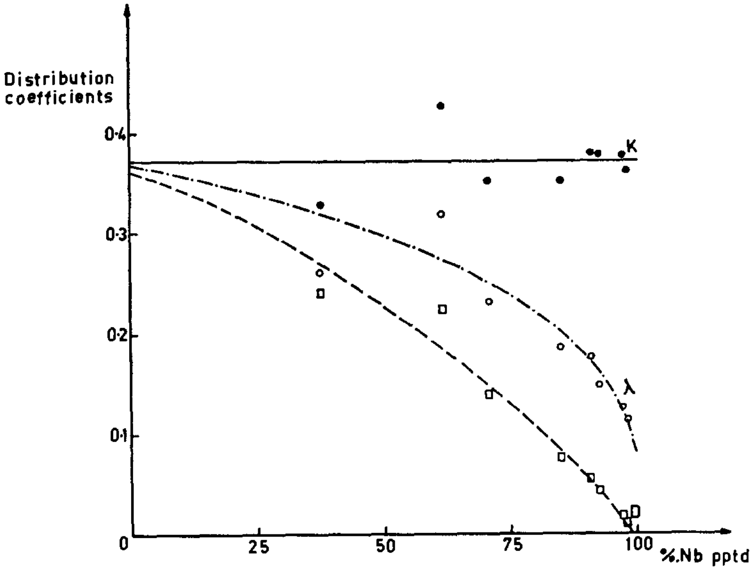

FIG. 3.—Distribution of tungsten on niobium:

□ - - - - - D,
○ - · - · - · λ,
● ——— K.

present of carrier and of coprecipitant are computed by analysis of the composite decay curve if the half-lives are sufficiently different.

Procedure

Introduce 168·9 mg of tantalum and 1·0 mg of tungsten or 129·5 mg of niobium and 5·2 mg of tungsten into a 400-ml conical flask fitted with a reflux condenser. Add ^{182}Ta or ^{95}Nb and ^{187}W tracers, 5 ml of hydrogen peroxide (30 %) and 100 mg of selenous acid. The volume of solution should be about 250 ml. The activities of the tracer solutions are chosen to correspond to approximately 1×10^7 cpm of each tracer.

Adjust the pH of the solution to between 7·5 and 8. Heat the solutions at 85° and at regular time intervals take 5-ml portions of the solution by reverse filtration through an asbestos filter. Count 4 ml of the filtrates and analyse the composite decay curves.

The results and the values of D, λ and K, computed according to equations (1), (2) or (3), are represented in Tables XI and XII. In Figs. 2 and 3 the values of D, λ and K are plotted as a function of the percentage precipitated carrier.

From Tables XI and XII it appears that the proportional distribution law is followed in both cases, *i.e.*, the amount of coprecipitant is directly proportional to the amount of precipitated carrier, the mean values of the proportional distribution coefficient being:

$$K_{\mathrm{Ta}} = 0{\cdot}84^4 \pm 0{\cdot}03^6 \quad \text{and} \quad K_{\mathrm{Nb}} = 0{\cdot}37^2 \pm 0{\cdot}008.$$

According to the views of Hahn,[8] proportional distribution occurs when no true homogeneous mixed crystals are formed, the process being caused by surface layer crystallisation.

Distribution constants of titanium were not studied because no suitable tracer is available and spectrophotometric determinations are not accurate enough because they lack specificity.

Zusammenfassung—Eine homogene Fällungsmethode zur gravimetrischen Bestimmung von Titan wurde entwickelt, wobei lösliches Peroxytitanat entweder in alkalischen oder in schwach salpetersauren Medien mit besseren Ausbeuten als 99,6% thermisch zersetzt wird. Die Mitfällung von Wolfram und Mangan wird beträchtlich verringert. Ferner können Tantal und Niob mit sehr zufriedenstellenden Ausbeuten aus homogener Salpetersäure-Wasserstoffperoxyd-Lösung gefällt werden. Die Mitfällung von Titan wurde untersucht und Korrekturfaktoren dafür berechnet. Die Erdsäuren können auch homogen aus Ammoniak-Wasserstoffperoxyd-Lösung gefällt werden, wobei die Mitfällung von Wolfram fast vernachlässigbar ist. Die Untersuchung der Mitfällung von Wolfram mit Tantal und Niob zeigt, daß auf beiden Trägern die Verteilungskoeffizienten linear verlaufen. Die Methode wurde an einigen vorgegebenen Mischungen der Oxyde getestet, wobei auf Grund der experimentellen Werte Korrektionen für unvollständige Fällung und Mitfällung angebracht wurden.

Résumé—On a élaboré, pour le dosage gravimétrique du titane, une méthode de précipitation en milieu homogène, par décomposition thermique du peroxytitanate soluble, en milieu soit alcalin, soit légèrement nitrique, avec des récupérations supérieures à 99,6%. Les coprécipitations du tungstène et du manganèse sont considérablement réduites. En outre, le tantale et le niobium peuvent être précipités, avec des rendements très satisfaisants, à partir d'une solution homogène acide nitrique–eau oxygénée. On a étudié la coprécipitation du titane, et calculé les corrections pour cette coprécipitation. Les oxydes terreux peuvent aussi être précipités par voie homogène, à partir d'une solution ammoniaque–eau oxygénée, la coprécipitation du tungstène étant à peu près négligeable. L'étude du processus de coprécipitation du tungstène sur le tantale et le niobium montre que les coefficients de distribution suivent un diagramme linéaire sur les deux supports. On a essayé la technique avec un certain nombre de mélanges synthétiques des oxydes, les corrections pour la précipitation incomplète et pour la coprécipitation étant appliquées en se basant sur les valeurs expérimentales.

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SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF ZIRCONIUM AND TITANIUM

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Summary—A method is described for the determination of trace amounts of zirconium and titanium. The two elements are separated from the sample matrix by precipitation with cupferron using iron as a carrier. Zirconium is determined after extraction with TOPO (tri-n-octylphosphine oxide), by colorimetric measurement of the zirconium–Pyrocatechol Violet complex. Titanium is determined by colorimetric measurement of its thiocyanate complex extracted with TOPO. The method is accurate to within ±5% (relative) or ±2·5 μg, whichever is greater, for both elements. Using the modifications suggested, the method is nearly specific for the determination of titanium (milligram amounts of niobium cause slightly high results), and only thorium and hafnium interfere with the determination of zirconium.

INTRODUCTION

By combining a number of known methods, an essentially specific determination of trace amounts of titanium and zirconium has been developed. Samples to be analysed are dissolved in the most appropriate manner and eventually obtained in a medium containing sulphuric acid, hydrochloric acid and citric acid. Iron is added as a carrier, and a cupferron precipitation is made. The precipitate is treated with nitric and perchloric acids, the solution evaporated nearly to dryness, and the residue dissolved in $8M$ nitric acid. Zirconium is extracted from an aliquot of this solution with $0{\cdot}02M$ TOPO (tri-n-octylphosphine oxide) in cyclohexane, and determined as its Pyrocatechol Violet complex.[1] Sulphuric acid is added to another aliquot of the $8M$ nitric acid solution, and this solution is evaporated to dryness. The residue is dissolved in $6M$ sulphuric acid and the titanium is extracted with $0{\cdot}02M$ TOPO in cyclohexane after the formation of the titanium-thiocyanate complex.[2]

EXPERIMENTAL

Apparatus

Cary Model 14 *Spectrophotometer*, with 2- and 5-cm cells
International Clinical Centrifuge, with 10 ml glass-stoppered centrifuge tubes
Mechanical shaker, Aloe Scientific

Reagents

Deionised water was used throughout the investigation.

Standard zirconium solutions. Dissolve 1 g of pure zirconium metal in dilute hydrofluoric acid. Add 20 ml of perchloric acid and evaporate to fumes of perchloric acid several times. Dilute to a suitable volume. Prepare two standard solutions, one containing 5 μg of zirconium/ml in $8M$

nitric acid and the other containing 1 μg of zirconium/ml in $8M$ nitric acid. Standardise the stock solution by precipitation with cupferron.

Standard titanium solutions. Dissolve 1 g of pure titanium metal in $6M$ hydrochloric acid at low heat. Oxidise the titanium with hydrogen peroxide and boil to remove the excess peroxide. Dilute to a suitable volume. Add sulphuric acid to an aliquot of this solution and heat to fumes of sulphuric acid. Dilute with $6M$ sulphuric acid to obtain two standard solutions of titanium, one containing 5 μg of titanium/ml and one containing 1 μg of titanium/ml. Standardise the stock titanium solution by precipitation with cupferron.

Ethyl alcohol, absolute

Thioglycolic acid (mercaptoacetic acid), 98% solution

Cyclohexane

Ammonium thiocyanate

Pyridine

Pyrocatechol Violet (pyrocatecholsulphonphthalein) solution, 0·05% (w/v) in absolute ethanol, prepared fresh daily.

Tri-n-octylphosphine oxide, $0{\cdot}02M$ in cyclohexane

Citric acid, 50% (w/v)

Hydrochloric acid, $12M$ and $1{\cdot}2M$

Nitric acid, $16M$ and $8M$

Perchloric acid, 70%

Sulphuric acid, $18M$, $6M$ and $1{\cdot}8M$

Hydrofluoric acid, $29M$

Cupferron, 6% (w/v), prepared just before use

Cupferron wash solution. Add 10 ml of 6% cupferron solution to 500 ml of $1{\cdot}2M$ hydrochloric acid. Prepare just before use.

Iron(III) chloride solution, 10 mg of iron/ml

Anion-exchange resin. Dowex 1X8, 100–200 mesh resin obtained from Bio-Rad Laboratories.

Filter paper, Whatman No. 40, 5·5 cm and 12·5 cm. Filter paper has been found to be the major cause of high blanks in the titanium procedure. If Whatman papers are unavailable, the papers to be used should be analysed for titanium before application of the procedure.

Filter paper pulp. Cut Whatman 40 filter paper into small (1 cm × 1 cm) pieces and shake vigorously with hot water in a stoppered Erlenmeyer flask.

Procedure

Dissolve the sample in the most appropriate manner and eventually obtain it in a volume of about 100 ml containing 5 ml each of sulphuric and hydrochloric acids and 10 g of citric acid. Add 1 ml of the iron(III) chloride solution, 0·5 g of filter paper pulp and cool to 10–15°. Also, cool an aqueous 6% solution of cupferron and the cupferron wash solution. Add an excess of cupferron to the sample solution. Filter the precipitate and wash 10 times with the cupferron wash solution. (It has been found very convenient to filter through a 6·3-cm i.d. Buchner funnel using suction. A piece of 5·5-cm filter paper is first placed in the bottom of the funnel, then a piece of 12·5-cm paper pushed down into the funnel using a 150-ml beaker. Finally, with the suction on, the paper is wetted with water.) Return the cupferrates to the original beaker, add 75 ml of nitric acid and 10 ml of perchloric acid, and evaporate using a Speedyvap cover glass. (The evaporation is continued until only a thin film of perchloric acid remains on the beaker walls. *Do not bake.*) Dissolve the residue in $8M$ nitric acid, transfer to a 50-ml volumetric flask and dilute to the mark with $8M$ nitric acid. This solution is hereafter referred to as the *prepared solution.*

Determination of Zirconium. Take an aliquot of the prepared solution, containing approximately 20 μg of zirconium, and transfer to a 125-ml separatory funnel. Add sufficient $8M$ nitric acid to give a total volume of 20 ml. Add 10 ml of $0{\cdot}02M$ TOPO solution and extract the zirconium by shaking for 10 min. Draw off and discard the aqueous phase. Wash the organic phase by shaking for 1 min with 20 ml of $8M$ nitric acid. Discard the wash solution. Transfer the extract to a glass-stoppered centrifuge tube and centrifuge for 2 min.

Add to a 25-ml volumetric flask, in the order listed, 9 ml of absolute ethanol, 5 ml of the centrifuged TOPO extract, 1 ml of Pyrocatechol Violet solution, 5 ml of pyridine, and dilute to the mark with absolute ethanol. Allow the colour of the zirconium-Pyrocatechol Violet complex to develop for 40 min and determine its absorbance at 655 mμ in 5-cm cells using absolute ethanol as a reference. The absorbance should be measured between 40 and 120 min after addition of the pyridine.

Determination of Titanium. Add a few drops of sulphuric acid to an aliquot of the prepared solution, containing 10 μg of titanium, and evaporate to dryness. Dissolve the residue by heating with 15 ml of $6M$ sulphuric acid. Cool and transfer to a 125-ml separatory funnel with $6M$ sulphuric acid. Add 5 ml of thioglycolic acid and 2 ml of 50% citric acid solution. Adjust the volume to about 60 ml with $6M$ sulphuric acid. Add 5 g of ammonium thiocyanate and, after the pink colour from the iron(III)-thiocyanate complex has faded, add 20 ml of $0{\cdot}02M$ TOPO solution. Extract the titanium by shaking for 5 min. After the phases have separated, withdraw and discard the aqueous phase. Add 30 ml of $6M$ sulphuric acid and 2 ml of thioglycolic acid to the organic phase and shake for 2 min. Discard the aqueous wash solution and transfer the extract to a 10-ml glass-stoppered centrifuge tube and centrifuge for 2 min. Measure the absorbance of the solution at 429 mμ in 2-cm cells using cyclohexane in the reference cell.

DISCUSSION

Determination of zirconium

A discussion of variables and other pertinent factors affecting the extraction and determination of zirconium is presented in the following paragraphs.

1. The efficiency of extraction will depend on both the amount of zirconium present and the TOPO concentration. The extraction coefficient is a function of nitric acid concentration and is 200, 400 and 550 when the concentration of nitric acid is $5M$, $8M$ and $10M$, respectively.[3]
2. The zirconium-Pyrocatechol Violet complex exhibits an absorbance maximum at 655 mμ. The absorbance is a linear function of concentration, at least from 0 to 0·75 μg of zirconium/ml. The effects of pyridine, ethanol, TOPO and water on the colour intensity have been discussed by Young and White.[1]
3. The colour development of the complex is concentration dependent. The higher the concentration of zirconium, the more rapidly full colour development is reached. In a solution containing 9·4 μg of zirconium/25 ml, 93% of the maximum absorbance was obtained after 2 min, 98% after 10 min and 100% after 45 min. After 2 hr, the absorbance had dropped to 99·5% of the maximum and no precipitate was visible. With 0·94 μg of zirconium/25 ml, the absorbance was 86% after 2 min, 94·5% after 10 min and 100% after 50 min. It was still 100% after 150 min, and no precipitate was visible. Nearly all solutions containing zirconium will eventually give rise to a precipitate.
4. The molar absorptivity of the zirconium complex is approximately 41,000 at 655 mμ, indicating an absorbance of about 0·8 for 0·4 μg of zirconium/ml in 5-cm cells.
5. Amounts of zirconium greater than the 20 μg referred to in the procedure can be satisfactorily extracted and determined using the procedure described. Up to 95 μg of zirconium can be extracted and determined by using a suitable aliquot. However, if the aliquot is diluted with TOPO solution and an aliquot taken of this solution, or if a measured amount of TOPO solution is added to an aliquot of the extract, low results are obtained.
6. Titanium interferes slightly with the determination of zirconium when present in a weight ratio (titanium to zirconium) of ten or greater. If the organic phase is back-washed with nitric acid, however, weight ratios (titanium to zirconium) of 100 and more are tolerated by the method.[1]
7. The extraction and absorbance measurement of the zirconium complex is quite reproducible as indicated by the fact that when 12 solutions containing 18·8 μg of zirconium were treated as described, all absorbance values were between 0·841 and 0·860.

Only a few additional remarks are necessary concerning the cupferron precipitation step and its effect on the final absorbance measurement.

1. Citric acid, between 0 and 20 g, had no effect (within experimental error) on the recovery of zirconium.
2. The recovery of 16 standards was 100 ± 5%.
3. A blank of 0·5 μg of zirconium is typical for the reagents used in the entire procedure.

Determination of titanium

A discussion of variables and other pertinent factors affecting the extraction and determination of titanium is presented in the following paragraphs.

1. The titanium-thiocyanate complex extracted in this manner exhibits an absorbance maximum at 429 mμ. At this wavelength, the molar absorptivity of the complex is about 43,000, indicating an absorbance of about 0·9 for 1 μg of titanium/ml in 1-cm cells. The extracted complex is stable (within experimental error) for at least 24 hr. The absorbance is a linear function of concentration, at least from 0 to 1 μg of titanium/ml, and obeys Lambert's law when 1-, 2- and 5-cm cells are used.
2. For quantitative extraction, the solution should be at least $6M$ with respect to sulphuric acid (mixtures of sulphuric and hydrochloric acids have no effect on the final absorbance if their total concentration is $6M$).[2]
3. Although equilibrium conditions are obtained in 3–4 min, a 5-min extraction time was used to ensure equilibrium.
4. The effect of TOPO concentration over the range 0·00002 to $0{\cdot}04M$ is slight but significant.[2] Using the procedure described, reasonable variations can be ignored.
5. The concentration of ammonium thiocyanate in the aqueous phase has no effect on the absorbance of the titanium complex provided the concentration exceeds 20 mg/ml.[2]
6. Using the procedure described, including the wash, no significant effect on the absorbance (of 10 μg of titanium in 20 ml of TOPO) was produced by 0–10 mg of iron, 0–5 g of citric acid or 0–10 ml of thioglycolic acid. Iron is present as a carrier, citric acid is added to prevent precipitation of other elements which might have been carried through the procedure, and thioglycolic acid is added to reduce iron and moderate or strong oxidants which might interfere in the determination.
7. There was no measurable effect on the absorbance of the titanium complex when the time between the addition of ammonium thiocyanate and the extraction of the complex was varied between 3 and 60 min, even though the iron(III)-thiocyanate colour was still visible after the shorter time period.
8. Up to 1 mg of titanium can be extracted using the procedure described, diluted appropriately with cyclohexane, and determined within experimental error.
9. The extraction and determination of titanium, if present in the tervalent state, is quantitative (within experimental error).
10. The extraction and absorbance measurement of the titanium complex is quite reproducible as indicated by the fact that when 10 solutions containing 10 μg of titanium were treated as described, all absorbance values were between 0·875 and 0·884.

Only a few additional remarks are necessary concerning the cupferron precipitation step and its effect on the final absorbance measurement.

1. Citric acid, between 0 and 20 g, had no effect, within experimental error, on the recovery of titanium.
2. The recovery of 50 μg of titanium(III) was quantitative within experimental error.
3. The recovery of 8 standards varied from 98·2 to 102·2%.
4. A blank of 2–3 μg of titanium is typical for the reagents used in the entire procedure.

Cupferron precipitation step

1. Quantitative recovery of 50 μg each of titanium and zirconium was obtained from:—
   (a) 100 ml of solution containing:
      i. 20 ml of 6*M* sulphuric acid, 5 ml of hydrochloric acid and 10 g of citric acid.
      ii. 50 ml of 6*M* sulphuric acid, 5 ml of hydrochloric acid and 10 g of citric acid.
      iii. No sulphuric acid, 10 ml of hydrochloric acid and 10 g of citric acid.
   (b) 250 ml of solution containing 60 ml of 6*M* sulphuric acid, 12·5 ml of hydrochloric acid and 10 g of citric acid.
2. Quantitative recovery of 3 mg each of titanium and zirconium was obtained using the procedure described. The 8*M* nitric acid solution was appropriately diluted before the determination of the two elements.

RESULTS

Effects of other elements

Table I indicates the results obtained in the study of the effect of other elements on the procedure described. The table also indicates whether the cupferron precipitation is necessary or sufficient to eliminate interference by an element.

The behaviour of hafnium (in the zirconium procedure) parallels that of zirconium. The absorbance spectrum and wavelength of maximum absorbance are apparently identical. The molar absorptivity of the hafnium complex is about 40,000 at 655 mμ. The absorbance of the hafnium complex is a linear function of concentration, at least from 0 to 1 μg of hafnium/ml.

Sulphate has an adverse effect on the extraction and determination of zirconium. The recovery of 18·8 μg of zirconium was 96·8, 95·4 and 94·2%, respectively, for 38, 384 and 676 mg of sulphate, present as sulphuric acid.

Both thorium and uranium interfere with the determination of zirconium if present when the zirconium is extracted. Results are within the accuracy limits described if less than 100 μg of uranium or 50 μg of thorium are present. The interference of uranium and thorium is shown in greater detail in Table II.

A discussion of the interferences indicated in Tables I and II is presented in the following paragraphs.

1. Barium interferes by precipitating as barium sulphate, which is insoluble in 8*M* nitric acid. To eliminate interference from barium, it would be necessary to make the cupferron precipitation from a hydrochloric acid solution.
2. Antimony(III) is carried to some extent with the cupferron precipitate and yields a residue insoluble in 8*M* nitric acid. Antimony must, therefore, be oxidised to antimony(V), which does not interfere.
3. Tin is partially carried and also yields a residue insoluble in 8*M* nitric acid. An anion-exchange separation is discussed in the following pages in which a 4% hydrofluoric acid solution is added to the column, and titanium and zirconium eluted

TABLE I.—THE EFFECT OF OTHER ELEMENTS ON THE DETERMINATION OF TITANIUM AND ZIRCONIUM

Element(s) added: 10 mg each^{a}	Recovery, %			
	Ti		Zr	
	Extraction procedure only^{b}	Entire procedure^{c}	Extraction procedure only^{b}	Entire procedure^{c}
Al	101, 98^{2}	(98^{13}), 96	97	100
$\mathrm{Sb^{III}}$	100, 100	u	99, 103^{g}	u
$\mathrm{Sb^{V}}$	103, 101	101, 100	101, 100^{g}	97, 96
$\mathrm{As^{III}}$	102	97^{9}	101	99^{9}
$\mathrm{As^{V}}$	—	102, 101	99, 96	98
Ba	102, $101^{3,f}$	100, 99^{t}	99^{5}	100, 99^{t}
Be	101, 98^{2}	99, (101^{d})	101^{e}, 100^{d}	103, $(104)^{d}$
Bi	101, 98^{2}	101^{10}	101	104^{10}
B	101, 98^{2}	97	101^{d}	99^{9}
$\mathrm{Br(Br^-)}$	100, 100	100, 100	*k*	99, (100^{e})
Cd	101, 98^{2}	97	97	101
Ca	102, $100^{3,f}$	99	99	102
$\mathrm{Ce^{IV}}$	102, 100	98, 98	n	98, 98
Cs	104, 102	98^{14}	99^{5}	97^{14}
$\mathrm{Cl(Cl^-)}$	101, 98	—	101	—
$\mathrm{Cr^{III}}$	100, 101	95, 99	102^{7}	98, 100
$\mathrm{Cr^{VI}}$	100	95	138^{h}	98
Co	101, 101	96^{11}	102^{7}	100^{11}
Cu	101, 101	100, 100	99^{5}	99, 100
Dy	102, 101^{1}	99, 100^{1}	99	98, 99^{1}
Er	102, 101^{1}	99, 100^{1}	98^{8}	98, 99^{1}
Eu	102, 101^{1}	99, 100^{1}	101	98, 99^{1}
$\mathrm{F(F^-)}$	104, 103	99, 100	40	102, 105
Gd	102, 101^{1}	99, 100^{1}	98^{8}	98, 99^{1}
Ga	97, 101	101^{10}	101	104^{10}
Ge	100, 100	100	102^{g}	101
Au	100, 101^{m}	100	102	98
Hf	98, 98	100	q	q
Ho	102, 101^{1}	99, 100^{1}	102	98, 99^{1}
In	101, 102	95^{12}	102	101^{12}
$\mathrm{I(I^-)}$	100, 100	100	j	98, 100
Ir	105, $104^{6,g}$	98	103	97
$\mathrm{Fe^{II}}$	100	99	98	101
$\mathrm{Fe^{III}}$	102, 101	95^{12}	103^{e}	101^{12}
La	102, 101^{1}	99, 100^{1}	99	98, 99^{1}
Pb	100, 100	100, 103	99	99, 99
Li	100, 98^{2}	98^{14}	99^{5}	97^{14}
Lu	102, 101^{1}	99, 100	98^{8}	98, 99^{1}
Mg	101, 98^{2}	102, 102^{4}	99^{5}	99, 98^{4}
$\mathrm{Mn^{II}}$	100, 101	95, 99	102^{7}	98, 100
$\mathrm{Mn^{VII}}$	100	100	94	100
Hg	101, 101	97, 98	100	95, 97
Mo	h	—	100	—
Nd	102, 101^{1}	99, 100^{1}	98^{8}	98, 99^{1}
Ni	101, 98^{2}	96^{11}	102^{7}	100^{11}
Nb	h	—	—	—
Pd	105, $104^{6,g}$	102, 102	101^{g}	99, 99
$\mathrm{P(PO_4^{3-})}$	100, (99^{e})	99, (99^{e})	98, (40^{e})	99, (100^{e})
Pt	105, $104^{6,g}$	96, 95	102^{g}	100, 99
K	101, 98^{2}	98^{14}	98	97^{14}
Pr	102, 101^{1}	99, 100^{1}	102	98, 99^{1}

Table I (*contd*)

Element(s) added: 10 mg each[a]	Recovery, %			
	Ti		Zr	
	Extraction procedure only[b]	Entire procedure[c]	Extraction procedure only[b]	Entire procedure[c]
Re	h	97	100	100
Rh	105, 104[6,g]	99	100	102
Rb	101, 98[2]	98[14]	101	97[14]
Sm	102, 101[1]	99, 100[1]	98[8]	98, 99[9]
Sc	102, 101	98, 101	100	100, 101
Se	102, 101	100, 100	101	95, 97
Si	102	(98[13]),104	104	102
Ag	100	100[v]	98	101[v]
Na	101, 98[2]	98[14]	98	97[14]
Sr	102, 100[3,f]	99	97	102
Ta	—	—	—	—
Te	97, 100	102, 100	101	97
Tb	102, 101	99, 100[1]	99	98, 99[1]
$\mathrm{Tl^{I}}$	100, 100	96	99	98, 95
Th	100, 100	99, 101	w	124, 134
Tm	102, 101[1]	99, 100[1]	98[8]	98, 99[1]
$\mathrm{Sn^{II}}$	97, 97	u	105[g]	u
$\mathrm{Ti^{III}}$	—	—	103	—
$\mathrm{Ti^{IV}}$	—	—	104	102
W	h	—	88[i]	—
$\mathrm{U^{VI}}$	102, 102	98, 100	w	100, 101
V	105, 104	101	103	103, 99
Yb	102, 101[1]	99, 100[1]	103, 104	98, 99[1]
Y	102, 101[1]	99, 100[1]	99	98, 99[1]
Zn	101, 98[2]	102, 102[4]	99[5]	99, 98[4]
Zr	100, 101	100	—	—
$HClO_4$[p]	—	99	101	100
Citric acid	—	—	98[d]	—
Oxalic acid	101	100 (100[d])	0·0[d]	99, (101[d])
H_2O_2[r]	100	—	—	—

Elements with numbered superscript were added with other elements with same number.

[a] Except as indicated.

[b] 10 μg of Ti and 18·8 μg of Zr added.

[c] 50 μg of Ti and 47 μg of Zr added.

[d] 1 g added.

[e] 100 mg added.

[f] Precipitated in extraction medium

[g] Added as chloride.

[h] Irreproducible high results.

[i] Precipitation occurred. When W was added before Zr, so as not to occlude Zr, 98% recovery was obtained.

[j] Oxidised to I_2, which oxidised the reagent and prevented colour formation

[k] Same effect as I (see j).

[m] Precipitated on addition of thioglycolic acid.

[n] Oxidised the reagent.

[p] 2 ml of 72% $HClO_4$.

[q] See discussion regarding interference of Hf.

[r] 0·5 ml of 30% H_2O_2.

[s] 101 and 100% recovery of Zr was obtained in the presence of 1 g of $\mathrm{U^{VI}}$ after a double pptn.

[t] Precipitated as $BaSO_4$. Results shown were obtained by filtering the solution before spiking.

[u] After cupferron pptn., residue insoluble in HNO_3 (1 + 1).

[v] AgCl ppt. soluble in HNO_3 (1 + 1).

[w] See Table II regarding interference of thorium and uranium.

with 9*M* hydrochloric acid. Faris[4] has shown that tin(IV) is very strongly adsorbed on an anion-exchange column from a dilute hydrofluoric acid solution. Also, Kraus and Nelson[5] indicate that tin(IV) in 9*M* hydrochloric acid solution would be strongly retained on such a column. Therefore, the determination of titanium and zirconium in the presence of tin should be no significant problem.

Table II.—The effect of uranium and thorium on the determination of 18·8 μg of zirconium (extraction only)

Element	Added, μg	Error,[a] %
U	50	2,3
U	100	5
U	250	11
U	500	22
Th	50	4,5
Th	100	35
Th	250	100

[a] All errors positive.

4. Ten mg of thorium interferes with the determination of zirconium even with a prior cupferron precipitation. This element is not felt to be especially significant or important in the analysis of most samples because of its scarcity. However, when it is present, several ways of separating it from zirconium are apparently available, among which are:
   (a) Anion exchange–Thorium is strongly adsorbed on an anion-exchange column from a solution 9*M* with respect to nitric acid, whereas zirconium is only very slightly adsorbed.[6] Also, zirconium is strongly adsorbed on an anion-exchange column from a solution 12*M* with respect to hydrochloric acid, whereas thorium is not adsorbed.
   (b) Moore,[7] using radioactive tracers, states that zirconium can be extracted from 2*M* (or higher) solutions of nitric or hydrochloric acids with 0·5*M* TTA (thenoyltrifluoracetone) in xylene. Among those elements he lists as not extracting are thorium and uranium(VI). Zirconium can be stripped from the organic phase either with 0·5*M* nitric acid-0·5*M* hydrofluoric acid, or by diluting with xylene to a TTA concentration of 0·05*M* and extracting for 10 min with an equal volume of 8*M* nitric acid (90% of the zirconium-95 removed).
5. Hafnium interferes with the determination of zirconium and can be separated from the latter by ion exchange according to:
   (a) Hague and Machlan,[8] who used a 3·5% sulphuric acid medium, and a Dowex-1X8 column.
   (b) Kolosova *et al.*,[9] who used the cation-exchange resin KU-2X12, and a 0·35*M* sulphuric acid medium.
6. Niobium, tantalum, molybdenum and tungsten give rise to interference for two reasons. Firstly, because of their insolubility in the nitric acid medium used to dissolve the cupferrate residues, and secondly, molybdenum, tungsten and niobium interfere markedly if present during the extraction and determination of titanium. Table III indicates the behaviour of these elements in the extraction procedure used for the determination of titanium.

Kallmann has reported[11] that 50 μg each of titanium and zirconium can be quantitatively separated and determined in the presence of 1-g amounts of niobium, tantalum, molybdenum or tungsten as follows.

From niobium and tantalum: Separation by anion exchange (Dowex 1X8) using 25% hydrochloric acid-20% hydrofluoric acid. Titanium and zirconium are eluted, whereas niobium and tantalum remain on the column.

From molybdenum: Precipitation with aqueous ammonia using 10 mg of iron as a carrier.

From tungsten: Precipitation with cupferron from a 50% tartaric acid solution using iron as a carrier.

TABLE III.—BEHAVIOUR OF MOLYBDENUM, TUNGSTEN, NIOBIUM AND TANTALUM IN TITANIUM EXTRACTION PROCEDURE

Element	λ_{max}, *mμ*	Present, *μg/ml*	A_{429}, *mμ*	Titanium equivalent (at 429 mμ)
Mo	473	1	0·030	1 μg of Mo = 0·017 μg of Ti
W	409	5	0·190	1 μg of W = 0·022 μg of Ti
Nb	384	5	0·410	1 μg of Nb = 0·046 μg of Ti
Ta	—	5	0·000	—

On the basis of information in the literature, in particular the work of Faris,[6] Kraus and Nelson[5] and Wilkins,[10] it was believed that if a solution of the seven elements (titanium, zirconium, iron, molybdenum, tungsten, niobium and tantalum) in 4% hydrofluoric acid was added to an anion-exchange column, iron would not be retained on the column. After removal of the residual hydrofluoric acid by washing with ethanol, the titanium and zirconium could be eluted with 9*M* hydrochloric acid, presumably free from the other refractory elements. The procedure used is as follows.

The sample solution, in 4% hydrofluoric acid, containing the elements mentioned, is added to the ion-exchange column (12 × 1·5 cm of anion-exchange resin), *ca.* 50–75 ml of acid being used for the transfer. The column is washed twice with 10 ml portions of 4% hydrofluoric acid and then with 70 ml of the same solution (to remove iron). Finally, the column is washed with 35 ml of ethanol to remove the 4% hydrofluoric acid. Titanium and zirconium are eluted with 100 ml of 9*M* hydrochloric acid, the eluate being caught in a 600-ml beaker containing 2 g of boric acid and 10 mg of iron(III) in 250 ml of water. A cupferron precipitation is performed as previously described, and the precipitate is filtered and treated with nitric and perchloric acids. (Plastic columns, beakers and stirring rods are used for all steps before the wet oxidation.)

It was found that both titanium and zirconium were quantitatively recovered using this procedure. Zirconium could be determined accurately in a solution originally containing 50 μg of titanium, 47 μg of zirconium and 10 mg each of iron, molybdenum, tungsten, niobium and tantalum. However, some niobium did "dribble' through the column as shown by a spectrum of the titanium extract. Results for titanium indicated that about 100 μg of niobium had not been retained on the column. This caused an error in the determination of 50 μg of titanium of about 10%.

Although this separation is not as satisfactory as could be desired, it indicates that samples containing a more favourable ratio of niobium to titanium could be accurately analysed in this manner.

Application of method

A number of samples have been analysed using the procedure described, or modifications thereof. The results obtained are shown in Tables IV and V.

Table IV.—Determination of titanium

Sample no.	Approximate composition	Titanium, %		Note
		Certificate	Found	
NBS 86C	Al Base-8 Cu-1 Fe	0·035	0·0341, 0·0342	—
			0·0349	1
NBS 169	77 Ni-20 Cr-1·4 Si	0·006	0·0058, 0·0057	—
			0·0057, 0·0057	1
NBS 170A	Ti Steel-0·006 Mo	0·281	0·281, 0·281	1
			0·280	1
NBS 462	Low Alloy Steel-Spec.	0·037	0·0371, 0·0372	2
			0·0358	2
NBS 467	Low Alloy Steel-Spec.	0·26	0·268, 0·268	2
			0·268	2
NBS 349	57 Ni-14 Co-20 Cr-3 Ti-4 Mo-0·4 Mn	3·05	3·05, 3·05	2
NBL 88	Beryllium Metal	—	0·0023, 0·0024	3

[1] Ti determined without previous cupferron pptn.

[2] 4% HF-ethanol-9*M* HCl anion-exchange separation used.

[3] Results obtained by S. Kallmann at Ledoux and Company using separation indicated in Note 2.

Table V.—Determination of zirconium

Sample no.	Approximate composition	Zirconium, %		Note
		Certificate	Found	
NBL 88	Beryllium metal	—	0·0362, 0·0365, 0·0366	1,2
NBS 169	77 Ni-20 Cr-1·4 Si	0·042	0·0394, 0·0394	3
NBS 170A	Ti Steel-0·006 Mo	0·037	0·0330, 0·0340	4
			0·0330	—
NBS 462	Low Alloy Steel-Spec.	0·063	0·057, 0·056, 0·058	5
NBS 467	Low Alloy Steel-Spec.	0·094	0·086, 0·087, 0·086	5
NBS 349	57 Ni-14 Co-20 Cr-3 Ti-4 Mo-0·4 Mn	0·081	0·083, 0·083, 0·086	—

[1] S. Kallmann found 0·038 and 0·040% of Zr using 4% HF-ethanol-9*M* HCl modification.

[2] O. Kriege found 0·038, 0·035, 0·039, 0·039% of Zr using his X-ray fluorescence technique.[12]

[3] Direct extraction of zirconium failed, presumably because of the chromium content.

[4] Results obtained by S. Kallmann at Ledoux and Company.

[5] Anion-exchange modification used.

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Zusammenfassung—Eine Methode zur Bestimmung von Spuren Zirkonium und Titan wird beschrieben. Die beiden Elemente werden vom Hauptteil der Probe durch Fällung mit Cupferron auf Eisenträger abgetrennt. Zirkonium wird mit TOPO (Tri-n-octylphosphinoxyd) extrahiert und kolorimetrisch als Zirkonium-Brenzkatechinviolett-Komplex bestimmt. Titan wird kolorimetrisch als Rhodanidkomplex bestimmt, der mit TOPO extrahiert wird. Die Methode ist für beide Elemente auf ±5% (relativ) oder höchstens auf ±2,5 μg genau. Mit den vorgeschlagenen Änderungen ist die Methode fast spezifisch für die Bestimmung von Titan (Milligrammengen Niob geben Plusfehler); nur Thorium und Hafnium stören die Zirkon-bestimmung.

Résumé—On décrit une méthode de dosage du titane et du zirconium. Les deux éléments sont séparés de la gangue échantillon par précipitation au cupferron, en utilisant le fer comme entraîneur. On dose le titane par mesure de son complexe thiocyanique extrait à l'oxyde de tri-n-octylphosphine (TOPO). Le zirconium est dosé après extraction au TOPO de la solution 8 M en acide nitrique, par mesure du complexe zirconium-violet de pyrocatéchol. Pour les deux éléments, la méthode est précise à ±5% ou 2,5 μg près. On prend la plus grande de ces deux valeurs. En utilisant les modifications suggérées, la méthode est spécifique pour le dosage du titane, et seuls le thorium et le hafnium interfèrent dans le dosage du zirconium.

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THE PRECIPITATION OF CADMIUM SULPHIDE BY THIOACETAMIDE FROM ACID CHLORIDE SOLUTIONS

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Summary—The rate of precipitation of cadmium(II) by thioacetamide from 0·030 *VF* to 0·040 *VF* chloride solutions has been found to conform to the expression

$$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]}{\mathrm{dt}} = k\,\frac{[\mathrm{Cd^{2+}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} + k'\,\frac{[\mathrm{CdCl^+}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{3/4}}$$

where k and k' are $8{\cdot}1 \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} and $1{\cdot}55 \times 10^{-4}$ litre$^{1/4}$ mole$^{-1/4}$ min^{-1}, respectively, at 90°. This rate expression applies to solutions having pH values above 3, where the so-called direct reaction between cadmium species and thioacetamide is predominant. At the above chloride concentrations, the observed rate of precipitation is greater than that which should have been observed if all of the cadmium(II) were present as aquated cadmium ion, Cd^{2+}. Rate measurements at 0·15 and 1 *VF* chloride have shown that the higher chloride complexes of cadmium(II), $CdCl_2$ and $CdCl_3^-$, react at a very much slower rate than does $CdCl^+$ or Cd^{2+}. The value of the dissociation constant for the monochlorocadmium ion,

$$K_{\mathrm{diss}} = \frac{[\mathrm{Cd^{2+}}][\mathrm{Cl^-}]}{[\mathrm{CdCl^+}]},$$

has been found to be $(2{\cdot}18 \pm 0{\cdot}07) \times 10^{-2}$ at 90° by means of a concentration cell with cadmium amalgam electrodes.

INTRODUCTION

BOWERSOX and Swift[1] found that in the pH region from 3·3 to 6·3 the rate of precipitation of cadmium sulphide by thioacetamide (TAA) from formic acid-formate buffered solutions conformed to the expression

$$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]}{\mathrm{dt}} = 8{\cdot}1 \times 10^{-4}\,\frac{[\mathrm{Cd^{II}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} \tag{1}$$

They also observed that chloride ion decreased the rate of precipitation, and this decrease was attributed to the formation of chloride complexes of cadmium. It was hoped that a quantitative investigation of this inhibition would provide information regarding the effect of complexing ligands on the rates and mechanisms of the direct reactions of hydrated metal ions with TAA. In addition, the analytical implications were of interest.

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I. THE DISSOCIATION CONSTANT OF MONOCHLOROCADMIUM ION

The rate measurements on the reaction of cadmium with thioacetamide in chloride solutions were carried out at 90°. Therefore a reliable value for the dissociation constant of the monochlorocadmium ion at this temperature was needed for quantitative interpretation of the results. A sufficiently accurate value could not be obtained by extrapolation of published values at other temperatures;[6,7,9] therefore, a concentration cell utilising cadmium amalgam electrodes was used for gathering the results required to calculate the desired dissociation constant at 90°. Approximate calculations from limited available values, indicated that at 90°, and the prevailing pH values, less than 0·0003 % of the cadmium would be present as $CdOH^+$.

EXPERIMENTAL

Reagents

Reagent-grade chemicals were used.

Cadmium perchlorate solution: 0·10*VF* (volume formal), prepared by dissolving cadmium carbonate in a measured volume of 9*VF* perchloric acid and diluting to volume.

Cadmium amalgam: 5%, made by mixing 15 g of cadmium metal turnings with 285 g of triply distilled mercury and warming the mixture in an atmosphere of nitrogen.

Sodium chloride solution: 0·50*VF* prepared by weight.

Sodium perchlorate solution: (chloride-free) 1·00*VF*, used to provide a constant ionic strength of 0·23.

Apparatus

A thermoregulated constant temperature bath was used to maintain the system at 90°. A Leeds and Northrup K-2 potentiometer was used for the potential measurements. The cell was a conventional polarographic H-cell with a sintered glass disc separating the two compartments. The cadmium amalgam was placed in the lower end of J-shaped 6-mm glass tubing having a length of platinum wire sealed in to maintain electrical contact with the cadmium amalgam in the cup. This apparatus was similar in nature to that used by Vanderzee and Rhodes[10] for the study of stannous chloride complexes.

Procedure

The method consisted of measuring the potential difference between two identical cadmium amalgam electrodes, one in a reference cadmium perchlorate solution of known concentration, the other in a solution of known cadmium and chloride concentrations and having the same ionic strength and pH as the reference solution. Fresh cadmium amalgam electrode surfaces were prepared for each experiment.

The empty H-cell was preheated in the constant temperature bath. The two cadmium solutions were deaerated with nitrogen, heated quickly to about 90°, and rapidly poured into the appropriate compartments of the cell, and the compartments were closed. An atmosphere of nitrogen was maintained over the solutions throughout each experiment. The electrodes were inserted, and potential difference readings were taken as soon as the temperature of the solutions stabilised at 90°. A series of readings was taken at approximately 3-min intervals for about 20 min; after this time the potential differences began to decrease because of the migration of chloride ion through the sintered glass disc. The values obtained during a given run agreed to within 0·3 mV; the average value of multiplicate runs agreed to within 0·2 mV. The reference solution in all measurements was a standard cadmium perchlorate solution, about 0·01 *VF* in cadmium and adjusted to ionic strength 0·23 with sodium perchlorate. The chloride-containing solutions were of the same ionic strength and same formal cadmium concentration.

RESULTS AND DISCUSSION

The reversible e.m.f. of the cell

$$Cd(Hg) \mid Cd^{2+}(C_1) \parallel Cd^{2+}(C_2) \mid Cd(Hg)$$

is given by

$$E_{cell} = \frac{RT}{2F} \ln c_2/c_1 \tag{2}$$

where c_2 represents the cadmium ion concentration of the standard solution and c_1 the cadmium ion concentration of the chloride-containing solution. In this work the junction potential has been neglected because the solutions are nearly identical in composition and of equal ionic strength; only the chloride and cadmium ion concentrations differ. There was no evidence of significant concentration changes caused by evaporation during the course of the measurements.

Checks on the experimental reliability of the method were made as follows:

1. The asymmetry potential resulting when the two cadmium amalgam electrodes were placed in identical solutions was measured at 25° and 90°, and in all cases, was within approximately ±0·5 mv.

2. The reversibility of the cadmium amalgam electrodes in these solutions at 90° was checked by measuring the potential difference between two solutions of the same ionic strength having a cadmium concentration ratio of 10:1 and comparing the value obtained with that predicted by equation (2); the calculated value was 36·4 mv, and the observed value 37·4 mv.

3. The dissociation constant of the monochlorocadmium ion at 25° was determined over a range of cadmium–chloride ratios and the value obtained compared with literature values. King[6] and Vanderzee and Dawson,[9] among others, have shown that a chloride concentration range exists in which cadmium and monochlorocadmium ions are the predominant species, and the results of Vanderzee and Dawson on the variation of the dissociation constant with ionic strength were used to calculate an approximate value for

$$K_{\text{diss}} = \frac{[Cd^{2+}][Cl^-]}{[CdCl^+]} \tag{3}$$

at 25° and $\mu = 0{\cdot}23$. (This ionic strength was used so that later comparison of the rate values with those of Bowersox and Swift[1] on the cadmium ion-TAA reaction

TABLE I.—DISSOCIATION CONSTANT OF MONOCHLOROCADMIUM ION AT 90° CALCULATED FROM CONCENTRATION CELL VALUES.
(Reference solution of cadmium perchlorate, 0·00968 *VF*; ionic strength, 0·23; 5% cadmium amalgam electrodes; nitrogen atmosphere)

Cd^{II}, *VF*	Cl^-, *VF*	E.m.f., mv	$K_{\text{diss}}{}^{a} \times 10^2$
0·00703	0·00978	4·8 4·8	2·20
0·00968	0·0190	8·1	2·22
0·00703	0·0244	10·2 10·4	2·25
0·00968	0·0476	16·4	2·24
0·00703	0·0487	18·2 18·4	2·00

$K_{\text{diss}} = (2{\cdot}18 \pm 0{\cdot}07) \times 10^{-2}$

[a] Calculated from the expression

$$K_{\text{diss}} = \frac{[Cd^{2+}][Cl^-]}{[CdCl^+]}$$

could be made.) The mean of the experimental values found for K_{diss} at 25° was $3{\cdot}2 \times 10^{-2}$; the value calculated from the results of Vanderzee and Dawson[9] was $3{\cdot}5 \times 10^{-2}$.

Dissociation constant of monochlorocadmium ion at 90°

Table I presents the results of two independent series of measurements of the e.m.f. of cadmium ion concentration cells at 90° and the resulting values for the dissociation constant at each chloride concentration. The average value of the dissociation constant, $2{\cdot}18 \times 10^{-2}$, was used during the rate study described below for calculating equilibrium concentrations of cadmium and monochlorocadmium ions under the conditions specified.

II. REACTION RATES OF CHLOROCADMIUM SPECIES WITH THIOACETAMIDE

EXPERIMENTAL

Reagents

Thioacetamide (*TAA*) *solutions:* 1·00*VF*, prepared by weight from Arapahoe thioacetamide.* These solutions were clear and were used for not longer than 3 weeks.

Disodium ethylenediaminetetra-acetate (EDTA): 0·011*VF*, prepared by weight and standardised with a standard zinc chloride solution. Eriochrome Black T in 1:1 ethanolamine-isopropanol was used as indicator.

Formic acid–formate buffer systems were used; the concentration of formate ion in the reaction solution was 0·15*VF*.

Buffer solution, pH 10: made by diluting a solution of 67·5 g of ammonium chloride and 570 ml of concentrated aqueous ammonia (stock reagent) to 1 litre, was used in the EDTA titrations.

Apparatus

The reaction vessel was a 38-mm × 200-mm Pyrex test-tube fitted with a three-hole stopper. Inserted in the stopper were a 6-mm siphon tube, a 6-mm outlet tube with a pressure bulb, and a thermometer. The vessel was immersed in the constant temperature bath and the temperature of the entire system was maintained at 90 ± 1°. In one experiment an additional 6-mm tube was inserted in the reaction vessel to allow nitrogen to bubble through the vessel.

Procedure

The cadmium perchlorate, sodium perchlorate, sodium chloride and buffer solutions were mixed in the reaction vessel at a temperature slightly above 90°. The TAA solution was heated quickly to about the same temperature and then added rapidly to the system. The initial concentration of cadmium(II) was 0·010*VF*, the chloride was 0·031–1·0*VF*, and the TAA concentration was varied from 0·100*VF* to 0·445*VF*. After temperature equilibration, samples of the reaction mixture were removed at timed intervals, quenched in an ice bath, and centrifuged to separate the cadmium sulphide. Duplicate 5·00-ml portions of each sample solution were pipetted into 15-mm × 125-mm test-tubes. An excess of ammonia was added to precipitate the cadmium sulphide, and the tubes were placed in hot water to coagulate the precipitate. Then the mixture was centrifuged, and the cadmium sulphide was transferred quantitatively to a flask. About 4 ml of 6*VF* hydrochloric acid were added, the solution was boiled to expel hydrogen sulphide, and was then partially neutralised with 6*VF* potassium hydroxide. The solution was cooled, and 10 ml of the pH 10 buffer solution and a few drops of Eriochrome Black T indicator were added. The solution was then titrated with 0·011*VF* EDTA to a blue-green end-point.

DISCUSSION AND RESULTS

The rate measurements were made with solutions, 0·030–0·040*VF* in chloride, which had approximately equal concentrations of cadmium and monochlorocadmium ions; the dissociation constant of $CdCl_2$, estimated from the results of Vanderzee and Dawson[9] at 25° and 45°, indicated that less than 5% of the total cadmium existed

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as this species. Evidence is presented later that $CdCl_2$ does not react with thioacetamide at a significant rate under the conditions prevailing.

A semi-logarithmic plot of the total or volume formal cadmium concentration *versus* time was made for each experiment, and as shown in Fig. 1 linear plots were obtained in all cases. The rate of decrease of the formal cadmium concentration under the conditions studied can be expressed in the form.

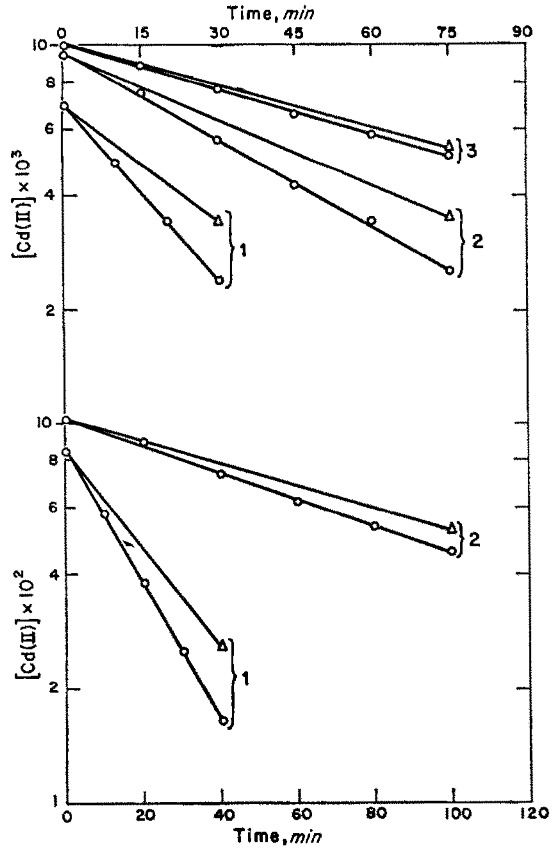

FIG. 1.—Effect of cadmium(II), thioacetamide and pH on the rate of precipitation of cadmium from chloride solutions by thioacetamide.

○ Experimental measurements.

Δ Calculated using equation (1), assuming no chlorocadmium(II) complexes formed.

A. CH_3CSNH_2 0·200*VF*; chloride 0·030*VF*; 90°
  (1) pH 4·30
  (2) pH 3·80
  (3) pH 3·30; chloride 0·040*VF*
B. pH 3·80; chloride 0·030*VF*; 90°
  (1) CH_3CSNH_2 0·445*VF*
  (2) CH_3CSNH_2 0·100*VF*

$$\frac{-d[Cd^{II}]}{dt} = K\,[Cd{-}II] \qquad (4)$$

Because essentially all of the cadmium exists as cadmium and monochlorocadmium ions under these conditions, the rate may be expressed also as

$$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]}{\mathrm{dt}} = -\left[\frac{\mathrm{d}[\mathrm{Cd^{2+}}]}{\mathrm{dt}} + \frac{\mathrm{d}[\mathrm{CdCl^{+}}]}{\mathrm{dt}}\right] \tag{5}$$

where $[\mathrm{Cd^{2+}}]$ and $[\mathrm{CdCl^{+}}]$ designate the concentrations of aquated cadmium and monochlorocadmium ions, respectively.

Bowersox and Swift[1] have shown that the rate of reaction of cadmium ion with thioacetamide in acid solution at 90°, in the pH region where the so-called direct reaction predominates, conforms to equation (1). Nearly exact reproducibility of the rate constant, $8{\cdot}1 \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} at 90°, reported by these investigators, was confirmed in separate experiments during the course of the present work. Therefore, the over-all reaction rate under these conditions becomes

$$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]}{\mathrm{dt}} = 8{\cdot}1 \times 10^{-4}\,\frac{[\mathrm{Cd^{2+}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}} + k_d[\mathrm{CdCl^+}]^n \tag{6}$$

where k_d is a constant for any given thioacetamide and hydrogen ion concentration.

If $\mathrm{CdCl^+}$ does not react with TAA at a measurable rate, the second term in equations (5) and (6) disappears, and the observed rate should conform closely to the rate calculated using the equilibrium concentrations of cadmium ion. The results presented in Table II show that the observed rate cannot be explained on this basis. Equilibrium concentrations of cadmium and monochlorocadmium ions were calculated at each experimental point, using the dissociation constant for $\mathrm{CdCl^+}$ previously determined. Cadmium(II) complexes are highly labile and there is no evidence for delay in establishing equilibrium.[8] The total observed rate of cadmium(II) precipitation and calculated rates of reaction of cadmium ion are tabulated for one representative set of conditions (Table II), and indicate that the monochlorocadmium ion reacts with TAA at a greater rate under these conditions than does the simple (aquated) cadmium ion. A similar representation of the relative reaction rates observed in all other experiments leads to the same conclusion.

TABLE II.—COMPARISON OF OBSERVED CADMIUM(II) PRECIPITATION RATE WITH PRECIPITATION RATE OF CADMIUM ION ($\mathrm{Cd^{2+}}$).

(pH 3·80; chloride 0·0300*VF*; $\mathrm{CH_3CSNH_2}$ 0·200*VF*; temp., 90°)

Time, *min*	$[\mathrm{Cd^{II}}]$, *VF*	$[\mathrm{Cd^{2+}}]$,[a] *M*	$[\mathrm{CdCl^+}]$,[a] *M*	$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]^{b}}{\mathrm{dt}} \times 10^5$	$\frac{-\mathrm{d}[\mathrm{Cd^{2+}}]^{c}}{\mathrm{dt}} \times 10^5$
0	0·00940	0·00440	0·00500	16·4	5·6
15	0·00745	0·00343	0·00402	13·0	4·4
30	0·00560	0·00255	0·00305	9·8	3·2
45	0·00425	0·00190	0·00235	7·4	2·5
60	0·00340	0·00150	0·00190	5·9	1·9

[a] Calculated from the expression

$$\frac{[\mathrm{Cd^{2+}}][\mathrm{Cl^-}]}{[\mathrm{CdCl^+}]} = 2{\cdot}18 \times 10^{-2} \quad (90°)$$

[b] Calculated from the expression

$$\frac{-\mathrm{d}[\mathrm{Cd^{II}}]}{\mathrm{dt}} = K[\mathrm{Cd{-}II}]$$

[c] Calculated from the expression (1)

$$\frac{-\mathrm{d}[\mathrm{Cd^{2+}}]}{\mathrm{dt}} = 8{\cdot}1 \times 10^{-4}\,\frac{[\mathrm{Cd^{2+}}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{1/2}}$$

Fig. 1 shows the relationships between the experimentally determined reaction rates of cadmium and TAA under the conditions specified [equation (4)], and the rate calculated using the Bowersox–Swift expression [equation (1)] assuming no complex formation. In every case, under the experimental conditions studied, the observed rate is greater than that calculated assuming that all cadmium in the system was present in the form of the aquated cadmium ion, represented as Cd^{2+}. The calculated plots were made by determining a rate constant, K, of the form in equation (4). These plots are consistent with the example results shown in Table II.

Rates of monochlorocadmium ion-thioacetamide reaction

Effect of monochlorocadmium ion: Because the term dependent on cadmium ion in equation (6) can be calculated, the results obtained from rate measurements at constant TAA and hydrogen ion concentrations can be used to determine the value of n in this equation. From equations (4), (5) and (6) it is seen that

$$\frac{-\mathrm{d}[\mathrm{CdCl}^+]}{\mathrm{dt}} = K[\mathrm{Cd^{II}}] - 8{\cdot}1 \times 10^{-4}\frac{[\mathrm{Cd}^{2+}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{1/2}} = k_d[\mathrm{CdCl}^+]^n \qquad (7)$$

The results were plotted as the term

$$K[\mathrm{Cd^{II}}] - 8{\cdot}1 \times 10^{-4}\frac{[\mathrm{Cd}^{2+}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{1/2}}$$

versus the equilibrium concentration of $CdCl^+$ at each experimental point.

The linearity of these plots (*cf.* Fig. 2) establishes a first order rate dependence on the concentration of monochlorocadmium ion. The value of n in equation (7), which has been calculated from the results is 1·01 ± 0·01.

Effect of thioacetamide: Experiments at three different TAA concentrations and at constant pH, permitted the calculation of the corresponding rate constants, K and k_d, in equation (7). The value of m in the expression

$$\frac{-\mathrm{d}[\mathrm{CdCl}^+]}{\mathrm{dt}} = k_d'[\mathrm{CdCl}^+][\mathrm{CH_3CSNH_2}]^m \qquad (8)$$

was then calculated as 1·03 ± 0·05.

TABLE III.—EFFECT OF THIOACETAMIDE CONCENTRATION ON THE MONOCHLOROCADMIUM ION—THIOACETAMIDE REACTION.
(Chloride 0·0300*VF*; pH 3·80; 90°)

$[CH_3CSNH_2]$, *VF*	$k \times 10^2$, sec^{-1} [a]	$k' \times 10$, $M^{-1}\,sec^{-1}$ [b]
0·100	1·04 ± 0·00	1·04
0·200	2·23 ± 0·01	1·11
0·445	4·93 ± 0·00	1·11

$k'_{\text{average}} = (1{\cdot}09 \pm 0{\cdot}03) \times 10^{-1}\,M^{-1}\,\mathrm{sec}^{-1}$

[a] Calculated from the expression

$$\frac{-\mathrm{d}[\mathrm{CdCl}^+]}{\mathrm{dt}} = k[\mathrm{CdCl}^+]$$

[b] Calculated from the expression

$$\frac{-\mathrm{d}[\mathrm{CdCl}^+]}{\mathrm{dt}} = k'[\mathrm{CdCl}^+][\mathrm{CH_3CSNH_2}]$$

In Table III the information on the effect of TAA is summarised, and shows that the rate of reaction of monochlorocadmium ion with TAA is first order with respect to the TAA concentration.

Effect of hydrogen ion: In order to establish the dependence on pH of the rate of the reaction of $CdCl^+$ with TAA, measurements were carried out in solutions varying from $5{\cdot}0 \times 10^{-4}$ to $5{\cdot}0 \times 10^{-5}$ *VM* in hydrogen ion. The measurements were not made over a wider range because at lower pH values precipitation by TAA hydrolysis becomes significant,[1] and at higher pH values the formate buffer system is inefficient.

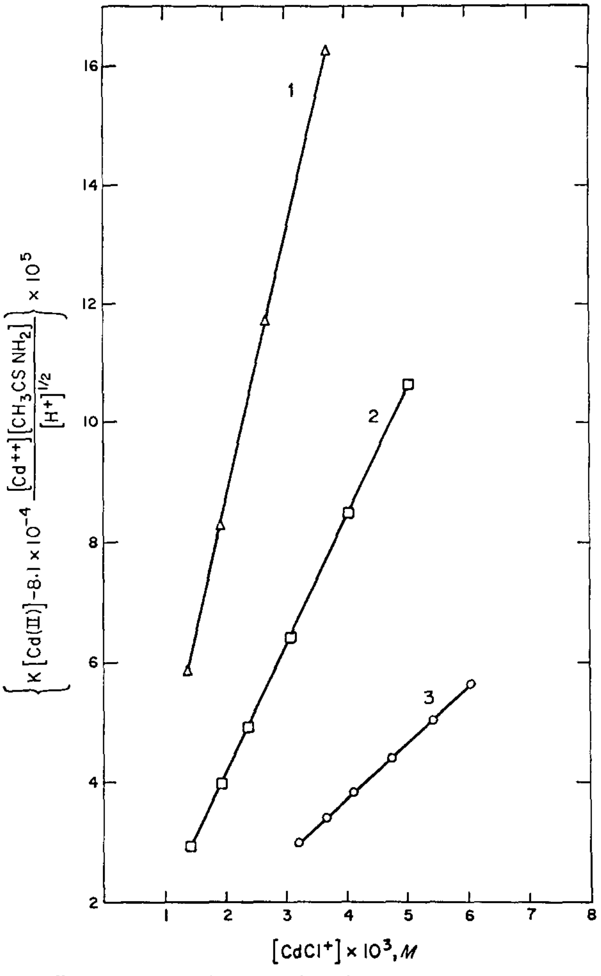

FIG. 2.—Effect of monochlorocadmium ion and pH on the rate of precipitation of monochlorocadmium ion by thioacetamide.

(CH_3CSNH_2 0·200*VF*; chloride 0·0300*VF*; 90°)
(1) pH 4·30
(2) pH 3·80
(3) pH 3·30; chloride 0·0400*VF*

It was desirable to retain the formate buffer system in order to utilise the information previously reported by Bowersox and Swift.[1] In this and similar work done in these laboratories the pH values reported were determined at 25° rather than at 90°.

Accurate and reproducible measurements at 90° are difficult to make, and reliable standards are not readily available. In some experiments, relative measurements of pH were made at 90° and gave essentially the same rate dependence. The measurements show that the reaction of monochlorocadmium ion with TAA is inhibited by hydrogen ion (Fig. 2) and that this inhibition is significantly different from the half-order inhibition observed in the direct reaction of the aquated cadmium ion.[1] The dependence observed in this case is inverse three-fourths order under the conditions shown in Table IV. The exact order calculated from the results is (—0·75 ± 0·00).

TABLE IV.—EFFECT OF pH ON THE MONOCHLOROCADMIUM ION—THIOACETAMIDE REACTION.
(Chloride 0·0300*VF*; CH_3CSNH_2 0·200*VF*; 90°)

pH	$k_1 \times 10^5$ [a]	$k_2 \times 10^3$ [b]	$k' \times 10^4$ [c]
3·30[d]	2·33	1·04	1·56
3·80	1·72	1·37	1·54
4·30	1·32	1·86	1·57

$k' = (1{\cdot}55 \pm 0{\cdot}01) \times 10^{-4}$ litre$^{1/4}$ mole$^{-1/4}$ min^{-1}.

[a] Calculated from the expression

$$\frac{-d[CdCl^+]}{dt} = k_1 \frac{[CdCl^+][CH_3CSNH_2]}{[H^+]}$$

[b] Calculated from the expression

$$\frac{-d[CdCl^+]}{dt} = k_2 \frac{[CdCl^+][CH_3CSNH_2]}{[H^+]^{1/2}}$$

[c] Calculated from the expression

$$\frac{-d[CdCl^+]}{dt} = k' \frac{[CdCl^+][CH_3CSNH_2]}{[H^+]^{3/4}}$$

[d] Nitrogen bubbled briefly through reaction vessel.

Rate expression: The experiments discussed above have shown that the rate of precipitation of cadmium by TAA from dilute chloride solutions having pH values from 3·3 to 6·3 follows the expression

$$\frac{-d[Cd^{II}]}{dt} = k \frac{[Cd^{2+}][CH_3CSNH_2]}{[H^+]^{1/2}} + k' \frac{[CdCl^+][CH_3CSNH_2]}{[H^+]^{3/4}} \tag{9}$$

where k and k' are $8{\cdot}1 \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} and $1{\cdot}55 \times 10^{-4}$ litre$^{1/4}$ mole$^{-1/4}$ min^{-1}, respectively, at 90°. This expression indicates that, as with the aquated cadmium ion, there is a direct reaction between the monochlorocadmium complex and the TAA.

Rates at higher chloride concentrations: It was of interest to determine the effect of increasing the chloride concentration on the precipitation rate. Especially of interest would be the rates of precipitation in chloride concentration regions where the higher chloride complexes of cadmium, $CdCl_2$ and $CdCl_3^-$, were present in significant quantities. Butler and Swift[5] have shown that arsenic(III) does not undergo a direct reaction with TAA in the same pH region as lead,[4] cadmium,[1] nickel[2] or zinc,[3] the reaction apparently being hydrolysis-controlled even at pH 6. In this pH region arsenic(III) exists in the form of a neutral complex species; thus more information on the reaction of neutral and negatively charged species was of interest.

Rate measurements were carried out in solutions 0·15*VF* and 1·0*VF* in chloride, where significant concentrations of $CdCl_2$ and $CdCl_3^-$, respectively, should be present. The results of King[6] show that at 25° the distribution of species should be approximately one-fifth total cadmium as $CdCl_2$ in a 0·15*VF* chloride solution: and one-third as $CdCl_2$, and one-half as $CdCl_3^-$ in a 1·0*VF* chloride solution.

The results are summarised in Fig. 3, where the rates at the higher concentrations are compared with one of the experiments at 0·0300*VF* chloride under the same conditions. The over-all rate of reaction of cadmium with TAA is greatly diminished as the chloride concentration increases. Also, it is to be seen that the rate of the reaction is still first order with respect to the volume formal cadmium concentration. This information indicates that the uncharged and negatively charged species, $CdCl_2$ and $CdCl_3^-$, react at a very much slower rate than does $CdCl^+$.

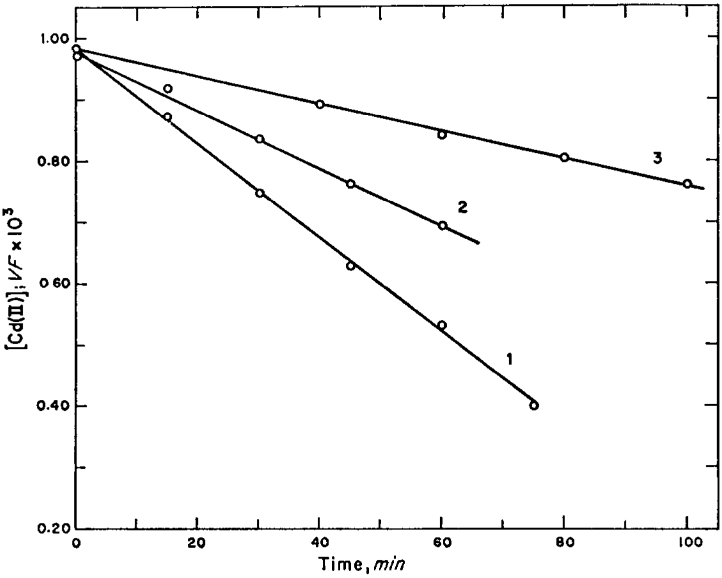

Fig. 3.—Effect of chloride concentration on the rate of precipitation of cadmium(II) by thioacetamide.

(pH 3·80; CH_3CSNH_2 0·200*VF*; 90°)
(1) chloride 0·0300*VF*
(2) chloride 0·146*VF*
(3) chloride 1·00*VF*

No quantitative conclusions can be drawn, because only very approximate values for the dissociation constants of $CdCl_2$ and $CdCl_3^-$ are available. In addition, the ionic strength of these more concentrated chloride solutions exerts a significant effect on the value of the individual dissociation constants. Nevertheless, attempts were made to calculate approximately the ionic strength and temperature effects on the available dissociation constants of $CdCl_2$ and $CdCl_3^-$ at lower temperatures and different ionic strengths.[6,9] These resulting approximate constants were applied in the calculation of the equilibrium distribution of the various cadmium species in the reaction solutions of chloride concentration 0·15*VF* and 1·0*VF*. Calculations made in this way indicate that $CdCl_2$ and $CdCl_3^-$ do not react with thioacetamide at a measurable rate under the conditions specified.

Comments on reaction rates of various species

As the results in Table II and Fig. 1 show, the rate of reaction of the monochlorocadmium ion with thioacetamide is greater than that of the aquated cadmium ion. A direct comparison of rate constants is not meaningful, because the rate constant of the $CdCl^+$—CH_3CSNH_2 reaction has different dimensions from that of the Cd^{2+}—CH_3CSNH_2 reaction because of the different hydrogen ion dependences of these reactions. If the Cd^{2+} and $CdCl^+$ rates had the same hydrogen ion dependence, the rate constant of the $CdCl^+$ reaction would be much greater than that of the Cd^{2+} reaction (Table IV); at pH 3·80, for example, k_2 would have been $1{\cdot}37 \times 10^{-3}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1}. As indicated by Fig. 3, and by the approximate calculations described in connection with the rate measurements in 0·146 and 1·00 *VF* chloride solutions, the $CdCl_2$ and $CdCl_3^-$ species react very slowly, if at all, under the conditions described. No information appears to be available by which one can explain these apparent relative rates by direct analogy with similar reactions.

Subsequent experiments in these laboratories[11] have indicated that nucleation and crystal growth phenomena can exert striking effects on precipitations by the direct reaction, and that under certain conditions reactions taking place at the surface of the precipitate particles constitute the rate-controlling step. These effects are being investigated further.

This investigation again shows the variety of effects which may occur when TAA is substituted for hydrogen sulphide as a precipitant, and the necessity for careful experimental verification of proposed analytical procedures based on this substitution.

Acknowledgement—We are indebted to David F. Bowersox for preliminary measurements which established that the aquated cadmium ion and the monochlorocadmium ion reacted with TAA at different rates. We have received valuable suggestions and comments from Fred C. Anson, Robert L. Causey, and David H. Klein. Financial support from the National Science Foundation is gratefully acknowledged.

Zusammenfassung—Die Fällungsgeschwindigkeit von Cadmium(II) mit Thioacetamid aus 0,03–0,04-molaren Chloridlösungen läßt sich durch die Gleichung

$$\frac{-d[Cd(II)]}{dt} = k\,\frac{[Cd^{2+}][CH_3CSNH_2]}{[H^+]^{1/2}} + k'\,\frac{[CdCl^+][CH_3CSNH_2]}{[H^+]^{3/4}}$$

darstellen, mit $k = 8{,}1 \cdot 10^{-4}\ l^{1/2}\ mol^{-1/2}\ min^{-1}$ und $k' = 1{,}55 \cdot 10^{-4}\ l^{1/4}\ mol^{-1/4}\ min^{-1}$ bei 90°C. Diese Geschwindigkeitsgleichung gilt für Lösungen mit pH-Werten über 3, wo die sogenannte direkte Reaktion zwischen Cadmium und Thioacetamid überwiegt. Bei den gennanten Chlorid-konzentrationen ist die beobachtete Fällungsgeschwindigkeit größer als die, die man erwarten würde, wenn alles Cadmium(II) als hydratisiertes Cadmiumion Cd^{2+} vorläge. Geschwindigkeitsmessungen bei 0,15 und 1-molarer Chloridkonzentration zeigten, daß die stärker chloridhaltigen Komplexe $CdCl_2$ und $CdCl_3^-$ viel langsamer reagieren als $CdCl^+$ und Cd^{2+}. Die Dissoziationskonstante des Monochlorocadmiumions

$$K_{diss} = \frac{[Cd^{2+}][Cl^-]}{[CdCl^+]}$$

wurde mit Hilfe einer Konzentrationszelle mit Cadmiumamalgamelektroden zu $(2{,}18 \pm 0{,}07) \cdot 10^{-2}$ bei 90°C gefunden.

Résumé—On a trouvé que la vitesse de précipitation du cadmium(II) par le thioacétamide, à partir de solutions de chlorure $0{,}030 VF$ à $0{,}040 VF$, est en accord avec l'équation:

$$\frac{-\mathrm{d}[\mathrm{Cd(II)}]}{\mathrm{d}t} = k\,\frac{[\mathrm{Cd}^{2+}][\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{1/2}} + k'\,\frac{[\mathrm{CdCl}^+][\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{3/4}}$$

où k et k' sont respectivement, à 90°C, $8{,}1 \times 10^{-4}$ litre$^{1/2}$ mole$^{-1/2}$ min^{-1} et $1{,}55 \times 10^{-4}$ litre$^{1/4}$ mole$^{-1/4}$ min^{-1}. Cette équation de la vitesse s'applique aux solutions dont le pH est supérieur à 3, et où prédomine la réaction dite directe entre le cadmium et le thioacétamide. Aux plus grandes concentrations en chlorure, la vitesse de précipitation observée est supérieure à celle que l'on devrait noter si tout le cadmium(II) était présent à l'état d'ion cadmium hydraté, Cd^{2+}. Les mesures de vitesse pour les valeurs 0,15 et 1F en chlorure ont montré que les complexes chlorés supérieurs du cadmium(II), $\mathrm{CdCl_2}$ et $\mathrm{CdCl_3}^-$, réagissent à des vitesses beaucoup plus lentes que CdCl^+ ou Cd^{2+}. On a trouvé, au moyen d'une cellule de concentration avec électrodes à amalgame de cadmium, que la valeur de la constante de dissociation pour l'ion monochlorocadmium,

$$K_{\mathrm{diss}} = \frac{[\mathrm{Cd}^{2+}][\mathrm{Cl}^-]}{[\mathrm{CdCl}^+]}$$

est de $(2{,}18 \pm 0{,}07) \times 10^{-2}$ à 90°C.

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A SELECTIVE AND SENSITIVE COLOUR REACTION FOR SILVER

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Summary—Bromopyrogallol red (BPR) and 1,10-phenanthroline (phen) may be used as a reagent system for the spectrophotometric determination of silver ions in aqueous solution in the range 0.02–0·20 ppm. Photometric and potentiometric methods have shown that the blue coloured ternary complex, which absorbs at 635 mμ, is most probably an ion-association system $[(\text{phen-Ag-phen})^+]_2\text{BPR}^{2-}$. The colour reaction, using EDTA, fluoride and hydrogen peroxide as masking agents, is free from interference of a 100-fold g ion excess over silver of some 24 cations and 11 anions investigated. Only gold(III), cyanide and thiosulphate were found to interfere. With a molar extinction coefficient of 51,000, the colour reaction is probably the most sensitive of all known colorimetric methods for silver.

FROM an examination of the literature it is apparent that there is considerable need for a selective colorimetric reagent for silver without the disadvantages of the existing organic reagents, dithizone and the rhodanine derivatives.[1] We felt it was unlikely that much success could be gained by designing similarly constituted reagents and have pursued a rather different approach to the problem.

We have previously described the use of pyrogallol red as a spectrophotometric reagent for silver ions.[2] This reagent forms a yellow complex [$\lambda_{\max} = 390$ mμ, $\epsilon_{390\text{ m}\mu} = 10{,}000$] with silver, but the colour development is protracted. The bromo-substituted reagent, bromopyrogallol red, behaves similarly and also forms a yellow colour. Subsequently, in the course of examining the use of 1,10-phenanthroline as a masking agent, we discovered that the presence of the latter caused a dramatic change in the course of the reaction between silver ions and the reagent. Instead of the slow removal of the red colour of the pyrogallol red, with the formation of a yellow colour of much lower intensity, we observed an instantaneous formation of a blue coloured solution of very high intensity. Because the colour formation was very rapid, sensitive and unaffected by the mass masking agent, EDTA, it was decided to investigate the reaction and develop it for the determination of trace amounts of silver.

The blue colour may be produced by the addition of a silver nitrate solution to an aqueous solution of 1,10-phenanthroline and pyrogallol red, buffered to pH 7 with ammonium acetate. The use of bromopyrogallol red increases the sensitivity of the reaction, which can be obtained over the pH range 3–10, although the optimum pH appears to be *ca.* 7. At pH values greater than 7 there is a risk of reagent oxidation, which becomes appreciable at pH > 9. The absorption of the bromopyrogallol red and 1,10-phenanthroline system at 560 mμ decreases with increasing amounts of

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silver and at the same time, another absorption peak builds up at 635 mμ. The ratio of silver:bromopyrogallol red, as deduced from this experiment at the position of maximum colour development, is 2:1 (*cf.* Fig. 1). It is worthy of note that the reaction is instantaneous. With more concentrated solutions of silver nitrate (*ca.* $10^{-3}M$) a blue gelatinous precipitate settles out on standing, but with lower concentrations of silver (*ca.* $10^{-5}M$) there is no obvious precipitation over a period of 2–3 days. Lastly, a considerable excess of 1,10-phenanthroline (*ca.* a 10-fold mole excess over silver) is required to give maximum colour formation.

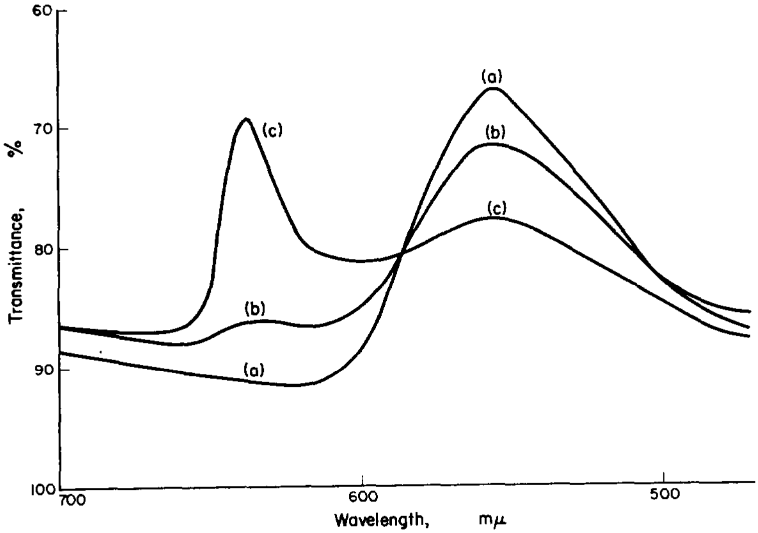

Fig. 1.—Transmission spectra:

(a) 5 ml of $10^{-5}M$ bromopyrogallol red plus 1 ml of $10^{-3}M$ 1,10-phenanthroline + 1 ml of 20% ammonium acetate diluted to 50 ml with distilled water.
(b) As (a) plus 5 ml of 10^{-5} M silver nitrate.
(c) As (a) plus 10 ml of 10^{-5} M silver nitrate.
(Measurements made at 635 mμ in 4-cm cuvettes with Beckman D.B. spectrophotometer.)

Preliminary calibration curves for silver in the range 1–10 μg (0·02–0·2 ppm) gave linearity only for 4–10 μg of silver. This appeared to indicate either the presence of a weak complex or the existence of a precipitate, the solubility product of which had not been reached with very small amounts of silver. There was no excess bromopyrogallol red at the upper silver limit (10 μg) in these experiments. The calibration curve was repeated using a 2-fold mole excess of bromopyrogallol red together with a 10-fold mole excess of 1,10-phenanthroline (both relative to silver). EDTA (1000-fold mole excess over silver) was also incorporated into the solution as a convenient masking agent for cations which would interfere by reacting with bromopyrogallol red [*e.g.*, lead(II)], with 1,10-phenanthroline [*e.g.*, iron(II)] or both [*e.g.*, mercury(II)]. By measuring the absorbance at 635 mμ in 4-cm cuvettes against a blank containing no silver, linearity was obtained from 1–10 μg (0·02–0·2 ppm) of silver. The solution colours slowly faded on standing, but were quite stable for 0·5 hr after preparation and subsequent dilution to 50 ml. The order of addition of reagents was unimportant.

Interferences

The permissible level of cation concentration, other than silver, depends largely on the concentration of EDTA employed, because it is intended that EDTA should function as the principal masking agent. Solutions were prepared, therefore, containing *ca.* 10 μg of silver (*ca.* 0·2 ppm), under the normal optimum conditions necessary for the preparation of a calibration curve. Each solution contained, in addition, varying concentrations of EDTA from a 100- to 10,000-fold mole excess over silver. It was found that there was no significant change in the absorbance of any of the solutions at 635 mμ. It should, therefore, be possible to determine silver in the presence of very large excesses of extraneous cations provided that they form reasonably stable EDTA complexes at pH 7, and that these complexes do not absorb appreciably at 635 mμ. Table I shows the effect of *ca.* a 100-fold (g ion) excess of various cations over silver in the presence of a 1,000-fold (mole) excess of EDTA.

TABLE I

Cation[a]	Absorbance[b]	Deviation from blank
Ag^+ (blank)	0·355	—
$Ag^+ + Al^{3+}$	0·354	−0·001
$Ag^+ + Au^{3+}$	0·258	−0·097
$Ag^+ + Ba^{2+}$	0·352	−0·003
$Ag^+ + Bi^{3+}$	0·352	−0·003
$Ag^+ + Ca^{2+}$	0·350	−0·005
$Ag^+ + Cd^{2+}$	0·349	−0·006
$Ag^+ + Ce^{3+}$	0·357	+0·002
$Ag^+ + Co^{2+}$	0·361	+0·006
$Ag^+ + Cr^{3+}$	0·357	+0·002
$Ag^+ + Cu^{2+}$	0·357	+0·002
$Ag^+ + Fe^{2+}$	0·010	−0·345
$Ag^+ + Fe^{3+}$	0·350	−0·005
$Ag^+ + Hg^{2+}$	0·352	−0·003
$Ag^+ + La^{3+}$	0·361	+0·006
$Ag^+ + Mg^{2+}$	0·360	+0·005
$Ag^+ + Mn^{2+}$	0·357	+0·002
$Ag^+ +$ Nb(V)	0·002	−0·353
$Ag^+ + Ni^{2+}$	0·351	−0·004
$Ag^+ + Pb^{2+}$	0·360	+0·005
$Ag^+ + Pd^{2+}$	0·356	+0·001
$Ag^+ + Th^{4+}$	0·060	−0·295
$Ag^+ + Tl^+$	0·353	−0·002
$Ag^+ + Ti^{4+}$	0·359	+0·004
$Ag^+ +$ U(VI)	0·005	−0·350
$Ag^+ + Zn^{2+}$	0·355	+0·000

[a] In a 100-fold g ion excess over silver.
[b] At 635 mμ in 4-cm cuvettes.

Except for gold(III), iron(II), niobium(V), thorium(IV) and uranium(VI), the deviation from the expected results is not greater than ± 0·006 absorbance unit, *i.e.*, $\not>$ 1·6% at a silver level of 0·18 ppm.

The red coloured tris-1,10-phenanthrolinium iron(II) complex was produced with iron(II) and 1,10-phenanthroline but its effect could be overcome by the addition of a sufficiently large excess of 1,10-phenanthroline to complex all of the iron(II) and to react with the silver-bromopyrogallol red. It does not absorb at 635 mμ. Uranium(VI), thorium(IV) and niobium(V) interfere because they all form blue-coloured complexes with bromopyrogallol red. However, these interferences could be eliminated completely at moderate concentrations of these cations [10-fold (g ion) excess over silver], by the addition of excess of fluoride for uranium and thorium, and of hydrogen peroxide for niobium. Only gold(III) continued to cause interference by producing a green-blue coloured precipitate.

It is obvious from this investigation that only silver and gold(III), of those ions examined, give, with 1,10-phenanthroline and bromopyrogallol red, ternary complexes which absorb at 635 mμ. Other complexes produced are complexes of either bromopyrogallol red or 1,10-phenanthroline.

Several anions were also examined at a level of a 10- to 100-fold mole excess over silver. There was no interference from acetate, bromide, carbonate, chloride, citrate, fluoride, nitrate, oxalate, sulphate, sulphite or phosphate. In addition, there was no interference from an appreciable excess of hydrogen peroxide, which is used to mask niobium(V). Only cyanide and thiosulphate were observed to interfere. Both of these ions completely inhibited formation of the blue ternary complex between silver and the reagents.

Reaction mechanism

The nature of this reaction in aqueous solution suggests that the colour is dependent on the formation of a precipitate. This is further indicated by its inability to extract into organic solvents; a blue precipitate normally settles out at the interface.

The composition of the complex was investigated by the following methods.

(a) *Photometric titration*

(i) *Bromopyrogallol red vs. silver nitrate (in excess 1,10-phenanthroline).* The ratio of *reagent:silver* at the end-point of the titration was 1:1·95 (*i.e.*, 1:2).

(ii) *Bromopyrogallol red plus silver nitrate (1:2 ratio) vs. 1,10-phenanthroline.* The ratio of *reagent plus silver:1,10-phenanthroline* at the end-point of the titration was 1:5·25. There was no excess of any one reagent throughout this titration. The actual amount of 1,10-phenanthroline will probably be less than the above because of the amount necessary to form and stabilise the precipitate.

(b) *Job plots*

(i) *Bromopyrogallol red:silver ratio (in excess 1,10-phenanthroline).* A continuous variation plot indicated a *reagent:silver* ratio of 1:2·16 (*i.e.*, 1:2) [Fig. 2(a)].

(ii) *Bromopyrogallol red: 1,10-phenanthroline ratio (in excess silver nitrate).* In this instance a *reagent:1,10-phenanthroline* ratio of 4:16 was given (*i.e.*, 1:4) [Fig. 2(b)].

(iii) *1,10-phenanthroline:silver ratio (in excess bromopyrogallol red).* Here the 1,10-*phenanthroline:silver* ratio was 13·85:6·15 (*i.e.*, 2:1) [Fig. 2(c)].

Thus, the over-all ratio of the reagents employed is $(\text{silver})_2$:$(\text{phen})_4$:$(\text{BPR})_1$.

(c) *Potentiometric measurements*

Potentiometric titration was investigated in order to show up differences in the reaction between Ag^+/BPR on the one hand and Ag^+/phen/BPR on the other. Silver is well known to form a co-ordinately-bound complex with 1,10-phenanthroline. It was felt possible that the BPR was reacting in some way with a $[\text{phen-Ag-phen}]^+$ complex or that the 1,10-phenanthroline was reacting with an Ag^+/BPR chelate by

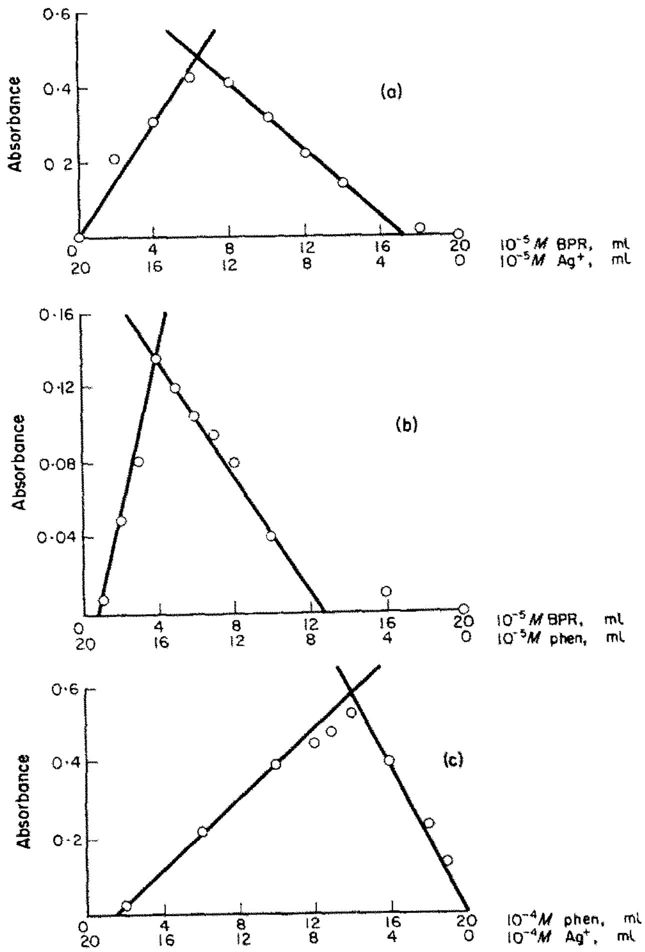

FIG. 2—Job plots:

(a) Bromopyrogallol red–silver (in excess 1,10-phenanthroline): Varying ratios of 10^{-5} M bromopyrogallol red and silver nitrate plus 1 ml of 20% ammonium acetate and 1 ml of $10^{-3}M$ 1,10-phenanthroline diluted to 50 ml with distilled water. Absorbance measured at 635 mμ in 4-cm cuvettes.

(b) Bromopyrogallol red-1,10-phenanthroline (in excess silver nitrate): Varying ratios of 10^{-5} M bromopyrogallol red and 1,10-phenanthroline plus 1 ml of 20% ammonium acetate and 5 ml of $10^{-4}M$ silver nitrate diluted to 50 ml with distilled water. Absorbance measured at 635 mμ in 4-cm cuvettes.

(c) 1,10-Phenanthroline–silver (in excess bromopyrogallol red): Varying ratios of 10^{-4} M 1,10-phenanthroline and silver nitrate plus 1 ml of 20% ammonium acetate and 20 ml of $10^{-4}M$ bromopyrogallol red diluted to 50 ml with distilled water. Absorbance measured at 635 mμ in 1-cm cuvettes. (Bromopyrogallol red solution prepared in 1% ammonium acetate.)

taking up co-ordination sites on the chelated silver ions. In the first instance the mechanism of colour production was likely only to involve ion-association or surface adsorption of the BPR on a colloidal [phen-Ag-phen]$^+$ salt, whilst in the second instance chelate formation with concomitant release of H^+ would be involved. Accordingly, this study was made to try and resolve which mechanism was the more probable.

Three types of curve were constructed:

1. titration of BPR with alkali,
2. titration of BPR + Ag^+ with alkali,
3. titration of BPR + 1,10-phenanthroline + Ag^+ with alkali.

It is obvious from the shape of the titration curves obtained that the silver:1,10-phenanthroline:bromopyrogallol red reaction is in no way related to the bromopyrogallol red-silver reaction. The half-wave pH for the titration of bromopyrogallol red with standard alkali occurs at *ca.* pH 8 and at 2 moles of base to 1 mole of reagent, *i.e.*, liberation of 2 hydrogen ions (*cf.* Fig. 3). This is, in fact, very similar to the titration of bromopyrogallol red plus silver nitrate plus 1,10-phenanthroline with standard alkali (*cf.* Fig. 4). However, the titrations of bromopyrogallol red and silver (*cf.* Fig. 5) give, not only more than one inflection, but also a considerably lower half-wave pH for the first inflection (*ca.* pH 5·0–5·5). Consequently, only in this latter instance is direct chelate formation indicated. Because the liberation of 2 hydrogen ions in the former titrations corresponds to the ionisation of the sulphonic acid and 1 hydroxyl group of bromopyrogallol red, the resulting silver/1,10-phenanthroline/bromopyrogallol red product is likely to be an ion-association system $[(\text{phen-Ag-phen})^+]_2\ \text{BPR}^{2-}$.

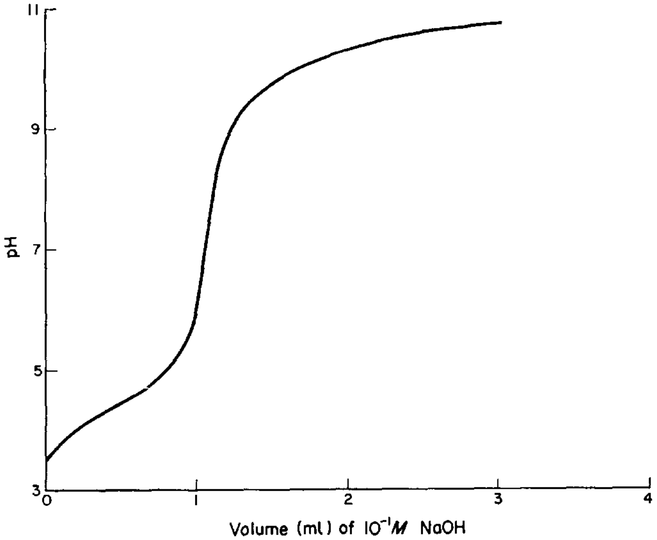

FIG. 3—Potentiometric titration of bromopyrogallol red (50 ml of $10^{-3}M$ reagent *vs.* $10^{-1}M$ sodium hydroxide).

DISCUSSION

The colour reaction described, using EDTA as masking agent, is reliably and virtually completely free from all cationic interference. In addition, with a molar, extinction coefficient of 51,000 (*cf.* Table II), it is the most sensitive of all colorimetric silver reagents known to us.

The system 1,10-phenanthroline/bromopyrogallol red has some useful indicator properties, *e.g.*, in silver cyanide titrations, *etc.*, although this has yet to be put on a more firm basis. The use of bromopyrogallol red as an adsorption indicator has been recently described.[3]

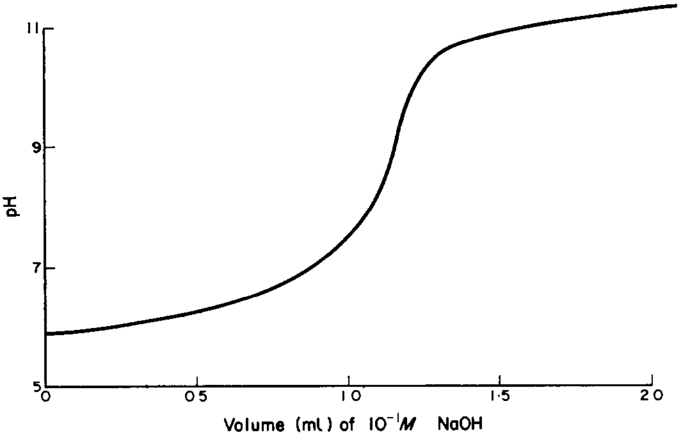

FIG. 4—Potentiometric titration of bromopyrogallol red/1,10-phenanthroline/silver (ratio of reagents was 1:10:2 with 50 ml of $10^{-3}M$ bromopyrogallol red).

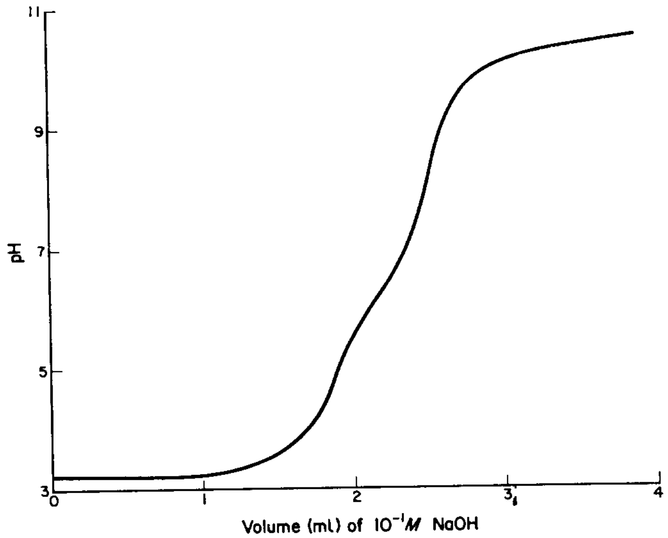

FIG. 5—Potentiometric titration of bromopyrogallol red/silver (ratio of reagents was 1:2 with 50 ml of $10^{-3}M$ bromopyrogallol red).

TABLE II

Method	Molar extinction coefficient (ϵ)
Phen/BPR	51,000 (635 mμ)
Dithizone	30,500 (462–465 mμ)
p-Dimethylamino-benzylidenerhodanine	23,200 (595 mμ)
$\alpha\beta\gamma\delta$-Tetraphenylporphine	39,000 (425 mμ)

The evidence obtained so far indicates either that we are dealing with an ion-association system between BPR^{2-} and [phen-Ag-phen]$^+$ or that the dyestuff BPR is physically adsorbed on the surface of a colloidal bis-1,10-phenanthrolinium-silver(I) salt. On currently accepted theories which explain the mechanism of the indicator action of adsorption indicators, it is readily possible thus to explain the formation of the blue colour-body in these experiments. Also, such an explanation is consistent with the destruction of the colour system by fairly large excesses of indifferent electrolytes, such as potassium nitrate. On the other hand, the stoichiometric ratios observed in the reaction between BPR^{2-} and [phen-Ag-phen]$^+$ tend to support the hypothesis that a stoichiometric compound is formed between the two rather than simple adsorption. It is also possible to explain the breakdown of the colour body by potassium nitrate, for example, on the basis of competition between the anions, NO_3^- and BPR^{2-}, in setting up the ion-association complex. It remains to be explained, however, why the blue colour of the ion-association system is different from that of the yellow-white $Ag(phen)_2^+$ ion and the red BPR^{2-} ion. A possible explanation is that a charge-transfer occurs between the oxidisable silver(I) ion in the [phen-Ag-phen]$^+$ part of the system and the reducible quinoid group in the associated BPR^{2-} molecule. Certainly, the intensity and sharpness of the adsorption band (c) at 630 mμ (Fig. 1) is consistent with this hypothesis.

This argument also raises the interesting speculation that the colour action of many adsorption indicator systems may be explained similarly on the basis of charge transfer mechanisms rather than on the currently accepted adsorption/electronic distortion theory. These matters are being further investigated and will be reported at a later date.

We also propose to continue this investigation with the aim of replacing bromopyrogallol red with alternative dyestuffs, which may offer an increase in sensitivity and may also eliminate the use of masking agents. This may be realised with dyestuffs which do not contain complexing centres, but nevertheless undergo this type of reaction. Work on an extraction system based upon this reaction will be described in a subsequent paper.

EXPERIMENTAL

Preparation of Calibration Curve

Reagents

10^{-5} *M Silver nitrate.* Prepared by dilution of standard 0·1*M* silver nitrate solution.

10^{-3} *M 1,10-Phenanthroline.* 49·56 mg of analytical reagent grade 1,10-phenanthroline dissolved in and diluted to 250 ml with distilled water.

10^{-4} *M Bromopyrogallol red.* 13·96 mg of bromopyrogallol red plus 2·5 g of analytical reagent grade ammonium acetate dissolved in and diluted to 250 ml with distilled water. This solution should be discarded after 5 days.

20% *Ammonium acetate.* 20 g of analytical reagent grade ammonium acetate dissolved in and diluted to 100 ml with distilled water.

10^{-1} *M* EDTA. 3·7225 g of analytical reagent grade disodium salt dissolved in and diluted to 100 ml with distilled water.

Apparatus

Unicam SP 600 spectrophotometer with 4-cm cuvettes.

Procedure

Pipette 1–10 ml of the 10^{-5} *M* silver nitrate solution into 50-ml volumetric flasks containing 1 ml of 10^{-1} *M* EDTA solution, 1 ml of 10^{-3} *M* 1,10-phenanthroline solution, 1 ml of 20% ammonium acetate solution and 2 ml of 10^{-4} *M* bromopyrogallol red solution. Dilute the solutions to 50 ml with distilled water and measure the absorbance immediately, or within 30 min, in 4-cm cuvettes at 635 mμ against a blank, containing all of the reagents except silver.

A plot of absorbance against concentration of silver gives a straight line graph over the range 1–10 μg of silver:

$$1 \text{ ml of } 10^{-5}\, M \text{ AgNO}_3 \equiv 1{\cdot}0787\ \mu\text{g of Ag.}$$

Determinations

Take an aliquot of the silver test solution (1–10 μg of silver in not more than 30–40 ml of solution) through the above procedure. If iron(II) is present, add sufficient 1,10-phenanthroline to complex it completely and to react with the silver and bromopyrogallol red. When uranium(VI), thorium(IV) or niobium(V) is present, add sufficient fluoride (for the first two) or hydrogen peroxide (for the last) to complex it before developing the colour with silver. The silver content is obtained from the calibration curve.

Acknowledgment—We wish to express our thanks to Professor R. Belcher for his interest in and support of this work.

Zusammenfassung—Brompyrogallolrot (BPR) und 1,10-Phenanthrolin (phen) können als Reagentien zur spektralphotometrischen Bestimmung von Silberionen in waßriger Lösung von 0,02–0,20 ppm verwendet werden. Photometrisch und potentiometrisch wurde gezeigt, daß der blaue ternäre Komplex, der bei 635 mμ absorbiert, höchstwahrscheinlich ein Ionenassoziat $[(\text{phen-Ag-phen}^+]_2\ \text{BPR}^{2-}$ ist. Wenn man mit EDTA, Fluorid und Wasserstoffperoxyd maskiert, ist die Farbreaktion auch bei hundertfachem Übershuß von Fremdionen über Silber (24 Kationen und 11 Anionen wurden untersucht) störungsfrei. Nur Gold(III), Cyanid und Thiosulfat störten. Mit einem molaren Extinktionskoeffizienten von 51,000 ist die Farbreaktion wahrscheinlich die empfindlichste aller bekannten kolorimetrischen Silberbestimmungsmethoden.

Résumé—On peut utiliser le rouge de bromopyrogallol (BPR) et la 1,10-phénanthroline (phen) comme système réactif pour le dosage spectrophotométrique des ions argent en solution aqueuse, aux concentrations comprises entre 0,02 et 0,20 p.p.m. Les méthodes photométrique et potentiométrique montrent que le complexe ternaire coloré en bleu, qui absorbe à 635 mμ, est très probablement une association ionique $[(\text{phen-Ag-phen})^+]_2\ \text{BPR}^{2-}$. A des concentrations en ionsgramme 100 fois supérieures à celle de l'argent, 24 cations et 11 anions étudiés n'interfèrent pas dans la réactions colorée, l'EDTA, le fluorure et l'eau oxygénée étant utilisés comme agents dissimulants. On a trouvé que seuls l'or(III), le cyanure et l'hyposulfite interfèrent. Avec un coefficient d'absorption moléculaire de 51,000 cette réaction colorée est probablement la plus sensible de toutes les méthodes colorimétriques connues pour l'argent.

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PRELIMINARY COMMUNICATION

Applications of precipitate membranes in analytical chemistry

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RECENTLY, several analytical procedures have been introduced which are based in some manner on the solubility of precipitates, on exchange reactions taking place with precipitates or on some other properties of precipitates. These include, for example, indirect colorimetric determination of anions with the aid of sparingly soluble metal chloranilates,[1] radiometric titrations using solid precipitate indicators,[2] and procedures involving radioactive precipitate exchange.[3]

However, all of these processes have the common drawback of requiring the separation of a precipitate from solid-liquid (aqueous) phases after the relevant reaction has reached equilibrium. In general, separation is carried out by filtration or centrifuging and the time required for the determination is thereby appreciably lengthened. Furthermore, in attempting to evolve automated techniques, difficulties are encountered when filtration or centrifuging is necessary.

These drawbacks can be eliminated when, instead of transferring the precipitate (which serves as the basis of the conventional method) in the form of a suspension to the solution containing the component to be determined, a precipitate fixed to a carrier is utilised. According to our experiments, chromatographic filter paper lends itself excellently to use as a carrier in that the precipitate is formed between the fibres of the paper. A precipitate membrane prepared in this way is fixed to a suitable framework, then immersed in the solution containing the component to be determined. Membranes of this type can be readily stored in the dry state, and when immersed in a solution, they behave exactly as freshly prepared precipitates. Suitably prepared membranes can be used for a great number of determinations, provided they are rinsed with water after each separate determination. Of the filter papers Whatman 1, Whatman 3, Whatman 4, Schleicher & Schüll 2043 b and Nagel 62 so far tested, Whatman 1 and Schleicher & Schüll 2043 b have proved best suited for the preparation of membranes. On applying such membranes, filtration or separation by centrifuging of the solid-liquid phases becomes superfluous.

In practice, the method is carried out as follows. The precipitate membrane, attached to a suitable framework, is immersed in a solution containing a component to be determined, then the solution is stirred or circulated until the equilibrium of the analytical reaction in question is set up. Subsequently, the extinction or radioactivity of the pure solution is measured.

In our preliminary experiments, the following determinations have been carried out with the aid of precipitate membranes:-

1. Indirect colorimetric determination of sulphate ions with the aid of a precipitate membrane of barium chloranilate.
2. Radiometric titration of calcium ions with EDTA solution as titrant, using a precipitate membrane of $^{110}AgIO_3$.
3. Determination of cyanide ions by radioactive precipitate exchange, using a precipitate membrane of $^{203}Hg(IO_3)_2$.

In all three cases, the results were in good agreement with those obtained by the more conventional techniques. Work is in progress to extend the fields of application of precipitate membranes and to design automatic analysing devices based on the use of precipitate membranes.

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Summary—The need for separation of a precipitate in the indirect colorimetric determination of anions with the aid of sparingly soluble metal chloranilates, in radiometric titrations using solid precipitate indicators and in procedures involving radioactive precipitate exchange, has been eliminated by the use of precipitate membranes.

Zusammenfassung—Bei der indirekten kolorimetrischen Bestimmung von Anionen mittels schwerlöslichen Metall-Chloranilaten, bei radiometrischen Titrationen mit festen gefällten Indikatoren und bei Verfahren mit radioaktivem Austausch in Fällungen wurde die Notwendigkeit, den Niederschlag abzutrennen, durch Gebrauch gefällter Membranen beseitigt.

Résumé—Par l'emploi de membranes de précipité, on a éliminé la nécessité de séparer un précipité lors du dosage colorimétrique indirect d'anions à l'aide de chloranilates métalliques faiblement solubles, lors de dosages radiométriques utilisant des indicateurs à l'état de précipité solide, et lors d'emploi de techniques comprenant un échange radioactif dans un précipité.

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SHORT COMMUNICATIONS

Contributions to the basic problems of complexometry—XVI:* Determination of thorium and scandium in the presence of each other

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Recently we have described the determination of zirconium, thorium and titanium in the presence of each other[1] and the successive determination of thorium, rare earths and some other elements.[2] However, the determination of thorium and scandium in their mixtures has not yet been solved. With EDTA these elements form complexes of the same strength ($pK_{ThY} = 23{\cdot}2$, $pK_{ScY} = 23{\cdot}1$) and their sum can be readily determined. *e.g.*, by direct titration with EDTA at pH 2·5-4 using Xylenol Orange as indicator. Obviously, their separate determination in the same solution is impossible unless a highly selective masking agent for one or the other element can be found and this is unlikely.

During some preliminary experiments we observed an interesting phenomenon in the behaviour of the Th- and Sc-EDTA complexes. Both complexes are quite stable in acidic media (pH 2–4). In solutions of pH higher than 5, however, the Th-EDTA complex again reacts with Xylenol Orange and forms a red-violet colour; the Sc-EDTA complex remains unchanged under these conditions. We deduced that, under given conditions of acidity and in the presence of another complexing agent X, it would be possible to shift the following equilibrium completely to the right

$$\mathrm{ThY} + \mathrm{X} \rightleftharpoons \mathrm{ThX} + \mathrm{Y} \qquad (1)$$

and liberate all of the EDTA bound to the thorium. Our previous experience[2] with the reaction between thorium and TTHA (triethylenetetraminehexa-acetic acid) and DTPA (diethylenetriaminepenta-acetic acid) is in accordance with these findings. The Th-TTHA and Th-DTPA complexes do not undergo a colour reaction with Xylenol Orange at pH 2-6. The use of DTPA cannot be considered for the displacement reaction (1) because, like EDTA, it forms 1:1 complexes and the equilibrium cannot be followed complexometrically by titration of the free X and Y. The situation is quite different if one uses TTHA, which forms 2:1 complexes with bivalent cations in a slightly acidic medium and has already been proposed with advantage as a complexometric reagent.[3] Reaction (1) can then be followed very simply by titration with zinc solution at pH 5-5·5 using Xylenol Orange as indicator. Determination of the liberated EDTA and of the excess TTHA occurs smoothly according to the reactions:

$$\mathrm{EDTA} + \mathrm{Zn} \rightarrow \mathrm{ZnEDTA} \qquad (2)$$

$$\mathrm{TTHA} + 2\mathrm{Zn} \rightarrow \mathrm{Zn_2TTHA} \qquad (3)$$

Suppose that an equivalent amount of TTHA is added to a solution of the Th-EDTA complex. The equilibrium is given by

$$\text{Th-EDTA} + \mathrm{TTHA} \rightarrow \text{Th-TTHA} + \mathrm{EDTA} \qquad (4)$$

If this reaction does not occur at all, the consumption of zinc corresponds to reaction (3); if it occurs quantitatively the consumption of zinc corresponds to reaction (2) and is halved. In the same way one should be able to test the following reaction of scandium

$$\text{Sc-EDTA} + \mathrm{TTHA} \rightarrow \text{Sc-TTHA} + \mathrm{EDTA} \qquad (5)$$

We have now shown experimentally that reaction (5) for scandium does not take place at all, and that reaction (4) for thorium proceeds quantitatively. This difference in behaviour of thorium and scandium enables their complexometric determination to be made in mixtures over a wide range of concentration ratios.

EXPERIMENTAL

Reagents

0·05*M EDTA solution.* Prepared by dissolution of 18·61 g of Chelaton (Lachema, Brno, Czechoslovakia) in 1 litre of redistilled water and standardisation by titration against lead nitrate using Xylenol Orange as indicator.

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* Part XV; see *Talanta*, 1964, **11**, 1319.

0·05*M TTHA solution.* Prepared by dissolution of 24·723 g of the free acid (J. R. Geigy, Basel, Switzerland) in 100–200 ml of 1*M* sodium hydroxide, with warming, then diluting to 1 litre. This solution was also standardised complexometrically.

0·05*M Zinc nitrate solution.* Prepared by dissolution of 14·874 g of $Zn(NO_3)_2 \cdot 6H_2O$ in 1 litre of water.

0·05*M Thorium nitrate solution.* Prepared by dissolution of 27·656 g of $Th(NO_3)_4 \cdot 4H_2O$ in 70 ml of nitric acid (1 + 1) and dilution to 1 litre (1 ml of solution = 11·6025 mg of thorium).

0·05*M Scandium nitrate solution.* Prepared by dissolution of 3·45 g of Sc_2O_3 in 70 ml of nitric acid (1 + 1) and dilution to 1 litre (1 ml of solution = 2·248 mg of scandium).

Buffer solution (pH 3). Prepared by neutralisation of 2*M* monochloracetic acid with aqueous ammonia (1 + 1) under potentiometric control with a glass electrode.

Other reagents include: 1*M* nitric acid, solid urotropine, 0·5% Xylenol Orange.

Procedure

Determination of sum of thorium and scandium. Thorium is readily determined by the well known direct titration with 0·05*M* EDTA at pH 2·5–4 using Xylenol Orange as indicator.[4] Titration of scandium under these conditions gives a somewhat sluggish end-point at room temperature. Therefore, the combined titration of the two elements should be carried out in hot solution (50°). The colour change of the indicator from red-violet to lemon yellow is very sharp.

Determination of thorium. After the above titration with EDTA, add to the hot solution an excess of 0·05*M* TTHA and adjust the pH to 5–5·5 with solid urotropine. Stand for 5 min, stirring occasionally. During this time reaction (4) proceeds quantitatively (even if a large amount of thorium is present). Titrate the excess of TTHA and the liberated EDTA with zinc solution [reactions (2) and (3)].

Calculations

Second titration: 2(ml of 0·05*M* TTHA) − ml of 0·05*M* Zn = ml of 0·05*M* Th.

First titration: ml of 0·05*M* EDTA − ml of 0·05*M* Th = ml of 0·05*M* Sc.

DISCUSSION

Table I shows a number of results using the above procedure for different concentration ratios of thorium and scandium (100:1 and 1:4). The last ratio can hardly be raised. Because of the atomic weights of thorium and scandium the ratio 1:4 appears as 1:20 in the consumption of EDTA. The method can only be applied to pure solutions of thorium and scandium, but these can easily

TABLE I.—DETERMINATION OF THORIUM AND SCANDIUM IN PRESENCE OF EACH OTHER

Taken, *mg*		0·05*M* EDTA consumed, *ml*	0·05*M* TTHA added, *ml*	Back titre with 0·05*M* Zn, *ml*	Found, *mg*		Difference, *mg*	
Th	Sc				Th	Sc	Th	Sc
11·13	2·34	2·11	5·09	9·12	11·23	2·36	+0·10	+0·02
11·13	11·69	6·30	5·09	9·09	11·55	11·71	+0·42	+0·02
11·13	23·30	11·48	2·04	2·98	11·65	23·33	+0·52	−0·07
11·13	46·80	21·95	5·09	9·81[a]	3·93	48·51	−7·20[a]	+1·71
33·29	7·01	6·30	10·18	17·30	32·44	7·06	−0·85	+0·05
55·45	2·34	6·28	10·18	15·03	56·51	2·14	+1·06	−0·20
111·11	2·34	11·55	12·22	14·49[a]	105·49[a]	3·59	−5·62[a]	+1·25
166·56	2·34	16·75	22·40	29·20	165·40	2·58	−1·16	+0·24
16·66	8·66	5·43	5·09	8·57	17·07	8·59	+0·41	−0·07
111·11	23·40	20·99	12·22	14·03	110·38	23·78	−0·73	+0·38
222·22	46·80	41·90	25·43	30·08	220·32	47·47	−1·90	+0·67
11·13	46·80	21·85	5·09	9·05	11·98	46·58	+0·85	−0·22
5·55	23·40	11·08	1·02	1·52	5·55	23·55	0	+0·15
111·11	1·17	11·03	15·27	20·20	109·63	1·55	−0·48	+0·38

[a] Titration with zinc solution carried out immediately after addition of TTHA and adjustment of pH.

be obtained by precipitation of the thorium and scandium from a triethanolamine medium, which separates them from iron, aluminium and other metals.[5]

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Summary—The first titrimetric determination of thorium and scandium in the presence of each other is described. It is based on complexometric determination of their sum with EDTA at pH 2·5–3·5 using Xylenol Orange as indicator. After the addition of an excess of TTHA (triethylenetetraminehexa-acetic acid) and adjustment of the pH to 5–5·5, the following displacement reaction then takes place:

$$\text{Th-EDTA} + \text{TTHA} \rightarrow \text{Th-TTHA} + \text{EDTA}$$

while the Sc-EDTA complex remains unchanged. The liberated EDTA and excess of TTHA are determined by titration with a solution of zinc, which forms 1:1 and 2:1 complexes with EDTA and TTHA, respectively. From the consumption of zinc solution the amount of thorium is calculated.

Zusammenfassung—Die erste Methode zur volumetrischen Bestimmung von Thorium und Scandium wird beschrieben. Zuerst wird die Summe beider komplexometrisch mit EDTA und Xylenolorange bei pH 2,5–3,5 bestimmt. Nach Zugabe eines Überschusses TTHA (Triäthylenstetraminhexaessigsaure) und Einstellung auf pH 5,0–5,5 findet folgende Verdrängungsreaktion statt:

$$\text{Th-EDTA} + \text{TTHA} \rightarrow \text{Th-TTHA} + \text{EDTA}.$$

Der Scandium-EDTA-Komplex reagiert nicht mit TTHA. Die freigesetzte EDTA und der Überschuss von TTHA wird dann mit Zinklösung bestimmt; Zink bildet mit EDTA bzw. TTHA einen 1:1- bzw. 2:1-Komplex. Aus dem Zinkverbrauch wird die Thoriummenge berechnet.

Résumé—On décrit la première méthode de dosage volumétrique du thorium et du scandium. Elle est basée sur le dosage complexométrique de la somme au moyen d·EDTA et de Xylenol Orange á pH 2,5–3,5. Après addition d'un excès de TTHA (acide triéthylènetétramine-*N*, *N*, *N'*, *N"*, *N'''*, *N"*-hexacétique) et adjustment du pH à 5,0–5,5, la réaction de déplacement suivante se produit:

$$\text{Th-EDTA} + \text{TTHA} \rightarrow \text{Th-TTHA} + \text{EDTA}$$

(cependant que le complexe Sc-EDTA ne réagit pas avec TTHA). L'EDTA libéré et l'excès de TTHA sont alors déterminés par dosage avec une solution de zinc, qui forme avec l·EDTA et le TTHA des complexes 1:1 et 2:1 respectivement. On calcule la teneur en thorium à partir de la quantité de solution de zinc consommée.

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The spectrophotometric determination of mercury in selenium

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In the determination of high purity selenium, mercury is an important impurity. At the level of 1 ppm, the precision of the blanks becomes most important. This paper discusses a dithizone[1–5] procedure with low consistent blanks, in which the other impurities, normally found in selenium, are non-interfering.

EXPERIMENTAL

Reagents

Standard mercury solution: 1 μg per ml in 0·5*M* sulphuric acid. Dissolve 0·1354 g of $HgCl_2$ in exactly 1000 ml of 0·5*M* sulphuric acid. Dilute 5 ml of this solution to exactly 500 ml with 0·5*M* sulphuric acid.

Selenium: 99·999% purity.

Dithizone: Chloroform solution (8·0 mg per 500 ml of chloroform). Dissolve 0·160 g of dithizone in 200 ml of chloroform. Dilute a 10-ml aliquot to 500 ml with chloroform.

Buffering and complexing solution: Dissolve 100 g of sodium acetate, 10 g of EDTA and 20 g of sodium thiocyanate in 500 ml of water.

Sulphuric acid: 0·5*M*

Aqueous ammonia:

Procedure

Sample dissolution procedure: Dissolve the sample of selenium in a minimum amount of nitric acid (1 : 1).[6] Transfer the solution to a volumetric flask such that aliquots containing 0·5 g of selenium will be contained in 25 ml or less. If the volume is less than 25 ml, adjust it with water.

To the aliquot of sample, add 20 ml of buffering solution and immediately adjust the pH to 4·5–5·0 with sulphuric acid (0·5*M*). Transfer the solution to separatory funnel *A*, and add 10 ml of the dithizone-chloroform solution. Shake for 2 min and allow the layers to separate. Reserve the lower layer in a second separatory funnel, *B*. Add 10 ml of chloroform to the aqueous layer of separatory funnel *A*, and shake for 0·5 min. Drain the lower layer into separatory funnel *B*. Discard the aqueous layer. To separatory funnel *B* add 50–60 ml of water and 13–15 drops of aqueous ammonia. Extract for 30 sec, allow the layers to separate, and drain the chloroform layer into separatory funnel *A*. Discard the aqueous layer. To separatory funnel *A* add 50–60 ml of water and 13–15 drops of aqueous ammonia. Extract for 30 sec and reserve the chloroform layer in a dry 25-ml volumetric flask. Make to volume with absolute ethanol. Determine the absorbance in a Beckman DU Spectrophotometer in 5-cm cells at a wavelength of 495 mμ.

RESULTS

TABLE I.—PRECISION OF BLANK SOLUTIONS

Blank	Absorption (495 mμ/5 cm) *vs.* water	Deviation from average
1	0·012	0·003
2	0·012	−0·001
3	0·011	−0·002
4	0·012	−0·001
5	0·018	+0·005
6	0·020	+0·007
7	0·011	−0·002
8	0·012	−0·001
	Average = 0·013	Average = ±0·003

[4] J. Körbl, R. Přibil and A. Emr, *Chem. Listy*, 1956, **50**, 1440; *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.
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The spectrophotometric determination of mercury in selenium

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In the determination of high purity selenium, mercury is an important impurity. At the level of 1 ppm, the precision of the blanks becomes most important. This paper discusses a dithizone[1-5] procedure with low consistent blanks, in which the other impurities, normally found in selenium, are non-interfering.

EXPERIMENTAL

Reagents

Standard mercury solution: 1 μg per ml in 0·5M sulphuric acid. Dissolve 0·1354 g of $HgCl_2$ in exactly 1000 ml of 0·5M sulphuric acid. Dilute 5 ml of this solution to exactly 500 ml with 0·5M sulphuric acid.

Selenium: 99·999% purity.

Dithizone: Chloroform solution (8·0 mg per 500 ml of chloroform). Dissolve 0·160 g of dithizone in 200 ml of chloroform. Dilute a 10-ml aliquot to 500 ml with chloroform.

Buffering and complexing solution: Dissolve 100 g of sodium acetate, 10 g of EDTA and 20 g of sodium thiocyanate in 500 ml of water.

Sulphuric acid: 0·5M

Aqueous ammonia:

Procedure

Sample dissolution procedure: Dissolve the sample of selenium in a minimum amount of nitric acid (1 : 1).[6] Transfer the solution to a volumetric flask such that aliquots containing 0·5 g of selenium will be contained in 25 ml or less. If the volume is less than 25 ml, adjust it with water.

To the aliquot of sample, add 20 ml of buffering solution and immediately adjust the pH to 4·5–5·0 with sulphuric acid (0·5M). Transfer the solution to separatory funnel *A*, and add 10 ml of the dithizone-chloroform solution. Shake for 2 min and allow the layers to separate. Reserve the lower layer in a second separatory funnel, *B*. Add 10 ml of chloroform to the aqueous layer of separatory funnel *A*, and shake for 0·5 min. Drain the lower layer into separatory funnel *B*. Discard the aqueous layer. To separatory funnel *B* add 50–60 ml of water and 13–15 drops of aqueous ammonia. Extract for 30 sec, allow the layers to separate, and drain the chloroform layer into separatory funnel *A*. Discard the aqueous layer. To separatory funnel *A* add 50–60 ml of water and 13–15 drops of aqueous ammonia. Extract for 30 sec and reserve the chloroform layer in a dry 25-ml volumetric flask. Make to volume with absolute ethanol. Determine the absorbance in a Beckman DU Spectrophotometer in 5-cm cells at a wavelength of 495 mμ.

RESULTS

TABLE I.—PRECISION OF BLANK SOLUTIONS

Blank	Absorption (495 mμ/5 cm) *vs.* water	Deviation from average
1	0·012	0·003
2	0·012	−0·001
3	0·011	−0·002
4	0·012	−0·001
5	0·018	+0·005
6	0·020	+0·007
7	0·011	−0·002
8	0·012	−0·001
	Average = 0·013	Average = ±0·003

TABLE II.—STANDARD CURVE BY MONO-COLOUR METHOD[7]

Hg, μg	Absorption (495 mμ/5 cm)	Corrected absorption for 0·016 average blank	Absorption/1 μg of Hg
0	0·011 0·012 0·018 0·020 Average 0·016		
5	0·318	0·302	0·0604
	0·320	0·304	0·0608
10	0·610	0·594	0·0594
	0·614	0·598	0·0598
15	0·935	0·919	0·0613
	0·930	0·914	0·0609
			Average = 0·0604
			Factor = 16·7 μg of Hg/1·000

TABLE III.—STANDARD CURVE BY MONO-COLOUR METHOD WITH 0·5 g OF SELENIUM

Hg, μg	Absorption (495 mμ/5cm)	Corrected absorption	Absorption
0	0·054 0·057 0·053 0·054 0·054		
5	0·358	0·304	0·0608
	0·354	0·300	0·0600
10	0·659	0·605	0·0605
	0·654	0·600	0·0600
15	0·968	0·914	0·0609
	0·960	0·906	0·0604
			Average = 0·0603
			Factor = 16·7 μg of Hg/1·000

TABLE IV.—DETERMINATION OF MERCURY IN SELENIUM SAMPLE

Sample	Sample, g	Absorption (495 mμ/5 cm)	Corrected absorption	Hg, μg
		0·012 0·010 0·011		
A	0·500	0·028	0·017	0·28
	0·500	0·025	0·014	0·23
A + 10 μg of Hg	0·500	0·615	0·589[a]	9·83
	0·500	0·612	0·586[a]	9·79
B	0·500	0·028	0·017	0·28
	0·500	0·035	0·024	0·40

[a] Corrected for absorbance of Sample A.

CONCLUSIONS

This procedure seems suitable for the determination of mercury in the low ppm in selenium. There is no interference from the presence of up to 25 μg each of silver, lead, or copper.

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Summary—Microgram quantities of mercury can be determined in the presence of as much as 0·5 g of selenium by a dithizone in chloroform extraction procedure. Common interferences are complexed by EDTA and sodium thiocyanate.

Zusammenfassung—Mikrogrammengen Hg können neben 0,5 g Selen durch Extraktion mit Dithizon in Chloroform bestimmt werden. Häufiger auftrende Störungen werden mit EDTA und Natriumrhodanid maskiert.

Résumé—En présence d'une quantité de sélénium pouvant atteindre 0,5 g, on peut doser des quantités de mercure de l'ordre du microgramme par une méthode d'extraction à la dithizone en chloroforme. Les substances interférentes sont complexées à l'EDTA et au thiocyanate de sodium.

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Radiochemical separation of cobalt by isotopic exchange

(*Received* 29 *May* 1964. *Accepted* 26 *August* 1964)

LANGER[1] in 1942 studied the exchange of silver ions between freshly precipitated silver chloride and an aqueous solution of silver nitrate, using radioactive silver tracer. He found that rapid isotopic exchange takes place between the silver atoms in the precipitate and the silver atoms in the solution. Sunderman and Meinke[2] made use of this fact to develop a rapid single-step, high-decontamination procedure for the separation of trace amounts of radioactive silver from solutions containing other activities. They also applied this technique for the separation of iodine-131[3] and for the preparation of β-ray sources of silver-III.[4]

By the use of isotopic exchange it is possible to devise simple separation procedures, and to shorten the existing radiochemical procedures, without sacrificing specificity or yield. In the present paper, the technique of isotopic exchange has been applied to develop a rapid procedure for the separation of trace amounts of cobalt from aqueous solutions.

If freshly precipitated cobalt(II) oxalate is agitated with an aqueous solution containing radioisotopes of cobalt, a high percentage of radioactive cobalt will, in a short time, exchange with the inactive cobalt in the precipitate. The necessary conditions of the exchange are that the concentration of inactive atoms in the precipitate should be much greater than that in the solution, and that the precipitate should have a low solubility.

CONCLUSIONS

This procedure seems suitable for the determination of mercury in the low ppm in selenium. There is no interference from the presence of up to 25 μg each of silver, lead, or copper.

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Résumé—En présence d'une quantité de sélénium pouvant atteindre 0,5 g, on peut doser des quantités de mercure de l'ordre du microgramme par une méthode d'extraction à la dithizone en chloroforme. Les substances interférentes sont complexées à l'EDTA et au thiocyanate de sodium.

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By the use of isotopic exchange it is possible to devise simple separation procedures, and to shorten the existing radiochemical procedures, without sacrificing specificity or yield. In the present paper, the technique of isotopic exchange has been applied to develop a rapid procedure for the separation of trace amounts of cobalt from aqueous solutions.

If freshly precipitated cobalt(II) oxalate is agitated with an aqueous solution containing radioisotopes of cobalt, a high percentage of radioactive cobalt will, in a short time, exchange with the inactive cobalt in the precipitate. The necessary conditions of the exchange are that the concentration of inactive atoms in the precipitate should be much greater than that in the solution, and that the precipitate should have a low solubility.

The separation technique involves a single isotopic exchange step, and can be represented by the following reaction:

$$CoC_2O_4 + Co^{*2+} \rightleftharpoons Co^{*}C_2O_4 + Co^{2+}$$

where the asterisk denotes the radio-isotope of cobalt.

EXPERIMENTAL

Apparatus

International Clinical Centrifuge

Centrifuge cones: Borosilicate glass, graduated, with cone point, 15 ml.

Planchets: 1-inch diameter cupped stainless steel.

Bottles: One-ounce, flint glass, square narrow mouth bottles with polyethylene screw caps were used for agitating the precipitate during separation. They were clamped in a *mechanical shaker* (Wrist-Action Shaker, Burrell Corp., Pittsburgh, Pa., U.S.A.), to which an extension arm of 9 inches was connected to give additional radial action.

Counters: The γ-ray measurements were made with a Baird-Atomic Model 810B Scintillation well-counter. The β-radioactivity was measured with a Tracerlab Geiger tube TGC-1.

Reagents

Cobalt chloride: May and Baker, analytical-reagent grade.

Oxalic acid: Baker analysed reagent.

Potassium chloride: Baker analysed reagent.

Sodium nitrate: Baker analysed reagent.

All other non-radioactive reagents used in this work were of C.P. or analysed-reagent grade.

All radio-isotopes used as tracers were obtained from The Radiochemical Centre, Amersham, England.

Preparation of cobalt(II) oxalate

Add an excess of 1% oxalic acid solution to a 1% solution of cobalt chloride. Digest the precipitate for 30 min at room temperature, with occasional stirring. Filter, and wash thoroughly with deionised water. Wash with acetone, and dry the precipitate in an oven at 90° for about 30 min.

Isotopic-exchange procedure

Place in a bottle 10 ml of 0·5*M* aqueous oxalic acid solution. Add cobalt-60 tracer (10^4–10^5 cpm), and agitate well to ensure thorough mixing. For contamination studies, add radioactive tracers (10^5–10^6 cpm) of the contaminating ions together with 1 μg of cobalt. Remove a 500-μl aliquot for counting. Add 200 mg of freshly prepared cobalt(II) oxalate precipitate, and shake mechanically for 3 min. Transfer the precipitate to a centrifuge cone. Centrifuge at top speed for a few sec, and remove the supernate. Wash the precipitate thoroughly twice with 1% oxalic acid solution and then with acetone. Count in the scintillation well-counter to determine the chemical yield. The total time for separation is about 6 min.

DISCUSSION AND RESULTS

To investigate the isotopic-exchange behaviour of cobalt, a number of insoluble compounds, *e.g.*, cobalt(II) sulphide, cobalt(II) ammonium phosphate, cobalt(II) oxalate, were agitated in different exchange media containing radioactive cobalt tracer. Yields of 21%, 98% and 85% were obtained for cobalt(II) sulphide, cobalt(II) ammonium phosphate and cobalt(II) oxalate, respectively, when 200 mg of their precipitates were agitated for 5 min in 0·5*M* sodium nitrate solution. Although cobalt(II) ammonium phosphate showed a high exchange, it did not exhibit good selectivity, probably because of the instability of the precipitate. Therefore cobalt(II) oxalate was used in the standard precedure.

To develop an optimum separation procedure, several experiments were performed, in which the agitation time, the amount of the precipitate, and the exchange medium were varied.

Of the various exchange media tried, 0·5*M* oxalic acid, 0·5*M* sodium nitrate, 0·5*M* potassium chloride and 0·5*M* ammonium chloride appeared to be favourable for the exchange, and gave yields of 83·6%, 81·3%, 80·5% and 80·2%, respectively, when 200 mg of the precipitate were agitated for 3 min.

The exchange yield is also dependent on the duration of agitation. A regular increase in exchange yield was observed during a 3-min agitation; after that, the rate of increase was considerably slowed down. Therefore a 3-min agitation was used in the separation. Using 200 mg of the precipitate in 0·5*M* oxalic acid solution, yields of 68·7%, 76·2%, 83·6%, 86·1% and 89·3% were obtained for 1-min, 2-min, 3-min, 5-min and 10-min agitations, respectively.

The recovery of cobalt tracer was studied by using different amounts of cobalt(II) oxalate precipitate. With increase in the amount of the precipitate from 50 mg to 100 mg, 200 mg and 300 mg, the yields were 34·1%, 65%, 83·6% and 85·2%, respectively. Therefore 200 mg of precipitate was chosen as the optimum quantity. A considerable decrease in the yield was observed when the precipitate was kept overnight and then used for the exchange. The best results are obtained with a freshly prepared precipitate but the mode of preparing the precipitate has no effect on the exchange properties.

The optimum separation procedure has been described above; this requires about 6 min for the entire separation, and gives an average yield of 83·6%.

In the interference studies it was observed that the presence of mineral acids or of aqueous ammonia significantly decreases the yield, because they dissolve the precipitate. It is, therefore, necessary that these reagents should be neutralised before the exchange step. Sodium hydroxide and potassium hydroxide, in concentrations below 0·1*M*, do not affect the exchange.

Decontamination

The extent of the separation of cobalt that can be obtained with this procedure was checked by making decontamination studies with tracers of 11 representative elements. (Unfortunately, tracers of Fe, Mn, Ni, and Zr-Nb were not available for this study.) The daughters of the tracers were tested with the parents, because no attempt was made to separate daughters from parents. The results are shown in Table I. Silver and mercury show high contamination, probably because of adsorption of their ions on the cobalt(II) oxalate precipitate. The contaminations from silver, mercury and thallium were reduced considerably when 1 mg of carrier for each of these elements was added to each of the exchange medium; this probably acts as a hold-back carrier, and reduces the adsorption of these ions on the precipitate. Similarly, contamination of other elements may be further reduced by adding mg-amounts of the corresponding carriers. Many elements, however, form insoluble oxalates; precipitation may, therefore, occur when the carrier is added to the exchange medium. In such cases, 0·5*M* sodium nitrate may be used in place of 0·5*M* oxalic acid as the exchange medium.

TABLE I.—SEPARATION OF COBALT AND CONTAMINANTS (ISOTOPIC EXCHANGE PROCEDURE)[a]

Tracer	Weight, μg[b]	Separated, %
Ra-DEF	0·9	0·09
^{131}I[c]	214	0·11
^{137}Cs	21	0·11
^{124}Sb	1·6	0·12
^{106}Ru–^{106}Rh	1·3	0·12
^{90}Sr–^{90}Y	2·1	0·21
^{51}Cr	347	1·1
^{144}Ce–^{144}Pr	13	1·7
^{204}Tl	0·4	3·3
^{204}Tl	1000	0·66
^{203}Hg	11·4	13·2
^{203}Hg	1000	4·1
^{110m}Ag	0·3	20·3
^{110m}Ag	1000	4·9
^{60}Co	0·1	83·6 ± 2·3

[a] Average of at least duplicate runs. Cobalt is average of 7 runs. "Error" is standard deviation.

[b] Weight of inactive element present before separation.

[c] Iodine in its lowest reduced state.

The rapidity of the method makes it suitable for the separation of short-lived isotopes of cobalt. It may be applied to the activation analysis of cobalt, using the short-lived cobalt-60m. The simplicity of the operation involved in this procedure allows it to be adapted to the remote handling of high-radiation levels.

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Summary—The radiochemical separation of cobalt by an isotopic exchange technique has been evaluated for an aqueous $0.5M$ oxalic acid system. The optimised procedure requires 6 min for the entire separation and gives cobalt yields of more than 83%. The specificity of this method was checked with the available tracers of 11 different elements. Mineral acids and aqueous ammonia interfere in the separation. This procedure may find useful applications in the separation of short-lived isotopes of cobalt and is adaptable to remote handling.

Zusammenfassung—Die radiochemische Abtrennung von Kobalt durch Isotopenaustausch wurde für ein wäßriges System mit 0,5 m Oxalsäure untersucht. Unter optimalen Bedingungen dauert die ganze Abtrennung 6 Minuten und gibt Kobaltausbeuten über 83%. Die Spezifität der Methode wurde mit 11 verschiedenen Elementen als Trägern geprüft. Mineralsäuren und Ammoniumhydroxyd stören bei der Trennung. Die Arbeitsvorschrift kann bei der Abtrennung kurzlebiger Kobaltisotope nützliche Anwendungen finden und kann auf Fernbedienung eingerichtet werden.

Résumé—On a étudié la séparation radiochimique du cobalt par une technique d'échange isotopique, dans le cas d'un système aqueux $0{,}5M$ en acide oxalique. La technique mise au point nécessite 6 min pour la séparation totale, et donne des rendements en cobalt supérieurs à 83%. La spécificité de cette méthode a été vérifiée avec 11 éléments traceurs différents. Les acides minéraux et l'ammoniaque interfèrent dans la séparation. Cette technique peut trouver des applications utiles dans la séparation des isotopes du cobalt à courte durée de vie, et elle est adaptable aux manipulations à distance.

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Observations on the atomic absorption spectroscopy of lead in aqueous solution, in organic extracts and in gasoline

(*Received* 27 *July* 1964. *Accepted* 10 *August* 1964)

In theory, atomic absorption spectroscopy affords a simple and rapid method for the analysis of lead in commercially available products such as gasoline.[1] However, our efforts to carry out this determination, using an air-propane flame, produced unaccountable results in this instance. In general, the lead standards (as nitrate and 8-hydroxyquinolate) prepared by us and diluted with the same solvent as tetra-ethyl lead standards were in good agreement with each other, but gave low results for tetra-ethyl lead in gasoline. This observation led us to undertake a detailed investigation of this phenomenon. The effects of extraneous ions, extraction procedures and solvents on the determination of lead by atomic absorption spectroscopy were also investigated.

EXPERIMENTAL

The equipment used in this work was the Hilger and Watts "Uvispek" and atomic absorption attachments.

A calibration curve for lead in aqueous solution in the range 20–145 ppm (absorbance: 0·053–0·372) was prepared using the following instrument conditions: slit width: 0·1 mm; wavelength: 2833 Å; lamp current: *ca.* 18 mA; air pressure: 25 lb/in.^{2}; propane pressure: just insufficient to

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The following aspects of the atomic absorption spectroscopy of lead were then examined.

Lead in aqueous solution

Extraneous ions

Cations. Of those cations investigated at *ca.* a 1000-fold mole excess over lead, *viz.*, Ag^+, Al^{3+}, Ba^{2+}, Be^{2+}, Bi^{3+}, Cd^{2+}, Ce^{3+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, K^+, La^{3+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Sn^{2+}, Sr^{2+}, Tl^+, Th^{4+}, Zn^{2+} and Zr^{4+}, only Al^{3+}, Be^{2+}, Th^{4+} and Zr^{4+} interfered by giving a reduction in absorbance. Be^{2+} interfered because of precipitate formation. The interference of Al^{3+}, Th^{4+} and Zr^{4+} is probably caused by the formation of refractory compounds in the flame with mechanical sequestration of the lead in the solid matrices.

Anions. A similar excess to that for cations was also investigated for the following anions: $B_4O_7^{2-}$, Br^-, Cl^-, ClO_3^-, ClO_4^-, CN^-, SCN^-, CO_3^{2-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, F^-, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, I^-, IO_3^-, MoO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, S^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, VO_3^- and WO_4^{2-}. Those anions which produced precipitates with lead interfered, but the addition of EDTA eliminated this and the subsequent interference. Only PO_4^{3-} and $S_2O_8^{2-}$ continued to interfere by slightly reducing the absorbance.

Organic anions. Of those anions examined at *ca.* a 1000-fold mole excess over lead, *viz.*, acetate, citrate, formate, oxalate, phthalate and tartrate, only formate and phthalate interfered because of the production of precipitates and a subsequent lowering of the absorbance.

Organic solvents (water-miscible). Solutions were examined containing 100 ppm of lead and 10% with respect to the following solvents: acetone, acetic acid, dioxan, ethanol, ethylene glycol, glycerol, methanol, methyl ethyl ketone and isopropyl alcohol. All increased the absorbance because of an increased efficiency of vaporisation, except for ethylene glycol and glycerol which decreased the absorbances because of an increase in the viscosity of the solutions (*cf.* Table I).

Determination of Lead in Organic Media Following Solvent Extraction

Extraction experiments were carried out with the following systems:

Lead 8-hydroxyquinolate in chloroform and isobutyl methyl ketone. Chloroform as a solvent was soon discarded because noxious gases were produced during the combustion and, furthermore, the vaporisation chamber quickly became clogged with solid 8-hydroxyquinoline because of rapid evaporation of chloroform. A far more suitable solvent for atomic absorption work was found to be isobutyl methyl ketone. Lead could be determined over the range 2 to 20 ppm (in the organic phase) by extracting with a 1% solution of 8-hydroxyquinoline in isobutyl methyl ketone (absorbance: 0·014–0·137) over the range pH 7–11. This represents *ca.* a 3-fold increase in sensitivity relative to aqueous solution.

TABLE I.—EFFECT OF 10% CONCENTRATIONS OF WATER-MISCIBLE ORGANIC SOLVENTS ON THE ABSORBANCE OF A 100-ppm SOLUTION OF LEAD

Solvent	Absorbance (2833 Å)
—	0·238
Isopropyl alcohol	0·366
Methyl ethyl ketone	0·352
Acetone	0·328
Acetic acid	0·307
Dioxan	0·294
Ethanol	0·291
Methanol	0·291
Ethylene glycol	0·212
Glycerol	0·190

Lead diethyldithiocarbamate in ethyl acetate. Lead was extracted at pH 7 into ethyl acetate as its diethyldithiocarbamate complex using 1 ml of a 2% aqueous solution of the disodium salt of the reagent. The calibration curve obtained was a straight line, passing through the origin, over the range 1–10 ppm of lead (in the organic phase). This gave *ca.* a 3-fold increase in sensitivity over the extraction system using 8-hydroxyquinoline as reagent in isobutyl methyl ketone. The sensitivities of these two methods are compared with that for aqueous solution in Fig. 1.

These extraction systems were subsequently employed to separate and concentrate lead for its determination in some commercially available products, *e.g.*, analytical reagent grade chemicals, chocolate samples and canned beer, by atomic absorption spectroscopy.

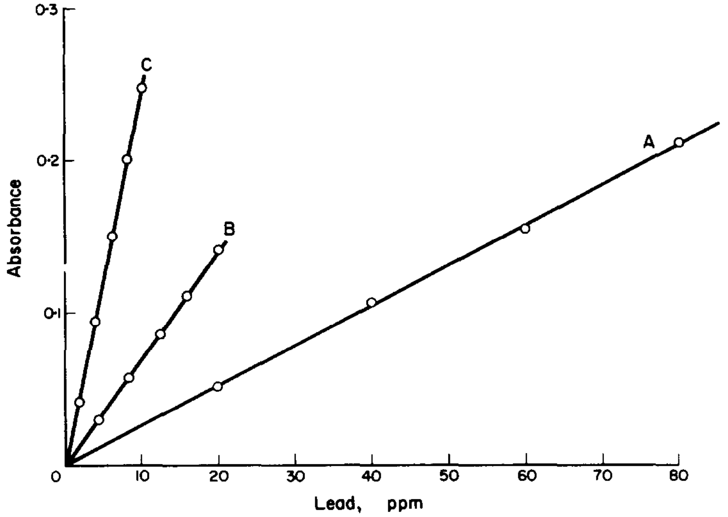

FIG. 1.—Comparative sensitivities of extraction systems at 2833 Å (calibration curves):
(A) lead nitrate in water;
(B) lead 8-hydroxyquinolate in isobutyl methyl ketone;
(C) lead diethyldithiocarbamate in ethyl acetate.

Determination of Lead in Gasoline

Following the success obtained in determining lead in non-aqueous extracts using reagents such as 8-hydroxyquinoline and disodium diethyldithiocarbamate, little difficulty was anticipated in dealing with the determination of lead as tetra-ethyl lead in gasoline. However, this did not prove to be the case.

The first difficulty encountered was the choice of solvent required to dilute the gasoline (iso-octane) samples. Several of these were examined, *e.g.*, ethanol, methyl ethyl ketone, isopropyl alcohol, isobutyl methyl ketone, hexane, iso-octane, but mostly they were either too volatile (hexane and iso-octane), or slowly increasing readings were obtained upon spraying the tetra-ethyl lead samples (tetra-ethyl lead was very difficult to wash out from the burner head with many solvents). The best solvent appeared to be methyl ethyl ketone.

Calibration curves were prepared subsequently from two standard substances, lead nitrate and lead 8-hydroxyquinolate dissolved in methyl ethyl ketone. In each instance 5·18–25·9 ppm of lead gave absorbances of 0·092–0·455. Tetra-ethyl lead diluted with the same solvent gave a straight line calibration curve, but with a 3-fold decrease in absorbance for the same lead content (11·2–67·7 ppm of lead gave absorbances of 0·067–0·402).

A similar series of results was obtained using ethyl acetate as solvent. Standard additions of lead as its nitrate were also made, but the same conclusions were reached, *i.e.*, disagreement between lead nitrate and lead 8-hydroxyquinolate on the one hand and tetra-ethyl lead on the other.

Subsequent experiments revealed that the position of measurement in the flame was a vital factor. When the absorbance measurements were made at progressively higher positions in the flame relative to its base, the absorbance from lead nitrate or 8-hydroxyquinolate in methyl ethyl ketone slowly increased. However, under the same conditions, the absorbance from tetra-ethyl lead in methyl ethyl ketone decreased significantly (Table II).

The lead contents of the lead nitrate and tetra-ethyl lead solutions used in this experiment were the same, *i.e.*, 21 ppm.

Similar results were obtained using other solvents, *e.g.*, isopropyl alcohol.

TABLE II.—EFFECT OF POSITION OF ABSORBANCE PATH IN FLAME IN RELATION TO ABSORBANCE BY LEAD NITRATE AND TETRA-ETHYL LEAD(TEL)
(Pb ≡ 21 ppm)

Position of absorption path in flame	Absorbance (2833 Å) in methyl ethyl ketone	
	$Pb(NO_3)_2$	$(C_2H_5)_4Pb$
Top [most suitable for $Pb(NO_3)_2$ and $Pb(C_9H_6ON)_2$]	0·350	0·130
Middle	0·326	0·156
Base (most suitable for TEL)	0·289	0·203

CONCLUSIONS

The determination of tetra-ethyl lead in gasoline by atomic absorption spectroscopy must be treated with caution. Satisfactory results will only be obtained if the standard solutions are prepared from tetra-ethyl lead. Our experiments on the position of the absorption path in the air-propane flame used in these experiments suggest that this is caused by a different "burn-off" rate or easier atomisation of tetra-ethyl lead compared with lead nitrate or 8-hydroxyquinolate. Consequently, the population of ground state atoms is highest at the base of the flame when tetra-ethyl lead is involved and measurements are best made at this point. The maximum population of ground state atoms of lead is obtained higher up in the flame when less readily atomised compounds of lead are present. It is probable that for the majority of lead compounds the upper regions of an air-propane flame may be preferable for absorption measurements.

In a previously reported method for the determination of lead in gasoline it may be noted that Robinson[1] has used tetra-ethyl lead rather than more conventional lead standards. He used an oxy-hydrogen flame and did not comment on the position of the absorbance path in the flame.

Obviously, there is no reason why this phenomenon should only apply to this particular compound. The so-called "organic solvent" effect[2] may be caused not only by an increase in the throughput of cation-solution vapour,[3] but also by a conversion of the particular cation into a more easily atomised species.

Acknowledgements—Thanks are expressed to D.S.I.R. for provision of the atomic absorption equipment used in this work and to Esso Research Limited for supplying the gasoline samples.

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Summary—The effects of extraneous ions, solvents and flame height on the determination of lead by atomic absorption spectroscopy at 2833 Å have been examined. In order to obtain satisfactory results for lead in gasoline, the standard solutions used in the preparation of the calibration curve must also be prepared from tetra-ethyl lead and the absorbance should be measured near the base of the air-propane flame. There are differences in atomisation efficiency of tetra-ethyl lead compared with lead nitrate or lead 8-hydroxyquinolate dissolved in the same solvent.

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Zusammenfassung—Der Einfluß von Fremdionen, Lösungsmitteln und der Flammenhöhe auf die Bleibestimmung durch atomare Absorptionsspektroskopie bei 2833 Å wurde untersucht. Um zufriedenstellende Bleiwerte in Benzin zu erhalten, müssen die Standardlösungen zur Aufstellung der Eichkurve ebenfalls aus Tetraäthylblei hergestellt und die Extinktion nahe bei der Basis der Luft-Propan-Flamme gemessen werden. Es bestehen Unterschiede in der Ausbeute an Bleiatomen zwischen Tetraäthylblei und Bleinitrat oder Blei-8-hydroxychinolat, auch im selben Lösungsmittel.

Résumé—On a examiné les influences d'ions étrangers, des solvants et de la hauteur de flamme sur le dosage du plomb par spectroscopie d'absorption atomique à 2833 Å. Afin d'obtenir des résultats satisfaisants pour le plomb dans l'essence, les solutions titrées utilisées pour la préparation de la courbe d'étalonnage doivent aussi être préparées à partir de plomb-tétraéthyle, et l'absorption doit être mesurée près de la base de la flamme air-propane. Il y a des différences dans l'efficacité d'atomisation du plomb tétraéthyle, par comparaison avec le nitrate de plomb ou le 8-hydroxyquinolate de plomb dissous dans le même solvant.

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LETTER TO THE EDITOR

The analytical importance of the methoxyl content of *Acacia* gum exudates

SIR,

Methoxyl groups occur frequently in plant gums as 4-methoxyglucuronic acid (*e.g.*, in *Albizzia*[1] and *Khaya*[2] species) or as ester groups (*e.g.*, in *Sterculia*[3] and *Astragalus*[4] gums). To date, however, the possibility of the presence of methoxyl groups in *Acacia* gum exudates appears largely to have been ignored, *e.g.*, in studies of *A. senegal*,[5] *A. pycnantha*,[6] *A. karroo*,[7] *A. cyanophylla*[8] and *A. sundra*,[9] although Stephen reported (without comment) a value of 0·35% for *A. mollissima*,[10] and Hulyalkar *et al.* found no methoxyl content in *A. catechu*.[11]

Recently, Anderson and Herbich observed[12] that the methoxyl content of a number of nodules of the gum from *A. seyal* ranged from 0·7–1·3%, and this has led us to analyse specimens of the gum from 12 further *Acacia* species, not hitherto studied chemically. We have also re-investigated three different specimens of *A. senegal syn. Verek* (gum arabic) and a sample of *A. karroo*. An infrared method,[13] specific for methoxyl groups, was used to analyse purified samples, prepared from authenticated single nodules of each species by electrodialysis so that artifacts arising from solvent retention[14] could not occur (*cf.* ref. 1).

The results shown in Table I indicate that the presence of methoxyl groups in *Acacia* gums is a more general occurrence than hitherto believed. In addition, the range of values found (0·75 to 1·44%) for 9 nodules of *A. nilotica* substantiates recent evidence[12,15] for inter-nodule variation in the composition of plant gums.

The viscosity of samples of gum tragacanth and of pectins is known[16] to be related to their methoxyl content. The limiting flow-time numbers for some of our *Acacia* samples, determined under standardised conditions, are also shown in the Table: a plot of methoxyl content *versus* limiting flow-time number gives a smooth curve.

TABLE I

Acacia species	Methoxyl, %*	Limiting flow-time number†
A. giraffae Burch	2·40	
A. nilotica (L.) Willd. ex Del.	1·14[a]	10·4
A. mellifera (Vahl) Benth.	1·06	
A. seyal Del.	1·02[b]	12·1
A. seyal Del. var. fistula	0·90	
A. arabica (Lam) *Willd.*	0·88	12·5
A. tortilis (Forsk.) *Hayne.*	0·57	
A. mearnsii De Wild.	0·45	
A. campylacantha Hochst. ex A. Rich.	0·42	16·0
A. drepanolobium Harms ex Sjöstedt.	0·40	16·6
A. senegal (L.) *Willd.*	0·36[c]	19·2
A. dealbata Link.	0·35	21·5
A. laeta R. Br. ex Benth.	0·33	23·0
A. nubica Benth.	0·15	
A. karroo Hayne.	0·13	

* Electro-dialysed, freeze-dried samples, corrected for trace residual moisture and ash content.

† In aq. 4% NaCl solution at 25°.

[a] Average of results for 9 nodules (range 0·75–1·44%).

[b] Average of results for 6 nodules (range 0·70–1·30%).

[c] Average of results for 3 nodules (range 0·34–0·37%).

It is therefore suggested that the methoxyl content of *Acacia* gums has some structural significance, and that greater analytical attention should be given to this in future studies. We do not subscribe to the view, recently expressed[17] in a study of gum Jeol, that a methoxyl content of 0·51 % can readily be dismissed as being very low and not structurally significant.

It is of interest that our re-examination of *A. senegal* and *A. karroo* has revealed the presence of methoxyl groups. Re-examination of other species, *e.g.*, *A. pycnantha*, may well provide an explanation for the complex behaviour observed[6] during examination of the aldobiuronic acid fraction.

Acknowledgements—We thank Professor Sir Edmund Hirst, F.R.S. for his interest, and record our indebtedness to (the late) Mr. M. P. Vidal-Hall, Gum Research Officer, El Obeid, and to Dr. Dyer, Botanical Research Institute, Pretoria, for collecting authenticated specimens of *Acacia* gums for our studies. We thank Samuel Jones and Co., Ltd. (Camberwell); James Laing, Son and Co., Ltd. (Manchester); Rowntree and Co., Ltd. (York); and the Director of Forests, Sudanese Government, for financial support.

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PUBLISHER'S NOTICE

Owing to pressure of other work, Professor C. L. WILSON is relinquishing his office as Editor-in-Chief of *Talanta* at the end of 1964. We owe him a great debt of gratitude for his work over seven years, especially in establishing the journal. Fortunately, it has been possible to maintain Professor Wilson's association with Talanta, for he is to continue as a Consulting Editor. His successor as Editor-in-Chief will be the current Associate Editor, Dr. M. WILLIAMS. Papers not normally submitted through a Regional Editor should now be sent to Dr. M. WILLIAMS, Department of Chemistry, College of Advanced Technology, Gosta Green, Birmingham 4, England.

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TALANTA REVIEW*

RECENT USES OF LIQUID ION EXCHANGERS IN INORGANIC ANALYSIS

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Summary—A review of recent uses of liquid ion exchangers in inorganic analysis is presented.

INTRODUCTION

Separations using liquid ion exchange may be said to date from the publication, in 1948, of a paper by Smith and Page[1] entitled "The Acid-Binding Properties of Long-Chain Aliphatic Amines". Since then, increasing interest has been shown in the use, as extractants, of those high molecular weight acids and bases which possess low solubility in water and high solubility in water-immiscible solvents.

The operation of liquid ion exchangers involves selective transfer of solute between two immiscible phases, an aqueous phase and an organic phase containing the liquid exchanger. The technique for liquid ion exchange separation is, therefore, identical to that employed in general solvent extraction separations. From the very first, liquid ion exchange has been compared with resinous ion-exchange because the behaviour of analogous functional groups in the two systems is frequently similar. From this similarity, by reference to available data on extractions with ion-exchange resins, it is possible to make a reasonable prediction of the likely course of the corresponding liquid ion-exchange extractions. Liquid ion exchangers may be employed in a similar manner to resinous exchangers except that, although the course of the reaction may involve 'salt-splitting', the ultimate products will not be acids or bases, as may be obtained with solid resins. They may be employed for the extraction of acids and bases, when the extraction from aqueous solution is by a neutralisation process to form a salt which is soluble in the organic solvent but insoluble in water, *e.g.*, $RNH + HX \rightarrow RNH_2X$. Alternatively, the same liquid exchangers may be used in the salt form when ions may be exchanged with those in the aqueous solution, *e.g.*, $RNH_2Cl + NaNO_3 \rightleftharpoons RNH_2NO_3 + NaCl$. This is, of course, a reversible reaction and when the organic phase contains the amine chloride a strong solution of sodium nitrate will strip the amine of chloride ions, while if amine nitrate in the organic phase is treated with a strong solution of sodium chloride the amine is stripped of nitrate ions. Regeneration of the appropriate amine salt is accomplished in these cases, and if the amine salt is treated with an alkaline solution, such as aqueous ammonia, sodium hydroxide or sodium carbonate, the free amine is obtained. Similar considerations apply in the case of cation exchangers, where regeneration can be achieved using suitable acid solutions. Selectivity is obtained when using liquid ion-exchangers by the usual means—control of pH and salt concentration, adjustment of valency, addition of complexing agents and probably most important of all choice of organic diluent.

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* For reprints of this Review see Publisher's Announcement at the end of this issue.

It will be seen that liquid ion exchangers combine many of the advantages of both solvent extraction and ion exchange. There are, however, a number of difficulties and disadvantages associated with their use, and an appreciation of these is essential if the full advantage of the combination of solvent extraction and ion exchange is to be obtained. The major difficulty is associated with the formation of emulsions between the organic and aqueous phases, making separation difficult and on some occasions impossible. The relative viscosities and densities of the two phases are of major importance here and, because liquid exchangers usually possess some surface activity, it is necessary to select those having a low activity and to use those conditions which will minimise the formation of stable emulsions. Such conditions are control of temperature, choice of acid and amount of free acid in the aqueous phase, organic diluent for the exchanger, relative volumes of organic and aqueous phases and concentration of the exchanger in the organic phase; the addition of 2–3% of a higher alcohol to the organic phase has proved effective in preventing emulsion formation in some cases.

The expense associated with the use of organic liquids for solvent extractions is not usually of major importance in laboratory applications, but organic solvents can be dangerous if care is not taken in handling and storage, and the exchangers themselves may constitute a certain hazard. For example, in the case of the aliphatic amines used as anion exchangers, the manufacturers point out that although the volatility is low, it is very important, particularly before dilution, to provide adequate ventilation to prevent inhalation of the vapours. Every precaution should be taken to avoid contact with the eyes or prolonged contact with the skin.

It is advisable to keep apparatus used for liquid ion-exchange extractions separate from that used for normal solvent extraction because separating funnels, in particular, are difficult to render completely free from the exchangers. If this is not possible, treatment with a solution containing 5 g of ammonium fluoride and 5 ml of hydrochloric acid in 100 ml of water followed by 10% sodium carbonate solution is usually an effective method of cleaning the glassware.

Another disadvantage in the use of liquid ion exchangers is the fact that, unlike many of the common solvent extraction separations, it is usually necessary to back-extract the required species from the organic phase to complete the determination. It is sometimes possible to use the organic phase directly for determination of the extracted ion or ions, *e.g.*, by aspirating directly into a flame and measuring by means of flame photometry or atomic absorption spectroscopy;[17] by employing a cellulose column impregnated with the liquid exchanger,[2] when metal ions may be recovered on ashing the cellulose and exchanger. If radioactive materials are under investigation, direct measurement of the activity present in the organic phase is possible. Back-extraction procedures can be very tedious where successive extractions are involved, because the organic layer is usually chosen to be the lower layer, when the extraction is being made, for ease of separation; if this layer has to be back-extracted manipulation is much more difficult. Before liquid ion exchange becomes as popular a method of separation as solvent extraction procedures have become, it will be necessary for simple techniques to be devised which utilise the organic phase directly. This is one of the great assets when employing normal solvent extraction methods.

Compared with resinous ion exchange the use of liquid ion exchangers offers a much more rapid method of separation of the required ionic species. In its normal method of use a liquid exchanger is closely similar to a solid resinous exchanger used in the 'batch analysis' technique. It does not, as yet, offer the same range of potential separations. For example, it is not possible to employ the technique of 'frontal analysis' in the same way as with solid resins except by the use of cellulose columns impregnated with the liquid exchanger referred to earlier. This does make possible the use of selected elution and it is claimed that the elution peaks are very narrow, but the preparation of the column appears to be a much longer process than the preparation of resin columns and the advantages accruing are rather marginal.

A comprehensive list of liquid ion exchangers has been given by Coleman, Blake and Brown,[3] but many of those listed have not been extensively used in analysis, and the exchangers mentioned here are those which have become generally accepted as the major materials for carrying out liquid ion exchange. Attention is also directed to a paper by Kunin and Winger.[4] Because of these authors' association with the Rohm and Haas Company, who manufacture Amberlite ion-exchange materials, the information given is invaluable as an introduction to the use of liquid ion-exchange materials.

Much of the earlier work up to 1960, covering extraction with liquid anion exchangers, has been reported by Moore.[5] The section in the present review dealing with liquid anion-exchangers is intended to cover the more important published work since then, with particular reference to the analysis of the more commonly encountered inorganic materials.

In order to prevent this review from becoming excessive in length, work carried out on the transuranic elements has not been included. Papers presented at the 1962 Conference on Solvent Extraction at Gatlinburg, U.S.A., many of which are now in the open literature,[6] effectively review the position regarding these elements.

LIQUID ANION EXCHANGERS

Liquid anion exchangers, at present available, are based on primary, secondary and tertiary aliphatic amines. They are of high molecular weight, water insoluble but soluble in many organic solvents, such as petroleum distillates, aliphatic and aromatic hydrocarbons, high molecular weight alcohols and chlorinated hydrocarbons. For laboratory separations only a small number of the amines which are commercially available have so far been examined and recommended for particular applications and of these the Amberlite exchangers have received by far the greatest attention. The important relevant properties of Amberlite LA.1 [*N*-dodecenyl(trialkylmethyl)amine] and Amberlite LA.2 [*N*-lauryl(trialkylmethyl)amine], both secondary amines, are summarised in Table I.

TABLE I.—SUMMARY OF RELEVANT PROPERTIES OF AMBERLITE EXCHANGERS LA.1 AND LA.2

Property	Amberlite LA.1	Amberlite LA.2
Molecular weight	351–393	353–395
Neutral equivalent	380–410	360–380
Acid binding capacity,		
mequiv/g	2·5–2·7	2·6–2·8
mequiv/ml	2·1–2·3	2·2–2·3
Density (25°), *g/ml*	0·84	0·83
Viscosity (25°), *cp*	72	18
Flash point, *°C*	*ca.* 105°	*ca.* 180°

These exchangers are usually employed at solution strengths varying from 2 to 20% in an inert organic solvent and, as may be expected, the capacity for ion exchange of a particular exchanger, for the same anion, is directly proportional to its concentration in the organic phase. Figures given by the manufacturers for Amberlite LA.1 show that, using kerosene as diluent, 1 litre of 0·05*M* amine has a capacity for $U_3O_8^{2-}$ ions of 1·78 g, while a 0·1*M* solution of amine has a capacity of 3·56 g and a 0·25*M* solution a capacity of 8·88 g/litre. A difference in capacity for ion exchange is exhibited for different ions. Table II shows how this capacity varies with the anion in question for Amberlite LA.1 and LA.2 when 0·1*M* solutions of the exchanger in kerosene are equilibrated with an equal volume of 0·1*M* acid in water. These extraction figures can be improved upon by the addition of a salt, such as sodium chloride, nitrate, sulphate, acetate or tartrate as appropriate, to increase the anion concentration.

TABLE II.—EXTRACTION OF ANIONS[a] BY AMBERLITE LA.1 AND LA.2

Acid	Extraction, %	
	Amberlite LA.1	Amberlite LA.2
Hydrochloric	77·3	88·6
Nitric	85·3	94·4
Sulphuric	74·5	88·0
Acetic	2·7	8·9
Tartaric	1	44

[a] In the form of the free acid.

Several metals form anionic complexes in solutions of mineral acids and it is possible to extract many of these complexes using anion exchangers. Such metals include niobium, tantalum, chromium, zirconium, zinc, uranium, titanium, vanadium and tin, while the anionic complexes may contain radicals such as sulphate, nitrate, oxalate, chloride or fluoride. Figure 1 shows the effect of variation in free sulphuric acid

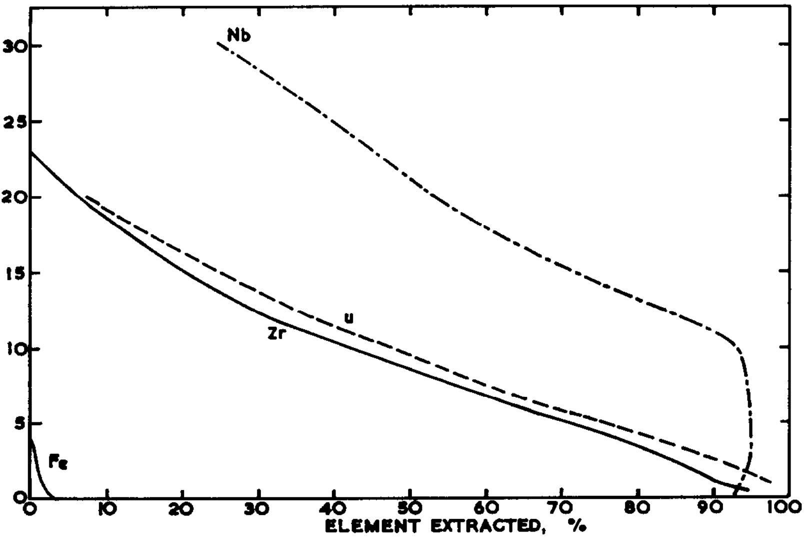

FIG. 1.—Typical curves for liquid ion-exchange extractions.
(Extractions made from sulphuric acid media using a 2:1 ratio of aqueous/organic phases and 4% of Amberlite LA.1 in chloroform[7,8,9].)

content of solution on degree of extraction of some metals as anionic sulphate complexes. Each extraction was made from a 100-ml volume of solution containing 0·02 g of the element and sulphuric acid only, except in the case of niobium when 0·1 g of oxalic acid was also present to prevent hydrolysis and precipitation of the hydrated pentoxide. Only one extraction was made in each case using 50 ml of 4% Amberlite LA.1 in chloroform. Iron(III) is seen to extract only slightly using sulphuric acid media and even then only at very low free acid contents. Zirconium and uranium give very similar extractions to one another, the degree of extraction increasing as the acid concentration decreases. Two extractions with 50-ml volumes of the exchanger at the 1–2% of free sulphuric acid level will then give virtually 100% extraction of both metals. Niobium extraction is appreciable even at the 30% of free sulphuric acid concentration, and from a 5% acid solution two extractions again give a virtual 100% removal.

Under similar conditions, Green[8] has shown that titanium and vanadium do not extract from sulphuric acid solutions alone using Amberlite LA.1. In fact, at the lower sulphuric acid concentrations titanium is hydrolysed. If sufficient fluoride ion is added to the solution of titanium containing 5% of free sulphuric acid to convert the titanium sulphate to titanium fluoride, then 95% of the titanium may be extracted with one 50-ml volume of the exchanger and virtually 100% using two 50-ml volumes. Vanadium gives only a partial and variable extraction in the presence of fluoride. When hydrogen peroxide is used in conjunction with the 5% sulphuric acid solution, 65–70% of the titanium is extracted with one 50-ml volume and 90–95% with two volumes of exchanger. Vanadium extraction is about 30% with one 50-ml volume of exchanger and about 50% with two volumes.

Conditions for the extraction of a number of metal ions from hydrochloric acid solutions, using a 10% solution of Amberlite LA.1 in xylene, have been investigated by Nakagawa.[10,11] A summary of his results is given in Table III. The range of

TABLE III.—EXTRACTIONS USING 10% AMBERLITE LA.1 IN XYLENE

Element	Optimum HCl range, *M*	Extent of extraction,[a] %
Cadmium(II)	2–6	95
Chromium(VI)	1–6	Almost quantitative[b]
Chromium(III)	—	Negligible
Copper(II)	7	35
Gallium(III)	>4	Quantitative
Germanium(IV)	8–11	Almost quantitative
Indium(III)	7	86
Iron(III)	6	Quantitative
Lead(II)	1·5	40
Manganese(II)	1–10	<12
Mercury(II)	1–8	Quantitative
Selenium(IV)	>9	Almost quantitative
Tellurium(IV)	4–6	Quantitative
Tin(IV)	5–6	Almost quantitative
Titanium(IV)	—	No extraction
Vanadium(V)	6–8	90[b]
Vanadium(IV)	—	No extraction

[a] One extraction.

[b] Reduction of V^{5+} to V^{4+} and of Cr^{6+} to Cr^{3+} occurs in solutions more than 6*M* in HCl.

hydrochloric acid concentration given in the table for each element is that over which maximum extraction occurs; outside this optimum range, extraction for any particular element may still be appreciable. Cadmium can be extracted from hydrochloric acid solutions as low as 0·1*M*, with maximum extraction at 2–6*M* and decreasing extraction with increased acid concentration to become 23% in concentrated acid. Tervalent chromium shows negligible extraction but sexivalent chromium gives almost quantitative extraction from solutions 1–6*M* in hydrochloric acid. More concentrated acid tends to reduce the chromium and lower the amount extracted. Back-extraction of the chromium from the organic phase only required that the aqueous phase contained a reducing agent, such as iron(II) sulphate or hydroxylamine hydrochloride.

Copper extracts from hydrochloric acid solutions greater than 3*M* with a maximum extraction of 35% from 7*M* acid. Extraction of germanium commences from 4*M* acid, becoming almost quantitative between 8 and 11*M*. The extraction of indium increases from 12% in 1*M* hydrochloric acid to 86% in 7*M*, decreasing again with increase in acid concentration to 20% in concentrated acid. Lead shows maximum extraction from 1·5*M* acid, decreasing to nothing at 10*M*. Tellurium is quantitatively extracted from hydrochloric acid solutions between 4 and 6*M* and was readily back-extracted with 0·5*M* acid. The extraction of tin commences at 0·5*M* hydrochloric and increases with increase in acid concentration, reaching a maximum between 5 and 6*M*, then decreasing above 6*M* acid; back-extraction using 1*M* nitric acid is recommended, dilute hydrochloric and sulphuric acids being stated as unsuitable. Quadrivalent vanadium does not extract from hydrochloric acid solutions, whereas up to 90% of quinquevalent vanadium may be extracted from 6*M* acid. When the acid concentration is greater than 6*M*, reduction of the vanadium occurs and extraction decreases.

Using Amberlite LA.1 as a 10% solution in kerosene, Nakagawa[12,13] has investigated the extraction of iron(III), nickel, cobalt, zinc, aluminium, titanium, arsenic, antimony and bismuth from hydrochloric acid solution. A summary of his results is given in Table IV.

TABLE IV.—EXTRACTIONS USING 10% AMBERLITE LA.1 IN KEROSENE

Element	Optimum HCl range, *M*	Extent of extraction, %
Aluminium(III)	—	Negligible
Arsenic(III)	8–11	92
Arsenic(V)	—	No extraction
Antimony(III)	1–4	Almost quantitative
Antimony(V)	>6	Quantitative
Bismuth(III)	0·3	Quantitative
Cobalt(II)	8	35
Iron(III)	6–10	Quantitative
Nickel(II)	—	No extraction
Titanium(IV)	12	10
Zinc(II)	2–3	90

Tervalent arsenic extracts from solutions greater than 4*M* in hydrochloric acid, a maximum extraction of 92% occurring in 8–11*M* acid. Tervalent antimony is almost quantitatively extracted from 1–4*M* acid solutions, extraction decreasing with increase in hydrochloric acid concentration. The extraction of quinquevalent antimony is, however, facilitated by an increase in acid concentration and only becomes quantitative from solutions greater than 6*M*. Bismuth extraction is complete from 0·3*M* acid; increasing the hydrochloric acid concentration results in decreasing extraction until at $10M$ acid no extraction occurs. It is recommended that tervalent antimony and bismuth be back-extracted using $0{\cdot}5M$ citric acid, and quinquevalent antimony with $1M$ sodium hydroxide, but not with mineral acids. Cobalt extraction starts from solutions more than $5M$ in acid, but maximum extraction at $8M$ acid is only about 35% complete. No extraction of titanium occurs from solutions below $8M$ in acid and only about 10% from concentrated hydrochloric acid solutions. Zinc extraction is maximum at 2–$3M$ acid, decreasing with increase in acid concentration.

The extraction data given by Nakagawa provide an excellent example of the parallelism which exists between liquid and resinous ion exchangers. The reader can qualitatively extend the data given in Tables III and IV by reference to the more comprehensive work on anion exchange in chloride media by Kraus and coworkers.[56]

Amberlite LA.1 has been used by Ishibashi and Komaki[14] for the determination of zinc in aluminium alloys. The zinc, present at about the 5-mg level, is extracted into a 15% solution of Amberlite LA.1 in kerosene from $6M$ hydrochloric acid. The procedure is to dissolve the sample in $6M$ hydrochloric acid and hydrogen peroxide, then extract the zinc with Amberlite LA.1/kerosene. The zinc is back-extracted into the aqueous phase using $0{\cdot}3M$ nitric acid, the solution made ammoniacal and triethanolamine and potassium cyanide added to mask iron and copper. Finally, the zinc is demasked using formaldehyde and titrated with standard EDTA.

For the determination of zirconium in cast iron, Green[15] employed a 4% solution of Amberlite LA.1 in chloroform. The precedure here is to dissolve the sample in sulphuric acid in the presence of a small amount of sodium fluoride. After mercury cathode separation, hydrogen peroxide is added and zirconium extracted with Amberlite LA.1/chloroform. The zirconium is back-extracted with hydrochloric acid and finally reacted with Pyrocatechol Violet for spectrophotometric measurement. Titanium and vanadium will be partially extracted by the exchanger under these conditions and a correction has to be applied if either or both are present.

Using the same exchanger, 4% of Amberlite LA.1 in chloroform, Green[16] has determined uranium in cast iron. The sample is dissolved in sulphuric acid solution and extracted directly with the ion exchanger. Under the conditions used, apart from the uranium, any niobium, tantalum and zirconium present will be extracted, along with a small quantity of iron. Back-extraction of the organic phase with sodium carbonate results in precipitation of these elements, while the uranium is extracted as the water-soluble uranyl-carbonate complex, $UO_2(CO_3)_3^{4-}$. After filtration, the uranium in the filtrate is reacted with hydrogen peroxide to yield the yellow peroxy complex, which is measured spectrophotometrically.

The use of Amberlite LA.1 has been described for the determination of zinc in bauxite.[17] Fifty ml of a 25% solution of the exchanger in xylene can be used to extract up to 5 mg of zinc from 1-g samples of bauxite. Despite the high concentration of exchanger, the organic phase can be fed directly to the burner of a Perkin-Elmer 214 atomic absorption spectrophotometer to complete the determination.

In an investigation into the separation and determination of chromium sesquioxide in chrome ores and refractories, Bennett and Marshall[18] used both Amberlite LA.1 and LA.2. The extraction of chromium from sulphuric acid solution, as the dichromate ion, increased with increasing acid concentration. However, at higher acid concentrations, increasing reduction of the sexivalent chromium took place. Because

Amberlite LA.2 is the more basic of the two exchangers and shows less tendency to emulsify, it was chosen for use in the final method. For decomposition of the sample a fusion is made using 7 g of anhydrous sodium carbonate and 2·5 g of boric acid with 0·5 g of sample. The cooled melt is extracted with dilute sulphuric acid and dilute aqueous ammonia added until a faint permanent precipitate forms. This precipitate is just dissolved by addition of dilute sulphuric acid and the solution extracted using a 10% solution of Amberlite LA.2 in chloroform. After two 25-ml extractions with the exchanger, further sulphuric acid is added to the aqueous phase and a third extraction made with 25 ml of exchanger. The extracts are combined and back-extracted using $1M$ potassium hydroxide. After acidification and reduction with sulphite, the chromium is reacted with EDTA and the determination completed by spectrophotometric measurement of the violet complex at 550 mμ. Under these conditions, other constituents of chrome ores and refractories, such as iron, titanium, manganese and silicon, are in no way affected by the ion-exchange separation and the aqueous phase can be used for their determination after being washed with chloroform.

The behaviour of tin(IV) and lead ions in extraction from hydrochloric acid solutions with a xylene solution of Amberlite LA.2 has been studied by Nakagawa.[19] Tin(IV) can be extracted from hydrochloric acid solutions between 5 and $9M$ up to 98%; lead extraction is about 40% from $2M$ acid, decreasing rapidly with increasing acid concentration to become negligible at concentrations above $8M$. A method for the separation of tin and lead was suggested in which the solution of the metal ions is adjusted to between 7 and $8M$ in hydrochloric acid. Two extractions are made using a 10% solution of Amberlite LA.2. The combined organic phases are then washed with fresh 7–$8M$ hydrochloric acid to remove traces of lead, and the tin returned to the aqueous phase by stripping with three consecutive volumes of $0{\cdot}5M$ nitric acid.

Hirano, Mizuike and Iida[20] have employed Amberlite LA.2 as a 10% solution in xylene for the determination of traces of cadmium in thorium compounds. The sample, containing about 10 g of thorium, is dissolved in hydrochloric acid and sodium fluoride solution, evaporated almost to dryness after addition of nitric acid, then taken up with 5 ml of concentrated hydrochloric acid and 35 ml of water. The cadmium in the solution is extracted with two 10-ml volumes of the exchanger. The combined extracts are washed twice with small volumes of $1M$ hydrochloric acid to remove iron and the cadmium back-extracted using two 5-ml volumes of $2M$ nitric acid. The cadmium in the extract is then determined polarographically. It is claimed that the separation can be applied to cadmium determinations as low as 0·01 ppm with a relative error of less than 10%.

Unpublished work, reported to the author,[59] shows that macro quantities of lead may be extracted using a 20% solution of Amberlite LA.2 in hexone. From a 100-ml volume of solution containing the equivalent of 0·13 g of PbO, 5 ml of concentrated hydrochloric acid and 1·5 g of potassium iodide, two extractions with the exchanger followed by one extraction with hexone alone will achieve a lead extraction of over 99%. The concentration of acid and iodide appears to be rather critical. Presumably, other metal iodides, such as those of tin, antimony, bismuth and cadmium, could be extracted under similar conditions.

Although the Amberlite exchangers have received the widest attention, other amines have proved of great value for certain separations. It has been shown by

Baeckmann and Glemser,[21] using a solution of a tertiary amine such as tribenzylamine (TBA) in chloroform, that it is possible to separate iron(III) chloride from elements which do not form anionic chloro complexes, such as aluminium, silicon, zirconium, titanium, hafnium, thorium, niobium, tantalum, nickel and alkali and alkaline earth metal ions. The extraction is made from 5*M* hydrochloric acid solution using a 0·2*M* solution of TBA in chloroform, when a quantitative separation can be achieved. The iron may be back-extracted into the aqueous phase using hydrochloric acid solutions less than 0·5*M*.

The separation of niobium and tantalum has been achieved by Ellenburg, Leddicotte and Moore,[22] using TBA in chloroform. Niobium can be extracted easily with equal volumes of aqueous and organic phases, whereas tantalum extraction was minimal. The extraction of niobium is dependent on the concentration of TBA in the organic phase—the distribution coefficient rising from 0·20 using 1·25% TBA to 74·4 using 8% TBA. The corresponding values for tantalum are 0·003 and 0·002, respectively. The concentration of acid is quite critical. Using 8% TBA in chloroform, practically no extraction occurs below 8*M* hydrochloric acid. At 9*M* acid the Kd value is 5·05 for niobium and 0·0013 for tantalum; from 11*M* hydrochloric acid the Kd values are 74·4 and 0·0025, respectively. When methylene chloride is used instead of chloroform the extraction is even better, niobium giving a Kd of 80·5 and tantalum 0·0023 from 11*M* hydrochloric acid. The reason for the success of the separation achieved under these conditions is explained by 'the extraction of niobium as an oxychloride complex of the type $H(NbOCl_4)$ or $H_2(NbOCl_5)$, while neither chlorotantalates nor oxychloride complexes of tantalum are presumed to exist in aqueous solution'. The investigation was extended to extraction from sulphuric acid solutions. Quantitative separation of tantalum and niobium is possible from 4·5*M* acid solution. The acid concentration is stated to be very critical. Both niobium and tantalum are extracted from oxalic acid solutions using TBA in chloroform and methylene chloride; on the other hand, if the solvent is changed to benzene, toluene, xylene or carbon tetrachloride, no extraction of either metal takes place.

Using a 5% solution of methyldioctylamine (MDOA) in xylene, Leddicotte and Moore[23] showed that niobium and tantalum could be separated satisfactorily. The radioactive isotopes ^{95}Nb and ^{182}Ta were used in the investigation. From hydrochloric acid solutions the extraction of tantalum is only 0·25% at 3*M* acid concentration, rising to only 1·4% in concentrated acid. With niobium, on the other hand, extraction is 2·4% at 3*M* hydrochloric acid with the percentage extraction increasing rapidly above 6*M* acid to reach over 99% at 8*M*. From nitric acid solutions neither niobium nor tantalum extracts appreciably up to 10·6*M*; from sulphuric acid solution up to 12*M* very little niobium extracts, but tantalum extraction is appreciable at 2*M* sulphuric acid, decreasing with increase in acid concentration.

Following the investigation into these separations for tantalum and niobium using MDOA and TBA, Mahlman, Leddicotte and Moore[24] examined the extraction of chromium, manganese, iron, nickel, copper, zinc and cobalt. In each case the course of the extraction was followed by using radioactive materials. From aqueous hydrochloric acid solutions using an 8% solution of MDOA in trichloroethylene, chromium extraction is only about 2%, and nickel less than 1%, irrespective of the acid concentration from 0·1 to 10*M*. Very little manganese is extracted below 5*M* hydrochloric acid and only 32% from 10*M*. Iron extraction becomes appreciable above about

0·5*M* and reaches a maximum at 94/95% between 4 and 5*M* acid, remaining at more than 90% even in 10*M* hydrochloric acid. Cobalt extraction is less than 2% in 3*M* acid, rising rapidly to 85% in 10*M* acid. Zinc, on the other hand, extracts readily from 0·5*M* acid, with quantitative extraction occurring from 2 to 10*M* acid. When chloroform is substituted for the trichloroethylene, cobalt does not extract until 8*M* acid, while zinc gives a maximum extraction of 85% at 3*M* acid. When the organic diluent is changed to xylene, cobalt extraction does not reach 2% until 4*M* hydrochloric acid, and is only 21% in 10*M* acid. Zinc again shows maximum extraction in 3*M* acid—over 99%, with over 95% extraction taking place from all solutions between 1 and 10*M*. When TBA is used in place of MDOA, maximum zinc extraction of 72% again occurs at 3*M* acid with negligible cobalt extraction occurring below 6*M* acid.

Other amines which have been used by a number of workers are tri-iso-octylamine and tri-n-octylamine. Marchart and Hecht[25] have examined the extraction behaviour of tantalum and niobium with tri-iso-octylamine from various acids and acid mixtures. The distribution coefficient is dependent on the acid concentration and on the nature of the complexing agent used. A method is given for the separation of the two metals from nitric/hydrofluoric acid solution.

The distribution of septivalent rhenium between nitric acid solutions and tri-iso-octylamine has been investigated by Kertes and Beck.[26] Variation in the rhenium molarity in the organic phase shows that the species extracted is free perrhenic acid, $HReO_4$.

Using tri-iso-octylamine hydrochloride, Lorenzini, Stoppa and Barbieri[27] separated gram-quantities of uranium from solutions of 8*M* hydrochloric acid before the spectrographic determination of the rare earth elements. A 6-g sample of uranium metal is dissolved in 50 ml of 8*M* hydrochloric acid and extracted with five 100-ml portions of 0·3*M* tri-iso-octylamine hydrochloride in a xylene/octanol mixture (19:1). Any iron present is extracted with the uranium.

White, Kelly and Li[28] have converted tri-n-octylamine (TOA) to its hydrochloric and perchloric salts before an investigation into the chloride complexes of iron(III) and indium(III). The tertiary amine is dissolved in benzene and equilibrated with equal volumes of 1*M* hydrochloric and perchloric acid to convert it to the appropriate salt. The amine itself is a light yellow colour; its hydrochloride and perchlorate salts in benzene are light yellow and slightly pink, respectively. The investigation was made using the radioactive materials ^{59}Fe and ^{114}In; the aqueous phase contained the metal ion in a concentration of the order of $10^{-7}M$ and varying concentrations of hydrochloric acid and/or perchloric acid. The organic phase contained the TOA salt in benzene and in each case was equilibrated with an equal volume of the aqueous phase to be used, without the radioisotope. Equal volumes of aqueous and organic phases were shaken for a number of hours at 25 ± 0·5°, then allowed to settle for 1 hr before measurement of the radioactivity of each phase. No extraction of iron or indium occurs from perchloric acid solutions less than 2*M* with no chloride present, indicating that the perchlorate ion does not form anionic complexes with either iron or indium in the organic phase. The distribution coefficient (defined as the concentration of metal ions in the organic phase divided by the concentration of metal ions in the aqueous phase) for both iron and indium are second power dependent on the

TOA/hydrochloric acid concentration in the benzene phase, indicating that the negatively charged complexes $FeCl_5^{2-}$ and $InCl_5^{2-}$ are formed in the organic phase.

The distribution of sulphuric acid between water and a benzene solution of TOA and tri-n-hexylamine (THA) has been investigated by Verstegen and Ketelaar.[29] Assuming that the organic activities of the amine salts, $(TOAH)_2SO_4$ and $(THAH)_2SO_4$, are equal to concentrations, then the law of mass action describes the equilibrium until the amine salt exceeds a certain value. The heat and entropy of the formation of $(TOAH)_2SO_4$ have been calculated and the equilibrium leading to the formation of $(THAH)_2SO_4$ studied at 25°. Finally, the relative basic strengths of tertiary amines, on the basis of infrared measurements of the proton-accepting properties, are discussed. It is emphasised by the authors that the results obtained using infrared measurements may only be interpreted as showing a certain trend because of small variation in the proton-accepting property. Furthermore, it is certainly not the only point governing the relative basicity of the amines.

An extensive investigation[30] has been made into the extraction of uranium from aqueous sulphate solutions by long-chain aliphatic primary, secondary and tertiary amines in various organic diluents. Tertiary amines have a remarkable preference for uranium over the other elements normally found in uranium leach liquors. Only molybdenum is extracted to any great extent. The extraction coefficients for uranium from sulphate solutions at a pH of about 1 are directly proportional to the concentration of the amine in the organic phase (see figures quoted earlier for Amberlite LA.1). At the same time, the extraction coefficients are dependent on temperature, pH, sulphate concentration and concentration of other anions in the aqueous phase. The back-extraction of uranium can be accomplished using dilute hydrochloric acid, sodium carbonate, sodium hydroxide or aqueous solutions. Using aqueous ammonia, the uranium is precipitated as it is returned to the aqueous phase. Again, there is a close parallel with the studies on ion exchange, such as those reported by Burstall *et al.*[58]

The tertiary amine didodecenyl-n-butylamine (Amberlite XE-204) has not been investigated to a great extent. However, Dono, Nakagawa and Wada[31] have employed it for the separation of micro amounts of nickel in cobalt. Approximately 95% of the cobalt can be extracted from an 8*M* hydrochloric acid solution, but nickel does not extract from hydrochloric solutions of any concentration.

Direct spectrophotometric determinations after liquid anion-exchange

Using a 1% solution of TBA in chloroform, Fasolo, Malvano and Massaglia[32] have extracted chromium(VI) from 1*M* hydrochloric acid solutions. The chloroform extracts can be measured spectrophotometrically to obtain the chromium content. Maximum absorption occurs at 355 and 458 $m\mu$. Only gold (100%), antimony (>90%) and mercury (>95%) give appreciable extraction under the conditions used. Negligible extraction (<1%) occurs for copper, cobalt, nickel, zinc, iron, chromium, manganese, cadmium, arsenic, uranium, cerium, molybdenum, rare earths and alkaline earths.

Direct spectrophotometric determination of the green cobalt complex in the organic phase, after extraction of cobalt thiocyanate using a 20% of TOA in carbon tetrachloride, is reported by Selmer-Olsen.[33] The absorption curve shows two maxima (340 and 627·5 $m\mu$). Bivalent manganese, nickel and zinc give no colour in the organic layer and do not interfere, while iron gives an absorption maximum at 475 mμ and practically no absorption at 627·5 mμ. It is, therefore, possible to determine small amounts of iron and cobalt in the presence of each other.

LIQUID CATION EXCHANGERS

Coleman, Blake and Brown[3] listed 24 liquid cation-exchange materials, but to-date only two of these have been used to any extent. These are di-(2-ethylhexyl)orthophosphoric acid (D2EHPA, DEHPA or HDEHP) and dinonylnaphthalene sulphonic acid (DNS).

DNS is obtained from the manufacturers as an approximately 48% solution in n-heptane, and is a mixture of isomers resulting from the sulphonation of dinonylnaphthalene, the dinonylnaphthalene being made by controlled alkylation of naphthalene with nonene. It is a monobasic acid with only slight solubility in water but readily soluble in many organic solvents. White, Tang and Li[34] analysed the material by extraction of a known volume of the solution in heptane with standard potassium hydroxide solution, followed by titration of the aqueous phase with standard hydrochloric acid. Kaufman and Singleterry[35] have demonstrated micelle formation by DNS in moist benzene, and White *et al.*[34] inferred from this 'that DNS in moist heptane may also exist as the polymer, $(\mathrm{DNS})_x$.'

The behaviour of DNS as a liquid cation exchanger has been examined by White, Tang and Li.[34] Using ^{60}Co, ^{54}Mn, ^{59}Fe, ^{114}In and ^{65}Zn as radioactive tracers, extractions were made from an aqueous phase, containing the metal radioisotope at a concentration of $10^{-6}M$, into a heptane solution of DNS in concentrations of the order of 10^{-3} to $10^{-4}F$. The heptane/DNS reagent was shaken for a number of hours with an equal volume of $0{\cdot}1M$ perchloric acid before use. Extractions were made using equal volumes of aqueous and organic phases of Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{3+} and In^{3+} as the perchlorates with a varying concentration of perchloric acid to obtain the desired pH, at a temperature of 25 ± 0·5°. After shaking for a number of hours, the two phases were allowed to settle for 1 hr and the activity of the metal ion in each phase measured.

The results show that the distribution coefficients of the bivalent and tervalent ions are inversely second power and third power, respectively, dependent on the pH of the aqueous phase and first power dependent on the DNS concentration of the heptane phase. At the same time, experiments were made to determine the formation constants of the indium(III) complexes of glycolate and bioxalate and the cobalt(II) complex of bioxalate. The formation constants obtained using DNS agree with the values obtained using a resinous cation exchanger.

The stability constants of the iron(III) and indium(III) chloride complexes were investigated by White, Kelly and Li[28] using DNS and radioisotopes ^{59}Fe and ^{114}In. Using metal ion concentrations of about $10^{-7}M$ and varying concentrations of hydrochloric and/or perchloric acid, extractions were carried out using equal volumes of aqueous and organic phases. In each case the organic phase was pre-equilibrated with an equal volume of the aqueous phase to be used, without the radioisotope. The total hydrogen ion concentration in each experiment was kept constant while the ratio of hydrochloric and perchloric acids varied. The solutions were shaken at 25 ± 0·5° for a number of hours, then allowed to settle for 1 hr before measuring the radioactivity of each phase.

A table is given showing the decrease in distribution coefficient for iron(III) with increase in hydrochloric acid concentration and corresponding decrease in perchloric acid concentration to maintain the total acid at 1*M*. The Kd value at 1*M* perchloric acid is 3·01 and on subsequent substitution of hydrochloric acid for the perchloric acid the Kd value becomes 0·65 at 0·8*M* hydrochloric acid/0·2*M* perchloric acid. By assuming that there is no complexing of M^{3+} and ClO_4^-, the stability constant for the reaction $M^{3+} + Cl^- \rightarrow MCl^{2+}$ was calculated by the method of White *et al.*[34] Good agreement was found for iron between the stability constants determined using DNS and the values in the literature obtained spectrophotometrically. The stability constant of the $FeCl^{2+}$ complex at ionic strengths varying from 0·2 to 1·0 is independent of whether H^+ or Na^+ is the cation associated with the perchlorate ion. With the indium(III) complex, the substitution of Na^+ for H^+ as the cation associated with the perchlorate ion decreases the value of the stability constant.

D2EHPA has been employed by McHenry and Posey[36] for the separation of strontium-90 and calcium. Calcium is extracted into the organic phase while the strontium remains in the aqueous phase to an extent greater than 95%. The effects of the addition of acetic acid, alcohol and 2-ethylhexanol on the recovery of calcium and strontium and on their distribution coefficients were investigated.

Using the same reagent, Butler and Ketchen[37] separated cerium-144 and yttrium-91 from other rare earth fission products, producing a highly pure ^{144}Ce in good yield. The extractions were made from nitric acid solution containing citric acid and the cerium was oxidised to the quadrivalent state with permanganate before extraction.

Using a D2EHPA solution in toluene, Peppard *et al.*[38] employed fractionation extraction of the lanthanides and yttrium from solutions containing various anions—nitrate, chloride and sulphate. The extracted lanthanide species do not contain any of the anion associated with the lanthanide in the original solution. Once this was established the rest of the investigations were carried out from hydrochloric acid solutions. Using radioisotopes it was found that, under the experimental conditions used, the distribution coefficients are directly third power dependent on the concentration of D2EHPA in the organic phase and inversely third power dependent on the hydrogen ion concentration of the aqueous phase. A further paper by Peppard *et al.*[39] examined the relative effectiveness of mono- and di-orthophosphoric esters for the extraction of the rare earths.

Using a 4% solution of D2EHPA in toluene, Arden[40] has determined the radioisotope ^{95}Zr in fission products. These products are allowed to cool for a minimum period of 15 days, then taken into solution with mineral acids, such as nitric, hydrochloric and sulphuric. A suitable aliquot of the solution is taken, such that the activity will not be less than 200 cpm. Niobium, iron and iodine carriers are added, together with hydrogen peroxide, and the solution is extracted with carbon tetrachloride. The organic phase containing any radio-iodine is discarded and the aqueous phase extracted with the toluene/D2EHPA. The aqueous phase is then discarded and the organic phase is extracted with potassium thiocyanate solution to remove any radio-iron. The organic phase, which contains the radio-zirconium, is then counted using a γ-scintillation counter.

The determination of total radio-strontium in milk using D2EHPA in toluene has been described by Butler.[41] The major problem in the analysis of milk for total radio-strontium is the removal of the large quantities of calcium that are present before counting. Using a 20% solution of D2EHPA in toluene, calcium is removed from hydrochloric acid solution by one extraction at pH 3·6–3·8, followed by a second extraction at pH 2·6–2·8, using equal volumes of aqueous and organic phases. These extracts are discarded and the strontium extracted at pH 4·8–5·0. The strontium is then back-extracted from the organic phase using 3*M* nitric acid and after suitable treatment the β-count of the strontium determined.

At a Symposium on Solvent Extraction Chemistry held at Gatlinburg, U.S.A., in 1962, a series of papers covering the theory and use of D2EHPA as an ion-exchanger was presented. A number of these papers have now been published in the open literature.[6] The reader who is about to use this reagent for the first time is recommended to consult these papers in view of the valuable information they contain.

At the same Symposium a paper on extraction with sulphur-containing organophosphorus compounds was presented by Handley.[42] Both mono- and di-substituted sulphur derivatives of the alkylphosphoric acids were investigated. In general, these new reagents extract from mineral acid solutions those metal ions which form insoluble sulphides. Because of their stability and wide range of acid tolerance it may be possible to use these reagents for many purposes where at the present time xanthates and diethyldithiocarbamates are employed.

CHROMATOGRAPHIC SEPARATIONS USING LIQUID ION EXCHANGERS

Chromatographic separations of a number of cations by means of paper treated with liquid ion exchangers have been reported by Testa and Cerrai. In the first report[43] the paper was treated with a 0·2*M* solution of TOA. Paper treated with TOA behaves very much like a film of anionic resin: it retains the chloride, nitrate and sulphate complexes of the various elements in accordance with the strength of the complex itself. The cations were used in concentrations of 20–50 μg in hydrochloric acid solution for each spot and development was carried out with appropriate reagents, such as potassium thiocyanate for iron(III), dimethylglyoxime for nickel and 8-hydroxyquinoline for cobalt. Using circular chromatography and 4*M* hydrochloric acid for elution, these three ions can be separated satisfactorily. Nickel follows the solvent front (R_f 0·97) because it is not complexed by hydrochloric acid and hence not retained by the amine. Cobalt is partially complexed and gives an R_f value of 0·50, while iron is completely complexed (R_f 0) and is retained in the original spot by the amine. Similarly, using 10*M* hydrochloric acid, uranium (R_f 0), zirconium (R_f 0·35) and thorium (R_f 0·95) can be separated or uranium, zirconium and titanium (R_f 0·85). Many other separations are possible using hydrochloric acid of suitable strengths. These include iron(III), copper and aluminium using 1*M* acid; uranium, vanadium and titanium using 3*M* acid; zinc and manganese using 3*M* acid; zinc, cobalt and manganese using 4*M* acid; zinc, manganese and nickel using 10*M* acid. Separation of zirconium (R_f 0·25) and hafnium (R_f 0·80) is made using 8*M* hydrochloric acid plus 5% concentrated nitric acid. When a 0·2*M* sulphuric acid solution is used, uranium and nickel can be separated from iron and copper, and using 0·5*M* sulphuric acid separation of molybdenum from iron, copper and nickel is possible.

Descending chromatography was used for the separation of some cation mixtures, such as zinc, cobalt and manganese, uranium, zirconium, thorium, vanadium and titanium. By judical selection of the strength of hydrochloric acid for elution, satisfactory separations were made of these mixtures.

The second report[44] dealt with the separation of uranium, thorium and lanthanum. In this case the chromatographic paper was treated with benzene solutions of various concentrations of TOA and elution was made using nitric acid, lithium nitrate, sodium nitrate, ammonium nitrate, calcium nitrate and aluminium nitrate. Lanthanum is not retained by the amine and so moved with the solvent front, while thorium and uranium form well defined spots. Lowering the TOA concentration on the paper effects a considerable increase in the R_f values of both thorium and uranium. Increasing the strength of the nitrate solution for elution decreases the R_f values for all three cations.

A third report[2] examined the use of TOA-cellulose in chemical separations. Whatman No. 1 cellulose powder was impregnated with $0{\cdot}1M$ TOA in benzene and then heated for 2 hr at 85° to volatilise the benzene solvent. The treated cellulose was crushed in a mortar, then packed into a column, fitted at the bottom with a fritted glass disc. This column was then used in a similar manner to a column of ion-exchange resin. Nickel, cobalt and iron can be separated by elution with hydrochloric acid, similarly, thorium, zirconium and uranium. The authors admit that the exchange capacity of this type of column is only 25–30% of that of the common resin but claim a number of advantages:

(1) Because of the white colour of the column the position and movement of coloured zones can be easily followed.
(2) Because the active functional groups are concentrated at the surface of the powder grains and the grain size is very small, the column has a high ability to fix large molecules, which often cannot penetrate the complex structure of anionic resins.
(3) Very narrow elution peaks are obtained.
(4) When working with radioactive tracers the column can be easily burned and the residue conveniently obtained for radioactive counting; the resins are less easily burned.

The chromatographic separation of the rare earths using paper treated with TOA and elution with lithium nitrate has been studied by Testa.[45] Previously reported work suggested that the rare earth elements formed anionic complexes in a concentrated solution of an alkaline nitrate. Based on this, Testa determined the R_f values for a number of rare earth elements, for various concentrations of lithium nitrate as eluting solution, using chromatographic paper treated with $0{\cdot}2M$ TOA in benzene. From these R_f values a number of separations of the rare earth elements was shown to be possible. The R_f values obtained increase on adding nitric acid to the lithium nitrate for elution, indicating that the presence of free nitric acid lowers the formation of the complex. The spots from the various elements were developed by means of a 1% solution of 8-hydroxyquinoline in 1:1 water/alcohol. On exposure of the paper strips to ammonia vapour the spots became clearly visible.

A further study of Cerrai and Testa[46] involved the separation of the rare earth elements on chromatographic paper treated with a $0{\cdot}1M$ solution of D2EHPA in cyclohexane. The R_f values for 9 rare earths (lanthanum, cerium, praseodymium, samarium, europium, gadolinium, dysprosium, erbium, ytterbium) and 7 additional elements (yttrium, scandium, thorium, uranium, zirconium, iron, aluminium) as functions of the molarity of the hydrochloric acid elutriant are given. The spots were developed using a 1% solution of 8-hydroxyquinoline in 1:1 water/alcohol solution. A relationship was established between the quantity log $(1/R_f - 1)$ and (1) the atomic number of the element, (2) the molarity of the acid used as elutriant, (3) the molarity of the solution with which the paper is treated; and (4) the operating temperatures. Under the same conditions, the R_f values increase as the atomic number decreases. For a given element, the R_f value increases with the strength of the acid used for elution and with the operating temperature, and it decreases with the concentration of D2EHPA on the paper. Examples are given of the chromatographic separation of the rare earth elements from each other and from the other 7 elements mentioned previously.

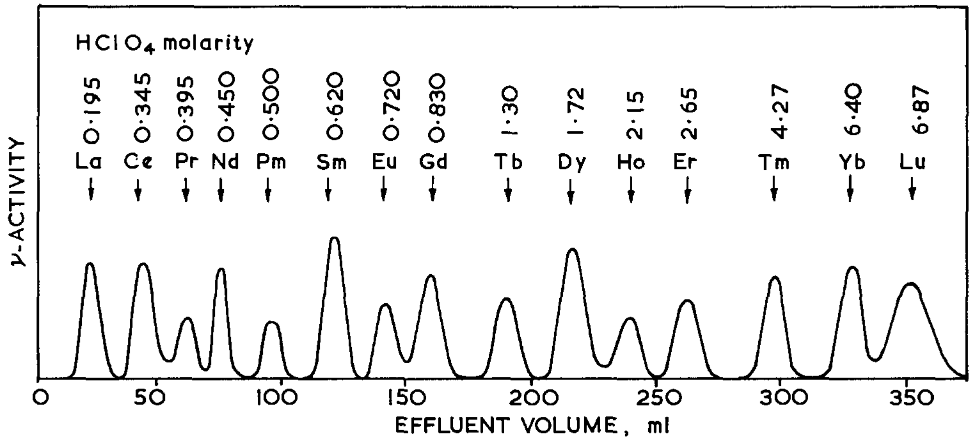

FIG. 2.—Separation of the rare earths by gradient elution from a Corvic/HDEHP column.[47]
(Reproduced by courtesy of Macmillan & Co. Ltd.)

The chromatographic separation of the rare earth elements using D2EHPA and reverse-phase partition chromatography has been described by Pierce *et al.*[47,48,49] A chromatographic column impregnated with D2EHPA was prepared using poly-(vinyl chloride/vinyl acetate) copolymer ('Corvic', Imperial Chemical Industries Ltd.) as supporting medium. Ten g of the copolymer (100–150 mesh) were mixed with 10 ml of solution containing 5 ml of chloroform plus 3 ml of toluene plus 2 ml of D2EHPA. The organic solvent was evaporated off and the resulting powder slurried in 0·002*M* perchloric acid and made into a column of the required size. The temperature of the column was thermostatically controlled at 60° and a flow rate of 2·0 ml.cm^{-2}.min^{-1} used throughout the experiments. It was shown that the separation of the rare earth element is possible using elution with perchloric acid. Separation of certain combinations of the rare earths, such as cerium with praseodymium and europium with gadolinium, proved difficult when perchloric acid of constant strength was employed for elution. Gradient elution using perchloric acid of gradually increasing strength is very successful in separating the rare earth series, the elements being eluted successively in the order of increasing atomic number. In order to check the separations, radioactive earths were used in dilute perchloric acid solution and the effluent from the column was passed through a γ-scintillation flow counter. The elution peaks were identified using a γ-spectroscope and the acidity of the eluate at the peak maxima was determined by titration with standard alkali. Fig. 2 illustrates the results obtained using gradient elution for separation of the rare earths on a Corvic/D2EHPA column.

Sastri and Rao[50] have described the use of paper impregnated with DNS for chromatographic separations. The paper was treated with a $0{\cdot}1M$ solution of DNS in n-heptane and the solvent removed by blowing hot air. The chromatograms were obtained using the ascending technique and the solvent front was allowed to move through a distance of 18 cm. More than 20 metal ions were examined using nitric and hydrochloric acids as elutriants at strengths between 0·1 and $1{\cdot}0M$. The R_f values increase with increase in the strength of the acid used to elute, and the R_f values for hydrochloric acid are somewhat greater than for nitric acid. The values obtained are in agreement with those expected from the cation-exchange mechanism. A number of separations were shown to be possible, *e.g.*, aluminium and beryllium; copper and cadmium; iron, titanium and vanadium; indium, gallium and zinc; calcium, barium and magnesium; in each case using $0{\cdot}25M$ hydrochloric acid.

NEUTRAL CO-REAGENTS

Reagents such as tri-n-butylphosphate and tri-n-octylphosphine oxide have been classed as 'neutral co-reagents' by Coleman *et al.*[3] They are frequently used for extraction of metal ions from aqueous solution. It is not the intention of this review to cover the use of these extractants. The reader is referred to the summary of much of the earlier work carried out with neutral co-reagents by Morrison and Freiser[51] and a more recent review by White and Ross.[52]

MISCELLANEOUS

The determination of amines and alkylphosphates in kerosene solutions, used for the extraction of uranium, has been reported by Ashbrook.[53] For the determination of an amine the kerosene is shaken with calcium hydroxide, when the sulphuric acid present is precipitated as calcium sulphate and the uranium absorbed on the calcium hydroxide. The solids are then removed by filtration and the amine determined in the filtrate by titration. If alkylphosphates are present it is necessary to extract the uranium first with 20% sulphuric acid, then to shake the kerosene with calcium acetate. The amine is titrated in chloroform solution with a dioxan solution of perchloric acid using Thymol Blue as indicator. For the determination of an alkylphosphate the kerosene is shaken with sodium methoxide. This precipitates the sulphuric acid as sodium sulphate, which is insoluble in chloroform. Excess methoxide is back-titrated with perchloric acid to the blue/yellow end-point (pH 8·9) of Thymol Blue. The titration with perchloric acid is then continued to the yellow/red end-point of the indicator (pH 1·7). At this stage both amine and alkylphosphate are titrated, and the difference between this volume of perchloric acid and that used to titrate the amine alone is equivalent to the amount of alkylphosphoric acid.

Damodaran[54] has recently found that a chloroform solution of tetra-n-hexylammonium iodide will extract the highly coloured anion $[Co(NH_3)_2(NO_2)_4]^-$ of Erdmann's salt, to give a deeply coloured liquid anion exchanger. Such a solution had been used to study exchange equilibria for a number of anions. Typical results are

(a) $F^- < Cl^- < Br^- < I^-$,

(b) $Cl^- < ClO_3^- < ClO_4^-$,

(c) $BF_4^- < ClO_4^- < IO_4^- < ReO_4^- < MnO_4^-$.

Anions such as SO_4^{2-} and PO_4^{2-}, which carried more than unit charge, are not extracted at all. The concentration of erdmannate ion displaced into the aqueous phase by the competing anion can be determined spectrophotometrically and so used for indirect determination of the anion in question.

The determination of perchlorate ion using this indirect technique with the erdmannate ion has been described by Clifford and Irving.[55] Interference of many other ions is overcome by pretreatment of the solution with silver sulphate. The interference of chlorate can be serious; when the ratio of ClO_3^- to ClO_4^- is 10:1 the error is 5%, and at a ratio of 100:1 it is about 35%. The error can be reduced by reduction of the chlorate ion to chloride using sulphurous acid or iron(II) sulphate. If the necessary constants are known a suitable correction for the chlorate ion can be calculated.

The use of reagents of the Erdmann or Morland $[Co(NH_3)_2(SCN)_4]^-$ type opens up some interesting possibilities and will undoubtedly extend the use of liquid anion exchange.

FUTURE OF LIQUID ION EXCHANGERS

It is not because of low potentiality that liquid ion exchangers have not been accorded the attention of other extraction systems. As already pointed out, the use of liquid ion-exchange extraction dates from 1948, compared to, say, resinous ion exchange, which may be said to have started in 1935 with the discovery by Adams and Holmes of the ion-exchange properties of certain synthetic resins.[57]

The reasons for the lack of attention to liquid ion exchangers are not easily defined. Partly the cause may be lack of knowledge of the fundamental principles of the technique, and partly the belief that extractions with such materials are only an extension of normal solvent extraction processes and not a separate technique at all. The tendency for emulsion formation between the aqueous and organic phases may be a contributory cause, again because of lack of basic knowledge to enable this to be avoided. In most cases the need for stripping the organic extract to complete the analysis, compared with the ease with which the extracts from chelate extractions may be utilised directly for spectrophotometric measurement, has undoubtedly contributed to lack of interest in their use. On the other hand, the rapidity with which the ion-exchange process is completed using liquid exchangers, instead of resinous exchangers, does not appear to have been of such wide interest to the users of ion exchange as might have been expected. This is probably because many analytical separations using resinous exchangers are made by the techniques of 'selective elution' or 'frontal analysis'.

What then is needed to make the technique of liquid ion exchange acceptable to more analysts?

1. Greater basic knowledge of the principles involved.
2. Some means of assessing the relative 'strengths' of the exchangers.
3. Investigations into the change in extraction properties of the exchangers which occurs when the organic diluent is changed.
4. Greater selectivity in separations, *e.g.*, by choice of a suitable exchanger for the particular separation or by a suitable selective back-extraction technique.
5. Easier ways of employing the organic phase directly for determination of the extracted ions.

The possibilities of liquid ion exchangers are slowly becoming apparent as analytical methods employing these materials are published. Bennett and Marshall[18] pointed out the tedious nature of the current methods for the analysis of chrome ores and chrome-bearing materials and the discrepancies which can occur between laboratories analysing these materials. By employing liquid ion exchange the time taken in analysis was reduced appreciably and reproducibility improved.

Green[16] showed that liquid ion exchange could be made to work directly for the separation of uranium in cast iron without prior separation stages other than removal of the graphitic carbon. Selectivity was achieved without the use of complexing agents or close control of pH.

In their work on chromatographic separations, Cerrai and Testa[2,43,44] and Pierce *et al.*[47,48,49] have demonstrated that the often difficult separation of rare earth mixtures can be achieved quite readily using paper cellulose treated with liquid ion exchangers, while Damodaran,[54] Clifford and Irving[55] and Handley[42] have shown that the field of liquid ion exchange separations may become very much wider.

In radiochemical analysis, the fact that the activity of the organic phase may be measured directly shows a distinct advantage over the use of resin exchangers, where the particular isotopes have first to be eluted, then their activity measured.

Zusammenfassung—Eine Übersicht über neuere Anwendungen flüssiger Ionenaustauscher in der anorganischen Analyse wird vorgelegt.

Résumé—On présente une revue sur les emplois récents des échangeurs d'ions liquides en analyse inorganique.

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DETERMINATION OF LOW CONCENTRATIONS OF ACETALDEHYDE IN ETHYLENE OXIDE

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Summary—The method is based on a qualitative test for acetaldehyde in which the reagents sodium nitroprusside and piperidine react with acetaldehyde to form a coloured substance that can be determined photometrically. This substance is unstable, however, and after reaching a maximum value in about 25 sec the absorbance decreases. Ethylene oxide also reacts with sodium nitroprusside to form brownish substances, but this reaction is slower, the colour not developing for 100–120 sec. If, therefore, the absorbance is measured about 25 sec after adding the reagents, any disturbance from the ethylene oxide is avoided.

INTRODUCTION

THE determination of impurities in ethylene oxide is complicated by its low boiling point and by its reactivity with a large number of substances, there being few reagents that do not produce disturbing side reactions. Gas chromatography and direct spectrophotometry can be applied for acetaldehyde concentrations down to about 20 μmole/ml, but it is necessary to be able to determine concentrations as low as 0.2 μmole/ml. The following photometric method has been worked out for this purpose.

PRINCIPLES

Sodium nitroprusside reacts with a number of substances to form coloured compounds. It also reacts with an aqueous solution of acetaldehyde in the presence of an organic base such as piperidine.[1,2] The mechanism of the reaction of sodium nitroprusside with acetaldehyde has been discussed by Williams.[3] The reaction was described for the first time by Simon,[4] and its use has since been reported in several papers.[5-9] The base used was piperazine. The reaction has been used as a qualitative test for acetaldehyde in water.[4] The resulting colour, which is bluish-red, attains its maximum intensity after 20–30 sec, and then quickly decreases, to be replaced after about 1 min by the same golden brown colour as is obtained from a blank. A method based on the sodium nitroprusside reaction with an aqueous solution of acetaldehyde has recently been published.[10]

When added to ethylene oxide, which reacts with amines, and consequently with piperidine, sodium nitroprusside and piperidine give a brownish colour after 100–120 sec. By mixing sample and reagents in the cell of a direct reading spectrophotometer the development of the colour may be followed. A maximum at 575 nm results from the reaction of acetaldehyde, and the absorbance reaches its highest value after about 25 sec and then decreases. After 90–120 sec the absorbance increases again, now because of the reaction of ethylene oxide with the reagents: the substances formed absorb all visible radiation strongly.

The procedure described below enables the absorbance maximum from the acetaldehyde reaction to be read off easily on the instrument. A calibration curve based on such readings obeys Beer's law, and gives a molar absorptivity of 2000–3500 litre.cm^{-1}.$mole^{-1}$, depending on the dilution of the sample. Experiments have shown that the logarithm of the absorbance is a linear function of the ethylene oxide concentration at a given acetaldehyde concentration, and that the absorbance increases with a decreasing ethylene oxide concentration. This means that a nomogram can be constructed in such a way that only one calibration curve is necessary to cover any dilution of the sample.

The reaction may be disturbed by a number of substances (*e.g.*, organic sulphides and mercaptans) but not by the impurities normally present in ethylene oxide made from ethanol or ethylene. Formaldehyde does not interfere with the reaction, because only aldehydes capable of forming aldoles, *i.e.*, compounds with at least two carbon atoms, react with sodium nitroprusside.[3]

EXPERIMENTAL

Reagents

Piperidine: Puriss.

Sodium nitroprusside: In aqueous solution, 10% w/w; dissolve 10 g of $Na_2[Fe(CN)_5NO]2H_2O$ in 90 ml of distilled water.

Apparatus

Beckman B spectrophotometer: Setting: wavelength, 575 nm; photomultiplier, position A; sensitivity, 2; slit width, *ca.* 0·11–0·12 mm.

Standard solutions

A calibration curve has to be drawn for a suitable dilution of freshly distilled ethylene oxide with distilled water. Two dilutions of the ethylene oxide samples may be used, one of 5% v/v (dilution A) for concentrations of acetaldehyde in the sample exceeding $2{\cdot}3 \times 10^{-6}$ mole/ml (0·01% w/v), and one of 20% v/v (dilution B) for lower concentrations. At room temperature it is difficult to obtain good results with samples of a higher ethylene oxide concentration than 20% because of the low boiling point of ethylene oxide.

If the dilutions A and B are chosen, prepare two series of standard solutions as follows: make stock solutions of dilutions A and B, each containing 0·005% of acetaldehyde w/v. Transfer known volumes of the stock solution to volumetric flasks, and make up to the mark to give the appropriate dilution A or B. Prepare at least 4 solutions in each series, with the acetaldehyde concentrations evenly distributed over the range of measurement.

Blanks

Prepare blanks for the adjustment of the instrument as follows (three blanks are recommended to ensure reliable adjustment): pipette 0·30 ml of sodium nitroprusside solution into a 1-cm cell. (Experiments, in which the volume of nitroprusside solution was varied from 0·1 to 0·4 ml, indicated that the optimum volume was 0·3 ml.) Pipette 2·00 ml of dilution A or B (without acetaldehyde) and 0·20 ml of piperidine into a 5-ml test-tube, and shake carefully for 10–15 sec to obtain a homogeneous mixture. To avoid the formation of bubbles do not invert the test-tube when mixing, but effect the mixing by small rapid lateral movements of the tube. Nor should the mixture be shaken too long, (at most 10–15 sec), because the heat of reaction may produce vapour bubbles. After shaking, transfer the solution to the cell by means of a pipette. To ensure complete mixing in the cell use a 2-ml pipette provided with a rubber bulb, or use a syringe. To avoid the formation of bubbles, direct the solution along the wall of the cell. Within the next 25 sec set the absorbance scale of the spectrophotometer at zero with the slit, because after this time the solution may turn brown. Repeat the procedure for 3 blanks. Only 1 zero adjustment is necessary for each test series.

Calibration curve

Treat the prepared standard solutions as described above under *Blanks*. Pipette 0·30 ml of sodium nitroprusside solution into a 1-cm cell. Pipette 0·20 ml of piperidine and 2·00 ml of the standard solution into a 5-ml test-tube, mix, and transfer the mixture to the cell. Perform the measurement at once and at room temperature. After the sample and reagents are mixed the absorbance increases to reach a maximum after *ca.* 25 sec: this lasts a few seconds, after which the absorbance decreases again. Read off the maximum value, and use this for drawing the calibration curve.

Dilution A gives a linear calibration curve in the concentration range of $0 - 2 \times 10^{-6}$ mole of acetaldehyde per ml of undiluted ethylene oxide ($0 - 9 \times 10^{-3}$% w/v; absorbance 0–0·6) and dilution B gives a linear curve in the range of $0 - 4{\cdot}5 \times 10^{-6}$ mole of acetaldehyde per ml of undiluted ethylene oxide ($0 - 20 \times 10^{-3}$% w/v; absorbance 0–0·6).

Measurements of samples

Dilute the unknown ethylene oxide sample with distilled water to 5% (dilution A) or 20% (dilution B), the dilution depending on the expected concentration of acetaldehyde. Set the spectrophotometer at zero as described under *Blanks*. Perform the measurements as described under *Calibration curve*, with the standard solution replaced by 2·00 ml of the diluted sample solution. As mentioned under *Principles*, there is a linear relationship between the logarithm of the absorbance and the degree of dilution of the ethylene oxide sample. Therefore a nomogram can be constructed where the calibration curve for a chosen dilution of ethylene oxide can be used for any dilution of the sample.

DISCUSSION

To obtain good results the determinations must be made with great care. Routine measurements have, however, been carried out at our laboratory for more than a year without difficulties.

The standard deviations are $1{\cdot}5 \times 10^{-8}$ and $2{\cdot}4 \times 10^{-8}$ mole per ml of ethylene oxide (original sample) for dilutions of 5 and 20 times, respectively, of the sample. Because the accuracy of the final results is dependent on the purity of the ethylene oxide used for making the calibration curve, it is important that this should be freshly and carefully distilled. We have used a Podbielniak column (120 theoretical plates) for the distillation.

The method is applicable to ethylene oxide samples diluted at least 4:1; otherwise bubbles appear which make it impossible to measure the samples in a spectrophotometer at room temperature. Large amounts of propionaldehyde or acrolein ($>0{\cdot}1$%) react with the sodium nitroprusside to increase the absorbance. The presence of formaldehyde does not affect the determination.

In most of the experiments piperazine has been used as the base. Lewin[1] describes experiments in which piperidine was used. A comparison between piperidine and piperazine that we carried out on samples with different concentrations of acetaldehyde showed that piperidine gives a 10 times higher absorptivity.

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Zusammenfassung—Bei einer qualitativen Probe auf Acetaldehyd reagiert dieser mit Nitroprussidnatrium und Piperidin zu einer photometrisch bestimmbaren farbigen Substanz. Die Substanz ist jedoch instabil; die Extinktion sinkt von einem nach etwa 25 Sekunden erreichten Maximalwert wieder ab. Äthylenoxyd readiert auch mit Nitroprussidnatrium zu bräunlichen Produkten; diese Reaktion ist langsamer, die Farbe tritt erst nach 100–120-Sekunden auf. Wird daher die Extinktion etwa 25 Sekunden nach Zugabe der Reagentien gemessen, so wird die Störung durch Äthylenoxyd vermieden.

Résumé—La méthode est basée sur un essai qualitatif de l'acétaldéhyde dans lequel le réactif: nitroprussiate de sodium et pipéridine, réagit avec l'acétaldéhyde pour donner une substance colorée, qui peut être dosée photométriquement. Cette substance est toutefois instable, et après avoir atteint une valeur maximale en 25 secondes environ, l'absorption décroît. L'oxyde d'éthylène réagit aussi avec le nitroprussiate de sodium pour former des substances brunâtres, mais cette réaction est plus lente, la couleur ne se développant pas pendant 100–120 secondes. Si, par conséquent, l'absorption est mesurée environ 25 secondes après l'addition des réactifs, toute perturbation dûe à l'oxyde d'éthylène est évitée.

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SEPARATION OF BISMUTH FROM LEAD, COPPER AND OTHER ELEMENTS BY MEANS OF ANION EXCHANGE

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Summary—The anion-exchange behaviour of bismuth and various other elements has been investigated in media consisting of methyl glycol and nitric acid. Through the determination of the distribution coefficients in such mixtures, a method for the anion-exchange separation of bismuth from many metal ions has been developed. A mixture of 90% methyl glycol and 10% 5*M* nitric acid is a suitable medium for this separation on the strongly-basic anion exchanger Dowex 1, X8. Only bismuth, thorium and lanthanum are strongly retained on the resin in these conditions. All other elements investigated, such as lead, copper, iron, *etc.*, are either only weakly adsorbed or are not absorbed. By means of this ion-exchange procedure, a series of analyses of copper-base alloys for bismuth has been carried out. The results show that this method can be used successfully for the quantitative isolation of bismuth from such materials. The final determination of bismuth in the eluates is performed by complexometric titration.

INTRODUCTION

THE anion-exchange behaviour of bismuth in pure aqueous nitric acid solutions has been investigated in detail by Buchanan and Faris,[1] who found that this element is rather weakly adsorbed on strongly basic anion-exchange resins, even at high concentrations of nitric acid; its adsorption is, however, markedly enhanced in the presence of ammonium nitrate. A similar increase has also been observed by Korkisch and Tera[2] in a 90% methanol–10% 5*M* nitric acid system, and Fritz and Greene[3] noted a similar phenomenon when they determined the distribution of bismuth in 1·5*M* nitric acid–85% isopropanol.

Because the adsorption of lead is comparatively high in both these organic solvent-nitric acid media, and also in 90% acetic acid–10% 5*M* nitric acid, as shown by Korkisch and Arrhenius,[4] a separation of these two elements from each other cannot easily be effected. Recent investigations by Korkisch and Feik[5] have shown that in a mixture consisting of 90% tetrahydrofuran and 10% 5*M* nitric acid the adsorption behaviour of bismuth and lead is such that a separation of these two elements can easily be carried out. Because bismuth is, however, accompanied by practically all other elements, its separation from metal ions such as copper, iron, nickel, zinc, *etc.*, is not feasible, and therefore a determination of bismuth in presence of all these elements is complicated by interferences. In order to overcome these difficulties several organic solvent-nitric acid mixtures have been studied. As a result of these investigations a medium consisting of methyl glycol and nitric acid has been found to be most suitable, not only for the separation of bismuth from lead, but also from practically all other elements usually present in copper-base alloys. The method described here can therefore be applied to the isolation and determination of bismuth in such alloys.

Because uranium can also easily be separated from bismuth, which is used in reactor cooling systems, this method might prove of importance in the field of reactor chemistry.

EXPERIMENTAL

Reagents

Ion-exchange resin: The strongly-basic anion exchanger Dowex 1, X8 (100–200 mesh, nitrate form) was used.

Standard solutions of bismuth and other elements: Solutions in $5M$ nitric acid, of precisely known element content, were employed.

Organic solvent: Methyl glycol of reagent-grade purity.

Wash solution: 90% (vol) of methyl glycol + 10% (vol) of $5M$ nitric acid.

Apparatus

The column operations were carried out in columns of the type and dimensions described earlier.[6] The height of the resin bed was 10 cm and its diameter 0·6 cm.

Quantitative determination of elements investigated

The determinations of bismuth and all other elements except uranium, which was determined fluorimetrically,[7] were performed by titration with $0{\cdot}01M$ or $0{\cdot}001M$ EDTA, using suitable indicators, *e.g.*, Xylenol Orange.

Determination of distribution coefficients

The distribution coefficients of all elements were determined in the manner described earlier.[8]

Column operations

All separations on resin columns were performed by the following working procedure.

Pretreatment of resin bed: Before passage of the sorption solution the resin was treated with 50 ml of the wash solution.

Sorption step: The sorption solution was prepared by diluting 2 ml of $5M$ nitric acid, containing the metal ions in question, with methyl glycol to 20 ml. This solution was passed through the column at a flow rate of 0·5 ml/min. During this operation, bismuth, thorium and lanthanum were strongly adsorbed, and lead to some extent; the other elements, such as copper, zinc, *etc.*, passed into the effluent.

Washing step: To remove lead completely from the column the resin bed was washed with 150 ml of the wash solution used in small portions.

Elution: The bismuth was eluted with 100 ml of $1M$ nitric acid. After evaporation of the eluate, bismuth was determined by titration with EDTA using Xylenol Orange as indicator.

In the analysis of copper-base alloys, 2 g of the sample were dissolved in nitric acid and the residue obtained after evaporation of the solution was dissolved in 10 ml of $5M$ nitric acid. To 1-ml aliquot of this solution 1 ml of a bismuth standard solution was added, and after dilution to 20 ml with methyl glycol the solution was passed through the column as described above. In blank runs, 1 ml of $5M$ nitric acid was used instead of the bismuth standard solution.

RESULTS

Investigation of the effect of methyl glycol concentration on the adsorption of bismuth at a constant over-all nitric acid concentration of $0{\cdot}5M$ (10% of $5M$ nitric acid) showed a linear decrease of the distribution coefficient with decreasing concentration of organic solvent.

An increase of the nitric acid concentration in solutions consisting of 90% methyl glycol caused the distribution coefficient of bismuth to increase linearly from 115 (in the presence of 10% of $2{\cdot}5M$ nitric acid) to 460 (in presence of 10% of $10M$ nitric acid). Although better adsorption can evidently be achieved in the latter case, mixtures with 10% of $5M$ nitric acid were invariably used for all other experiments, such as the separations, because the solubility of the nitrates of the investigated metal ions is still high enough in these media, whereas at much higher concentrations of nitric acid the solubility is low.

Loading experiments showed that the distribution coefficient of bismuth decreases with increasing load from 230 to 185, when equilibrating 5–30 mg of bismuth with 1 g of the resin.

Investigation of the adsorption of various other elements in 90% methyl glycol–10% 5*M* nitric acid media showed that besides bismuth only lanthanum and thorium are strongly retained on the resin. The results of these experiments are recorded in Table I.

TABLE I.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL–10% 5*M* NITRIC ACID ON DOWEX 1, X8

Metal ion	Distribution coefficient, 5 mg/20-ml load
Bi^{III}	230·
Pb^{II}	28·6
Cu^{II}	<1·
Zn^{II}	<1·
Cd^{II}	5·
Al^{III}	<1·
Ga^{III}	2·2
In^{III}	7·7
Mn^{II}	<1·
Fe^{III}	<1·
Co^{II}	<1·
Ni^{II}	<1·
Zr^{IV}	<1·
Hf^{IV}	3·
Th^{IV}	1,700·
Mg^{II}	<1·
Ca^{II}	5·
Sc^{III}	<1·
La^{III}	9,000·
Yb^{III}	4·
UO_2^{II}	6·6

It is seen that bismuth can easily be separated from most of the elements listed in Table I. Fractions of micrograms of the element can be separated from milligram quantities of other metals. For the quantitative separation from lead, however, a prolonged treatment with the wash solution is necessary (see *Experimental*).

Based on all these investigations several samples of copper-base alloys to which known amounts of bismuth were added have been analysed using the working procedure described above. From the results of these experiments, which are shown in Table II, it is seen that in all cases a quantitative separation of bismuth from the elements present in the samples was achieved, the error being within small limits. From a number of experiments with varying amounts of the elements, a relative standard deviation of ±1·65% was calculated.

In order to demonstrate the effectiveness of the separation method more clearly, a typical separation of lead from bismuth is shown in Fig. 1 from which it is seen that even when washing with 260 ml of the wash solution no trace of bismuth appears in the effluent. Because practically all other elements investigated except lanthanum

TABLE II.—DETERMINATION OF BISMUTH IN COPPER-BASE ALLOYS

Composition of alloy (major constituents)	Bismuth added, *mg*	Bismuth found, *mg*
1. Cu (65%), Zn (35%)	0·0	0·0
	0·5	0·51
	5·0	5·02
	10·0	9·98
2. Cu (65%), Zn (16%) Ni (17%), Pb (1%) Fe (0·7%)	0·0	0·01
	0.5	0·5
	5·0	5·02
	10·0	10·03
3. Cu (70%), Zn (30%)	0·0	0·0
	0·5	0·48
	5·0	5·01
	10·0	10·0
4. Cu (80%), Zn (10%) Pb (8%)	0·0	0·0
	0·5	0·51
	5·0	4·98
	10·0	9·99
5. Cu (75%), Zn (10%) Ni (5%), Pb (5%)	0·0	0·02
	0·5	0·52
	5·0	5·03
	10·0	10·04

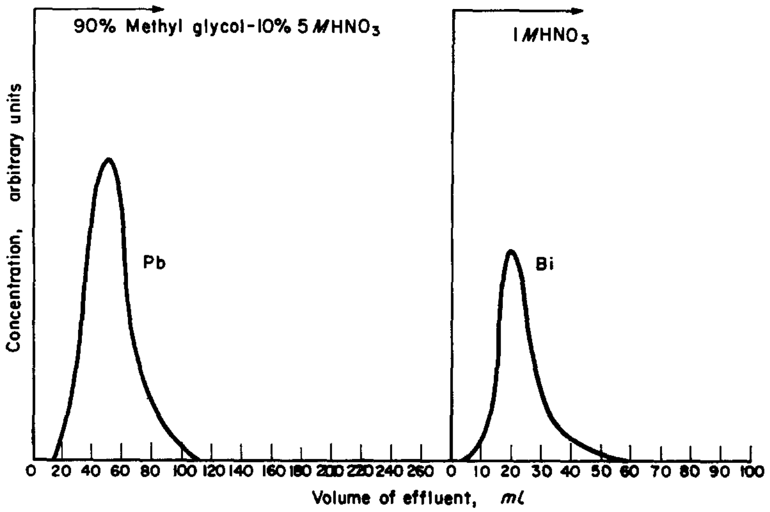

FIG. 1.—Separation of lead from bismuth.

and thorium have distribution values smaller than that of lead (see Table I), their quantitative separation from bismuth can effectively be carried out even if present in large amounts (see Table II).

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Zusammenfassung—Das Anionenaustauschverhalten von Wismuth und verschiedener anderer Elemente wurde in Medien bestehend aus Methyl-Glykol und Salpetersäure untersucht. Auf Grund von Bestimmungen der Verteilungskoeffizienten in solchen Mischungen wurde eine Methode zur Anionenaustauschtrennung des Wismuts von vielen Metallionen entwickelt. Eine Mischung bestehend aus 90% Methyl-Glycol und 10% $5M$ Salpetersäure erwies sich als am besten geeignet zur Trennung am stark basischen Anionenaustauscher Dowex 1, X8. Unter diesen Bedingungen werden nur Wismut, Thorium und Lanthan stark am Harz adsorbiert während alle anderen Elemente wie z.B. Blei, Kupfer, Eisen etc. überhaupt nicht oder nur schwach festgehalten werden. Mittels dieses Verfahrens wurde Wismut in einer Anzahl von Kupferlegierungen bestimmt. Die Ergebnisse dieser Untersuchungen zeigten, daß diese Methode erfolgreich zur quantitativen Abtrennung des Wismuts aus solchen Materialien angewendet werden kann. Die Endbestimmung des Wismuts in den Eluaten erfolgte durch komplexometrische Titration.

Résumé—On a étudié le comportement, au point de vue échange anionique, du bismuth et de divers autres éléments dans des milieux propylèneglycol-acide nitrique. Par la détermination des coefficients de distribution dans de tels mélanges, on a élaboré une méthode de séparation par échange anionique du bismuth de nombreux autres ions métalliques. Un mélange composé de 90% de propylèneglycol et 10% d'acide nitrique $5M$ s'est révélé être le milieu le plus convenable pour cette séparation, sur l'échangeur anionique fortement basique Dowex 1, X8. Seuls, le bismuth, le thorium et le lanthane sont fortement retenus sur la résine dans ces conditions, cependant que tous les autres éléments étudiés, tels le plomb, le cuivre, le fer, etc . . . , ne subissent qu'une adsorption faible ou nulle. Au moyen de cette méthode d'échange d'ions, on a effectué une série d'analyses, concernant le bismuth, sur des alliages à base de cuivre. Les résultats de ces recherches ont montré que cette méthode peut être utilisée avec succès pour l'isolement quantitatif du bismuth de tels matériaux. Le dosage final du bismuth dans les éluats a été effectué par titrage complexométrique.

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NUCLEATION OF LEAD CHROMATE FROM HOMOGENEOUS SOLUTION

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Summary—On the basis of the Christiansen-Nielsen model for nucleation, the nucleus of lead chromate precipitated from homogeneous solution has been found to consist of about five ions. The critical supersaturation values of solutions of lead chromate are dependent upon the method of filtration; however, a change in supersaturation of about 25% is without effect on the size of the critical nucleus.

THE nucleation of sparingly soluble salts may be considered to take place in two steps, the first being the production of supersaturation within the system and the second the formation of the nucleus within the supersaturated system.[1,2] In the present investigation an attempt is made to elucidate the mechanism of nucleation of lead chromate, to determine the degree of supersaturation which must be attained for nucleation to occur, and to learn the effect of the degree of supersaturation on the size of the critical nucleus.

Christiansen and Nielsen[3] proposed that the mechanism of nucleation proceeds by a series of bimolecular collisions between precipitating ions and subcritical embryos. Klein, Gordon and Walnut[4] modified the Christiansen-Nielsen approach to make it applicable to the determination of the critical nucleus size in precipitations from homogeneous solution. In their modification, they obtained

$$N = k\int[\mathrm{I.P.}]^n\,dt \tag{1}$$

where N = number of nuclei and hence number of particles found,
k = a constant,
I.P. = ion product,
n = nucleus size,
and t = time.

Thus, by determining N, the number of particles formed, and evaluating the variation of the ion product with time, one can determine n, a measure of the number of ions in the critical nucleus. Klein *et al.*[4] studied the precipitation of silver chloride from homogeneous solution and determined that the critical nucleus consisted of five ions.

The present investigation was undertaken to study the nucleation of lead chromate from homogeneous solution. The chromate ion was generated by the reaction[5] of chromium(III) with bromate in the presence of lead ion, the stoichiometry of the reaction being:

$$10Cr^{3+} + 6BrO_3^- + 22H_2O \rightarrow 10CrO_4^{2-} + 3Br_2 + 44H^+.$$

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EXPERIMENTAL

Reagents

All stock solutions were prepared from reagent-grade chemicals. All solutions, except lead and chromium(III) nitrates, were prepared by weighing the dry reagent and diluting to volume. The necessary dilutions were made with distilled water previously filtered through a Millipore HA filter. There was no further standardisation of these solutions.

The stock solution of lead was standardised gravimetrically by precipitation of the sulphate. The chromium(III) solution was standardised by oxidation to chromate with sodium peroxydisulphate, followed by addition of a known amount of iron(II) sulphate and titration with standard potassium permanganate.[6]

Apparatus

Spectrophotometric measurements were performed with a Beckman DU spectrophotometer fitted with a dual thermospacer set, which permitted circulation of water around the cell housing compartment to maintain constant temperature in the cells. Fused 10-mm silica cells were used.

Turbidimetric measurements were made using a Phoenix-Brice light scattering instrument equipped with a thermostatted jacket which encircled a cylindrical cell; a 430-mμ filter was used.

Procedure

Appropriate amounts of stock solutions of lead nitrate, potassium bromate, potassium nitrate and equimolar acetic acid-sodium acetate buffer were drawn through a Millipore filter into a 500-ml volumetric flask; potassium nitrate was used to vary the ionic strength of the medium. The resulting solution was diluted to approximately 400 ml with pre-filtered distilled water. A solution of chromium(III) ions was then introduced into the reaction mixture through the Millipore filter and the contents were diluted to volume with water. The time was measured from the moment of addition of chromium(III) ions to the other reagents. Portions of the solution were transferred to optical cells for spectrophotometric and turbidimetric measurements and to Erlenmeyer flasks for later use in sampling studies. All reaction vessels were maintained at 25° ± 0·2°.

Spectrophotometric determination of chromate. The photometer was used to determine the concentrations of chromate ion in the solution up to the onset of precipitation. The wavelength used was 340 mμ, at which the molar extinction coefficient for chromate ion is $1{\cdot}51 \times 10^6$ cm^2.mole^{-1}. Because the precipitate particles acted as light scattering centres, thus introducing an uncertainty in the absorbance readings, it was necessary to extrapolate the absorbance-time curve in order to determine the total chromate ion produced.

Titrimetric determination of lead. To determine the amount of lead ion precipitated and therefore the concentration of lead ion remaining in solution, it was necessary to pipette 50-ml portions of the reacting solution and transfer these into 50-ml Erlenmeyer flasks suspended in the constant temperature bath. Then, approximately 40 min after the start of precipitation and every 20 min thereafter, one of the samples was filtered through a Millipore VC filter. The precipitate particles on the walls of the flask and on the filter were dissolved in concentrated potassium hydroxide, the solution transferred to a 100-ml volumetric flask and analysed for chromate; the amount of lead ion precipitated was determined from this measurement.

Turbidimetric determination of onset of precipitation. Turbidimetric measurements were made to determine the time at which precipitation began. The relative turbidity was plotted as a function of time and the inception of precipitation taken to be the time at which there was a sharp increase in the slope of the turbidity-time curve.

RESULTS AND DISCUSSION

Size of nucleus

The solution concentrations of lead and chromate ions were determined from the analytical results; a typical plot of the variation of the ion product ($[Pb^{2+}].[CrO_4^{2-}]$) with time is shown in Fig. 1. The lead concentration in solution was considered to be that remaining uncomplexed by acetate.[7] According to equation (1), when the variation of the ion product with time and the quantity of nuclei, *i.e.*, the particle count, is known, it is possible to determine the number of ions in the critical nucleus. (The particle count was determined microscopically.)

For each experiment, the *ion product* was plotted as a function of *time*. If the ion product, raised to a power x (selected integral values), is plotted *versus* time the area under the curve is the value $\int(\mathrm{I.P.})^x\,dt$. If this value is divided by the particle count N, a value of $1/k$ is obtained. For each selected value of x, $1/k$ for each run was plotted *versus* $\int(\mathrm{I.P.})^x\,dt$. Where $d(1/k)/d\int(\mathrm{I.P.})^x\,dt$ *versus* x was zero, the term $1/k$ was taken as constant and x to be equal to n, where $2n - 1$ represents the number of ions in the critical nucleus. The limits for the integration of $(\mathrm{I.P.})^x$ *versus* time were chosen to include essentially all ion products at which nucleation was occurring. For these experiments the limiting ion product chosen was $1{\cdot}70 \times 10^{-9}$ mole^2.l.$^{-2}$.

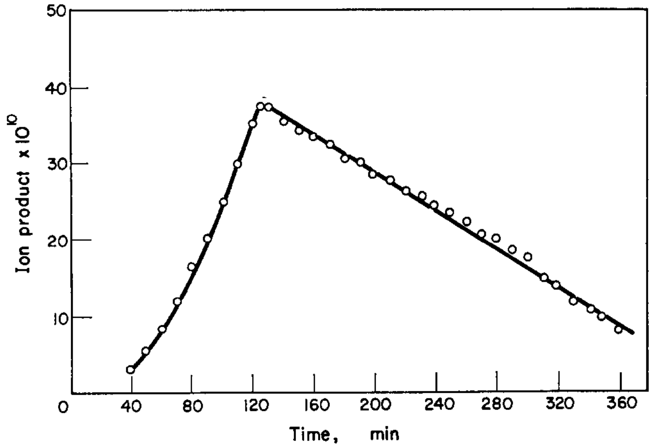

FIG. 1.—Ion product of lead chromate as a function of time during the precipitation.

Table I summarises the values used in the determination of the critical nucleus size. The results indicate n to be three; therefore, the number of ions in the critical nucleus is five.

TABLE I.—DETERMINATION OF THE SIZE OF THE NUCLEUS OF LEAD CHROMATE[a]

$[\mathrm{Pb}^{2+}]$, *mole.l.*$^{-1}$ $\times 10^4$	Number of particles, N.*l.*$^{-1}$ $\times 10^{-7}$	$\frac{\int(I.P.)^1\,dt}{N} \times 10^{15}$	$\frac{\int(I.P.)^2\,dt}{N} \times 10^{23}$	$\frac{\int(I.P.)^3\,dt}{N} \times 10^{32}$	$\frac{\int(I.P.)^4\,dt}{N} \times 10^{40}$	$\frac{\int(I.P.)^5\,dt}{N} \times 10^{48}$
7·46	1·92	2·28	1·03	3·38	0·95	2·48
9·95	1·40	0·29	1·32	4·36	2·43	3·12
14·9	8·78	3·12	0·13	0·38	0·11	0·30
19·9	4·53	0·61	0·26	0·78	0·23	0·72
29·9	1·44	2·94	1·74	6·26	2·07	9·03
Slope of plot of $\frac{\int(I.P)^n\,dt}{N}$ *vs.* $\int(I.P.)^n\,dt$		$1{\cdot}06 \times 10^{-7}$	$1{\cdot}20 \times 10^{-7}$	$6{\cdot}82 \times 10^{-7}$	$0{\cdot}94 \times 10^{-7}$	$0{\cdot}82 \times 10^{-7}$

[a] Millipore HA filter used.

The values presented in Table I are for experiments conducted with Millipore HA filters (pore size = 0·45 μ). In order to determine whether the filtration process has any effect on the nucleus size, an analysis of the results from experiments using Millipore VC filters (pore size = 0·1 μ) was made. These results are shown in Table II. Again, n was found to be three, showing the number of ions in the critical nucleus to be independent of the filter pore size.

This part of the study demonstrates the use of kinetic methods to determine the size of the critical nucleus of lead chromate, thus supporting the model for nucleation proposed by Christiansen and Nielsen. Although the critical nucleus of lead chromate consists of five ions, the significance of this number is its order of magnitude. Christiansen and Nielsen's induction time experiments, used to determine the nucleus size, have been criticised because the use of direct mixing of reactants may possibly cause nucleation to occur during the mixing process rather than having it occur after the system becomes homogeneous. The present work eliminates the effect of direct mixing by using the technique of precipitation from homogeneous solution, with, however, the results still in agreement with the model for nucleation as proposed by Christiansen and Nielsen.

TABLE II.—DETERMINATION OF THE SIZE OF THE NUCLEUS OF LEAD CHROMATE[a]

[Pb^{2+}], *mole.l.*$^{-1}$ × 10^4	Number of particles, N.*l.*$^{-1}$ × 10^{-7}	$\frac{\int(I.P.)^1\,dt}{N}$ × 10^{15}	$\frac{\int(I.P.)^2\,dt}{N}$ × 10^{23}	$\frac{\int(I.P.)^3\,dt}{N}$ × 10^{32}	$\frac{\int(I.P.)^4\,dt}{N}$ × 10^{40}	$\frac{\int(I.P.)^5\,dt}{N}$ × 10^{48}
9·95	2·59	8·65	4·09	7·80	5·40	1·69
19·9	9·36	0·97	0·51	2·10	0·36	0·30
24·9	3·99	2·83	1·67	7·99	3·36	1·56
29·9	15·6	0·36	0·20	0·92	0·34	0·14
Slope of plot of $\frac{\int(I.P.)^n\,dt}{N}$ *vs* $\int(I.P.)^n\,dt$		$5{\cdot}18 \times 10^{-8}$	$5{\cdot}40 \times 10^{-8}$	$25{\cdot}9 \times 10^{-8}$	$4{\cdot}28 \times 10^{-8}$	$3{\cdot}93 \times 10^{-8}$

[a] Millipore VC filter used.

Effect of supersaturation

This phase of the investigation involved a study of the effect of filtration, the rate of generation of the chromate ion and the variation of the ionic strength of the medium upon the supersaturation ratios which were reached before precipitation was first observed. The "critical"* supersaturation ratio, S_{crit}, is defined as $[(I.P.)/K_{sp}]^{\frac{1}{2}}$, where K_{sp} is the equilibrium solubility product. The turbidimetric measurements were used to determine the time of inception of precipitation. The concentration of chromate ion used for the ion product was taken from the absorbance-time curve and the lead ion concentration was taken as the uncomplexed ion initially present.

Effect of filtration on S_{crit}. Two filters of different pore size were used in the preparation of the reacting solutions; these were Millipore HA filters with a nominal pore size of 0·45 μ and Millipore VC filters with a nominal pore size of 0·1 μ. The results of these experiments are shown in Table III, S_{crit} being calculated on the basis of concentration. The supersaturation ratios varied inversely with the pore size of the filter. With the HA filter, S_{crit} is 104 ± 3; with the VC filter, it is 128 ± 8, *i.e.*, a 25% change for the four-fold variation in filter pore size.

If nucleation occurs by a heterogeneous process involving a foreign body, then the finer filter must remove some of the larger (or more active) nucleation sites so that the

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* A purely critical value does not exist (*cf.* Nielsen[13]). It appears to be critical only because the rate of formation of nuclei changes drastically with supersaturation. As a result, the experimental range, within which the rate of nuclei formation can be followed, is quite restricted.

system can become more supersaturated before nucleation occurs. Thus the first step in the nucleation mechanism, rather than being a reaction between the two ions comprising the precipitate, is a "reaction" between either one or other of their ions (or both) and a foreign site M, as follows:

$$\mathrm{M} + \mathrm{Pb}^{2+} = \mathrm{MPb}^{2+}$$

or

$$\mathrm{M} + \mathrm{CrO_4}^{2-} = \mathrm{MCrO_4}^{2-}$$

TABLE III.—EFFECT OF FILTRATION ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

Filtration	$[\mathrm{Pb}^{2+}]$, *mole.l.*$^{-1} \times 10^4$	S_{crit}
Millipore HA	7·46	102
Millipore HA	9·95	102
Millipore HA	14·9	100
Millipore HA	19·9	104
Millipore HA	29·9	110
Millipore VC	9·95	116
Millipore VC	19·9	124
Millipore VC	24·9	138
Millipore VC	29·9	136

Effect of rate of generation of chromate ion. The rate was altered by varying the concentration of chromium(III) and bromate ions in the reacting solutions. The results of these experiments are shown in Table IV; the times indicated are those at which precipitation was first detected turbidimetrically. It was noted, although the times varied considerably (45–157 min), that there was no change in S_{crit}. If the value of the supersaturation ratio were not critical, but merely dependent upon the time required for the system to reach a particular supersaturation,[8] one might expect that the value of the supersaturation ratio atwhich precipitation is first detected should change. This result was not observed for the nucleation of lead chromate. Thus, the supersaturation ratio is truly "critical" at least for the particular set of experimental conditions utilised here.

TABLE IV.—EFFECT OF THE RATE OF GENERATION OF CHROMATE ION ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

$[\mathrm{Pb}^{2+}]$, *mole. l.*$^{-1}$ $\times 10^4$	$[\mathrm{Cr}^{+3}]$, *mole. l.*$^{-1}$ $\times 10^3$	$[\mathrm{BrO_3}^{-}]$, *mole. l.*$^{-1}$ $\times 10^3$	S_{crit}	Time, *min*
9·95	3·77	4·00	118	157
19·9	3·77	4·00	100	89
9·95	4·71	5·00	102	128
19·9	4·71	5·00	104	84
9·95	5·65	6·00	104	75
19·9	5·65	6·00	109	45

Effect of ionic strength of reacting solution. The ionic strength was varied by adding known quantities of potassium nitrate; the mean activity coefficient for lead chromate was calculated from the Debye-Hückel equation. The results of these experiments are shown in Table V. The critical supersaturations show no apparent variation with change in ionic environment. This is a surprising result, for if the mechanism for nucleation involves an ionic dependence, then a large concentration of foreign ions would decrease the electrostatic attraction between the ions which can form the precipitate. Possible explanations for the results obtained are either (1) that the range over which the ionic strength was varied was insufficient or (2) that these experiments were conducted above a limiting value of the ionic strength. If the latter were the case, any further increase in the ionic strength would be without effect upon nucleation. Further, the values used for the mean activity coefficient for lead chromate may be inaccurate; LaMer and Dinegar[10] comment in a similar manner in their study of the precipitation of barium sulphate.

TABLE V.—EFFECT OF IONIC STRENGTH ON THE CRITICAL SUPERSATURATION RATIO OF LEAD CHROMATE

Method of filtration	Ionic strength, $\mu \times 10^2$	Mean activity coefficient, f	S_{crit}[a]	S_{crit}[b]
Millipore HA	8·5	0·356	100	35·6
	8·5	0·356	102	36·3
	8·5	0·356	102	36·3
	8·5	0·356	104	37·0
	8·5	0·356	110	39·2
	9·8	0·337	114	38·4
	10·5	0·328	117	38·4
	10·5	0·328	120	39·3
	11·0	0·321	116	37·2
	13·5	0·294	136	40·0
	13·7	0·292	113	33·0
	18·5	0·256	118	32·3
				(ave.) 37 ± 2
Millipore VC	8·5	0·356	116	41·3
	8·5	0·356	124	44·2
	8·5	0·356	132	47·0
	8·5	0·356	138	49·1
				(ave.) 45 ± 3

[a] Calculated from concentrations.

[b] Calculated from activities.

Relation between nucleus size and supersaturation

It is informative to examine the relationship between supersaturation and nucleus size according to the Ostwald-Freundlich equation:[11]

$$r = \frac{2\sigma M}{RT\rho \ln S}$$

where r = radius of the nucleus,
σ = interfacial tension,
M = molecular weight,
ρ = density,
S = supersaturation,
and R and T have their usual meanings.

When this equation is used to calculate the size of the nucleus of lead chromate, using values of 40 for the supersaturation and of 150 dynes/cm² for the interfacial tension,[11] the radius is found to be 40 Å. This radius is considerably greater than that of the Christiansen-Nielsen model, for which the rather small nucleus size of five ions is found. Furthermore, there is no interdependence of nucleus size and supersaturation as with the Ostwald-Freundlich equation. A homogeneous 40-Å radius nucleus would contain hundreds of ions. It seems improbable that a nucleus of such size could be built up either by a kinetic process or by concentration fluctuations. One possibility is that the bulk of such a nucleus might consist of a heterogeneous site (solvent or foreign impurity) with the ions contributing little volume to its actual size. Thus, it has been suggested that the Ostwald-Freundlich nucleus consists of the ions and the foreign site while the Christiansen-Nielsen nucleus is the ion aggregate only.[12]

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Zusammenfassung—Auf Grund des Keimbildungsmodells von Christiansen-Nielsen wurde gefunden, daß der Keim für die Fällung von Bleichromat aus homogener Lösung aus etwa 5 Ionen besteht. Die Werte für die kritische Übersättigung von Bleichromatlösungen hingen von der Filtrationsmethode ab; eine Änderung der Übersättigung um etwa 25% wirkte sich aber auf die Größe des kritischen Keimes nicht aus.

Résumé—Sur la base dur modèle Christiansen-Nielsen pour l'amorçage on a trouvé que le germe de chromate de plomb précipité d'une solution homogène est constitué par environ cinq ions. Les valeurs critiques de sursaturation des solutions de chromate de plomb dépendent de la méthode de filtration; toutefois, un changement d'environ 25% dans la sursaturation est sans effet sur la dimension du germe critique.

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SEPARATION AND DETERMINATION OF TANTALUM AND NIOBIUM BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—An attempt to separate niobium and tantalum by precipitation from homogeneous solution by thermal decomposition of their peroxy complexes, in the presence of tannin and oxalate, has been only moderately successful. A more satisfactory separation of tantalum and niobium for ratios from 50:1 to 1:30 is obtained by extracting the bisulphate melt with ammonium oxalate before adding hydrogen peroxide, hydrochloric acid and tannin. For a tantalum/niobium ratio of 1:1 the niobium coprecipitation is reduced to 5%. Furthermore, two alternative possibilities are presented: (1) a quantitative recovery of a tantalum precipitate at small oxalate and high tannin concentration, leaving 90% of the tantalum-free niobium in solution; (2) an 85% recovery of niobium-free tantalum at high oxalate and small tannin concentration. A study of the coprecipitation process of niobium shows that the distribution coefficients follow a logarithmic pattern, true homogeneous mixed crystals being formed.

INTRODUCTION

BECAUSE of the similarity of their chemical properties, the gravimetric separation of tantalum and niobium from each other has always presented a very difficult problem in analytical chemistry. Probably the most reliable, but tedious, procedure for the separation is a fractional tannin precipitation. This procedure, developed by Powell and Schoeller,[1] is based on the difference in the stability of the oxalato-complexes. Precipitation from homogeneous solution was recently proposed by the present authors for the separation and determination of tungsten,[2] titanium, tantalum and niobium,[3] based on the thermal decomposition of soluble peroxy complexes from a hydrogen peroxide medium. An analogous procedure can readily be adapted for the separation and determination of niobium and tantalum. Radioactive tracer techniques were used to develop the proposed method.

EXPERIMENTAL

Radioisotopes

Tantalum. ^{182}Ta, β,γ-emitter, half-life ± 111 days, produced by irradiation of Ta_2O_5 in the BR-1 reactor.

Niobium. ^{95}Nb, β,γ-emitter, half-life ± 35·5 days, obtained from the Radiochemical Centre, Amersham, England.

Counting techniques. Integral γ-counting was performed for ^{182}Ta and ^{95}Nb using a standard scintillation counter with a well-type sodium iodide (thallium activated) crystal. In the presence of each other they were measured by differential γ-counting, using a 3″ × 3″ sodium iodide (thallium activated) crystal connected to a 400-channel analyser.

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Procedure

Precipitation of tantalum. Fuse the mixture of the oxides with potassium bisulphate and remove the cold melt from the crucible by warming with 5% ammonium oxalate. Rinse the contents of the crucible into a beaker and heat with water until a clear solution is obtained. Add 2 ml of 30% hydrogen peroxide, an adequate amount of 12*M* hydrochloric acid and an amount of tannin corresponding to 20 times the weight of the acids. Dilute the solution with water to obtain a final concentration of earth acid oxides of 0·02%, an ammonium oxalate concentration of 1% and an acidity of 2·5*M* hydrochloric acid. Decompose the peroxides by heating at 85° for 7–8 hr, and collect the dense precipitate. Some results are summarised in Table III.

Precipitation of niobium. Evaporate the filtrate from the tantalum precipitation to about 200 ml, and add 5–10 ml of nitric acid (sp. gr. 1·4) to clarify the dark-coloured solution. Oxidise the excess of oxalate with an adequate amount of sodium bromate, added dropwise. Neutralise with aqueous ammonia and precipitate the niobium with a ten-fold excess of tannin. Heat the solution to boiling over 5 min.

Precipitation of Tantalum from Homogeneous Solution

Tantalum is incompletely precipitated (95%) by the thermal decomposition of soluble peroxy-tantalate and -niobate in a homogeneous ammonia-hydrogen peroxide solution at pH 10 or 11; niobium is coprecipitated (at least 40%). Thermal decomposition of peroxytantalate in an acetate, citrate or tartrate solution, in the presence of tannin, results in an incomplete and voluminous precipitation. In an acid oxalate-tannin solution, however, a dense and readily filterable precipitate was obtained. Preliminary experiments showed that optimum results were obtained in an acidic medium (5*M* nitric acid); recoveries of 99·8% were achieved.

Separation of tantalum and niobium

In the present case, γ-spectrometric measurements offer a relatively simple means of determining the amounts of coprecipitated niobium as a function of the amount of precipitated tantalum. The gamma rays at 1·12, 1·15, 1·19, 1·22 and 1·23 *MeV* of ^{182}Ta can be measured independently from the activity of ^{95}Nb. The ^{95}Nb content can be computed from the activity under the 0·776 *MeV* peak, after subtraction of the Compton continuum of ^{182}Ta. For ^{182}Ta, the ratio of the activity under the peaks at about 1·2 *MeV* to the activity in the energy range about 0·776 *MeV* is, under standard conditions, a constant.

It appears that for the precipitation of tantalum from the homogeneous peroxide solution, optimum results are obtained in the presence of 1200 mg of oxalic acid, together with tannin and selenous acid. The respective amounts of the latter should correspond to 7 and 0·5 times the weight of the pentoxides. Different amounts of tantalum were precipitated from 200 ml of solution. The results are given in Table I.

TABLE I.—PRECIPITATION OF THE EARTH ACIDS AS A FUNCTION OF THEIR CONCENTRATION

Taken, *mg*		Heating period, *hr*	Ta left in solution, %	Nb coprecipitated, %
Ta_2O_5	Nb_2O_5			
20·0	20·0	24	0·6	10·5
50·1	50·0	10	0·9	19
75·2	75·1	5	1·3	34

From Table I it appears that from the most dilute solution 99·4% of the tantalum was recovered, the niobium coprecipitation being reduced to 10·5%.

A decrease of the coprecipitation was observed by extracting the bisulphate melt of 20 mg of tantalum pentoxide and 20 mg of niobium pentoxide with ammonium oxalate before adding the hydrogen peroxide. The precipitations were also carried out in the presence of different amounts of nitric, hydrochloric and selenous acids, ammonium oxalate and tannin, the volume of the solution being 200 ml.

Typical results are given in Table II.

TABLE II.—SEPARATION OF THE EARTH ACIDS IN THE PRESENCE OF AMMONIUM OXALATE

$(NH_4)_2Ox$, %	Acid	Ratio to the oxides (w/w)		Heating period, *hr*	Ta left in solution, %	Nb coprecipitated, %
		H_2SeO_3	Tannin			
1	4·5*M* HNO_3	1	10	20	1·5	7·2
1	3*M* HNO_3	1	10	10	4·9	6·4
1	1·5*M* HCl	1	10	10	26·5	1·1
1	2·5*M* HCl	1	10	20	3·3	2·7
1	3·5*M* HCl	1	25	12	5·1	2·9
1	2·5*M* HCl	0	25	7	0·3	8·4
0·75	2·5*M* HCl	0	25	7	1·7	7·0
0·50	2·5*M* HCl	0	25	12	0·5	12·5
0·50	2·5*M* HCl	2	25	14	0·1	11·5
1·25	2*M* HCl	0	7	7	15·0	<0·5

From Table II it appears that, from a 0·5% ammonium oxalate solution and in the presence of a large amount of selenous acid, tantalum can be precipitated homogeneously with recoveries of 99·9%. From the γ-ray spectrum of the solution before and after precipitation, it is clear that the ^{182}Ta activity in the filtrate is undetectable. The last result given in Table II shows that it is possible to precipitate 85% of practically niobium-free tantalum. In the γ-ray spectrum of the precipitate, the niobium-peak at 0·776 *MeV* can barely be seen, although in the original solution it was as important as in the standard. These precipitations are interesting for preparative purposes. For a rapid analysis, however, optimum results were obtained by following the procedure, as shown in Table III.

TABLE III.—PRECIPITATION OF TANTALUM FROM HYDROGEN PEROXIDE OXALATE SOLUTION

Ta_2O_5 taken, *mg*	Ta left in solution, %
140·1	0·60
109·8	0·49
79·9	0·71
57·3	0·64
42·1	0·65
33·4	0·81
20·7	0·87
16·6	1·5^3
10·0	1·9^0
8·0	2·1^8

From Table III it appears that precipitation of tantalum from a homogeneous hydrogen peroxide-oxalate solution gives satisfactory tantalum recoveries.

Coprecipitation of niobium

The coprecipitation of niobium was investigated for niobium/tantalum ratios varying from 2 × 10^{-2} to 30. The absolute amount of tantalum precipitated varied from 100 mg for small ratios to 5 mg for larger ratios. The results are given in Fig. 1.

From Fig. 1 it appears that for a Nb_2O_5/Ta_2O_5 ratio equal to one the error on the tantalum determination is 5·5 %. If the precipitation is repeated, the error is reduced to 1 %. A correction can be made after a single precipitation if this ratio is higher than unity.

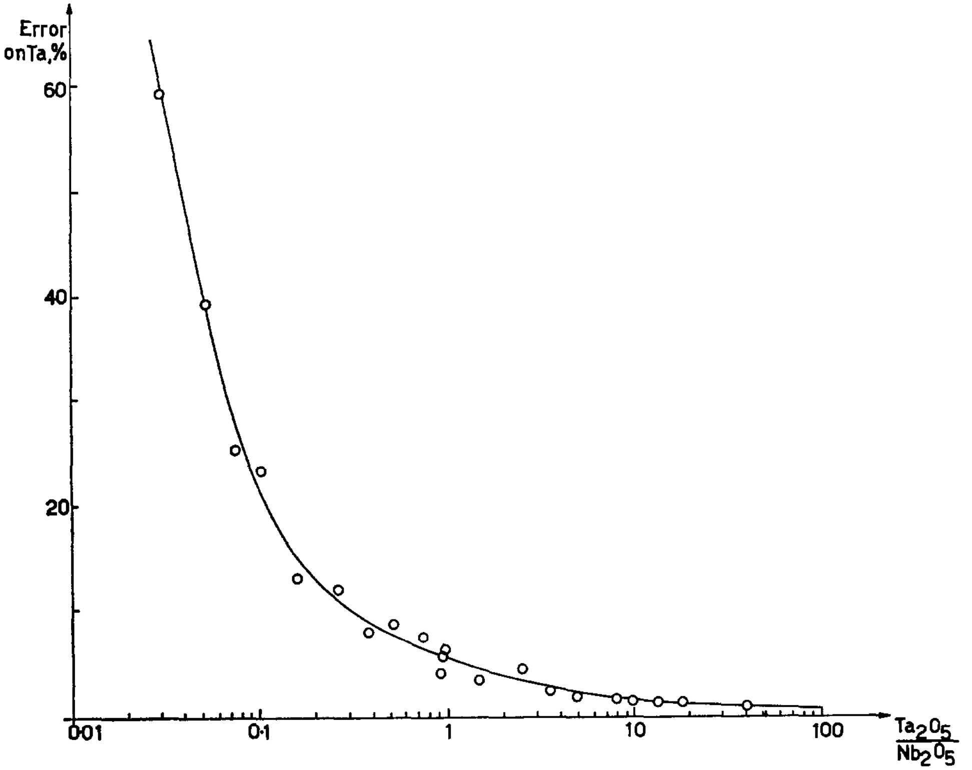

FIG. 1.—Coprecipitation of niobium with tantalum.

Precipitation of niobium from the filtrate after precipitation of tantalum

The amount of niobium left in solution was computed by adding, before the fusion, an adequate amount of ^{95}Nb of known activity (*ca.* 1 × 10^6 cpm) and counting an aliquot of the filtrate. The results are summarised in Table IV. It appears that this precipitation gives highly satisfactory niobium recoveries. The small amounts of tantalum and titanium present are coprecipitated quantitatively.

Determination of Distribution Coefficient

A coprecipitant can be distributed between solid and liquid phase according to an homogeneous,[4] logarithmic[5] or proportional distribution law.[6] As was shown in previous papers,[2,3] the coprecipitation process of molybdenum and vanadium with tungstic acid and of tungsten with the earth acids follows a linear pattern. In the present case, measurements of the radioactive isotopes offer a relatively simple means of determining the amount of coprecipitant as a function of the amount of precipitated carrier. To effect this, a small quantity of solution was removed at regular time intervals. The amount of each element present was then computed by γ-ray spectrometric analysis.

TABLE IV.—PRECIPITATION OF NIOBIUM IN THE FILTRATE

Taken, *mg*		Nb left in solution, %
Ta_2O_5	Nb_2O_5	
19·7	100·4	0·05
20·6	80·0	0·10
20·5	60·3	0·09
20·2	40·1	0·13
20·7	20·8	0·13
20·5	10·6	0·07
40·5	10·4	0·12
60·1	10·1	0·14
80·2	10·2	0·07

Procedure

Extract with 50 ml of 5% ammonium oxalate after bisulphate fusion of 43·8 mg of tantalum, and 5·6 mg of niobium, labelled with ^{182}Ta and ^{95}Nb, and transfer to a 400-ml conical flask fitted with a reflux condenser. Add 2 ml of 30% hydrogen peroxide, 50 ml of 12*M* hydrochloric acid and 1·5 g of tannin. Make the volume up to 300 ml. The activities of the tracer solutions are chosen to correspond respectively to *ca.* 3×10^6 and 5×10^6 cpm of ^{182}Ta and ^{95}Nb. Heat the solution for 7 hr at 85° and remove 5-ml portions by reverse filtration through an asbestos filter. Count 4-ml portions of these filtrates in standard vials with a multichannel analyser. The values of D, λ and K, corresponding to the different distribution constants, are presented in Table V.

From Table V it appears that the logarithmic distribution law is followed, the mean value being $\lambda = 0{\cdot}030_4 \pm 0{\cdot}001_3$.

TABLE V.—COPRECIPITATION OF NIOBIUM WITH TANTALUM

Ta pptd., %	Nb copptd., %	Distribution coefficients		
		D	λ	K
$42{\cdot}5_1$	$1{\cdot}7_4$	$0{\cdot}023_9$	$0{\cdot}031_8$	$0{\cdot}040_9$
$72{\cdot}6_3$	$4{\cdot}3_8$	$0{\cdot}017_4$	$0{\cdot}034_6$	$0{\cdot}060_3$
$83{\cdot}7_8$	$6{\cdot}3_6$	$0{\cdot}013_1$	$0{\cdot}036_1$	$0{\cdot}075_9$
96·38	$9{\cdot}9_7$	$0{\cdot}0041_6$	$0{\cdot}031_6$	$0{\cdot}10_3$
97·56	$10{\cdot}4_9$	$0{\cdot}0029_3$	$0{\cdot}029_8$	$0{\cdot}10_7$
$98{\cdot}82_5$	$11{\cdot}3_6$	$0{\cdot}0015_2$	$0{\cdot}027_1$	$0{\cdot}11_5$
$99{\cdot}17_6$	$11{\cdot}6_7$	$0{\cdot}0011_0$	$0{\cdot}025_8$	$0{\cdot}11_8$
$99{\cdot}25_9$	$12{\cdot}2_3$	$0{\cdot}0010_4$	$0{\cdot}026_5$	$0{\cdot}12_3$
			$\bar{\lambda} = 0{\cdot}030_4 \pm 0{\cdot}001_3$	

Furthermore, the experiments showed that the coprecipitation of niobium on tantalum also follows a logarithmic distribution if the bisulphate melt of the earth acids is extracted with hydrogen peroxide, the mean value of the distribution coefficient being $\lambda = 0{\cdot}067 \pm 0{\cdot}005$.

In this case, 61·5 mg of tantalum were precipitated in the presence of 5·25 mg of niobium. The concentration of oxalic acid was 1·5%; the solution contained 50 ml of 14*M* nitric acid and the precipitation was carried out with 0·75 g of tannin for a volume of *ca.* 200 ml. The results are presented in Table VI.

TABLE VI.—COPRECIPITATION OF NIOBIUM WITH TANTALUM (MELT EXTRACTED WITH HYDROGEN PEROXIDE)

Ta pptd., %	Nb copptd., %	Distribution coefficients		
		D	λ	K
34·1	$2{\cdot}1_2$	$0{\cdot}041_9$	$0{\cdot}052_2$	0·062
65·1	$6{\cdot}5_0$	$0{\cdot}037_3$	$0{\cdot}063_4$	$0{\cdot}10_0$
84·5	$13{\cdot}8_0$	$0{\cdot}029_4$	$0{\cdot}079_6$	$0{\cdot}16_3$
87·6	$14{\cdot}8_1$	$0{\cdot}024_6$	$0{\cdot}077_1$	$0{\cdot}16_9$
95·94	$18{\cdot}2_4$	0·0094	$0{\cdot}062_8$	$0{\cdot}19_0$
			$\bar{\lambda} = 0{\cdot}067_0 \pm 0{\cdot}005_0$	

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Zusammenfassung—Einem Versuch zur Niob-Tantal-Trennung durch homogene Fällung in Gegenwart von Tannin und Oxalat durch thermische Zersetzung der Peroxykomplexe war nur mäßiger Erfolg beschieden. Eine bessere Tantal-Niob-Trennung in Verhältnissen von 50 : 1 bis 1 : 30 wurde jedoch erzielt durch Extraktion des Bisulfataufschlusses mit $(NH_4)_2Ox$ vor der Zugabe von H_2O_2, HCl und Tannin. Beim Niob-Tantal-Verhältnis 1 : 1 wird die Mitfällung von Niob auf 5% gedrückt. Darüber hinaus werden zwei Alternativen vorgeschlagen: 1) quantitative Tantalausbeute im Niederschlag bei kleiner Oxalat- und großer Tanninkonzentration, wobei 90% des Tantal-freien Niob in Lösung bleiben; 2) 85%-ige Ausbeute von Niob-freiem Tantal bei hoher Oxalat- und niedriger Tanninkonzentration. Die Verteilungskoeffizienten der Mitfällung von Niob verlaufen logarithmisch; es werden homogene wahre Mischkristalle gebildet.

Résumé—Un essai de séparation du niobium et du tantale par précipitation en milieu homogène en présence de tanin et d'oxalate, en effectuant la décomposition thermique des peroxy complexes, n'a été que moyennement satisfaisant. On a toutefois obtenu une séparation plus satisfaisante du tantale et du niobium, pour des rapports allant de 50 : 1 à 1 : 30, en extrayant la masse de fusion au bisulfate avec $(NH_4)_2Ox$ avant addition de H_2O_2, HCl et tanin. Pour un rapport tantale/niobium 1 : 1, la coprécipitation du niobium est réduite à 5%. En outre, on présente deux possibilités: 1) une récupération quantitative d'un précipité de tantale à faible concentration en oxalate et forte concentration en tannin, laissant 90% du niobium exempt de tantale en solution; 2) une récupération de 85% en tantale exempt de niobium, à forte concentration en oxalate et faible concentration en tanin. L'étude du processus de coprécipitation du niobium montre que les coefficients de distribution suivent un diagramme logarithmique; il se forme un vrai cristal mixte homogène.

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GRAVIMETRIC ANALYSIS OF TANTALOCOLUMBITES BY PRECIPITATION FROM HOMOGENEOUS SOLUTION*

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Summary—An analysis of complex tantalocolumbites has been carried out by precipitation from homogeneous solutions. A homogeneous precipitation of tungsten, titanium, tantalum and niobium by thermal decomposition of the soluble peroxytungstates, described in previous papers, is used. Corrections for incomplete precipitation and coprecipitation phenomena are applied on the basis of the experimentally found values. Silicon and tin are separated by volatilisation as fluoride and iodide, respectively. Iron is extracted by means of isopropyl ether and the rare earth metals are precipitated homogeneously from an oxalate solution. Manganese is precipitated as the ammonium phosphate. The results are in good agreement with an independent method, the standard deviations being within 1% for the major constituents.

INTRODUCTION

As shown in previous papers,[1-3] tungsten, titanium, tantalum and niobium can be separated and determined by precipitation from a homogeneous hydrogen peroxide solution. In the present work the method is tested on a number of synthetic and natural minerals, containing tantalum and niobium.

Qualitative analysis

Before carrying out the quantitative determination of three natural minerals, a spectrochemical qualitative analysis by means of a d.c. arc was effected. A quartz-prism spectrograph was used in the wavelength range of 2600–3950 Å and 2750–4200 Å. The results are given in Table I.

TABLE I.—Spectrochemical analysis of the minerals

Mineral	I	II	III
Major constituents	Nb, Ta, Fe, Mn	Nb, Ta, Fe, Mn, Ti	Nb, Ta, Fe, Mn, Ti, Cr, rare earths
Minor constituents	Ti, Si, Sn, W	W, Si, Sn, Mn	W, Sn, Si, Mg, Mo, Th
Traces	Cr, Zr, Al, Mo, Mg	Cr, Zr, Al, Mo, Pb	As, Zr, Al, Pb

Discussion of method

Because tin(IV) oxide and silica are only slightly attacked by a bisulphate fusion, and because the melt is only extracted with hydrogen peroxide-nitric acid, tin(IV) oxide and silica are found almost quantitatively in the residue. They are volatilised as the tetra-iodide and tetrafluoride, respectively; the content of silicon and tin is then computed by difference.

Tantalum, niobium and tungsten are separated by precipitation from a homogeneous hydrogen peroxide-nitric acid solution. They are separated and determined by homogeneous precipitation from a slightly alkaline hydrogen peroxide and from an oxalate-tannin-hydrogen peroxide medium. From the filtrate of the earth acids

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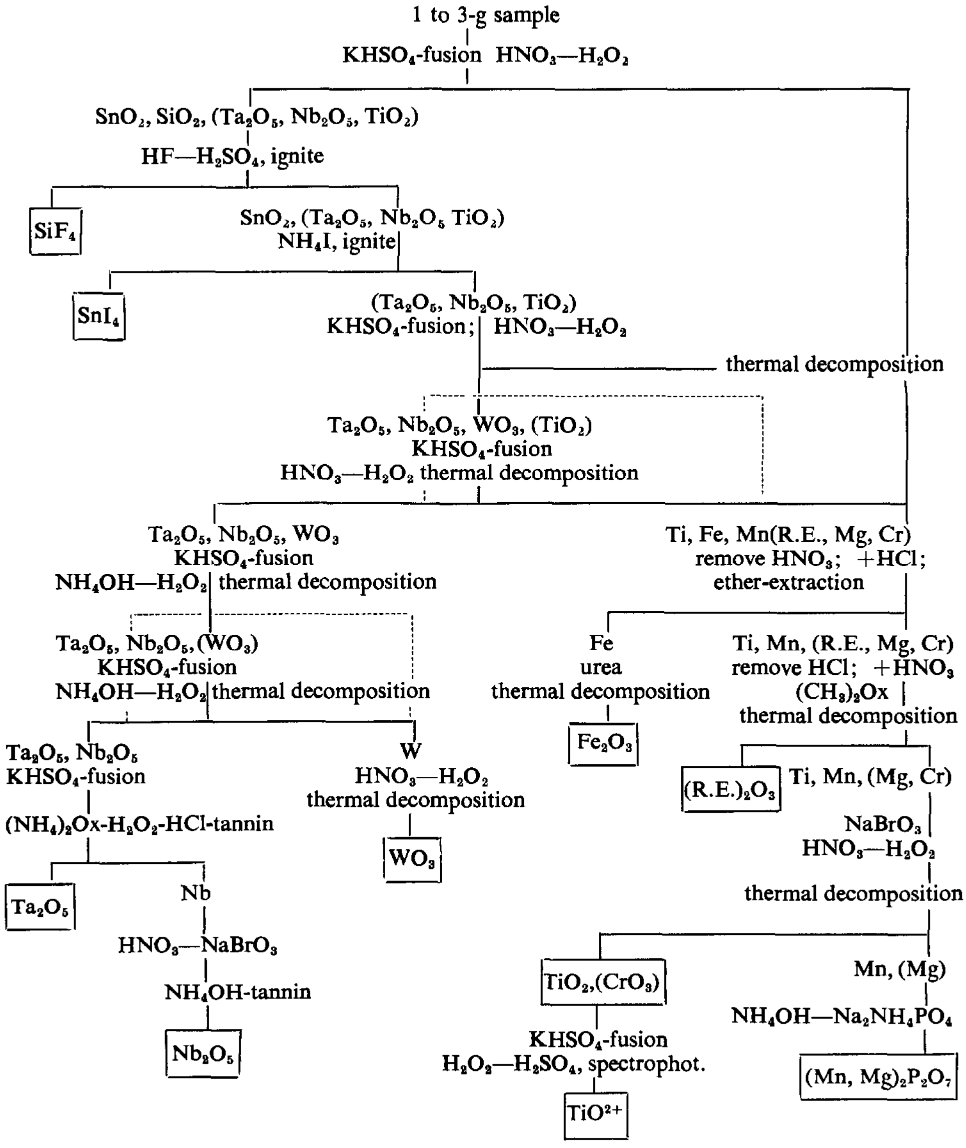
precipitation, iron is extracted with isopropyl ether, without manganese and titanium interference.[4] From a homogeneous hydrogen peroxide-nitric acid solution (pH 2·5) titanium precipitates practically quantitatively.[2] Manganese is obtained as manganese ammonium phosphate,[5] contaminated with small amounts of magnesium. The rare earths present in Mineral III are separated and determined as oxalates by a homogeneous precipitation with dimethyl oxalate.[6] In the presence of chromium (Mineral III), the precipitate of titanium is contaminated and was determined colorimetrically as peroxide in this precipitate.

An outline of the general scheme of the analysis is given in Fig. 1.

FIG. 1.—General scheme of analysis



Procedure. Fuse 1–3 g of finely powdered mineral with 5–15 g of bisulphate and dissolve the melt in hot 3% hydrogen peroxide. After neutralising with aqueous ammonia, acidify the solution to obtain 5*M* nitric acid. Filter the solution into an 800-ml beaker and transfer the precipitate to a platinum crucible. Add 4 ml of concentrated hydrofluoric acid and 1 ml of sulphuric acid and volatilise the silicon as silicon tetrafluoride. Take the residue twice to dryness with 2–3 ml of 14*M* nitric acid. Ignite the residue to constant weight at 950° to convert the sulphates and nitrates into the oxides. The silica content is found by difference. Add a ten-fold excess of ammonium iodide and 1 ml of hydriodic acid and stannictetriodide and heat at 475°. Repeat the process to ensure complete removal of tin. The loss in weight represents the amount of tin(IV) oxide. Fuse the residue with bisulphate and dissolve the melt in a few ml of 3% hydrogen peroxide and transfer the solution to the original filtrate. Heat at *ca.* 85° for 7 hr, in the presence of 0·1 g of selenous acid. Filter the hot solution and wash the precipitate with hot 1% nitric acid until free from sulphate. Incinerate and ignite the precipitate at 950° for 1 hr to constant weight. Fuse the mixed oxide residue with bisulphate in a silica crucible and leach the melt with 3% hydrogen peroxide and with dilute aqueous ammonia. Carefully adjust the pH of the solution to 7·5–8. After adding 0·1 g of selenous acid, heat the solution at 85° for 8 hr; tantalum and niobium are precipitated from this homogeneous solution. Collect the precipitate on a filter paper and wash with hot 2% alkaline ammonium nitrate until free from sulphate. Ignite the precipitate at 950° to constant weight as $(Ta, Nb)_2O_5$. For the determination of small amounts of titanium and tungsten repeat the precipitation steps from nitric acid and from slightly alkaline solution to reduce the coprecipitation of the latter. Evaporate the filtrate from the precipitation from alkaline medium, containing the bulk of the tungsten to *ca.* 150 ml and add 2 ml of 3% hydrogen peroxide and 75 ml of 14*M* nitric acid. Heat the solution at 60° for 2 hr. As soon as the precipitate has settled, filter from the hot solution, wash with hot 1% nitric acid, incinerate and ignite to constant weight at 900°. Weigh as WO_3. Fuse another two fractions, of *ca.* 125 mg, of the mixed oxides with bisulphate and transfer the crucible to an 800-ml beaker. Dissolve the melt in 120 ml of hot 5% ammonium oxalate solution. Add 120 ml of 12*M* hydrochloric acid, 2 ml of hydrogen peroxide (30%) and 2·5 g of tannin, dilute the solution to 600 ml. Heat for 7 hr at 85°. Filter the precipitate from the hot solution, wash with hot 2% ammonium chloride and ignite at 950° for 1 hr to constant weight. Weigh as Ta_2O_5. Evaporate the filtrate to *ca.* 200 ml. Remove the oxalate by adding a few ml of 14*M* nitric acid and a suitable amount of sodium bromate (3 g). Neutralise the solution with aqueous ammonia and add a ten-fold excess of tannin to the boiling solution. Boil for a few minutes until the precipitate settles. Filter and wash with hot 2% ammonium nitrate. Ignite the residue at 950° for 1 hr to constant weight as Nb_2O_5.

The filtrate from the earth acids precipitations contains titanium, iron, manganese and, in the case of Mineral III, chromium, rare earths and magnesium. Take almost to dryness and treat the residue with 50 ml of 12*M* hydrochloric acid. Repeat the operation to ensure complete removal of the nitric acid. Dissolve the residue in 300–800 ml of 8*M* hydrochloric acid and extract the iron repeatedly with isopropyl ether. Test for complete iron removal with thiocyanate. Shake the ether-phase three times with water to back-extract the iron. Neutralise the solution with aqueous ammonia and reacidify with dilute hydrochloric acid. Add 10 g of urea and boil the solution until neutrality is obtained; allow the precipitate to settle. To ensure complete precipitation of the iron, add a few ml of aqueous ammonia. Filter, wash and ignite the precipitate to constant weight as Fe_2O_3. For the determination of titanium, manganese and the rare earths, hydrochloric acid must be removed by the addition of 14*M* nitric acid and evaporation. Repeat the process twice. If rare earths are present, neutralise the solution with aqueous ammonia to pH 0·2, add 2 ml of 30% hydrogen peroxide and 30 ml of dimethyloxalate reagent solution (40 g of dehydrated oxalic acid dissolved in 100 ml methanol) to the solution and boil gently for 1 hr. Add an excess of 4 g of oxalic acid and boil for 0·5 hr. Filter the precipitate, wash with hot 2% oxalic acid and ignite at 950° to constant weight. Cover the crucible during cooling, and weigh quickly without removing the cover because the oxides absorb moisture and carbon dioxide from the air. Oxidise the excess of oxalate in the filtrate with sodium bromate in a nitric acid medium. Add 1 ml of hydrogen peroxide (30%), neutralise the solution to pH 2·5 and subject the peroxytitanates to thermal decomposition at 85° for 6 hr. Collect the precipitate and wash with hot 2% ammonium nitrate. Ignite the precipitate to TiO_2 at 950°. In presence of much chromium fuse the precipitate and extract with sulphuric acid. Add a few ml of hydrogen peroxide (30%) and determine the titanium by spectrophotometry at 410 mμ. To the filtrate from the titanium precipitation add aqueous ammonia and disodium ammonium phosphate. Collect the precipitate on a Gooch crucible and redissolve with sulphuric acid. Reprecipitate manganese and magnesium, if present, as ammonium phosphates. Collect the precipitate and ignite to constant weight at 650° as $(Mn, Mg)_2P_2O_7$. The tantalum, niobium, tungsten and titanium precipitates are filtered on SS 589^3 and the iron precipitate on SS 589^1 filter papers.

The results for tantalum, niobium, tungsten, titanium and manganese were corrected for incomplete recovery and for coprecipitation, corrections being applied according to the experimentally found values.[1–3]

TABLE II.—Analysis of synthetic mixture

Sample, g	SiO_2, %	SnO_2, %	Ta_2O_5, Nb_2O_5, WO_3, %	Ta_2O_5, Nb_2O_5, %	TiO_2, % Colorimetry	TiO_2, % Gravimetry	WO_3, %	Ta_2O_5, %	Nb_2O_5, %
1·0005	6·38	—	65·26	64·43	1·73^6	—	—	29·88 28·83 28·91	35·06 34·83 34·54
1·0014	6·07	—	65·47	64·05	1·67^1	—	—	—	—
1·0009	6·33^5	6·22^5	65·04	64·15	—	1·65^8	—	—	—
3·0014	6·40	6·30^5	64·95	64·02	—	1·70^5	0·96^5	—	—
Mean, %	6·30 ± 0·07^5	6·26^5 ± 0·03^9	65·13 ± 0·12	64·16 ± 0·10	1·70^5 ± 0·03^3	1·70^0 ± 0·01^4	0·96^5	29·21 ± 0·33^5	34·81 ± 0·15
Taken, %	6·24	6·25	65·05	64·21	1·66^8		0·83^5	29·15	35·02

Fe_2O_3 = 10·01%; Mn_2O_3 = 10·84%.

TABLE III.—Analysis of Mineral I

Sample, g	SiO_2, %	SnO_2, %	FeO, %	MnO, %	TiO_2, %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Sum, %
1·0002	0·74	0·62	7·71	12·90^{2}	0·91^{0}	—	35·49^{8} 35·44^{9}	43·04^{5} 43·22^{5}	—
1·0008	0·88	0·58	7·69^{2}	12·99^{0}	0·87^{5}	—	35·68^{3} 35·53^{7}	43·25^{1} 43·15^{2}	—
1·0000	0·88	0·49	7·68^{1}	12·83^{4}	0·74^{1}	—	35·29^{8} 35·57^{1}	(44·83^{6}) 42 91^{7}	—
1·0004	0·76	0·54	—	—	—	—	—	—	—
3·0005	0·89	0·42	7·66^{1}	12·95^{3}	0·82^{2}	—	35·20^{8} 35·31^{7}	42·84^{0} 42·94^{0}	— —
3·0009	0·66	0·43	7·70^{3}	12·88^{0}	0·87^{1}	—	35·25^{0} 35·48^{2}	42·86^{3} 42·69^{7}	—
Mean, %	0·80 ± 0·03^{9} s = ±0·09^{5}	0·51^{5} ± 0·03^{3} s = ±0·08^{1}	7·69 ± 0·00^{9} s = ±0·02^{0}	12·91 ± 0·02^{6} s = ±0·05^{8}	0·84^{5} ± 0·01^{8} s = ±0·04^{1}	—	35·43 ± 0·04^{9} s = ±0·15^{5}	42·99 ± 0·10^{7} s = ±0·32^{0}	101·1^{8}
Analysis[a]	0·86	0·48^{2}	7·72	13·32	0·90	0·22	35·32	42·77	101·5^{9}

[a] Analysis by Société Genérale Métallurgique de Hoboken.

TABLE IV.—Analysis of Mineral II

Sample, g	SiO_2, %	SnO_2, %	FeO, %	MnO,[a] %	TiO_2, %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Sum, %
1·0019	0·73^5	0·61	11·27^0	10·24^5	2·45	—	25·49^2 25·51^2	47·17^0 47·10^0	—
1·0284	0·82	0·50	(10·63)	(9·26)	(2·11)	—	25·88^5 25·73^9	47·02^5 47·66^6	—
1·0004	0·97	0·41	11·35^2	10·20^5	2·29	—	25·54^0	47·80^1	—
							25·67^0	47·96^1	
2·9997	0·82	0·46^5	11·28^0	10·29^4	2·18^8	0·84^2	25·65^8 25·75^4	47·88^8 47·99^8	—
2·9999	0·68	0·48^5	11·24^3	10·28^2	2·30^1	0·97^8	25·83^7 25·85^9	47·84^5 47·71^1	—
Mean, %	0·80^5 ± 0·04^5 s = ±0·10^1	0·49^5 ± 0·03^3 s = ±0·07^3	11·28^5 ± 0·02^4 s = ±0·04^7	10·25^5 ± 0·02^0 s = ±0·04^0	2·26^0 ± 0·04^1 s = ±0·08^1	0·91 ± 0·06^8	25·69^5 ± 0·04^6 s = ±0·14^5	47·61^5 ± 0·11^0 s = ±0·35^0	99·32^0
Analysis[b]	0·28	0·54^6	11·55	10·24^5	2·29	1·02	25·69	47·30	98·92^1

[a] Magnesium present (<0·2%) determined as manganese.
[b] Analysis by Société Genérale Métallurgique de Hoboken.

TABLE V.—Analysis of Mineral III

Sample, *g*	SiO_2, %	SnO_2, %	FeO, %	MnO,[a] %	TiO_2,[b] %	WO_3, %	Ta_2O_5, %	Nb_2O_5, %	Rare earths R_2O_3, %	CrO_3,[b] % (minimum)	Sum, %
1·0006	1·13	1·15	12·03^{1}	10·22^{5}	5·43^{9}	—	23·10^{5} 23·03^{6}	36·04^{4} 36·26^{2}	4·51	1·55	
1·0001	0·95	0·92	12·13^{8}	10·17	5·57^{7}	—	23·63^{6} 23·01^{6}	37·00^{3} 36·60^{4}	4·55	1·52	
0·9997	0·96	1·00	12·10^{3}	10·33	5·50^{4}	—	23·61^{7} 23·18^{0}	36·98^{8} 36·95^{8}	4·45	1·44^{5}	
3·0004	0·93	0·95^{5}	12·00^{0}	10·18	5·44^{8}	0·72^{6}	23·41^{3} 23·29^{8}	36·81^{9} 36·74^{5}	4·48	1·42	
2·9999	0·95^{5}	1·13^{5}	12·00^{7}	10·20^{5}	(4·89^{4})	0·83^{3}	23·70^{0} 23·78^{1}	36·87^{0} (39·76^{3})	4·53	(2·06)	
Mean, %	0·98^{5} ± 0·02^{3} s = ±0·05^{0}	1·03 ± 0·04^{7} s = ±0·10^{5}	12·05^{5} ± 0·02^{7} s = ±0·06^{1}	10·22 ± 0·02^{9} s = ±0·06^{5}	5·46 ± 0·01^{1} s = ±0·02^{2}	0·78 ± 0·05^{4}	23·38 ± 0·09^{4} s = ±0·29^{6}	36·70 ± 0·11^{6} s = ±0·34^{8}	4·50^{5} ± 0·01^{8} s = ±0·04^{0}	1·49 s = ±0·06^{2}	96·60^{5}
Analysis[c]	0·73	1·29^{5}	12·22	9·20	5·27	1·06	23·91	35·73	—	—	89·41^{5}

[a] Magnesium present determined as manganese.

[b] Titanium content determined colorimetrically, the difference between the colorimetric and gravimetric determination being given as chromium.

[c] Analysis by Société Genérale Métallurgique de Hoboken.

The double precipitation used for the analysis of the 3-g samples reduces the coprecipitation of titanium and tungsten to a considerable extent. When calculating the weighed mean values and the standard deviations for the titanium and tungsten, a three-fold weight was given to these results.

Before carrying out the analyses of the 3 minerals, the tantalum, niobium, tungsten, titanium, silicon and tin contents of a synthetic mixture were determined following the same procedure. The results are given in Tables II, III, IV and V.

From Tables III–V it appears that the results are mostly in good agreement with the results of an analysis performed elsewhere by an independent procedure. The deviation of the results of the major elements (tantalum, niobium, iron and manganese) are within 1 %. The larger deviation in the case of tungsten and titanium is obviously caused by the fact that the contents are only small in the presence of large amounts of earth acids. Chromium interferes with the gravimetric determination of titanium.

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Zusammenfassung—Eine Analyse komplizierter Tantalocolumbite wurde mittels Fällungen aus homogener Lösung ausgeführt. Homogene Fällung von Wolfram, Titan, Tantal und Niob durch thermische Zersetzung der löslichen Peroxywolframate wird verwendet, wie in den vorhergehenden Arbeiten beschrieben. Korrekturen für unvollständige Fällung und Mitfällung werden auf Grund der experimentell gefundenen Werte angebracht. Silicium und Zinn werden durch Abdestillieren als Fluorid bzw. Jodid abgetrennt. Eisen wird mit Isopropyläther extrahiert, die seltenen Erden homogen aus Oxalatlösung gefällt und Mangan als Ammoniumphosphat niedergeschlagen. Die Ergebnisse stimmen gut mit einer unabhängigen Methode überein, die Standardabweichungen für die Hauptbestandteile liegen unter 1 %.

Résumé—On a effectué une analyse de tantalocolumbites complexes par précipitation à partir de solutions homogènes. On emploie une précipitation homogène des tungstène, titane, tantale et niobium par décomposition thermique des peroxytungstates solubles, qui a été décrite dans des mémoires antérieurs. Sur la base des valeurs trouvées expérimentalement, on applique des corrections pour la précipitation incomplète et pour les phénomènes de coprécipitation. Le silicium et l'étain sont séparés par volatilisation à l'état de fluorure et d'iodure. Le fer est extrait au moyen d'éther isopropylique et les métaux des terres rares sont précipités en milieu homogène à partir d'une solution oxalique. On précipite le manganèse avec le phosphate d'ammonium. Les résultats sont en bon accord avec une méthode indépendante, les écarts types étant à 1 % près pour les principaux constituants.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XVII*

DETERMINATION OF ZINC AND CADMIUM IN THE PRESENCE OF EACH OTHER

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Summary—A new method for separating cadmium from zinc by precipitation as $Cd(phen)_2I_2$ is reported. Even very small amounts of zinc can be determined complexometrically in highly ammoniacal media by back-titration of an added excess of DCTA with calcium(II) using Methylthymol Blue as indicator.

CADMIUM and zinc form complexes with EDTA of almost identical stability ($\log K_{CdY} = 16{\cdot}46$, $\log K_{ZnY} = 16{\cdot}50$), so it is necessary to separate them for their complexometric determination in mixtures. Some years ago Přibil[1] proposed diethyldithiocarbamate for precipitation of cadmium after the complexometric determination of the sum of zinc and cadmium in slightly ammoniacal solutions. Kinnunen and Wennestrand[2] removed small amounts of cadmium by precipitation with thiourea. The adsorbed zinc was then removed by extracting its thiocyanate complex into an ether-amyl alcohol mixture. Recently, Fabregas, Prieto and Garcia[3] masked cadmium with a lead-EDTA complex. The displaced equivalent amount of lead was then precipitated as sulphate and removed from the solution by filtration. In the filtrate zinc was determined by EDTA titration with Eriochrome Black T as indicator. The results are satisfactory up to the weight ratio Zn:Cd = 1:17. Only one method for the determination of cadmium in the presence of zinc without previous separation is known; Flaschka and Ganchoff[4] titrated cadmium with ethyleneglycol-bis-(β-aminoethylether)-*N*,*N*-tetra-acetic acid (EGTA) solution, using copper sulphate as indicator. The end-point was detected spectrophotometrically by the appearance of the first traces of a blue copper-EGTA complex. With this method cadmium can be determined up to a 1:500 ratio of Cd:Zn.

None of the mentioned methods is, however, suitable for the determination of zinc in the presence of high concentrations of cadmium. Because one can hardly expect to find a specific masking agent for cadmium, we have searched for a new method for its separation from zinc. From preliminary experiments it was ascertained that cadmium precipitates quantitatively in a well filtrable form as $Cd(phen)_2I_2$. We have now found simple conditions where no adsorption of zinc occurs. The precipitation of cadmium as a phenanthroline-iodide complex is much more selective than the analogous precipitation as a phenanthroline-thiocyanate complex which has been used for the gravimetric determination not only of cadmium but also of copper, manganese, nickel and cobalt.[5]

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* Part XVI: *Talanta*, 1964, **11**, 1545.

The last three elements do not precipitate at all in the presence of iodide with phenanthroline. Amounts of cadmium even smaller then 5 mg can be separated by the proposed method.

EXPERIMENTAL

Reagents:

0·1*M o-Phenanthroline solution:* Add 1·8 g of solid *o*-phenanthroline to 50 ml of water, dissolve by dropwise addition of 1*M* hydrochloric acid, then dilute to 100 ml.

0·05*M DCTA solution:* Dissolve 17·72 g of 1,2-diaminocyclohexanetetra-acetic acid (J. R. Geigy, Basel, Switzerland) in hot water by adding 130 ml of 1*M* sodium hydroxide. Dilute to 1 litre. The pH of the solution should be *ca.* 5. Standardise by a complexometric titration with lead nitrate using Xylenol Orange as the indicator.

Other reagents: 0·05*M* cadmium nitrate, 0·05*M* zinc nitrate (prepared by dissolving metallic zinc in nitric acid), 0·05*M* calcium chloride (prepared by dissolving calcium carbonate in hydrochloric acid), solid potassium iodide, solid urotropine, Methylthymol Blue (1:100 with solid potassium nitrate).

Precipitation of cadmium as Cd(phen)$_2$I$_2$

To precipitate cadmium in a well defined crystalline form without adsorption of zinc great care has to be taken. The original pH of the solution must be 2·5–3·5, otherwise a voluminous precipitate adsorbing zinc is formed; also, the washing out of the precipitate on the filter is very important. The following procedure is considered to be most advantageous. Adjust the pH of the solution containing cadmium and zinc to 2·5–3·5, add 0·5–1·0 g of potassium iodide and heat to boiling. Add, dropwise, 0·1*M o*-phenanthroline solution until no further precipitate is formed. Cease boiling the solution and adjust the pH to 4·5–5 with solid urotropine. Intense stirring with a glass rod speeds up the formation of a crystalline precipitate, which settles easily. With small amounts of cadmium (< 5 mg) let the solution stand for 1 hr in a water-bath. Filter the precipitate through a paper filter (Black or White ribbon) and wash out the precipitate on the filter 8–10 times with a warm (50–60°) wash solution.[*] All of the zinc is in the filtrate.

Determination of zinc

In slightly acidic media zinc is completely complexed by *o*-phenanthroline,[6] but in strongly ammoniacal media the Zn(phen)$_2^{2+}$ complex is broken down. An ammonia-ammonium chloride buffer of pH 9–10, suitable for titrations with Eriochrome Black T, is not sufficiently concentrated and aqueous ammonia is required. Under these conditions the titration with EDTA does not have a sufficiently sharp change of pZn^{2+} at the equivalence point and it is better to use an indirect determination with DCTA solution.

Procedure. To the filtrate from the separation of cadmium add an excess of 0·05*M* DCTA (at least 30%) and 20–30 ml of concentrated aqueous ammonia. Add Methylthymol Blue and back-titrate with a solution of 0·05*M* calcium chloride to an intense blue coloration. The end-point is very sharp and reversible. A greater excess of aqueous ammonia than that given has no influence on the titration.

A number of determinations of zinc in the presence of small and high concentrations of cadmium have been made following the procedure. The results are shown in Table I.

TABLE I.—DETERMINATION OF ZINC AND CADMIUM

Taken, *mg*		Found, *mg*		Difference, *mg*		Ratio of Cd:Zn, *mg*
Cd	Zn	Cd	Zn	Cd	Zn	
56·50	10·24	56·50	10·25	0	+0·01	5·5:1
5·65	34·00	5·90	33·90	+0·25	−0·10	1:55
2·82	68·00	3·37	67·80	+0·55	−0·20	1:20
1·12	68·00	1·57	67·92	+0·45	−0·08	1:43
84·70	1·70	85·00	1·54	+0·30	−0·16	55:1
141·20	1·70	141·90	1·64	+0·70	−0·06	85:1
5·65	74·99	6·51	74·70	+0·86	−0·29	1:12
28·25	17·00	28·70	16·83	+0·45	−0·17	1·5:1
5·65	3·40	6·40	3·08	+0·75	−0·32	2:1
5·65	340·00[a]	—	338·00	—	2·00	1:60

[a] 1/10th Aliquot for determination of Zn.

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[*] 10 ml 0·1*M o*-phenanthroline in 500 ml of water.

DISCUSSION

The separation of cadmium as $Cd(phen)_2I_2$ is rather selective. Manganese, nickel and cobalt are not precipitated, but copper and lead must be absent. This offers a further possibility of determining cadmium gravimetrically as $Cd(phen)_2I_2$. In this case, iron(III), lead, *etc.*, could be screened with EDTA. This enables some simplified analyses of alloys containing cadmium, zinc and other elements to be made. These practical applications will be discussed elsewhere.

Zusammenfassung—Eine neue Methode zur Trennung von Cadmium und Zink durch Fällung von Cadmium als Cd-Phenanthrolin-Jodid $Cd(phen)_2J_2$ wird angegeben. Auch sehr kleine Zinkmengen werden in stark ammoniakalischem Medium komplexometrisch durch Rücktitration von DCTA mit Calciumsalz bestimmt. Methylthymolblau wird als Indikator verwendet.

Résumé—On décrit une nouvelle méthode pour séparer le cadmium du zinc, par précipitation à l'état d'iodure de cadmium-phénanthroline, $Cd(Phen)_2I_2$. Même de très petites quantités de zinc sont dosées par complexométrie en milieu fortement ammoniacal, par titrage en retour du DCTA au moyen d'un sel de calcium. On prend pour indicateur le bleu de méthylthymol.

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THE DETERMINATION OF ACETONE IN BUTANONE-2 BY PHASE SEPARATION

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Summary—Binary solutions of acetone in butanone-2 have been analysed by adding a constant amount of water and determining the temperature at which phase separation takes place. Because butanone-2 and water have a lower critical solution temperature, solutions are clear at lower temperatures and opalescent at higher temperatures. The weight percent of acetone in the original binary solution of ketones is a function of the phase-separation temperature, enabling the analyst to construct a calibration curve and determine unknown solutions directly. The error is about 0·1 absolute %.

MANY binary solutions exhibit a miscibility gap and, at certain concentrations, separate into two phases. Each phase is, itself, a binary solution. As the temperature of the system is increased, the composition of each phase usually approaches that of the other. Normally, at some temperature, the compositions of the phases become the same and the components become miscible in all proportions. This temperature is called the upper critical solution temperature. Less commonly, the liquid components become more soluble in each other as the temperature decreases and are completely miscible in all proportions below a temperature minimum. Such a temperature minimum is called a lower critical solution temperature. Some systems have both lower and upper critical solution temperatures.

Small amounts of impurities have a profound effect on the solubility curves of partially miscible binary solutions.[1] As long ago as 1914, Findlay suggested the critical solution temperatures as a criterion of purity,[2] and phase separation is the basis of a number of analytical methods, including the cloud-point method of determining water[3–7] and binary mixtures,[8–9] and the cloud- and aniline-point methods of characterising petroleum products[10] and fats.[11]

Because many binary solutions have miscibility gaps which are displaced by any one of an indefinite number of impurities, the phenomenon of phase separation should be capable of much wider analytical application than it now enjoys. This work is an example of the application of the phenomenon of phase separation to the subtle analytical problem of the accurate determination of the ratio of acetone to butanone-2 in binary solutions. It is novel in the application of the lower critical solution temperature to an analytical problem.

THEORY

Butanone-2 and water have an upper and a lower critical solution temperature. Because the lower critical solution temperature is more readily accessible, we will consider it in the following discussion. Acetone, being completely miscible with both

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butanone-2 and water, increases their mutual solubility and increases the lower critical solution temperature. If a calibration curve were constructed of the critical solution temperature of butanone-2 in ternary solutions with water and acetone, as a function of the ratio of acetone to butanone-2, unknowns could be determined by comparison. Critical solution temperatures would be determined by varying the amount of water in combination with a given ratio of acetone to butanone-2 and recording the minimum temperature of phase separation. The method would not be useful for determining the amount of water in any ternary solution because the temperature of phase separation is not very sensitive to small changes in composition of the system with respect to water.

Because the shape of the solubility curve is flat over a wide composition range in the region of the critical solution temperature, a considerable experimental simplification can be achieved. A convenient composition near the critical solution composition is selected, keeping the amount of water constant throughout, and the temperature of phase separation is determined. This avoids the necessity of determining the entire lower part of the solubility curve. The exact critical solution composition is not selected because it is not accurately known and it may change with increasing amounts of acetone.

EXPERIMENTAL

Reagents

Reagent-grade acetone and butanone-2 and distilled water were used throughout.

Procedure

Ten ml of a binary solution of acetone in butanone-2 are put in a test-tube with an equal amount of water. After cooling the solution below the temperature at which it becomes homogeneous and clear, it is allowed to warm slowly and, at the appearance of the first slight haze, the temperature is recorded to the nearest 0·1°. To prevent separation into two layers, the solution is stirred using a magnetic stirrer and a short stirring bar rotating at low speed. If turbidity occurs above room temperature, a water bath is used. In all cases, the rate of heating is less than 1° per min.

RESULTS

Fig. 1 is the calibration curve of the solution temperature of ternary solutions of acetone, butanone-2 and water at constant water composition. The temperature is plotted as a function of the weight percent of acetone in the original binary solution to which the water was added. The lower limitation of the curve is the point at which ice begins to separate from the water-rich phase and the upper limit is the boiling point of the organic rich phase. These are about −6 and 60°, respectively. The calibration curve has not been taken to these extremes because at the lower temperature, bubbles, arising from stirring, interfere with the observation of turbidity. They do not float out because of the increased viscosity of the solution at low temperatures. The upper extreme was avoided to prevent slight changes in composition from vaporisation. Any solution outside the useful composition range can be adjusted by standard addition of one of its components.

Observation of phase separation

Because the refractive indices of the phases are not very different, the turbidity which appears as the system goes from one to two phases is light. Viewed against a black background with cross illumination, phase separation produces a slight haze which, despite its unspectacular nature, is unmistakable and occurs within 0·1°. Stirring should be slow and intermittent up to the point of phase separation to prevent interference by bubbles.

The solution temperatures were approached from both lower and higher temperatures. Agreement was within 0·4°, indicating little kinetic lag. For maximum reproducibility, only those solution temperatures observed on increasing the temperature were used for analytical purposes.

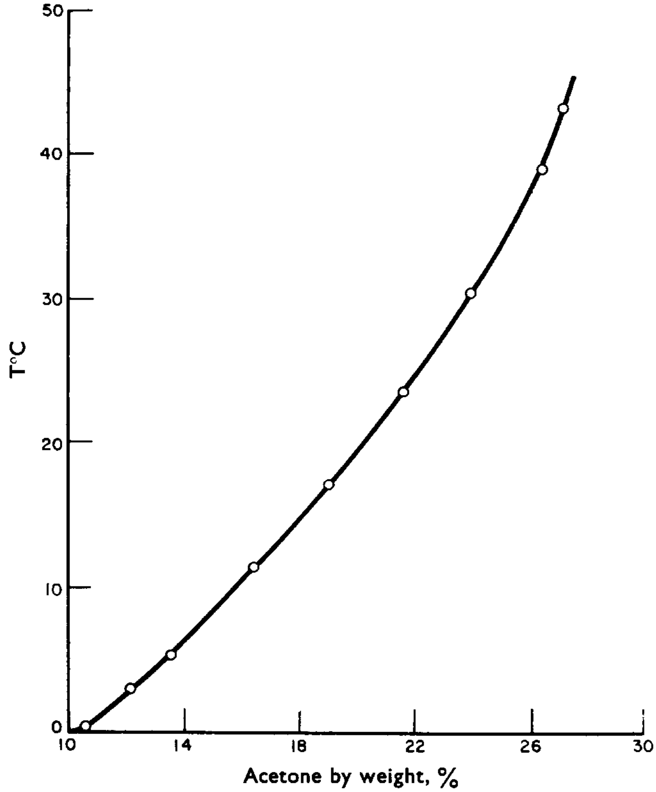

FIG. 1.—The temperature above which phase separation takes place for solutions of acetone, butanone-2 and water. The composition is constant with respect to water.

Potential accuracy of the method

The phase separation temperature can be determined with an error of less than 0·2° for replicate samples. The minimum slope of the calibration curve is 0·65% per degree and its maximum slope is 0·21% per degree at higher temperatures. Therefore, the minimum error should be about 0·13% at lower temperatures and 0·04% at higher temperatures. The extreme sensitivity of the solubility of butanone-2 in water to the presence of acetone makes this method one of high potential accuracy.

Comparable methods of analysing binary solutions are by density and refractive index measurements. The difference in density between acetone and butanone-2 is 0·0140 g/ml.[12] Assuming a minimum error of 0·0002 g/ml in density measurements, the error is about 1·4%.

The difference in refractive index between acetone and butanone-2 is 0·0216.[12] Assuming a minimum error of 0·0002 in refractive index measurement, the resulting analytical error is slightly less than 1%.

Interferences

All foreign substances interfere with analysis by phase separation. Like the comparable physical methods of density and refractive index, analysis by phase separation is strictly applicable only to binary solutions or solutions in which the amount of interfering substance is absolutely constant from one sample to the next.

One common impurity, water, does not interfere to a serious extent if its concentration is low. Because of the flat shape of the solubility minimum, small variations in the ratio of water to the organic components do not cause large changes in the solution temperature. The addition of 0·1 ml of water in excess of the usual amount increases the solution temperature by 0·1° for a solution showing phase separation at 30·4°. The addition of 0·1 ml of ethanol to the same system raised the solution temperature by more than 6°.

If the amount of water, the most common impurity, is less than 1% there will be no noticeable effect on the solution temperature. The amount of water which may be tolerated varies with the composition of the solution being analysed because the shape of the solubility curve varies with composition.

Applications

Like density and refractive index, phase separation will usually be useful only when the solutions being analysed are known to be binary solutions. An example is in the determination of the theoretical plates of a distilling column by analysis of the distillate and residue of a solution which is known to be binary.

Routine analysis is most convenient by phase separation when acceptable limits of concentration have been set. One constant temperature bath can be set to the temperature of the lower limit of concentration and another to the temperature of phase separation of the upper limit. Duplicate samples can be allowed to come to temperature equilibrium, one in each bath. If one is turbid and the other is not, the sample is within the concentration limits specified.

Phase separation is a method of cross checking other methods applicable to binary solutions. If a solution is assumed to be binary but is contaminated by a third substance, density, refractive index or phase separation measurements, taken singly, will give false results. If analysis by all three methods gives results which check with each other, the original solution was binary.

CONCLUSION

Analysis of binary solutions by phase separation at a lower consolute temperature has been illustrated by the system acetone in butanone-2. The method has the advantages of accuracy, simplicity and generality. It has the disadvantage of great susceptibility to interference.

Zusammenfassung—Binäre Lösungen von Aceton in Butanon-2 wurden analysiert durch Zusatz einer konstanten Wassermenge und Bestimmung der Temperatur, bei der Phasentrennung eintritt. Da Butanon-2 und Wasser eine untere kritische Lösungstemperatur haben, sind die Lösungen bei tiefen Temperaturen klar und bei höheren trübe. Der

Gewichtsprozentsatz von Aceton in der binären Ketonlösung ist eine Funktion der Trübungstemperatur. Damit kann man eine Eichkurve aufstellen und unbekannte Lösungen direkt bestimmen. Der Fehler beträgt etwa 0,1% absolut.

Résumé—On a analysé des solutions binaires d'acétone et de butanone-2, par addition d'une quantité constante d'eau et détermination de la température à laquelle on observe une séparation de phases. La butanone-2 et l'eau ayant une température critique inférieure de miscibilité, les solutions sont claires aux plus basses températures, et opalescentes aux températures plus élevées. Le pourcentage en poids de l'acétone dans la solution binaire initiale des cétones est une fonction de la température de séparation des phases. L'analyste peut ainsi construire une courbe d'étalonnage et doser directement des solutions inconnues. L'erreur est d'environ 0,1% absolu.

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ANION-EXCHANGE SEPARATION OF BERYLLIUM, VANADIUM AND OTHER ELEMENTS FROM LARGE AMOUNTS OF URANIUM

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Summary—A method is described for the anion-exchange separation of small quantities of beryllium, vanadium, magnesium, calcium, aluminium, gallium and indium from gram-amounts of uranium. For this purpose, a medium consisting of 95% methanol and 5% $5M$ nitric acid is passed through a resin bed of Dowex 1, X8. By subsequent washing of the resin with a methanol-nitric acid mixture of the same composition, these metal ions are preferentially eluted from the column, whereas uranium is still retained by the anion exchanger. In the eluates the elements are determined by means of spectrophotometric or titrimetric procedures.

INTRODUCTION

RESEARCH work carried out by Buchanan and Faris[1] has shown that uranium is only weakly adsorbed on strongly basic resins from aqueous nitric acid solutions. This fact has been employed to separate uranium, together with other weakly adsorbed elements, from those which are strongly adsorbed, such as thorium and bismuth.

When the nitrate concentration of such solutions is increased, as, for instance, by adding the nitrates of ammonium,[2] aluminium[3,4] or nickel,[4] the uptake of uranium by these resins is considerably enhanced, and quantitative adsorption can be achieved. These methods, however, suffer from the disadvantage that large amounts of salts will be present in the effluent in which the non-adsorbable elements have to be determined. In addition, gross quantities of vanadate and other anions would compete with uranium for resin sites, thus limiting the quantitative retention of uranium.

In mixed aqueous-organic solvent systems, in which the distribution coefficients of most elements are considerably higher than in pure aqueous nitric acid solutions, uranium is also more strongly adsorbed, as has been shown in detail by Korkisch and coworkers.[5,6]

Based on these observations an attempt has been made to find a means of separating large amounts of uranium as the nitrate from milligram or microgram quantities of other metal ions, such as beryllium and vanadium, which might be present in uranium used as a reactor fuel, or in uranium compounds obtained after the processing of uraniferous materials such as carnotite ores.

EXPERIMENTAL

Reagents

Ion-exchange resin: The strongly basic anion exchanger Dowex 1, X8 (100–200 mesh; nitrite form) was used.

Standard solutions of uranium and other elements: $5M$ nitric acid solutions of the nitrates, of exactly known element content, were employed.

Organic solvent: Reagent-grade methanol.

Wash solution: 95% (v/v) methanol- 5% (v/v) 5*M* nitric acid.

Apparatus

Ion-exchange columns: The column operations were carried out in resin columns of 75 cm length and a diameter of 1 cm.

Spectrophotometer: For the spectrophotometric determination of all elements investigated, with the exception of uranium which was determined fluorimetrically, the Beckman Model B spectrophotometer was employed.

Fluorimeter: The photoelectric fluorimeter employed was a Galvanek Morrison Fluorimeter, Mark V.

Quantitative determinations

Determination of uranium: The quantitative determination of uranium in the effluents was performed fluorimetrically by means of a procedure described by Schönfeld, El Garhi, Friedmann and Veselsky.[7]

Determination of other elements: The convenient and accurate photometric procedures described by Sandell[8] and by Snell and Snell[9] were used to determine microgram amounts of all metal ions investigated except beryllium, for the assay of which the following method was developed:

To 1 ml of 5*M* nitric acid, containing not more than 20 μg of beryllium, are added 1 ml of a 1% solution of Neothoron in methanol and 1 ml of 0.1*M* EDTA solution (disodium salt), and the solution is diluted to 10 ml with 2*M* sodium acetate solution. Spectrophotometric measurement is carried out at 570 mμ.

Under these experimental conditions, Beer's law is obeyed from 0 to 20 μg of beryllium/10 ml of measured solution. The addition of EDTA reduces the number of interfering elements considerably, so that in practice only appreciable amounts of aluminium and iron interfere slightly. Uranyl ions would cause strong interference when present, but they are removed by the ion-exchange step.

The determination of milligram quantities of the elements investigated was performed by using suitable titrimetric methods, mostly employing titration with 0.01 or 0.001*M* solutions of EDTA.

Column operations

Through the resin bed, pretreated with 100 ml of the wash-solution, were passed 20 ml of a mixture consisting of 1 ml of 5*M* nitric acid (containing uranium and the other element to be separated from uranium) and 19 ml of methanol, at a flow rate of 0.5 ml/min. The column was washed at the same rate with the wash solution, effecting the preferential elution of the second element; uranium passes only slowly down the column. When performing the test runs, each 5-ml portion of the effluent was collected and analysed for the metal ion in question and for uranium. After complete elution of the element, uranium is removed from the column by washing with a mixture consisting of 50% methanol–45% water–5% 5*M* nitric acid. The composition of this mixture is not critical, but after elution the resin can be regenerated better than if aqueous nitric acid only were used. In addition, excessive bubble formation is prevented.

RESULTS AND DISCUSSION

In Table I, the results of a series of separation experiments, carried out according to the ion-exchange procedure described above, are recorded. In all cases quantitative separation can be achieved, even when 10 g of uranium are present in the sorption solution. To demonstrate the effectiveness of this separation procedure the break-through volumes of uranium and the elution volumes of the other elements have been included in the table. As the elution volume, the ml of wash solution necessary to elute completely the element in question was taken. The break-through volumes of uranium are the ml of effluent in which uranium is detectable by means of the fluorimetric procedure.[7] Because the elution and break-through volumes are always more or less distinct, quantitative separation can thus be ensured.

Attempts to separate cadmium or strontium from uranium were unsuccessful.

Investigations carried out using other aliphatic alcohols in place of methanol have shown that in these solvents the separation of uranium from the metal ions investigated here is less advantageous, because of stronger adsorption by the resin.

TABLE I.—SEPARATION OF BERYLLIUM, VANADIUM(V), MAGNESIUM, CALCIUM, ALUMINIUM, GALLIUM AND INDIUM FROM URANIUM

Amount of uranium taken, *g*	Amount of other element taken, *mg*		Amount of other element recovered, *mg*	Elution volume, *ml*	Break-through volume of uranium, *ml*
10	Be	5	5.007	80	100
5	Be	5	5.001	80	130
1	Be	5	5.002	80	130
1	Be	0.1	0.098	80	130
1	Be	0.01	0.010	80	130
0.1	Be	0.01	0.010	80	180
10	V	5	4.98	80	90
5	V	0.1	0.10	60	130
0.05	V	12.	12.02	120	225
0.1	V	5.	5.004	80	250
1	Mg	5	5.01	80	150
0.5	Mg	5	4.98	80	150
1	Ca	5	5.01	90	140
0.5	Ca	5	5.02	90	140
1	Al	10	9.987	80	130
1	Al	0.1	0.101	80	130
1	Al	5	5.01	80	130
1	Ga	4	4.01	90	130
7	Ga	0.1	0.10	90	120
1	Ga	5	5.008	90	130
1	In	5	5.01	100	130
1	In	0.1	0.10	100	130
0.5	In	5	4.99	100	130

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Zusammenfassung—Es wird eine Methode beschrieben mittels der geringe Mengen an Beryllium, Vanadium, Magnesium, Calcium, Aluminium, Gallium und Indium von Grammengen Uran durch Anionenaustausch getrennt werden können. Zu diesem Zweck wird eine Lösung bestehend aus 95% Methanol und 5% 5*M* Salpetersäure durch ein Harzbett aus Dowex 1, X8 fließen gelassen. Beim darauffolgenden Waschen des Harzes mit einer Methanol-Salpetersäuremischung derselben Zusammensetzung werden diese Metallionen bevorzugt von der Säule eluiert während Uran weiterhin vom Anionenaustauscher festgehalten wird. In den Eluaten werden dann die Elemente mittels spektrophotometrischer oder titrimetrischer Verfahren quantitativ bestimmt.

Résumé—On décrit une méthode de séparation, par échange anionique, de petites quantités de beryllium, vanadium, magnésium, calcium, aluminium, gallium et indium, à partir de quantités d'uranium de l'ordre du gramme. Dans ce but on fait passer, à travers une couche de résine Dowex 1, X8, un milieu constitué de 95% de méthanol et 5% d'acide nitrique 5*M*. Par lavage ultérieur de la résine avec un mélange méthanol-acide nitrique de même composition, on élue préférentiellement ces ions métalliques de la colonne, cependant que l'uranium reste retenu par l'échangeur anionique. Dans les éluats, les éléments sont dosés par des techniques spectrophotométriques ou volumétriques.

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A SELECTIVE EXTRACTION SYSTEM FOR TRACE AMOUNTS OF SILVER

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Summary—Silver can be extracted from near-neutral aqueous solution into nitrobenzene as the ion-association system formed between its 1,10-phenanthroline complex and bromopyrogallol red. In the presence of EDTA, mercury(II) and bromide ions as masking agents, the extraction system is highly selective. Of 42 ions examined, only thiosulphate and large amounts of gold interfere. The colour system is very sensitive ($\epsilon = 32{,}000$). Also, it can readily be applied to the indirect determination of concentrations of cyanide down to 0·026 ppm by determination of an added excess of silver.

THE few extraction systems that exist for silver are, in the main, dependent on chelation and are, as a consequence, somewhat unselective in action. Notable exceptions are the ion-association systems developed by Betteridge and West[1] and by Ziegler *et al.*[2] However, even these systems have some limitations, especially with anions which form strong silver complexes. In addition, some cations interfere,[1] among the more prominent being mercury(II).

In our examination of the very sensitive and selective silver/1,10-phenanthroline/bromopyrogallol red method,[3] it was noted that very large amounts of anions completely prevented the development of the colour system. Even nitrate, when present in greater than a 1000-fold mole excess over silver, completely prevented all colour development. This is, of course, in keeping with the behaviour of ion association systems of which the above is an example. In addition, with large amounts of silver ($10^{-4}M$ solutions) there is danger of precipitation. Thus, although this reaction is extremely sensitive in aqueous solution ($\epsilon = 51{,}000$), its usefulness is limited by interference from anions and it cannot be used for the determination of amounts of silver larger than 10 μg.

With these restrictions in mind, the possibilities of extracting the blue ternary complex, produced between silver, 1,10-phenanthroline and bromopyrogallol red, from near-neutral solution were investigated.

Water-immiscible solvents, such as ether, benzene, carbon tetrachloride, chloroform, methyl isobutyl ketone, amines, higher alcohols, *etc.*, all caused the blue complex to collect at the interface of the two phases. In addition, water-miscible solvents prevented or completely destroyed the colour. Only nitrobenzene was found to be capable of extracting the complex. In this medium the maximum absorption peak was at 590 mμ (*cf.* 635 mμ in aqueous solution) when compared with a blank of distilled water or nitrobenzene. Although the colour slowly faded to brown after several days, there was no sign of any precipitation at any time. The colour

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could also be developed directly in the nitrobenzene phase by first extracting an aqueous solution of silver nitrate and 1,10-phenanthroline at pH *ca.* 7 with nitrobenzene, followed by an equilibration with an aqueous solution of bromopyrogallol red in 1% ammonium acetate. The dyestuff itself is not extracted by nitrobenzene.

Procedures were subsequently developed along these lines for the determination of 10-50 μg of silver directly in the nitrobenzene phase. The molar extinction coefficient was calculated to be 32,000, which is equal to that of the standard dithizone and *p*-dimethylaminobenzalrhodanine methods. In addition, amounts of silver down to 1 μg, can be determined with but slight alteration in the recommended procedure. Small concentrations of silver can be determined by using the extraction system as a means of concentration.

The major difficulty encountered in this investigation was the slowness of the phase separation, following the final extraction with an aqueous solution of bromopyrogallol red. An ice-water treatment of the separating funnels was unsuccessful and the addition of a very large excess of electrolyte merely destroyed the colour of the final complex in the nitrobenzene phase.

The turbidity of the organic phase could be removed, without prolonged standing, by running it into a beaker containing a few pellets (*ca.* 5) of sodium hydroxide. Upon swirling, the turbidity disappeared in about 1 min. However, under these conditions the stability of the solutions was somewhat reduced and the absorbance measurements had to be made within 0·5 hr of this treatment. Other drying agents, such as calcium chloride, oxide and sulphate, *etc.*, merely adsorbed the blue complex, *cf.* however Note 1.

The effect of the 1,10-phenanthroline concentration on the efficiency of the extraction system was determined. It was concluded that, provided a 5-fold mole excess over silver was present, there was no significant increase or decrease in the expected absorbances. The effect of EDTA was similarly investigated, but once again it had no pronounced effect, even with amounts such as 10 ml of a $10^{-1}M$ solution. Furthermore, the order of addition of reagents was found to be equally unimportant.

Interferences

Because of the anionic interference in aqueous solution, this examination was restricted, in the first instance, to about a 1000-fold g ion excess over silver of the following anions: sulphate, phosphate, carbonate, chloride, bromide, iodide, fluoride, cyanide, thiocyanate, chlorate, thiosulphate, nitrate, acetate, oxalate and citrate. Provided that the aqueous phase is removed after the initial extraction of the silver/1,10-phenanthroline with nitrobenzene, and before the final extraction with an aqueous solution of bromopyrogallol red, only cyanide, thiocyanate, iodide and thiosulphate interfere. With the aid of a *double masking action* with mercury(II) ions, only thiosulphate continued to interfere. A sufficient excess of mercury(II) ions is added to the solution containing silver and 1,10-phenanthroline to complex cyanide, thiocyanate and iodide. Excess EDTA is then added to complex the excess mercury(II). Under these conditions only silver and 1,10-phenanthroline are extracted and the colour can be developed in the usual way.

Only mercury(II) and copper(II), of those cations previously investigated[3] and found not to interfere in aqueous solution in the presence of excess EDTA, were re-investigated in the extraction procedure. Neither was, however, found to interfere in the recommended procedure, which incorporates, once again, the use of EDTA as a general masking agent.

The cation examination was confined primarily to those ions which were found to interfere in aqueous solution, *i.e.*, niobium(V), gold(III), thorium(IV) and uranium(VI).[3] To these antimony(V) was added because it had been found to give, with bromopyrogallol red, a blue coloured complex, which was stable to EDTA. Under those conditions outlined in the recommended procedure only gold(III) continued to interfere. In addition, it was now unnecessary to add further masking agents, such as hydrogen peroxide or fluoride.

Gold(III), when present in a 5-fold excess over silver, no longer interfered if a sufficient amount of bromide ions was added to form the $AuBr_4^-$ complex before the initial extraction. Alternatively, the extraction can be carried out from ammoniacal solution at pH 10. The ammine complex of gold now prevents its extraction, but a decrease in sensitivity (*ca.* 4-fold) is obtained because of the less efficient extraction of silver/1,10-phenanthroline at this elevated pH.

Thus, the proposed extraction is completely free from the interference of the 26 cations and 14 anions examined, *viz.*, aluminium(III), ammonium, antimony(V), barium(II), bismuth(III), cadmium(II), calcium(II), cerium(III), chromium(III), cobalt(II), copper(II), iron(II), iron(III), lanthanum(III), lead(II), magnesium(II), manganese(II), mercury(II), niobium(V), nickel(II), palladium(II), thallium(I), thorium(IV), titanium(IV), uranium(VI), zinc(II) and acetate, bromide, carbonate, chloride, chlorate, citrate, cyanide, fluoride, iodide, nitrate, phosphate, sulphate, tartrate and thiocyanate. Only thiosulphate and large amounts of gold(III) caused interference.

EXPERIMENTAL

Reagents

$10^{-4}M$ *Silver nitrate solution.* Prepare by dilution of standard $10^{-1}M$ silver nitrate solution.

$10^{-3}M$ *1,10-Phenanthroline solution.* Dissolve 49·56 mg of analytical reagent grade 1,10-phenanthroline in distilled water and dilute to 250 ml.

20% *Ammonium acetate solution.* Dissolve 20 g of analytical reagent grade ammonium acetate in distilled water and dilute to 100 ml.

$10^{-4}M$ *Bromopyrogallol red solution.* Dissolve 13·96 mg of bromopyrogallol red plus 2·5 g of analytical reagent grade ammonium acetate in distilled water and dilute to 250 ml. This solution should be discarded after 5 days.

$10^{-1}M$ *EDTA solution.* Dissolve 3·7225 g of the analytical reagent grade disodium salt in distilled water and dilute to 100 ml.

$1M$ *Sodium nitrate solution.* Dissolve 8·5 g of analytical reagent grade sodium nitrate in distilled water and dilute to 100 ml.

Nitrobenzene, Reagent grade

Sodium hydroxide, Reagent grade pellets

Apparatus

A Unicam SP 600 spectrophotometer was used for the absorbance measurements.

Procedure

Calibration curve. Pipette 1–5 ml of $10^{-4}M$ silver nitrate solution, 1 ml of 20% ammonium acetate solution, 5 ml of $10^{-3}M$ 1,10-phenanthroline solution, 1 ml of $10^{-1}M$ EDTA solution and 1 ml of $1M$ sodium nitrate solution into 100-ml separating funnels. Add sufficient distilled water to give a constant volume of solution in each funnel, then add 20 ml of nitrobenzene and shake by continuous inversion for 1 min. Allow about 10 min for the layers to separate, then transfer the lower organic layers to different 100-ml separating funnels and add to the latter 25 ml of $10^{-4}M$ bromopyrogallol red solution. Again shake by continuous inversion for 1 min and allow about 30 min for the layers to separate. Run the lower nitrobenzene layers into 100-ml beakers, each containing about 5 pellets of sodium hydroxide (*Note 1*) and swirl each beaker until all cloudiness disappears (*ca.* 1 min). Finally, transfer the solutions to 1-cm cuvettes and, as soon as possible (within 0·5 hr), measure the absorbance at 590 mμ against a blank carried through the same procedure, but containing no silver:

$$1 \text{ ml of } 10^{-4}M \text{ AgNO}_3 \equiv 10{\cdot}788\ \mu\text{g of Ag}.$$

The graph of absorbance *vs.* micrograms of silver is a straight line from 10 to 50 μg of silver and passes through the origin.

Determinations. Take an aliquot of the silver test solution, containing between 10 and 50 μg of silver, and add sufficient EDTA to complex all those cations present which form an EDTA complex. If gold is present (<250 μg), add, in addition, sufficient bromide ion to form the $AuBr_4^-$ complex. If cyanide, thiocyanate or iodide is present, add sufficient mercury(II) ions to complex these anions followed by sufficient EDTA to complex any excess mercury(II). Add 1 ml of 20% ammonium acetate solution, *etc.*, and proceed as under *Calibration Curve*. Only thiosulphate interferes in this determination.

The determination of smaller amounts of silver can be carried out in a similar manner by using 4-cm cuvettes (for 1–10 μg of silver) or by using the extraction system as a means of concentration.

DISCUSSION

The proposed method is, in most respects, superior to the existing spectrophotometric procedures for the determination of silver. It is simple and quick in operation; there is no need for a special purification of reagents and the usual disadvantages associated with the dithizone and rhodanine methods are, therefore, eliminated. The method is equally as sensitive ($\epsilon = 32{,}000$) as the hitherto most sensitive silver reagent *p*-dimethylaminobenzalrhodanine. In addition, because of the use of masking agents and the selectivity of the nitrobenzene extraction system, only thiosulphate was found to interfere. The solution colours are stable for 0·5 hr after complete colour development and, provided the bromopyrogallol red reagent solution is not kept for longer than about 5 days, reproducible results can be obtained. With large amounts of silver (10–50 μg) there is no danger of precipitation, and smaller amounts of silver can readily be determined with the minimum of alteration in the recommended procedure.

Furthermore, the method can be readily applied to the indirect determination of trace amounts of cyanide by determination of an added excess of silver. Thus, by employing 10 ml of a $10^{-4}M$ silver nitrate solution and extracting into 40 ml of nitrobenzene in the recommended procedure, 2·602–13·01 μg of cyanide (1–5 ml of $10^{-4}M$ potassium cyanide solution) can be determined. Smaller concentrations of cyanide can be determined by using the extraction system as a means of concentration. Cyanide, in the range 0·026–2·6 ppm, has been determined in this way. The advantages of this method are that, of the common anions, only thiocyanate, iodide and thiosulphate interfere; in addition, only those cations which form a more stable complex with cyanide than silver (*e.g.*, Hg^{2+}), will interfere.

The complex produced in aqueous solution between silver, 1,10-phenanthroline and bromopyrogallol red is an ion-association system, $([\text{Phen-Ag-Phen}]^+)_2 \cdot \text{BPR}^{2-}$. This accounts for the selectivity and sensitivity of the method and for the instability towards anions in aqueous solution. However, there is still some doubt as to the mechanism of the extraction into nitrobenzene. Preliminary experiments suggest the existence of a differently constituted species in this solvent, probably $[\text{Phen-Ag-Phen}]^+ \cdot \text{BPR}^{2-}$, which would account for the decrease in the value of the molecular extinction coefficient and for the shift in wavelength of maximum absorption. Work is now proceeding on this aspect and on the possibility of using chromogens which do not contain chelating groups. Ligand bases other than 1,10-phenanthroline are also being investigated.

Note 1. The sodium hydroxide is the source of instability of the colour system, which is otherwise as stable as that of the aqueous one.[3] We have found more recently that the use of sodium hydroxide is unnecessary. Effective clarification of the nitrobenzene extract can be obtained by swirling a portion of it in a clean dry beaker before transference to the cuvette.

Zusammenfassung—Silber kann aus fast neutraler wäßriger Lösung als Ionenassoziat zwischen seinem 1,10-Phenanthrolinkomplex und Brompyrogallolrot mit Nitrobenzol extrahiert werden. In Gegenwart von EDTA, Quecksilber(II) und Bromid zur Maskierung ist das Extraktionssystem hochselektiv. Unter 42 untersuchten Ionen störten nur Thiosulfat und große Mengen Gold. Die Farbreaktion ist sehr empfindlich (ϵ = 32 000). In gleicher Weise kann die Methode zur indirekten Bestimmung von Cyanid bis herunter zu 0,026 ppm verwendet werden durch Bestimmung eines zugesetzten Silberüberschusses.

Résumé—On peut extraire l'argent au nitrobenzène, à partir de solutions aqueuses voisines de la neutralité, à l'état de système d'association ionique formé entre son complexe 1,10-phénanthrolinique et le rouge de bromopyrogallol. En présence d'EDTA, et d'ions mercure (II) et bromure comme agents dissimulants, le système d'extraction est hautement sélectif. Parmi 42 ions examinés, seuls l'hyposulfite et de fortes quantités d'or interfèrent. Le système coloré est très sensible (E = 32 000). On peut aussi appliquer aisément cette méthode au dosage indirect de concentrations en cyanure aussi faibles que 0,026 p.p.m. par dosage d'un excès d'argent ajouté.

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DETERMINATION OF BERYLLIUM BY MEANS OF HEXAMMINECOBALT(III) CARBONATOBERYLLATE—I

COMPOSITION OF THE PRECIPITATE AND ITS SUITABILITY AS A WEIGHING FORM FOR BERYLLIUM

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Summary—The precipitate obtained when hexamminecobalt(III) chloride is added to a solution of beryllium in excess ammonium carbonate has been analysed and its behaviour under different humidity conditions examined. The composition is that of hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot xH_2O$, as suggested by Sen Gupta, rather than that of Pirtea $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$. x depends on the humidity of conditioning, varying between 10·8 and 11·1 at relative humidities between 32 and 80%. Drying the precipitate *in vacuo* over anhydrous magnesium perchlorate or phosphorus pentoxide results in 3 molecules of water being retained. The compound as normally precipitated may be a mixture of the deca- and dodecahydrates that Sen Gupta prepared. After conditioning at a definite humidity and if an empirical factor is used, the precipitate may be suitable as a gravimetric form for determining beryllium where precision requirements are not too exacting.

OVER the past few years the development of beryllium metallurgy has resulted in the production of increasingly pure metal and consequently in heavier demands on the analytical chemist. The purest metal now available has a total impurity content of not more than 0·05%, most of which is oxygen, and it is desirable to have a highly accurate and precise beryllium assay method to supplement other analytical information.

The accurate determination of beryllium is a matter of some difficulty because the element does not readily form complexes or insoluble compounds of definite stoichiometric composition. The oxide has, perhaps, been most used for the gravimetric determination of beryllium, the hydroxide being precipitated in the presence of ethylenediaminetetra-acetate (EDTA) ion, which complexes a wide range of other cations. Unfortunately, this is not completely successful in preventing coprecipitation of impurities and it is usually necessary to carry out a spectrographic analysis of the oxide to enable suitable corrections to be made. This method also suffers from the usual difficulties associated with the high temperature ignition and weighing of a hygroscopic oxide. The determination as pyrophosphate suffers from similar disadvantages.

A number of organic precipitants have been proposed for the determination of beryllium, including 8-hydroxyquinaldine, β-hydroxy-α-naphthaldehyde and dimethylhexandione, but none of the resulting procedures is of a sufficiently high order of precision for the present purpose.

A method based on the potentiometric titration of the hydroxyl ion liberated in the reaction

$$Be(OH)_2 + 4F^- \rightarrow BeF_4^{2-} + 2OH^-$$

has been described by McClure and Banks[1] and has been used quite widely. This is an empirical procedure and the acid titrant must be standardised against beryllium. It was used routinely in this Establishment for some time, for moderately pure beryllium metal, giving results reproducible to 0·1–0·2 %. However, on occasions the method broke down completely and a more reliable procedure was required.

A number of papers by Pirtea[2–4] and coworkers describe a gravimetric method for determining beryllium in which the element is precipitated as a hexamminecobalt(III) compound of a carbonatoberyllate anion. Good results were obtained with quantities of beryllium between 0·9 and 72 mg, the reproducibility being about 0·1 % of the beryllium added at the higher levels; a micro-adaptation was shown to be satisfactory for quantities of beryllium between 70 and 350 μg. In this procedure the beryllium solution is neutralised and a large excess of ammonium carbonate added, forming the basic carbonatoberyllate anion. Any precipitated beryllium hydroxide or carbonate dissolves fairly readily in ammonium carbonate and a clear solution is obtained. Excess saturated hexamminecobalt(III) chloride is then added. After standing for some time the precipitate is collected on a sintered glass crucible, washed successively with 0·2 % hexamminecobalt(III) chloride solution, 60 % alcohol, absolute alcohol and ether. The precipitate is first dried by suction, then left in a vacuum desiccator for 15 min and weighed. The method was shown to be highly selective for beryllium if carried out in the presence of a suitable complexing agent, such as tartrate or EDTA, to prevent the precipitation of metals giving insoluble hydroxides or carbonates.

The above method appeared to be the most promising of available procedures from which a highly precise beryllium assay method might be developed and it was decided to investigate it further. The composition assigned to the complex by Pirtea disagrees with the results of other workers on carbonatoberyllates, although these are not entirely consistent with each other, as is shown below.

Compounds of basic beryllium carbonate were first prepared in 1855 by Debray,[5] who dissolved beryllium hydroxide in aqueous potassium carbonate solution. From this solution he isolated the potassium salt to which he assigned the formula $3K_2Be(CO_3)_2 \cdot Be(OH)_2$; he and Klatzo[5] prepared the corresponding ammonium salt. More recently, Sen Gupta[6] dissolved beryllium hydroxide in aqueous potassium bicarbonate and from the resulting solution he isolated a hygroscopic compound which he considers to be a hydrated form of $K_6[Be_4O(CO_3)_6]$; he similarly obtained the corresponding sodium salt. Ignoring the water content, Debray's and Sen Gupta's products are identical in composition. The formula proposed by Sen Gupta contains the anion $[Be_4O(CO_3)_6]^{6-}$, which has the typical basic beryllium carboxylate structure as found in the basic acetate $Be_4O(CH_3COO)_6$.

In contrast with the above observations, Humpidge,[5] in 1886, prepared an ammonium carbonatoberyllate whose formula he gave as $2(NH_4)_2Be(CO_3)_2 \cdot Be(OH)_2$. As regards the hexamminecobalt(III) compound, Pirtea gives it the formula $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3] \cdot 3H_2O$, whereas Sen Gupta considers it to have the same anion as the other salts and writes the formula as $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]$. Sen Gupta finds it to contain 10 or 12 molecules of water "according to the amounts of ammonium carbonate or alkali bicarbonate utilised for complexing beryllium". The $10H_2O$ compound gives tetrahedral and octahedral crystals, while the crystals of the $12H_2O$ are said to be feather-like. He states that the latter can be used for the gravimetric determination of beryllium, but gives no details as to how each hydrate can be produced or how he dried his precipitates.

The formulae given by Sen Gupta for his compounds are all supported by analytical results for N, Be, C and H. However, no such evidence is given by Pirtea and it is difficult to see on what grounds he arrives at his rather odd formula. The only statement made in its justification, literally translated from the Rumanian, is as follows: "Given the high molecular weight of the compound obtained, 440, corresponding to an empirical formula $[(H_2O)_2Be_2(CO_3)_2(OH)_3][Co(NH_3)_6]\cdot 3H_2O$ and the small atomic weight of beryllium, 9·02, beryllium enters into this compound in the proportion of only 4·10%." The experimental results obtained by Pirtea, using 4·10% as the beryllium content of the precipitate, appear to be good, in-so-far as the weight of beryllium found agrees with the amount added, but here the paper is obscure in another respect. It appears that the beryllium was added as a standard solution of $Be(NO_3)_2\cdot 4H_2O$ but it is not stated how the solution was standardised.

From the foregoing it was evident that it would first be necessary to establish the composition of the precipitate and experiments for this purpose are described below.

EXPERIMENTAL

Preliminary experiments showed that vacuum desiccation of hexamminecobalt(III) carbonatoberyllate over anhydrous magnesium perchlorate or phosphorus pentoxide resulted in continuous weight loss over a period of a day or two before constant weight was reached. The short drying period of 15 min in a vacuum desiccator as recommended by Pirtea could not, therefore, be regarded as a satisfactory procedure. Experiments were therefore performed to determine whether a suitable conditioning procedure at a definite humidity would give a product of sufficiently stable composition for weighing.

Stability of Compound at Various Humidities

Reagents

Standard beryllium solution (about 2% by weight). Prepared by dissolving beryllium metal flake of 99·8% purity (based on impurity analysis) in hydrochloric acid in a tared flask, diluting and weighing. Portions of the solution were weighed out as required from a polythene ampoule drawn out to a fine jet.

25% Ammonium carbonate solution (containing EDTA). 250 g of ammonium carbonate and 4 g of disodium ethylenediaminetetra-acetate were dissolved by stirring with 500 ml of water containing 120 ml of concentrated aqueous ammonia, and the solution diluted to 1 litre.

Hexamminecobalt(III) chloride. 5% aqueous solution

Wash solutions. 0·2% aqueous hexamminecobalt(III) chloride
60% v/v ethanol and water

Procedure

A weighed portion of beryllium solution was diluted to about 25 ml, 1*M* aqueous ammonia added until a permanent precipitate was formed and the latter dissolved by the addition of 1*M* hydrochloric acid. 20 ml of ammonium carbonate solution were added and the solution heated to about 60° for a few minutes until it became completely clear. An excess (20–50%) of 5% hexamminecobalt(III) chloride solution was then added and the solution allowed to cool to room temperature. The precipitate was collected on a tared X4 sintered glass crucible and washed successively with 0·2% hexamminecobalt(III) chloride solution and 60% v/v ethanol. It was then dried by suction (about 15–20 min). Washing with absolute ethanol was avoided to prevent possible dehydration of the compound.

The crucible and contents were weighed and transferred to a desiccator in which an atmosphere of controlled humidity was maintained. The humidifying agents used were moistened crystals of ammonium chloride (about 80% R.H. at 20°), magnesium nitrate (about 55% R.H. at 20°) and calcium chloride (about 32% R.H. at 20°). When constant in weight the sample was transferred to a vacuum desiccator containing anhydrous magnesium perchlorate or, in one experiment, phosphorus pentoxide.

Constant weight, reproducible to about 0·03%, was reached in 10–20 hr at relative humidities of 30–80%. However, dehydration took much longer and the reproducibility was only about 0·3% in these experiments because the desiccated material was very hygroscopic.

The results are shown in Table I.

TABLE I.—EFFECT OF HUMIDITY ON HEXAMMINECOBALT(III) CARBONATOBERYLLATE

Experiment no.		1	2		3		4		5
Weight (*g*) after exposure for 24 hr at:									
80% R.H.		0·8285							
55% R.H.			0·8685						
32% R.H.		0·8236	0·8655		1·2303		0·5213		0·6216
	Hr			Hr		Hr		Hr	
Weight (*g*) after drying *in vacuo* over magnesium perchlorate	2	0·7226	0·7588	20	1·1382	15	0·4466	7	0·5437^a
	67	0·7005	0·7356	69	1·0472	22	0·4481	72	0·5344^a
	70	0·7029	0·7389	72	1·0507	84	0·4440	104	0·5347^a
						116	0·4454	170	0·5337^a
Weight relative to that at 32% R.H. after exposure to:									
80% R.H.		1·0059							
55% R.H.			1·0035						
magnesium perchlorate^b		0·851	0·850		0·851		0·852		0·859^a

^{a} Dried over phosphorus pentoxide.

^{b} Ratios were calculated from the minimum weights observed.

Analysis for Elementary Constituents

Early experiments showed that conditioning at 30–80% R.H. gave a product sufficiently stable to handle in the ordinary laboratory atmosphere without the occurrence of sudden weight changes. Further experiments were carried out in which the complex was conditioned for 24 hr at 32% R.H., then analysed for cobalt, carbon, hydrogen and nitrogen. Four precipitations were carried out and cobalt determined on all four precipitates by the method to be described in Part II. Duplicate determinations of carbon, hydrogen and nitrogen by micro-combustion were made on two of the precipitates. The beryllium content of the precipitate was calculated from the known amounts added on the assumption of complete precipitation.

These results are shown in Table II.

DISCUSSION

It is clear, from the atomic ratios of carbon to the other elements shown in Table II, that the precipitate has the composition stated by Sen Gupta and not that of Pirtea. The compound should, therefore, be termed hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate and has the formula $[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot xH_2O$. The value of x may be calculated from the cobalt content, which was the most accurate of the determinations carried out. The mean value of the cobalt content of the compound conditioned at 32% R.H. was 12·696 ± 0·003%, corresponding to a molecular weight of 928·4 and giving x the value of 10·8. From the results in Table I, x has the value of 11·0 and 11·1 for the material conditioned at 55% and 80% R.H., respectively. 3·0 molecules of water are retained by the precipitate after drying *in vacuo* over magnesium perchlorate. In view of Sen Gupta's identification of the deca- and dodecahydrates it is possible that these species are of very similar

TABLE II.—COMPOSITION OF HEXAMMINECOBALT(III) CARBONATOBERYLLATE

Experiment no.	Be taken, *g*	Ppt. at 32% R.H., *g*	Composition, % *by weight*					Atomic ratios			
			Co	Be	C	N	H	N/C	C/Be	C/Co	Be/Co
6	0·02433	0·6237	12·695	3·901	—	—	—	—	—	—	2·009
7	0·01702	0·4367	12·693	3·897	—	—	—	—	—	—	2·008
8	0·04924	1·2628	12·691	3·899	8·0 8·1	18·8 18·9	6·2 6·2	2·01	1·54	3·11	2·009
9	0·05120	1·3154	12·704	3·892	7·7 7·8	18·6 18·8	6·4 6·2	2·07	1·49	2·99	2·003
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 10H_2O$			12·889	3·942	7·88	18·38	6·17	2·00	1·50	3·00	2·000
$[Co(NH_3)_6]_2[Be_4O(CO_3)_6]\cdot 12H_2O$			12·400	3·793	7·58	17·68	6·36	2·00	1·50	3·00	2·000
$[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$			13·386	4·094	5·46	19·09	7·10	3·00	1·00	2·00	2·000

stability and that the precipitates normally obtained are mixtures of the two. It is difficult to account for the continuous change in composition between 32 and 80% R.H. that we observed, but equilibrium is certainly reached quite rapidly at any humidity in the range. The loss in weight *in vacuo* over magnesium perchlorate also took place rapidly in the initial stages, and in Experiments 1 and 2 over 80% of the total water lost came off in the first 2 hr. Drying the precipitate in a vacuum desiccator for 15 min as recommended by Pirtea would, therefore, be expected to give a large loss in weight and a product of variable composition.

Since completing the above work we have seen the paper of Vinogradov[7] *et al.* on the same subject. They used Pirtea's method for precipitating beryllium and after determining the cobalt, carbonate and water contents of the precipitate, also concluded that it has the Sen Gupta formula. However, they find the beryllium content to be 3·95%, corresponding to 10 molecules of water. Because they followed Pirtea it is presumed that they also dried the precipitate for 15 min *in vacuo* over an unspecified desiccant. Because Pirtea and Vinogradov obtained results of reasonable reproducibility it is presumed that whatever desiccant was used was relatively slow in action. However, even in this case, the system cannot have been in equilibrium and the compound must have been losing weight continuously, if slowly. Vinogradov also measured the rate of decomposition of the compound on heating. He showed that it begins to lose weight at 30° and decomposition proceeds rapidly up to 60°. After a short halt there is another sharp increase in the decomposition rate at 75–85°. The results were rather variable and inconclusive, but about half of the water was lost on drying for 2 hr at 60°.

The rather variable and non-stoichiometric water content of the precipitate renders it unsuitable for the gravimetric determination of beryllium for work of the highest precision. However, as reasonably good reproducibility of composition is attainable by conditioning at a definite humidity it is considered that the method, used empirically, could find application in circumstances where a precision of 0·1–0·2% is adequate. The beryllium content of the precipitate conditioned at 32% R.H. is 3·883%. It should be noted that precipitation conditions in our experiments were not quite optimum. From the Be/Co ratios in Table II it may be calculated that only 99·5–99·8% of the beryllium was precipitated and this is attributed to insufficient dilution of the solution after adding the hexamminecobalt(III) chloride. This point will be dealt with in Part II in which a highly precise method for determining beryllium will be described, based on the determination of the cobalt in the hexamminecobalt(III) hexacarbonato-oxo-tetraberyllate precipitate.

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Zusammenfassung—Der beim Zusatz von Hexamminkobalt(III)-chlorid zu einer Lösung von Beryllium in überschüssigem Ammoniumcarbonat entstehende Niederschlag wurde analysiert und sein Verhalten bei verschiedenen Feuchtigkeiten untersucht. Die Zusammensetzung entspricht Hexamminkobalt(III)-hexacarbonato-oxo-tetraberyllat $[Co(NH_3)_6]_2[Be_4O(CO_3)_6].xH_2O$, wie von Sen Gupta vorgeschlagen, besser als der Formel von Pirtea

$$[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3\ H_2O$$

x hängt von der Feuchtigkeit bei der Aufbewahrung ab, es variiert bei

relativen Feuchtigkeiten von 32 bis 80% zwischen 10,8 und 11,1. Beim Trocknen im Vakuum über wasserfreiem Magnesiumperchlorat oder Phosphorpentoxyd werden 3 Moleküle Wasser zurückgehalten. Die normalerweise gefällte Verbindung ist vielleicht eine Mischung der von Sen Gupta hergestellten Deka- und Dodekahydrate. Nach Aufbewahrung bei einer definierten Feuchtigkeit und bei Gebrauch eines empirischen Faktors kann sich der Niederschlag als Wägeform bei der Beryllium-bestimmung eignen, wenn die Genauigkeitsansprüche nicht zu streng sind.

Résumé—On a analysé le précipité obtenu par addition de chlorure de cobaltihexammine à une solution de beryllium dans un excès de carbonate d'ammonium, et étudié son comportement dans différentes conditions d'humidité. La composition est celle de l'hexacarbonate-oxo-tétraberyllate de cobaltihexammine $[Co(NH_3)_6]_2[Be_4O(CO_3)_6],xH_2O$, ainsi que l'a suggéré Sen Gupta, plutôt que celle de Pirtea $[Co(NH_3)_6][(H_2O_2)Be_2(CO_3)_2(OH)_3],3H_2O$. x dépend de l'humidité ambiante, variant entre 10,8 et 11,1 pour des humidités relatives comprises entre 32 et 80%. Après séchage sous vide sur perchlorate de magnésium anhydre ou sur anhydride phosphorique, 3 molécules d'eau sont retenues. Le composé normalement précipité peut être un mélange des déca- et dodécahydrates que Sen Gupta a préparés. Après traitement sous une humidité définie, et par emploi d'un facteur empirique, le précipité peut convenir au dosage gravimétrique du béryllium, lorsque les exigences quant à la précision ne sont pas trop grandes.

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PRECIPITATION OF COPPER 8-HYDROXYQUINALDATE FROM HOMOGENEOUS SOLUTION

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Summary—Copper can be precipitated quantitatively, over a wide range of pH, by 8-hydroxyquinaldine produced from the hydrolysis of 8-acetoxyquinaldine. The copper 8-hydroxyquinaldate can be weighed as either the monohydrate or the anhydrous dichelate. Differences in the appropriate pH conditions, between the PFHS and conventional precipitation methods, and between thorium and copper precipitations from homogeneous solution, are accounted for.

ALTHOUGH precipitation from homogeneous solution (PFHS) has been extensively investigated and used for about twenty-five years, the generation of organic precipitants *in situ* received little attention until three or four years ago. Interest in this field is increasing, as a recent survey[1] of the literature shows. Since that review, studies[2,3] have revealed advantages, for the precipitation of zinc and of indium, of 8-acetoxyquinaldine as a source reagent for the precipitant 8-hydroxyquinaldine.

A study[4] of the precipitation of thorium 8-hydroxyquinaldate [thorium 2-methyloxinate, $Th(C_{10}H_8ON)_4$] *via* the hydrolysis of 8-acetoxyquinaldine disclosed a disadvantage of the PFHS method: the pH conditions for the quantitative precipitation of the pure chelate can be much more restrictive than in the conventional method. It was anticipated that, with regard to the pH conditions for successful precipitation, the difference between the conventional and PFHS methods would be much less with copper than with thorium. The present work demonstrates that this is so, and that copper can be determined with high precision and accuracy through the agency of 8-acetoxyquinaldine.

EXPERIMENTAL

Reagents and procedures

Copper(II) solution: Copper foil (AnalaR) was dissolved in nitric acid, and the solution was diluted with water to a concentration ~1·0 mg of Cu/ml. Standardisation was done iodometrically, using procedures recommended by Hammock and Swift.[5]

8-Acetoxyquinaldine (8-AQD): The sources of, and method of storing, this reagent were the same as in an earlier study.[4] The infrared spectra (in Nujol) of the commercial and synthesised products were the same; in neither was the hydroxyl stretching band at about 3400 cm^{-1} detected. Solutions were made by dissolving in 2·0 ml of glacial acetic acid the amount of 8-AQD required to give 20% or 200% excess of reagent, and diluting with water to 10 ml (100 mg of 8-AQD are equivalent to 15·8 mg of copper, for the 1:2 chelate).

All other chemicals were reagent-grade. Weights and volumetric ware were calibrated. The thermobalance has been described previously.[4]

The pH values of precipitation were determined by measurements on the filtrates at room temperature; the meter was standardised before use by an appropriate buffer solution, and readings of pH >10 were corrected for sodium-ion error.

Precipitation of copper 8-hydroxyquinaldate

Twenty-five ml of copper(II) solution (1 mg/ml) were diluted with water to 225 ml and 10 ml of a freshly prepared solution of 8-AQD (*vide supra*) were added. The pH was adjusted using 1·5–3*M* aqueous ammonia (or, for precipitations at pH values >10, using 2–5*M* sodium hydroxide), added drop by drop with vigorous stirring. (To allow for drift during precipitation, the pH was brought to a value higher than that desired after precipitation: about 0·1 unit higher at pH 5; about 1 unit at pH 7.) The solution was warmed for 2 hr at ~80°, filtered (medium porosity frit), and the precipitate washed, using for the transferring and washing about 100 ml of hot water. The precipitate was dried for 2 hr at 105–110° or for 1 hr at 125–130°, cooled over phosphorus pentoxide, and weighed as $Cu(C_{10}H_8ON)_2$.

RESULTS AND DISCUSSION

Character and composition of the precipitate

Precipitation began after some minutes of heating. The delay at pH 5.2 was less than half that at pH 4·0: this is a consequence of a sharp increase in the rate of hydrolysis of 8-AQD with increasing pH in the range 3·0 to 5·5.[6] The precipitate was distinctly crystalline, consisting of large, well-formed, thin, brown plates that were readily washed.

On being heated at 105–130°, the precipitate became dark green. That this reflects the dehydration of $Cu(C_{10}H_8ON)_2{\cdot}H_2O$ was established by the following (all precipitations at pH 4·5–9·5): weights of the brown product, dried at 60° for 16 hr, corresponded to quantitative recovery of the copper as the dichelate monohydrate; weights of the green product, dried for 2 hr at 105–110° or 1 hr at 125–130°, corresponded to quantitative recovery as the anhydrous dichelate; the green compound had a copper content (by ignition) of $16{\cdot}7_1$% with an average deviation of $0{\cdot}0_2$% (theoretical, for $Cu(C_{10}H_8ON)_2$, 16·73%); and thermogravimetric curves for precipitates previously dried at room temperature for 72 hr showed a break beginning at 102° followed by another plateau from about 130° to 230°, the decrease in weight corresponding to the loss of the hydrate water. (These temperatures are reasonably close to those found by Borrel and Pâris,[7] and we agree that the oxide level is reached at about 600°.)

pH Range for quantitative precipitation

The recommended procedure, even with an excess of reagent of only 20%, permits the quantitative recovery of copper (from solutions of concentration ~90 mg of Cu/litre or $1{\cdot}4 \times 10^{-3}M$) as the dichelate, with high precision, over a wide range of pH. Sixteen determinations in the pH range 4·5–9·5 had an average deviation, from the 100·0% recovery value, of only 0·1%.

The pH range for quantitative precipitation can, of course, be extended by increasing the excess of reagent (Fig. 1). The pH values for both "incipient" and quantitative precipitation of a metal chelate depend on several factors, including the concentration of any complexing anions in the solution; in spite of such differences, our values (pH 3·2 and 4·5 for 20% excess reagent; pH 2·9 and 3·9 for 200% excess) are in good agreement with other results[8,9] obtained using 8-hydroxyquinaldine directly.

No work bearing on the upper limit of pH for the quantitative precipitation of copper 8-hydroxyquinaldate is known to us. With 20% excess reagent, we found that precipitation—calculated as the dichelate—beyond pH 10 began to fall below 100%, decreasing to 94% at pH 13·9. In this same range, the copper contents of the precipitates (dried at 105–130°) rose from $16{\cdot}7_1$% (proper for the anhydrous dichelate) to $16{\cdot}8_6$%. These results indicate that precipitation beyond pH 10 occurs as an hydroxychelate or a mixture of the normal chelate and hydrous copper oxide. Moreover, more than one kind of experiment showed that (regardless of the composition of the precipitate), at least at and beyond pH 12·8, copper was not quantitatively precipitated; this, too, is likely due to hydroxo complexing.

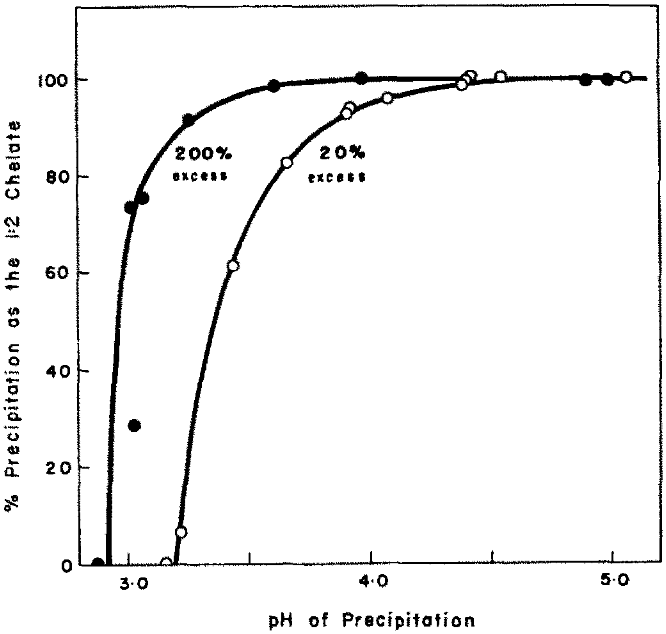

FIG. 1.—Precipitation of copper 8-hydroxyquinaldate from homogeneous solution in relation to pH of precipitation and excess of reagent.
(Copper in original solution = 0·1 mg/ml.)

Comparison of PFHS and conventional methods

With 20% excess reagent, precipitation of copper, by this PFHS method ceased to be quantitative (100·0 ± 0·1%) *as the dichelate* at pH 10; recovery of copper in this form was 99·5% in the pH range 10–12, thereafter decreasing more sharply with increasing pH, to 94% at pH 13·9 as has been mentioned. In contrast, in precipitations in which 8-hydroxyquinaldine was used directly, but which otherwise were comparable, quantitative precipitation of copper as the dichelate was obtained at pH values up to 12.

This wider pH range for successful precipitation using the conventional precipitation method is consistent with what was found with thorium,[4] although the effect is much less pronounced with copper. The differences in the useful pH range of the two methods likely arise from the different concentrations of the chelating quinaldate anion during adjustment of the pH and the consequences of this, as elaborated in the earlier paper.[4] That copper shows this effect in much lesser degree than thorium is to be expected. The effect stems from a competition between hydroxyl-ion and chelating anion for the metal-ion, and thorium-ion is, of course, relatively very prone to hydrolysis. Of the bivalent metal-ions of the first transition period, copper may have the widest pH range for successful precipitation of the 8-hydroxyquinaldate, because of the high stability of copper chelates. Another relevant factor, though, is the intrinsic solubility[10] of the chelate, and the intrinsic solubilities of these metal chelates may differ appreciably. In fact, pronounced differences in the intrinsic solubilities of the 8-hydroxyquinolates of cobalt, copper and zinc have recently been reported[11] and, moreover, the intrinsic solubilities of these chelates do not follow their stability order.

In any event, copper can be quantitatively precipitated as the 8-hydroxyquinaldate over a wide pH range: 6 to 8 or more pH units, depending on the excess of reagent and whether 8-acetoxyquinaldine or 8-hydroxyquinaldine directly is used.

Acknowledgement—We gratefully acknowledge financial support from the National Research Council of Canada.

Zusammenfassung—Kupfer kann quantitativ in einem weiten pH-Bereich mit 8-Hydroxychinaldin gefällt werden, das durch Hydrolyse von 8-Acetoxychinaldin erzeugt wird. Das Kupfer-8-hydroxychinaldinat kann entweder als Monohydrat oder als wasserfreies Dichelat gewogen werden. Unterschiede in den geeigneten pH-Werten zwischen der Fällung aus homogener Lösung und konventionellen Fällungsmethoden und zwischen Thorium- und Kupferfällungen aus homogener Lösung werden berücksichtigt.

Résumé—On peut précipiter quantitativement le cuivre, dans un large domaine de pH, au moyen de 8-hydroxyquinaldine produite par hydrolyse de la 8-acétoxyquinaldine. Le 8-hydroxyquinaldinate de cuivre peut être pesé à l'état de monohydrate ou de dichélate anhydre. On interprète les différences observées, dans des conditions de pH appropriées, entre la méthode de précipitation en milieu homogène et les méthodes de précipitation usuelles, et entre les précipitations du thorium et du cuivre en milieu homogène.

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SPECTROPHOTOMETRIC INVESTIGATION OF THE NATURE AND STABILITY OF SILVER(II) IN ACIDIC SULPHATE MEDIA

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Summary—A spectrophotometric study of silver(II) in sulphuric acid solution indicates the formation of two sulphato complexes, in the range 4–18*M* H_2SO_4, with absorbance peak maxima at 361 and 260 mμ, respectively. In 15*M* H_2SO_4 the molar absorptivity of silver(II) is $3{\cdot}11 \times 10^4$ at 361 mμ. Kinetic studies of the reduction of silver(II) by the solvent suggest a rate-determining step first order in silver(II) and yield a pseudo first-order rate constant of $1{\cdot}9 \times 10^{-1}$ min^{-1}. Further studies as a function of H_2SO_4 concentration show that the specific decomposition rate of the two complexes is identical and that changes in H_2SO_4 concentration only serve to shift the concentration equilibrium between the two complexes.

INTRODUCTION

IN a previous paper[1] we reported preliminary observations concerning the powerful oxidising agent, silver(II), in aqueous solution at low pH values. Silver(II) was found to be complexed even in perchlorate media and to undergo reduction by the solvent at rates proportional to the square of the silver(II) concentration and inversely proportional to the silver(I) concentration with an over-all activation energy of 11·6 kcal. mole^{-1}.

The present paper describes the results of systematic experiments aimed at elucidating the nature of silver(II) in sulphuric acid media and the details of the reduction of such species by the solvent. In particular, we were interested in establishing the effect of sulphate complexation on the stability of silver(II) with regard to its decomposition to silver(I) to learn whether or not the rate determining step of the over-all oxidation-reduction process involves a change in co-ordination number.

Because of uncertainties in the actual nature of solid silver(II)oxide,[2] employed as starting material in our preliminary experiments, we used an electrolytic generation method, similar to that of Davis and Lingane,[3] to prepare homogeneous solutions of silver(II). Previously unknown data on the nature and optical properties of sulphate-silver(II) complexes are reported in detail.

EXPERIMENTAL

Reagents

All solutions were prepared from reagent-grade materials, except where noted, and used without further purification.

Silver(II) oxide. AgO of 98·5% minimum purity was obtained from Handy & Harmon Company, New York, U.S.A., and was weighed as needed.

Silver(II) sulphate. $AgClO_4{\cdot}H_2O$ (G. F. Smith Chemical Co., Columbus, Ohio, U.S.A.) was used to produce silver(II) sulphate complexes in sulphuric acid media by electrolysis. Best results were obtained by making serial dilutions from 0·2400*M* $AgClO_4{\cdot}H_2O$ in 15*M* H_2SO_4 stock solutions to a final concentration of 0·0024*M* in 15*M* H_2SO_4.

Cerium(IV) sulphate. Pipette 10 ml of 0·1021*M* cerium(IV) sulphate (G. F. Smith Chemical Co.) in 0·5*M* sulphuric acid solvent and dilute with 15*M* sulphuric acid solvent to a total volume of 100 ml. Make further serial dilutions of $5{\cdot}0 \times 10^{-3}$, $1{\cdot}0 \times 10^{-3}$, $5{\cdot}0 \times 10^{-4}$, $1{\cdot}0 \times 10^{-4}$, $5{\cdot}0 \times 10^{-5}$, and $1{\cdot}0 \times 10^{-5}M$ in 15*M* sulphuric acid.

Cerium(III) sulphate. Weigh 0·3250 g of $Ce_2(SO_4)_3{\cdot}8H_2O$ (G. F. Smith Chemical Co.), dissolve in water and dilute with 18*M* sulphuric acid to a final concentration of $2{\cdot}04 \times 10^{-3}M$ in 15*M* sulphuric acid.

Apparatus

Spectra. Spectra and decomposition curves were recorded using a Beckman Model DB ultraviolet-visible spectrophotometer equipped with 1·00-cm matched silica cuvettes. Temperature of both the spectrophotometer and electrolysis cells was held at 25·0° ± 0·15° by a Wilkins-Anderson Co. Lo-Temp Bath system. An E. H. Sargent Model SRL recorder was employed for all absorbance measurements.

Electrolysis. The electrolysis current was provided by a Heathkit Model EUW-17 transistorised power supply. The current and voltage were monitored by Simpson Model 269 and 260 meters, respectively. A cylindrical platinum gauze cathode, 1·40 cm by 3·80 cm, and anode, 2·70 cm by 5·10 cm, were employed to provide proper cell geometry. The cathode was isolated from the anode by a glass cylinder 2·50 cm by 6·20 cm, closed at the bottom by either an "A" or a "C" sintered glass frit. The electrodes, isolation cylinder and electrolysis solution were contained in a thermostatted double-walled glass cell.

Procedure

Silver(II) in sulphuric acid solution was obtained both by dissolution of silver(II) oxide and by electrogeneration at constant current from silver(I). Dissolution was carried out by weighing the desired amount of silver(II) oxide into a 125-ml Erlenmeyer flask and adding 25 ml of sulphuric acid solvent. The flask was swirled until all the silver(II) oxide was dissolved and spectra or decomposition curves were recorded in the usual manner, with correction for initial decomposition time effects where necessary.

Electrolytic production of silver(II) complexes in sulphuric acid. Place 70 ml of silver(I) perchlorate in 15*M* H_2SO_4 into the electrolysis cell and stir vigorously. Adjust the power supply to furnish currents of 87–90 *mA*, which cause the voltage to be greater than the minimum 1·98 *V* needed with the cell used.[3] After rapid initial production of silver(II), a steady-state concentration of silver(II) is reached because the rate of silver(II) decomposition approaches the electrolysis rate. Because silver(I) inhibits the decomposition of silver(II), the steady-state concentration of the latter can be adjusted by changing the initial silver(I) concentration.

Withdraw samples by pipette and record spectra or decomposition curves in the usual manner, correcting for the time elapsed during sample withdrawal and transfer.

Beer's law was checked for the silver(II) complexes in sulphuric acid by allowing silver(I) to oxidise cerium(III) to cerium(IV) and measuring the absorbance of the stable cerium(IV) complex produced. A typical procedure is given for the determination of the molar absorptivity for the silver(II)-sulphate complex in 15*M* sulphuric acid at 361 mμ. Spectra of cerium(IV) sulphate in 15*M* sulphuric acid solvent were obtained in the $1{\cdot}0 \times 10^{-2}$–$1{\cdot}0 \times 10^{-5}M$ range, yielding $\epsilon_{380} = 2{\cdot}36 \times 10^3$ and $\epsilon_{360} = 3{\cdot}86 \times 10^3$, respectively.

Electrolytically generate silver(II)-sulphate complexes from 0·0024*M* silver(I) perchlorate in 15*M* sulphuric acid. Withdraw aliquots of the electrolysis solution and follow its decomposition as A_λ *vs. t*, at $\lambda = 361$ mμ. When suitable absorbance readings are reached, rapidly empty the cuvette into a beaker containing 10 ml of $2{\cdot}04 \times 10^{-3}M$ cerium(III) sulphate in 15*M* sulphuric acid, which provides a large excess of cerium(III). After the redox reaction has taken place, record the spectra of the stable cerium(IV) complex formed. Record the spectra of silver(I) perchlorate and cerium(III) sulphate in 15*M* sulphuric acid and of 15*M* sulphuric acid so that wavelengths can be chosen where silver(II) will not be interfered with by cerium(IV), cerium(III), silver(I) or sulphuric acid.

Calculate the actual concentrations of silver(II) corresponding to the measured absorbances at the appropriate wavelength from the amount of cerium(IV) produced by oxidation of cerium(III) by silver(II). Finally, plot A_λ (at $\lambda = 361$ mμ) of the silver(II)-sulphate complex (from decomposition curves) *vs.* the calculated silver(II) concentration. Beer's law is obeyed and the molar absorptivity, ϵ_λ, is calculated.

A further test of the applicability of Beer's law can be obtained using silver(II) from silver(II) oxide. Weigh 0·0023–0·0100 g of silver(II) oxide into 125-ml Erlenmeyer flasks. Add 10 ml of $2{\cdot}0 \times 10^{-3}M$ cerium(III) sulphate in 15*M* sulphuric acid. When all silver(II) has been reduced to silver(I), record the spectra of the cerium(IV) complex produced. Beer's law plots of A_λ [cerium(IV) produced] *vs.* initial concentration of silver oxide are obtained at $\lambda = 460$, 440, 420 and 410 mμ, all producing excellent straight lines.

RESULTS AND DISCUSSION

Spectra of silver(II) as a function of sulphuric acid concentration

Ultraviolet and visible spectra of an initial concentration of 0·0065 g of silver(II)-oxide in 25 ml of sulphuric acid solvent at 25·0° ± 0·15° suggest that two sulphate complexes of silver(II) are predominant in the range 4–18*M* sulphuric acid. One complex predominates in 10–18*M* acid with absorption maxima between 368 and 343 mμ (visible complex); the second complex predominates between 4 and 9*M* acid with absorption maxima between 262 and 245 mμ (ultraviolet complex). An isosbestic point, occurring in 12 and 18*M* acid at 310 mμ, further confirms the fact that significant concentrations of only two complexes in equilibrium are present in these media. Absorbances, at the respective maxima for the two complexes, are equal in 10*M* sulphuric acid.

The visible complex appears only as a shoulder between 339 and 332 mμ on spectra of the ultraviolet complex in the range 4–9*M* sulphuric acid. In the range 0·25–2·5*M* acid no measurable peak of either complex can be distinguished; undissolved particles of silver(II) oxide colour the solutions pale grey initially. Between 4 and 18*M* sulphuric acid, the solutions initially are brownish-yellow and decompose first to pale yellow and then, within a few hours, to water white. The highest absorbance for a given silver(II) concentration is obtained in 15*M* sulphuric acid at 356 mμ and in 5*M* acid at 250 mμ for the visible and ultraviolet complexes, respectively. Spectra of silver(I) perchlorate in sulphuric acid and of sulphuric acid showed no interference at the above wavelengths.

Definite shifts in location of the maxima occur for both complexes and are probably the result of several effects. Spectra taken at various times during the silver(II) decomposition process, but at constant sulphuric acid concentration, show small (3 mμ or less) wavelength shifts; changes in the acid concentration result in substantial changes in peak heights described above. All the above results are summarised in Table I.

Molar absorptivity of silver(II) in sulphuric acid

Beer's law was tested for the visible complex of silver(II) sulphate at 15*M* sulphuric acid at 361 mμ. This acid concentration and wavelength correspond to conditions where the absorbance of the visible complex reaches its maximum value for any given silver(II) concentration. A molar absorptivity of $3{\cdot}11 \times 10^4$ at 361 mμ was calculated for the silver(II) complex. No interference by perchlorate could be noted in the electrogeneration experiments where silver(I) perchlorate was used as a starting material.

Decomposition kinetics of silver(II) complexes in sulphuric acid media

The decomposition of silver(II)-sulphate complexes obtained by dissolution of 0·0050 and 0·0100 g of silver(II) oxide in 15*M* sulphuric acid was followed at 356 mμ (visible complex), 310 mμ (isosbestic point) and 260 mμ (ultraviolet complex), respectively, at 25·0 ± 0·15°. Plots of log absorbance *vs.* time yielded pseudo first-order rate constants of $8{\cdot}44 \times 10^{-2}$, $8{\cdot}79 \times 10^{-2}$ and $9{\cdot}43 \times 10^{-2}$ min^{-1}, respectively. Reliable values are difficult to obtain in such experiments, however, because silver(II) oxide does not instantly dissolve in these media and rate constants are not obtainable from initial slopes. All decomposition experiments were carried out in triplicate.

Silver(II)-sulphate complexes were also obtained by electrogeneration of 0·0024*M* silver(I) perchlorate in 15*M* sulphuric acid and their decomposition followed at 361 mμ at 25·0 ± 0·15°. Good straight lines were obtained for the early portions of log absorbance *vs.* time plots and yielded calculated pseudo first-order rate constants of 1·98 × 10^{-1} and 1·85 × 10^{-1} min^{-1} for electrolysis currents of 90 *mA* and values of 1·85 × 10^{-1} and 1·90 × 10^{-1} min^{-1} at 87 *mA*.

TABLE I.—SPECTROPHOTOMETRIC DATA FOR SILVER(II)-SULPHATE COMPLEXES AS A FUNCTION OF SULPHURIC ACID CONCENTRATION

H_2SO_4, *M*	Visible complex maximum, $\lambda(m\mu)$	Absorbance	Ultraviolet complex maximum, $\lambda(m\mu)$	Absorbance
18	368	0·557	260	0·149
17·5	368	0·293	260	0·085
17	364	0·835	260	0·228
16·5	362	0·790	260	0·241
16	362	0·436	260	0·128
15·5	363	0·905	260	0·277
15	356	0·967	260	0·398
14	353	0·758	260	0·309
13	352	0·874	260	0·470
12	346	0·813	260	0·543
11	346	0·973	260	0·805
10	340	0·659	260	0·557
9	339 (shoulder)	0·690	245	0·722
8	334 (shoulder)	0·468	247	0·568
7	334 (shoulder)	0·308	249	0·463
6	332 (shoulder)	0·360	251	0·585
5	334 (shoulder)	0·486	256	0·800
4	334 (shoulder)	0·203	262	0·325
2·5	(360)	0·055	260	0·115
0·5	(360)	0·080	260	0·065
0·25	(360)	0·125	260	0·110

TABLE II.—RATIO OF PSEUDO-RATE CONSTANTS FOR THE DECOMPOSITION OF SILVER(II) SULPHATE COMPLEXES

H_2SO_4, *M*	Ratio of rate constants, K	H_2SO_4, *M*	Ratio of rate constants, K
18	1·078	11	0·993
17·5	1·145	10	1·011
17	1·085	9	1·060
16·5	1·047	8	0·997
15	0·906	7	0·794
14	0·911	5	1·016
13	0·936	4	1·001
12	0·997		

In order to establish whether or not the extent of complexation of silver(II) by sulphate has any influence on the kinetics of silver(II) decomposition to silver(I), the absorbance *vs.* time behaviour of the visible and ultraviolet complexes was compared by a ratio method. For each acid concentration (see Table II) complete spectra were recorded at preselected intervals. From these absorbance *vs.* wavelength scans, absorbance *vs.* time data for each of the two complexes could be derived and corrected for any shifts in location of peak maxima and for decomposition during the time required to record each spectrum. A comparison of the specific decomposition rates can be obtained from the slopes, m, of the resulting plots as follows:

$$\frac{A_1 - A_{11}}{t_{11} - t_1} = m_1\,, \qquad \text{for } \lambda_1 \tag{1}$$

$$\frac{A_2 - A_{21}}{t_{21} - t_2} = m_2\,, \qquad \text{for } \lambda_2 \tag{2}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\frac{A_{m(n)} - A_{m(n+1)}}{t_{m(n+1)} - t_{m(n)}} = m_n\,, \qquad \text{for } \lambda_m \tag{3}$$

The standard rate expression, with concentration, C, pseudo-rate constant, k^1, and and reaction order, n^1, is

$$\frac{dC}{dt} = k^1[C]^{n^1} \tag{4}$$

and if $n^1 = 1$, then

$$\frac{dC}{dt} = k^1[C] \tag{5}$$

Substituting absorbance for concentration with $A_1 - A_{11} = \Delta A_{1-11}$, $A_2 - A_{21} = \Delta A_{2-21}, \ldots A_{m(n)} - A_{m(n+1)}$ and $t_{11} - t_1 = \Delta t_{11-1}, t_{21} - t_2 = \Delta t_{21-2}, \ldots t_{m(n+1)} - t_{m(n)}$, then combining (3) with (5)

$$\frac{\Delta A_{m(n)-m(n+1)}}{\Delta t_{m(n+1)-m(n)}} = k_m{}^1 A_{m(n+1)} \tag{6}$$

Divide $k_1{}^1$ by $k_2{}^1$ and let $\Delta t_{11-1} = \Delta t_{21-2}$, then

$$\frac{\dfrac{\Delta A_{1-11}}{A_1}}{\dfrac{\Delta A_{2+21}}{A_2}} = \frac{k_1{}^1}{k_2{}^1} = K \tag{7}$$

where K is the ratio of rate constants.

In the system under present consideration, it is experimentally observed that in the ranges of 4–18*M* sulphuric acid at constant initial silver(II) oxide concentration, K, the ratio of pseudo-rate constants, is a constant. Furthermore, the ratio of the pseudo-rate constants for the decomposition of the visible and ultraviolet silver(II)-sulphate complexes is 1·000 ± 0·015 (see Table II). Because the relative concentrations of the two complexes vary widely over the range of acid concentrations studied, one can conclude from the fact that the ratio of rate constants is a constant, that the rate determining step in the silver(II) decomposition is independent of both sulphate and hydrogen ion concentrations. Also, the decomposition reaction must indeed be pseudo first-order, in the range studied, in order to yield a rate constant ratio of unity.

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Zusammenfassung—Eine spektralphotometrische Untersuchung von Silber(II) in schwefelsaurer Lösung zeigt die Bildung zweier Sulfatokomplexe im Bereich von 8–36*n* H_2SO_4 mit Absorptionsmaxima bei 361 mμ und 260 mμ. In 30*n* H_2SO_4 ist der molare Extinktionskoeffizient von Silber(II) 3,11 × 10^4 bei 361 mμ. Kinetische Untersuchungen der Reduktion von Silber(II) durch das Lösungsmittel deuten auf einen geschwindigkeitsbestimmenden Schritt erster Ordnung bezüglich Silber(II) und liefern eine scheinbare Geschwindigkeitskonstante erster Ordnung von 1,9 × 10^{-1} min^{-1}. Weitere Untersuchungen, bei denen die H_2SO_4-Konzentration variiert wurde, zeigen, daß die spezifische Zersetzungsgeschwindigkeit der beiden Komplexe gleich ist und Änderungen in der H_2SO_4-Konzentration nur das Konzentrationsgleichgewicht zwischen den beiden Komplexen verschieben.

Résumé—Une étude spectrophotométrique de l'argent (II) dans l'acide sulfurique montre, dans le domaine 8–36*N* en SO_4H_2, la formation de deux complexes sulfato, avec des pics d'absorption maximale à 361 et 260 mμ respectivement. En SO_4H_2 30*N*, l'absorption molaire de l'argent (II) est de 3,11 × 10^4 à 361 mμ. Des études cinétiques sur la réduction de l'argent (II) par le solvant suggèrent un stade déterminant la vitesse d'ordre un en argent (II), et donnent une constante de vitesse d'ordre pseudo-un de 1,9 × 10^{-1} min^{-1}. Des études ultérieures en fonction de la concentration en SO_4H_2 montrent que la vitesse spécifique de décomposition est identique pour les deux complexes et que les variations dans la concentration de SO_4H_2 servent seulement à déplacer l'équilibre de concentration entre les deux complexes.

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PHOTOMETRIC TITRATIONS—X*

THE EDTA TITRATION OF IRON(III) IN THE PRESENCE OF HIGH CONCENTRATIONS OF BISMUTH

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Summary—In solutions containing a high concentration of ammonium chloride, bismuth is masked as the chloro complex, and iron(III) can be titrated with EDTA to a photometric end-point using sulphosalicylic acid as the indicator. Up to a mole ratio Bi:Fe of about 2,000, good results are obtained. At higher ratios slightly high results are obtained for the iron. The influence of some other metal ions on the titration has been studied.

THE direct chelometric titration of bismuth when present as the chloride is usually difficult, because of the formation of the insoluble oxychloride. It is known that high chloride concentrations prevent the formation of the oxychloride, or redissolve it once it has formed, provided that the pH is lower than about 3. It was thought that addition of high concentrations of chloride might offer a possibility for the direct titration of bismuth because, in such a solution, no precipitate would form. However, under these conditions bismuth gave only a faint colour or no colour at all with several metal indicators tried, and the rate of reaction of bismuth with EDTA was, from all indications, slow. These experimental findings suggested the possibility of using chloride for the "low stability masking" of bismuth. Masking by complex formation is commonly accomplished by employing low concentrations of complexing agents which form fairly stable complexes. However, a few cases are known where high concentrations of complexing agents which form weak complexes are employed. Notable examples are the masking of thorium with sulphate[1] and, recently, of cadmium with iodide.[2] Thus the term "low stability masking" was coined,[3] and investigations indicated that this approach offers further interesting possibilities.

To test this idea an attempt was made to titrate iron in the presence of bismuth, masking the latter by chloride. The stabilities of the EDTA complexes of iron and bismuth are of nearly the same order. Consequently the metals mutually interfere in titration. Although it is not difficult to titrate bismuth in the presence of iron when the latter is masked by reduction to iron(II) with ascorbic acid, the determination of iron in the presence of bismuth is possible only by difference methods. The sum iron + bismuth is titrated in one aliquot and the bismuth is titrated in a second aliquot, after the iron is masked by reduction; the iron is obtained by difference. This procedure yields good results for iron only if the Bi:Fe ratio is close to or below unity. With bismuth present in increasing excess, the results for iron rapidly become less accurate.

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* Part IX: *Talanta*, 1964, **11**, 1067.

Sulphosalicylic acid was employed as the indicator for the titration of iron at pH 2–3. Preliminary experiments revealed that the colour of the iron-sulphosalicylic acid complex is discharged only slowly after the addition of excess EDTA, when the amount of ammonium chloride added is not higher than that required to redissolve the bismuth oxychloride initially formed. But with the solution nearly saturated with ammonium chloride, the colour disappeares rapidly and with seemingly equivalent amounts of EDTA. However, the disappearance of the red colour at the end-point was only gradual, especially with a large excess of bismuth present. Thus, in this particular case, no visual end-point could be obtained and a photometric titration was used.

EXPERIMENTAL

Apparatus

The phototitrator described by Flaschka and Sawyer[5] was employed with a heat filter mounted in the light path.[6] An interference filter with the nominal wavelength of 508 mμ was used. All titrations were performed in a glass cell with a 2-cm path length and a 200-ml capacity.

Reagents

All solutions were prepared from reagent-grade materials. Deionised water was used exclusively.

An approximately 0·1*M EDTA solution* was prepared by dissolving 37 g of the disodium salt dihydrate and making the volume to 1 litre.

An approximately 0·1*M iron solution* was prepared by dissolving 40 g of iron(III) nitrate in 1 litre.

A 0·6*M bismuth solution* was prepared by dissolving 290 g of bismuth nitrate in water to which several ml of concentrated nitric acid had been added, and diluting to 1 litre.

The EDTA solution was standardised against 0·10000*M* zinc solution which had been prepared by dissolving 6·538 g of zinc metal (99·99% purity) in the minimum amount of dilute nitric acid, and diluting to 1 litre. The standardisation was performed by titration at pH 5, using Xylenol Orange as indicator. This EDTA solution was used as the reference in the standardisation of the iron(III) solution, using sulphosalicylic acid as indicator at pH 2–3 in a photometric titration. Appropriate dilutions of the stock solutions were performed in order to obtain 0·01*M* iron and EDTA solutions.

Ammonium chloride was used as the solid and as a saturated aqueous solution.

The *indicator solution* was prepared by dissolving 1 g of sulphosalicylic acid in 10 ml of water.

Procedure

An accurately measured amount of the metal ion solution was transferred to the titration cell and enough hot water was added to make the solution volume 75–100 ml. Then 20–30 g of solid ammonium chloride were added in 5-g portions, with vigorous stirring, until no more solid was observed to dissolve readily. The remaining solid was dissolved by adding small amounts of hot water, and the solution volume was then brought to about 150 ml with a saturated ammonium chloride solution. The solution was cooled to room temperature, and the pH was adjusted to between 2 and 3 by dropwise addition of dilute sodium hydroxide, with vigorous stirring to minimise the local precipitation of bismuth salts. The cell was positioned in the phototitrator, which was then adjusted to indicate a transmittance of 85–90%. Finally, 4–5 drops of indicator were added and the titration was carried out at 508 mμ in the usual manner, with 0·01–0·1*M* EDTA.

RESULTS AND DISCUSSION

The results of several titrations of iron(III), alone and in the presence of bismuth and other metals, are presented in Table I. Using the procedure presented above, solutions with a molar ratio of Bi:Fe of 2,100 were titrated, and showed the precision and accuracy to be expected with the apparatus and technique employed. When the ratio was increased to 3,000 and slightly above, a tendency towards increasing positive errors was observed. Impurities of iron or other titratable metals in the bismuth salt may be responsible for this trend, but it is more likely that at this high ratio some bismuth is also titrated.

Table I.—Representative results for the EDTA titration of iron(III) in the presence of bismuth and some other metal ions

Fe taken, *mg*	$1{\cdot}14 \times 10^{-1}M$ EDTA, *ml*			Metal (M) added	Molar ratio M:Fe
	Calculated	Found	Difference		
5·70	0·89	0·89	0·00	—	—
5·70	0·89	0·88	−0·01	—	—
5·70	0·89	0·89	0·00	Bi	2
5·70	0·89	0·87	−0·02	Bi	2
5·70	0·89	0·88	−0·01	Bi	50
5·70	0·89	0·87	−0·02	Bi	100
5·70	0·89	0·89	0·00	Bi	210
5·70	0·89	0·90	+0·01	Bi	420
	$5{\cdot}70 \times 10^{-2}M$ EDTA, *ml*				
2·85	0·89	0·90	+0·01	Bi	1050
	$1{\cdot}14 \times 10^{-2}M$ EDTA, *ml*				
1·14	1·79	1·79	0·00	—	—
1·14	1·79	1·79	0·00	Bi	2100
1·14	1·79	1·80	+0·01	Bi	2090
1·14	1·79	1·87	+0·08	Bi	3140
1·14	1·79	1·86	+0·07	Bi	3140
	$1{\cdot}00 \times 10^{-2}M$ EDTA, *ml*				
1·23	2·20	2·20	0·00	Bi	1570
1·14	2·05	2·08	+0·03	Bi	1450
1·14	2·05	2·14	+0·09	Al	9
1·14	2·05	2·47	+0·42	Al	9
1·14	2·05	2·04	−0·01	Zn	25
1·14	2·05	2·04	−0·01	Ca	25
1·14	2·05	2·04	−0·01	Pb	25
1·14	2·05	2·05	0·00	Pb	125
1·14	2·05	2·05	0·00	Co	50
1·14	2·05	2·04	−0·01	Co	250
1·14	2·05	2·06	+0·01	Hg(II)	500
1·14	2·05	2·06	+0·01	In	1
1·14	2·05	2·06	+0·01	In	10
1·14	2·05	2·05	0·00	Mn	125

The rate of fading of the colour of the iron-sulphosalicylic acid complex upon the addition of an increment of titrant solution decreases considerably for Bi:Fe ratios above 1,000, and it becomes necessary to wait 4–5 min for the reaction to go to virtual completion after each addition of titrant. However because only a few points are required for locating the end-point graphically, this delay is not too serious. A reasonable explanation for the delayed reaction may be suggested. As the EDTA is added to the solution containing such a high concentration of bismuth, complex formation first occurs with that metal; then the iron exchanges with the bismuth, and this exchange reaction takes place slowly.

A mole ratio, Bi:Fe, of 3,000 is equivalent to a weight ratio of approximately 11,200. Thus the situation in the artificial solutions parallels the determination of about 0·01% of Fe in a bismuth metal sample of which 12 g were taken. The determinations at this ratio were precise to about 4% relative. At these levels of amounts and ratios, the success of a titrimetric determination is rather unusual. It must, of course, be considered that in an actual analysis less favourable results may be obtained because of the presence of interfering impurities.

For the titration of iron at the high Bi:Fe ratios it is necessary to obtain the maximum amount of dissolved chloride. In order to incorporate as much ammonium chloride as possible, it is helpful to warm the saturated ammonium chloride solution in contact with excess solid salt, before using it to raise the volume of the solution in the titration cell to 150 ml.

Predictions about elements that may interfere with the iron titration may be made cautiously from a comparison of the stability constants, and from knowledge of the situation in the absence of extreme chloride concentrations. Because iron(III) is known to form chloro complexes, the effective stability constant of the iron(III)-EDTA complex may be lowered to such an extent that the metals which are of no influence under normal conditions may interfere at high chloride concentrations. Several metals were added in order to see if there was a noticeable effect on the position and quality of the end-point. No effects were observed with calcium, magnesium, mercury, indium, lead, manganese or zinc in solutions containing the ratios of metal:Fe indicated in Table I. No attempt was made to establish limiting ratios. Cobalt slowed the rate of reaction considerably at a ratio of 250. Nickel and copper could only be tolerated in concentrations up to about that of iron(III). As expected, aluminium interfered and high results were obtained, implying that this metal is partially titrated. Zirconium and hafnium were fully titrated under these conditions. Gallium, in contrast to indium, was not completely masked by the chloride and high results for iron were obtained at a ratio Ga:Fe as low as 1. Titanium slowed the reaction between iron and EDTA to such an extent that the titration became impracticable, even with equal concentrations of titanium and iron.

The interference studies reported are only exploratory in nature, because the main concern of the present investigation was masking of bismuth and the determination of iron. A study of the application of low stability masking with chloride, and of the exclusion of some interfering metals by addition of further masking agents is under way on a broader basis, and any results of interest will be published at a later date.

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Zusammenfassung—In Lösungen, die hohe Konzentrationen an Ammoniumchlorid enthalten, wird Wismut als Chlorokomplex maskiert; Eisen(III) kann dann mit AeDTE gegen Sulfosalicylsäure als Indicator photometrisch titriert werden. Bis zu einem Molverhältnis Bi/Fe von etwa 2000 werden gute Resultate erhalten. Bei höheren Verhältnissen ergeben sich leichte Überwerte. Der Einfluss einiger anderer Metall wird studiert.

Résumé—Dans les solutions à forte concentration en chlorure d' ammonium, le bismuth est dissimulé à l'état de chloro-complexe, et l'on peut doser le fer (III) au moyen d'EDTA, avec virage final photométrique, en utilisant comme indicateur l'acide sulfosalicylique. On obtient de bons résultats jusqu'à un rapport molaire Bi/Fe de 2000 environ. Pour des rapports plus grands, on obtient, pour le fer, des résultats légèrement trop élevés. On étudie l'influence de quelques autres ions métalliques sur le dosage.

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SOME ANTIPYRINE DERIVATIVES IN THE ANALYTICAL CHEMISTRY OF THE PLATINUM METALS

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Summary—The reaction of quadrivalent osmium and iridium with antipyrine and some of its derivatives has been studied, and it has been shown that in acidic solutions the compounds $(R.H)_2MeX_6$ are formed. The extraction of the halide complexes of osmium, iridium, ruthenium, rhodium, platinum and palladium with diantipyrylpropylmethane by dichloroethane has been investigated. An extraction–photometric method is proposed for determining 2–20 μg/ml of osmium in the presence of 40 mg of ruthenium and for determining 4–40 μg/ml of iridium in the presence of 4 mg of rhodium. The error of the determination is ±10%. A gravimetric method is proposed for determining 5–13 mg of osmium and iridium with diantipyrylpropylmethane and diantipyrylmethane. The error of the determination is ±3%. The possibility is shown of the extractive separation of small amounts of iridium and rhodium, platinum and rhodium, and palladium and rhodium, using diantipyrylpropylmethane.

THE platinum metals form stable complex anions with a number of monodentate inorganic ligands. During the analysis of the platinum metals, they frequently pass into solution in the form of anionic chloride and bromide complexes: $Me^{IV}X_6^{2-}$ and $Me^{II}X_4^{2-}$. where X is Cl^- or Br^- and Me is a platinum metal. These anions form compounds with many organic bases. Some of the organic bases (strychnine,[1–3] brucine,[4] acridine,[5,6] tetraphenylarsonium chloride,[7–10] fatty amines[15]), and tributyl phosphate,[11–14] have been used for the gravimetric and photometric determination or extractive separation of the platinum metals.

We have made a detailed study of the reaction of the halide complexes of the platinum metals with antipyrine and its derivatives (diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane) in order to develop new and improved analytical methods for the determination and separation of the platinum metals. These reagents are widely used in analytical chemistry at the present time. In acid solutions they are present in the form of cations, and these react with the anionic metal complexes:

$$[Me^{m}X_{n}]^{-(m-n)} + (m + n)RH^{+} \rightleftharpoons (RH)_{(m-n)}[Me^{m}X_{n}] \qquad (1)$$

It was found that quadrivalent osmium, iridium and platinum, and also bivalent platinum and palladium, are precipitated from hydrochloric acid solutions (0·5–2M) and hydrobromic acid solutions by antipyrine, diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane. The compounds formed possess valuable analytical properties—a high molecular weight, low water solubility, the capacity for being extracted with organic solvents, a characteristic coloration, *etc.* We have used these properties to develop extraction-photometric and gravimetric methods for the determination of osmium and iridium and for the extractive separation of rhodium from platinum, palladium and iridium.

EXPERIMENTAL

Reagents

Osmium, ruthenium, iridium and platinum were used in the form of the following salts: $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$;[16] $(NH_4)_2RuOHCl_5$;[17] $(NH_4)_2RuOHBr_5$;[18] $(NH_4)_2IrCl_6$;[19] $(NH_4)_2IrBr_6$;[20] $(NH_4)_2PtCl_6$;[21] $(NH_4)_2PtBr_6$.[22]

The content of metal in the products was determined by calcining a weighed sample in a current of hydrogen (in air in the case of the platinum preparation) to constant weight of metallic osmium, ruthenium, iridium or platinum. Standard solutions were prepared by dissolving weighed amounts of the salts.

The hydrochloric and hydrobromic acid solutions of the rhodium and palladium salts were prepared from metallic rhodium and palladium by known methods.[23-25] The contents of rhodium and palladium in the prepared solutions were determined gravimetrically by means of thionalide[26] and dimethylglyoxime,[27] respectively.

The antipyrine was a commercial preparation with a melting point of 113·5–114·5°. The diantipyrylmethane,[28] diantipyrylpropylmethane[29] and diantipyrylphenylmethane[30] were synthesised from antipyrine by condensing it with the corresponding aldehydes. The materials obtained were purified by recrystallisation from ethanol.

Preparation and Composition of Compounds of Osmium(IV) and Iridium(IV) with Antipyrine and Its Derivatives

When acidic solutions of $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$, $(NH_4)_2IrCl_6$ or $(NH_4)_2IrBr_6$ and of the various antipyrine derivatives were mixed, curdy precipitates of low water-solubility immediately separated. To study the composition and properties of these precipitates, they were obtained in a pure state by the following method.

A hydrochloric (or hydrobromic) acid solution, containing 20–30 mg of osmium or iridium in the form of $(NH_4)_2OsCl_6$, $(NH_4)_2OsBr_6$, $(NH_4)_2IrCl_6$ or $(NH_4)_2IrBr_6$, was treated with 5–8 ml of a 2% solution of diantipyrylmethane, diantipyrylpropylmethane or diantipyrylphenylmethane in acetic acid (1:1).* The curdy precipitates which separated were filtered off and washed three or four times with water acidified with hydrochloric acid (or hydrobromic acid) and then three or four times with water alone.

The materials obtained were purified by recrystallisation from a 1:1 mixture of methanol and acetone and were analysed for their contents of osmium and iridium by calcining a weighed sample in a current of hydrogen to constant weight of metallic osmium or iridium.

Table I gives the formulae of the compounds (from the results of chemical analysis) and also some of their properties.

To elucidate the structure of the compounds, their infrared spectra were recorded in the crystalline state. The spectra were taken on a IKS-14 spectrophotometer in Nujol over the frequency range 4000—700 cm^{-1}.

As can be seen from Table II (Fig. 1), the band of carbonyl absorption at 1650–1660 cm^{-1}, present in antipyrine, diantipyrylmethane and diantipyrylpropylmethane,

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* Because of their high solubility in water, the compounds with antipyrine were isolated by adding dry antipyrine to a solution of the osmium or iridium salt.

TABLE I.—COMPOSITION AND PROPERTIES OF THE COMPOUNDS OF OSMIUM (IV) AND IRIDIUM (IV) WITH ANTIPYRINE AND ITS DERIVATIVES OBTAINED

Formula[a]	Colour and form of crystals	λ_{max}, *mμ*	ε	Solubility in 0·5*M* HCl, *moles/l.*
$(C_{11}H_{12}ON_2{\cdot}H)_2OsCl_6$	Yellow	346 378	10600 8000	Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsCl_6$				$10{\cdot}7 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$				$3{\cdot}5 \times 10^{-5}$
$(C_{29}H_{28}O_2N_4{\cdot}H)_2OsCl_6$				$1{\cdot}8 \times 10^{-5}$
$(C_{11}H_{12}ON_2{\cdot}H)_2OsBr_6$	Dark red	425 457 500	6000 9500 6500	Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$				$3{\cdot}7 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsBr_6$				—
$(C_{29}H_{28}O_2N_4{\cdot}H)_2OsBr_6$				—
$(C_{11}H_{12}ON_2{\cdot}H)_2IrCl_6$	Dark red	442 498	4500 5000	Very soluble
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrCl_6$				$14{\cdot}2 \times 10^{-5}$
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$				$3{\cdot}8 \times 10^{-5}$
$(C_{23}H_{28}O_2N_4{\cdot}H)_2IrCl_6$				$1{\cdot}1 \times 10^{-5}$
$(C_{11}H_{12}ON_2{\cdot}H)_2IrBr_6$	Dark blue needles or plates	540 555 605 700	2300 2300 4150 2150	—
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrBr_6$				—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrBr_6$				—
$(C_{29}H_{28}O_2N_4{\cdot}H)_2IrBr_6$				—

[a] $C_{11}H_{12}ON_2$—antipyrine; $C_{23}H_{24}O_2N_4$—diantipyrylmethane; $C_{26}H_{30}O_2N_4$—diantipyrylpropylmethane; $C_{29}H_{28}O_2N_4$—diantipyrylphenylmethane.

TABLE II.—FREQUENCIES OF THE VIBRATIONS OF SOME GROUPS OF ANTIPYRINE, ITS DERIVATIVES AND THEIR SALTS

Compound	Frequency of bond, *cm*$^{-1}$			
	C═O	C═C	HO—	$C\overset{\cdots}{=}O \cdots HX$
$C_{11}H_{12}ON_2$	1662	1586	—	—
$(C_{11}H_{12}ON_2{\cdot}H)_2OsBr_6$	—	2573	3560m	2452s
		1593	3470s	
			3226s	1830m
$(C_{11}H_{12}ON_2{\cdot}H)_2OsCl_6$	—	1576	3470m	—
			3070s	
		1616	—	—
$(C_{23}H_{24}O_2N_4$	1656	1592	—	—
		1620	3058s	2205s
$C_{23}H_{24}O_2N_4{\cdot}HCl$	—	1590		
		1605	3370w	2240w
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$	—	1584	3000w	
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsCl_6$	—	1597	3450w	—
		1596	3470s	2470w
$(C_{23}H_{24}O_2N_4{\cdot}H)_2IrBr_6$	—	1588	3280w	
$C_{26}H_{30}O_2N_4$	1658; 1650	1595	—	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsBr_6$	—	1610	3400w	2400w
		1598	3480w	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$	—	1584		
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrBr_6$	—	1596	3470w	2400w
		1582		

m = medium-intensity, s = strong, w = weak.

disappears and bands of comparatively low intensity appear in the region of 1500–1560 cm^{-1}. In the region of absorption of the O—H and $\overset{+}{N}$—H groups, broad intense bands appear (3500–3000 cm^{-1}), the intensity of these bands in the antipyrine complexes being considerably higher than in the diantipyrylmethane and diantipyrylpropylmethane complexes. A number of the spectra are characterised by intense absorption in the region of 3500–1800 cm^{-1}.

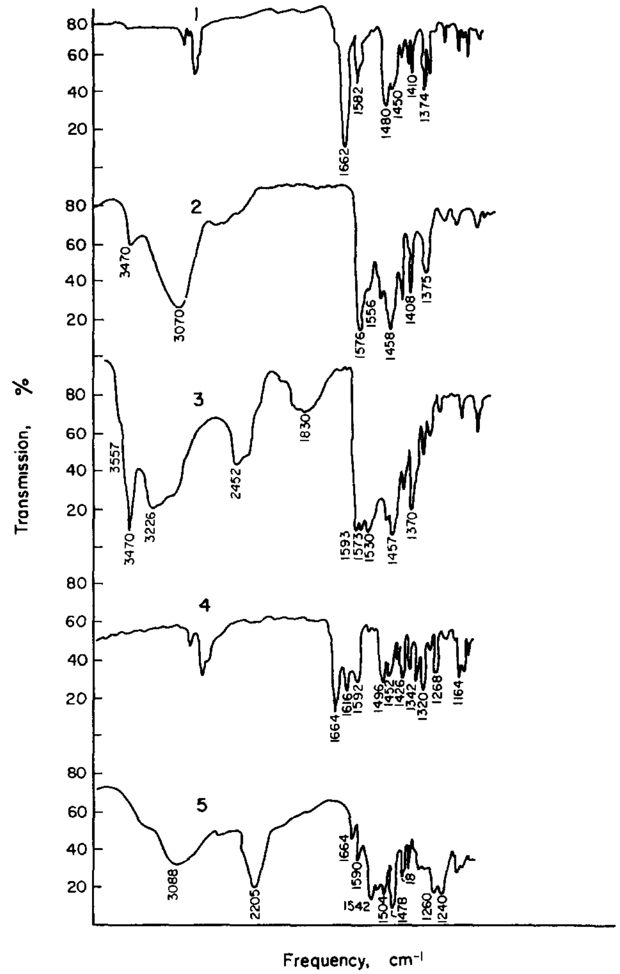
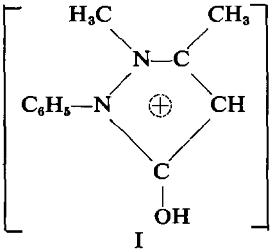


FIG. 1.—Infrared spectra of compounds in the crystalline state (in Nujol):

1. antipyrine,	4. diantipyrylmethane,
2. antipyrine hexachloro-osmate,	5. diantipyrylmethane hydrochloride.
3. antipyrine hexabromo-osmate,	

The assignment of the absorption bands, in the complexes investigated, in the region of 3500—3000 cm^{-1} to the stretching vibrations of the $\overset{+}{N}$—H bond does not agree with the behaviour of the carbonyl band. In fact, the interaction of the protons with the N_1 or N_2 nitrogen atoms must lead to a displacement of the C=O band to the high-frequency region, *i.e.*, under these conditions, the conjugation of the C=O bond with the unshared pair of electrons of the nitrogen atom will decrease and their electronegativity will increase.[31]

Thus, the appearance of bands in the region of 3500–3000 cm^{-1} in compounds of antipyrine and its derivatives with acids is connected with the addition of a proton to the carbonyl oxygen atom with subsequent opening of the carbonyl bond and formation of a hydroxyl group, which leads to the formation of onium salts of types I and Ia.



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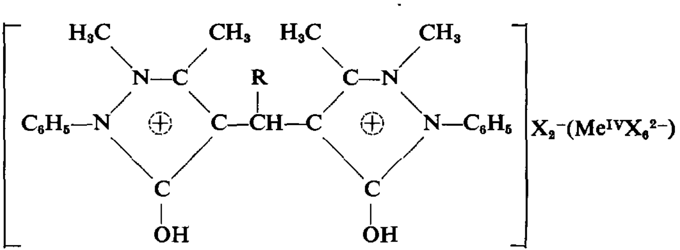


Ia

However, the appearance in the spectra of the compounds studied (Fig. 1, Table II) of absorption bands in the region of 2500–1800 cm^{-1} evidently shows an interaction of the antipyrine cation with the anions not only through electrostatic forces but also as a consequence of the formation of hydrogen bonds:

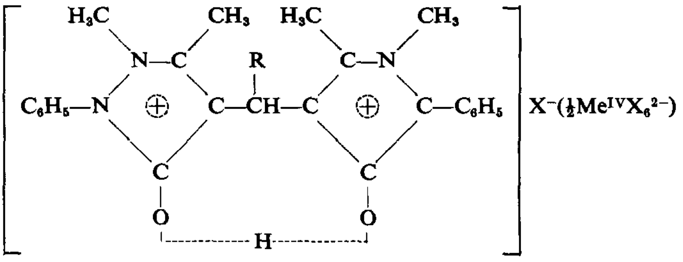
$$>\mathrm{C—O—H}\cdots\mathrm{X}\,(\mathrm{H_2MeX_6}) \rightleftharpoons\ >\mathrm{C}\overset{\cdots}{-}\mathrm{O}\cdots\mathrm{HX}\,(\mathrm{H_2MeX_6}).$$

The bands in the region of 1500–1560 cm^{-1} are apparently connected with the absorption of the strongly polarised $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ bond in the complexes

$$>\mathrm{C}\overset{\cdots}{-}\mathrm{O}\cdots\mathrm{HX}\,(\mathrm{H_2MeX_6}).$$

The considerably increased intensity of the hydroxyl absorption bands in the compounds of diantipyrylmethane and diantipyrylpropylmethane with osmium(IV) and iridium(IV) is probably connected with the formation of strong intramolecular hydrogen bonds between one proton and two carbonyl oxygen atoms (see formula II below). This is in agreement with the aromatic nature of antipyrine. In actual fact, in the formation of complex II (see below), the proton evidently adds first to one of the two carbonyl oxygen atoms in the diantipyrylmethane (or diantipyrylpropylmethane) with subsequent formation of a strong intramolecular hydrogen bond in which the proton is attached to the two carbonyl oxygen atoms to the same extent. The intensity of the absorption of such hydroxyl groups is particularly strongly reduced.[32]

The results obtained on the structure of the compounds of antipyrine and its derivatives with quadrivalent osmium and iridium are in good agreement with the fact that in all of the compounds formed in an acidic medium antipyrine and its



II

derivatives participate as singly charged cations (see I above). This fact is difficult to explain if the basicity of antipyrine and its derivatives is connected with the basicity of the heterocyclic nitrogen atoms. In actual fact, in the case of antipyrine, the formation of a singly charged cation can be connected formally with a weakening of the basic properties of the nitrogen present in the α-position to the C═O group. In the case of diantipyrylmethane, diantipyrylpropylmethane and other derivatives having two nitrogen atoms of equivalent basicity in the molecule, however, it is difficult to see why protonation takes place only in respect of one of them.

Thus, the compounds of antipyrine and its derivatives that have been obtained with quadrivalent osmium and iridium are, in the crystalline state, salts of the cations of antipyrine, diantipyrylmethane and diantipyrylpropylmethane with the anions $OsCl_6^{2-}$, $OsBr_6^{2-}$, $IrCl_6^{2-}$ and $IrBr_6^{2-}$. The formation of these compounds may be expressed by the equation:

$$2R + Me^{IV}X_6^{2-} + 2H^+ \rightleftharpoons (R\cdot H)_2MeX_6.$$

Solubility of Compounds of Osmium(IV) and Iridium(IV) with Antipyrine and Its Derivatives in Aqueous Solution

The hexachloro- and hexabromo-osmates and the hexachloro- and hexabromo-iridates of diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane are sparingly soluble in water, but readily soluble in certain organic solvents—dichloroethane and chloroform. The compounds of osmium(IV) and iridium(IV) with antipyrine, on the other hand, are readily soluble in water and sparingly soluble in organic solvents. As a rule, the bromine-containing complexes are less soluble in water than the corresponding chlorine-containing complexes (see Table I).

The influence of the concentrations of the acid, the reagent and alkali-metal chlorides on the solubility of diantipyrylpropylmethane hexachloro-osmate and -iridate and of diantipyrylmethane hexabromo-osmate has been studied. The procedure used was as follows.

A freshly produced precipitate, carefully washed with water, was placed in a bottle containing 50 ml of hydrochloric acid (or hydrobromic acid) of the appropriate concentration and shaken in a thermostat at 25° for 2–3 hr (it was established by preliminary experiments that this time was sufficient for saturation). The resulting saturated solution was rapidly filtered through filter paper, the first portion of the filtrate being rejected. The content of metal in an aliquot of the clear filtrate was determined: osmium with thiourea[33] or with diantipyrylpropylmethane (for the method, see below), and iridium with diantipyrylpropylmethane (for the method, see below).

The results obtained are given in Figs. 2–4. In the presence of sodium chloride, the solubility of the iridium compound diminishes somewhat; the solubility of the osmium compound remains practically unchanged.

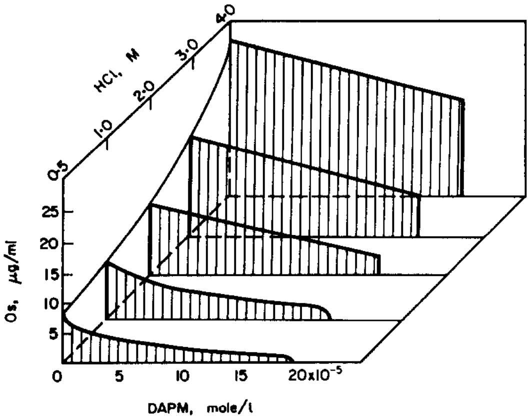


FIG. 2.—Influence on the solubility of $(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$ of the concentration of hydrochloric acid and diantipyrylpropylmethane (DAPM).

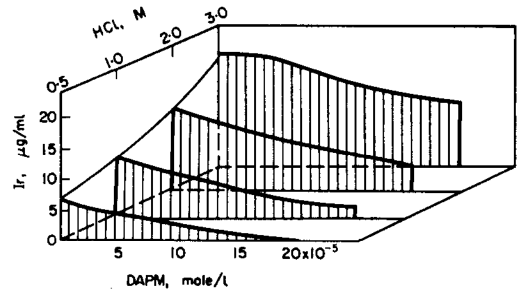


FIG. 3.—Influence on the solubility of $(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$ of the concentration of hydrochloric acid and diantipyrylpropylmethane (DAPM).

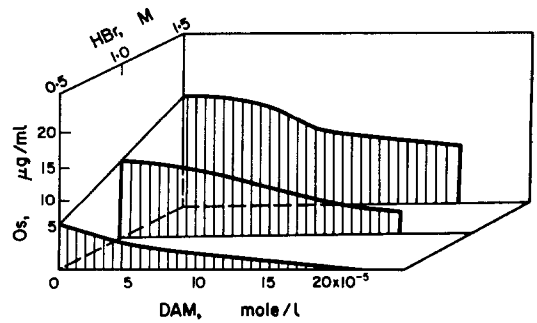


FIG. 4.—Influence on the solubility of $(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$ of the concentration of hydrobromic acid and diantipyrylmethane (DAN).

Extractability of Osmium and Iridium, and also of Platinum, Palladium, Ruthenium and Rhodium with Dichloroethane in Presence of Diantipyrylpropylmethane

In the presence of diantipyrylpropylmethane, quadrivalent osmium, iridium, platinum and ruthenium, and also bivalent palladium, are well extracted by dichloroethane from hydrochloric and hydrobromic acid solutions.

Tervalent ruthenium, rhodium and iridium are extracted considerably less well.

TABLE III.—EXTRACTABILITY OF CHLORIDES OF COMPLEXES OF PLATINUM, PALLADIUM, IRIDIUM AND RHODIUM FROM HYDROCHLORIC ACID SOLUTIONS (1*M*) WITH DICHLOROETHANE IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Metal	Metal taken, *mg*	Metal found, *mg*		Percentage extraction, E	Distribution coefficient, D[b]
		Aqueous phase	Organic phase		
Pt^{IV}	5·28	0·01	5·30	99·8	—
	6·60	0·01	6·60	99·8	—
	7·92	0·01	8·00	99·8	—
Pd^{II}	3·12	0·02	3·11	99·2	—
	6·24	0·05	6·15	99·2	—
	4·68	0·03	4·70	99·4	—
Ir^{IV}	1·31	0·02	1·29	98·5	129
	5·24	0·08	5·15	98·5	132
	7·86	0·12	7·85	98·6	125
Rh^{III}	5·11	0·45	0·78	15·3	0·35
	10·23	8·80	2·50	14·7	0·34
	10·23	8·80	1·54	15·0	0·35

[a] Extraction carried out with 10 ml of a 1% solution of diantipyrylpropylmethane in dichloroethane. Contents of platinum, palladium, iridium and rhodium in each of the phases determined by means of tin(II) chloride.[34–37]

[b] $D = \frac{\text{mg/ml of metal in organic phase}}{\text{mg/ml of metal in aqueous phase}}$.

The greatest difference in extractability is found with hydrochloric acid solutions. Thus, the extractability of osmium is 94–96%, of iridium 98·5%, of platinum > 99%, of palladium > 99%, of ruthenium(IV) 96·5%, of ruthenium(III) 1·5% and of rhodium(III) 15%, in extraction from solutions 1*M* with respect to hydrochloric acid by a 1% solution of the reagent in dichloroethane (Tables III and IV).

The extractability of the platinum metals depends on the acidity of the aqueous solution and on the excess of reagent.

A 6- to 10-fold excess of diantipyrylpropylmethane is sufficient for the complete extraction of osmium(IV), iridium(IV), platinum(IV) and palladium(II) (Fig. 5; the study was carried out spectrophotometrically from the optical density of the extracts).

TABLE IV.—EXTRACTABILITY OF CHLORIDES OF COMPLEXES OF RUTHENIUM AND OSMIUM FROM HYDROCHLORIC ACID SOLUTIONS (1*M*) WITH DICHLOROETHANE IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Concentration of reagent solution, %	Percentage extraction, E		
	Ru^{IV} (64 μg/ml)	Ru^{III} (3·15 mg/ml)	Os^{IV} (8 μg/ml)
0·1	33·8	0·4	96·28
0·2	41·0	0·6	94·9
1·0	80·6	1·3	—
2·0	93·5	2·8	—
3·0	95·0	3·6	—
4·0	96·5	5·6	—

[a] Extraction carried out with 10 ml of a solution of the given concentration of the reagent in dichloroethane (volume of aqueous phase: 20 ml). Extraction of osmium and ruthenium studied by means of the radioactive isotopes ^{191}Os and $^{106}Ru + ^{106}Rh$.

Ruthenium(IV) requires a 150-fold excess of the reagent (Table IV). The percentage extraction of tervalent ruthenium and of rhodium, even with a large excess of diantipyrylpropylmethane, did not exceed 6% and 15%, respectively (Tables IV and V).

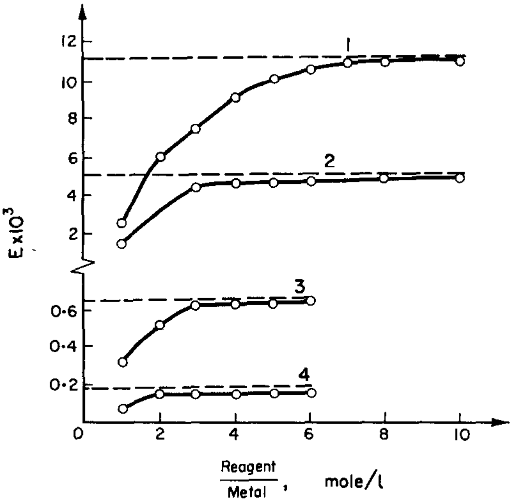


FIG. 5.—Influence of an excess of diantipyrylpropylmethane on the extraction of:
1. osmium, 3. platinum,
2. iridium, 4. palladium.

The extractability of osmium(IV), iridium(IV), platinum(IV) and palladium(II) remains practically constant over a wide range of concentrations of acid (0.5–5*M* hydrochloric acid) (Fig. 6). The percentage extraction of ruthenium and rhodium (Table VI) decreases with an increase in the concentration of the hydrochloric acid.

Photometric Method for Determination of Osmium(IV) and Iridium(IV) by Means of Antipyrine Derivatives

The dichloroethane extracts of quadrivalent osmium and iridium are intensely coloured. The absorption curves (Fig. 7) for all three complexes of osmium and

TABLE V.—EXTRACTABILITY OF RHODIUM FROM HYDROCHLORIC ACID SOLUTIONS (1*M*) IN PRESENCE OF DIANTIPYRYLPROPYLMETHANE[a]

Concentration of reagent solution, %	Rh taken, *mg*	Rh found in organic phase, *mg*	Percentage extraction, E
0·1	24·70	0·60	2·4
0·2	0·99	0·66	6·0
0·2	1·97	0·09	4·5
0·2	2·96	0·13	4·4
0·2	3·95	0·18	4·5
0·5	24·70	1·30	5·3
1·0	10·23	1·55	15·15

[a] Extraction carried out with 10 ml of a solution of the given concentration of the reagent in dichloroethane (volume of aqueous phase: 20 ml).

TABLE VI.—DEPENDENCE OF EXTRACTION OF RHODIUM ON ACIDITY OF INITIAL SOLUTION[a]

HCl, *M*	Rh found in organic phase, *mg*	Percentage extraction, E
0·5	0·74	3·0
1·0	0·66	2·7
2·0	0·49	2·0
3·0	0·46	1·9
4·0	0·44	1·8
5·0	0·42	1·7
6·0	0·40	1·6
7·0	0·10	0·4
8·0	none	0·0

[a] 24·70 mg of Rh taken.

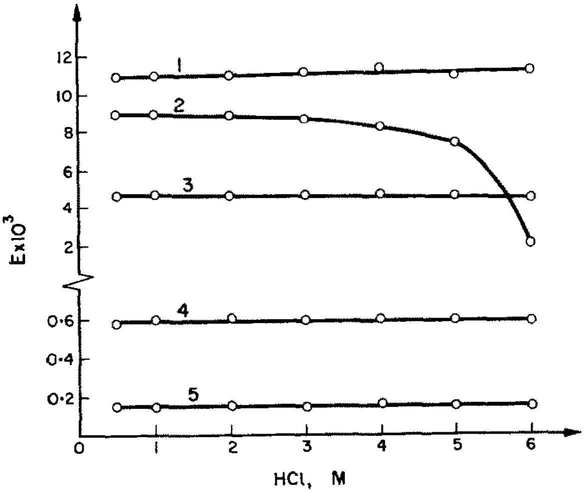


FIG. 6.—Influence of the concentration of hydrochloric acid on the extraction of:
1. osmium, 4. platinum,
2. ruthenium(IV) 5. palladium.
3. iridium,

iridium with diantipyrylmethane, diantipyrylpropylmethane and diantipyrylphenylmethane are identical with one another, and the coefficients of molar absorption are practically the same. Curves 2 and 4 (Fig. 7) show the light absorption of solutions of ammonium hexachloro-osmate and -iridate in 1*M* hydrochloric acid, respectively. By comparing curves 1 and 2 with 3 and 4, the light absorption of the extracts arises from the absorption of the $OsCl_6^{2-}$ and $IrCl_6^{2-}$ anions. A slight displacement of the absorption curves of the extracts to the long-wave region of the spectrum and an increase in the intensity of the absorption are connected with the replacement of the ammonium cation in the compounds $(NH_4)_2MeX_6$ by the large organic cations $(C_{23}H_{24}O_2N_4{\cdot}H)^+$, $(C_{26}H_{30}O_2N_4{\cdot}H)^+$ and $(C_{29}H_{28}O_2N_4{\cdot}H)^+$ and with the change of solvent. Analogous phenomena are found in the case of the bromine-containing compounds. The light-absorption curves of solutions of the pure materials in dichloroethane proved to be identical with the absorption curves of the extracts.

It was found by the method of isomolar series that the ratio of metal to reagent in the extracted compounds was 1:2, *i.e.*, the extracted compounds had the same composition as those isolated in the crystalline state.

The optical density of the extracts is proportional to the concentration in the range 2–20 μg/ml of osmium and 4–40 μg/ml of iridium. This has permitted the development of simple photometric methods for determining osmium and iridium.

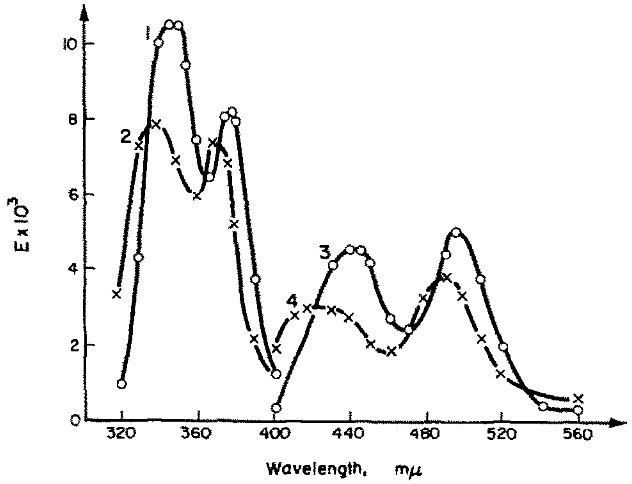


Fig. 7.—Absorption curves of the chlorides of complexes of osmium (1) and iridium (3) with antipyrine derivatives, and of ammonium hexachloro-osmate (2) and ammonium hexachloro-iridate (4).

The most suitable reagent for the extraction and subsequent photometric determination of osmium and iridium is diantipyrylpropylmethane and the most suitable organic solvent is dichloroethane.

Ruthenium does not interfere with the determination of osmium if it is first converted to the tervalent state. As mentioned above, in the presence of a small excess of reagent (10 ml of a 0·1 % solution in dichloroethane for 0·8 mg of osmium) it is not appreciably extracted.

Rhodium does not interfere with the determination of iridium if the content of the former in the initial solution does not exceed 4 mg. In this case, the amount of rhodium passing into the organic phase does not exceed 0·2 mg (on extraction with a 0·2 % solution of the reagent). The light absorption of an extract containing 0·2 mg of rhodium at 498 mμ (maximum of the light absorption of the iridium complex) is insignificant.

After a detailed study of the reaction of osmium and iridium tetrachlorides with the antipyrine derivatives and an investigation of the behaviour of the other platinum metals under the conditions of the formation of the osmium and iridium complexes, extraction-photometric methods were developed for the determination of osmium in the presence of ruthenium and of iridium in the presence of rhodium. The methods are simple to carry out and are as follows.

Determination of osmium in presence of ruthenium. A hydrochloric acid solution (3–6*M* with respect to this acid), containing osmium in the form of $OsCl_6^{2-}$ and ruthenium, is heated with hydrazine hydrochloride or hydrazine sulphate for 10–15 min until the dark red colour of the solution changes to pale yellow. Under these conditions, the ruthenium is reduced to the tervalent state while the osmium remains in the quadrivalent state.

After cooling, the solution is transferred to a separating funnel and the osmium tetrachloride extracted with 10 ml of a 0·1 % solution of diantipyrylpropylmethane in dichloroethane. The optical density of the extract is measured at 346 mμ or 378 mμ and the osmium content found from a calibration curve. The method permits the determination of 2–20 μg of osmium/ml in the presence of 40 mg of ruthenium (Table VII).

TABLE VII.—SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM AND IRIDIUM WITH DIANTIPYRYLPROPYLMETHANE

Amount taken, μg		Amount added, mg		Found, μg		Error, %	
Os	Ir	Ru	Rh	Os	Ir	Os	Ir
19·0	—	6·10	—	19·0	—	0·0	—
38·0	—	30·52	—	39·7	—	+4·5	—
57·0	—	27·46	—	62·5	—	+9·6	—
171·2	—	18·30	—	163·0	—	−4·8	—
152·1	—	36·61	—	150·0	—	−1·3	—
133·1	—	45·76	—	141·0	—	+5·9	—
114·1	—	18·30	—	110·0	—	−3·6	—
—	38·6	—	0·988	—	40·5	—	+4·9
—	77·2	—	4·09	—	75·3	—	−2·5
—	347·6	—	4·09	—	351·4	—	+1·1
—	38·6	—	2·04	—	36·7	—	−4·9
—	154·5	—	3·952	—	152·5	—	−1·2
—	77·2	—	1·976	—	81·1	—	+5·0
—	231·7	—	1·02	—	237·5	—	+2·5

The error of the above determination is ±10%. Thus, the extraction-photometric method for determining osmium by means of diantipyrylpropylmethane is not inferior in sensitivity to the widely used thiourea method,[33] but its selectivity is superior to that of all known photometric methods of determining osmium.

The method may be used for the analysis of hydrochloric acid distillates and other solutions of osmium after this had been converted to $OsCl_6^{2-}$.

Determination of iridium in presence of rhodium. A solution, containing iridium and not more than 4 mg of rhodium, is twice evaporated on a water-bath with concentrated hydrochloric acid, in the presence of sodium chloride and hydrogen peroxide, to the state of moist salts to convert the iridium to $IrCl_6^{2-}$. The residue is dissolved in water, the solution transferred to a separating funnel and the iridium extracted with 10 ml of a 0·2 % solution of diantipyrylpropylmethane in dichloroethane. The optical density of the extract is measured at 490 mμ and the content of iridium found from a calibration curve. The method permits the determination of 4–40 μg of iridium/ml in the presence of up to 4 mg of rhodium with an accuracy of ±10% (Table VII).

The extraction-photometric method for determining iridium by means of diantipyrylpropylmethane is equal in sensitivity to the method used in practice,[38–40] being inferior in this respect to the majority of other photometric methods for determining iridium. However, it is favourably distinguished from them in respect of selectivity, permitting the determination of up to 4 μg/ml in the presence of 100-fold amounts of rhodium. In our opinion, the method can be used for the analysis of any solution of iridium after its conversion to $IrCl_6^{2-}$.

The extraction-photometric determination of osmium and iridium in the form of the bromide complexes is not selective, *i.e.*, all platinum metals, including tervalent ruthenium and rhodium, are extracted well from hydrobromic acid solutions with the formation of coloured extracts.

Gravimetric Methods for Determination of Osmium and Iridium by means of Antipyrine Derivatives

Because the development of gravimetric methods for osmium and iridium is of practical importance, we have studied the possibility of using for this purpose the compounds of quadrivalent osmium and iridium with antipyrine derivatives that we have obtained.

Diantipyrylmethane (with precipitation from hydrobromic acid solution) and diantipyrylpropylmethane (with precipitation from hydrochloric acid solution) must be considered the most suitable reagents for the gravimetric determination of osmium and iridium. Diantipyrylphenylmethane is unsuitable because of the low solubility of its hydrochloride and hydrobromide. For the same reason, it is also undesirable to use diantipyrylpropylmethane in precipitation from hydrobromic acid solutions.

In the presence of a small excess of the reagent, quadrivalent osmium and iridium are precipitated practically completely from hydrochloric acid solutions by diantipyrylpropylmethane; quadrivalent osmium is also precipitated quantitatively from hydrobromic acid solutions by diantipyrylmethane (Figs. 2–4). Thus, in a solution $0{\cdot}5M$ with respect to hydrochloric acid and containing 20×10^{-5} mole/l. of reagent in excess, osmium cannot be detected with thiourea[33] nor iridium with a mixture of acids (H_2SO_4—H_3PO_4—$HClO_4$). From the results obtained, a gravimetric method for the determination of osmium and iridium has been developed.

Determination of osmium and iridium. A 2% solution of diantipyrylpropylmethane (or diantipyrylmethane in precipitation from hydrobromic acid solutions) in acetic acid (1:1) is added slowly with stirring to 60–70 ml of hydrochloric acid solution ($0{\cdot}1$–$0{\cdot}5M$) or a corresponding hydrobromic acid solution, containing osmium in the form of $OsCl_6^{2-}$ or $OsBr_6^{2-}$ or iridium in the form of $IrCl_6^{2-}$, until the addition of a fresh portion of the reagent causes no further precipitation. A further 1 ml of the reagent solution is then added and the solution containing the precipitate is allowed to stand for 2–3 hr. The resulting precipitate is filtered off through a No. 4 filter crucible, washed 4–5 times with a 0·05–0·1% solution of the reagent in $0{\cdot}5M$ hydrochloric acid, dried to constant weight at 100–110° and weighed. As can be seen from Table VIII, using diantipyrylmethane and diantipyrylpropylmethane it is possible to determine 5–13 mg of osmium and iridium by precipitation and weighing in the form of $(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$, $(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$ or $(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$.

The error of the above determination is ±3%. Platinum and palladium interfere with the determination, forming sparingly soluble compounds with the antipyrine derivatives. Ruthenium and rhodium, although they do not give sparingly soluble compounds, nevertheless undergo considerable coprecipitation with the osmium and iridium precipitates. Thus, they precipitate to the extent of 2–3% from hydrochloric acid solutions of quadrivalent and tervalent ruthenium, as was found by means of the $^{106}Ru + {}^{106}Rh$ isotope. On precipitation from hydrobromic acid solutions, the amount of quadrivalent ruthenium coprecipitated increases to 20% and that of tervalent ruthenium to 7%.

The gravimetric methods for the determination of osmium and iridium by means of diantipyrylmethane and diantipyrylpropylmethane are favourably distinguished from many other gravimetric methods, firstly, because they do not require calcination of the precipitate to the metal and, secondly, because they permit the determination of milligram-amounts of osmium and iridium with great accuracy because of the small conversion factor to the metal. The disadvantage of these methods is their low selectivity: all platinum metals interfere with the determination.

TABLE VIII.—GRAVIMETRIC DETERMINATION OF OSMIUM AND IRIDIUM BY MEANS OF ANTIPYRINE DERIVATIVES

Form of precipitate	Amount taken, *mg*		Found, *mg*		Error, %	
	Os	Ir	Os	Ir	Os	Ir
	6·06	—	6·15	—	+1·5	—
$(C_{26}H_{30}O_2N_4{\cdot}H)_2OsCl_6$	8·65	—	8·55	—	−1·1	—
	4·33	—	4·47	—	+3·2	—
Factor = 0·1503	10·38	—	10·16	—	−2·1	—
	12·98	—	12·75	—	−1·8	—
	4·11	—	4·20	—	+2·2	—
$(C_{23}H_{24}O_2N_4{\cdot}H)_2OsBr_6$	3·69	—	3·69	—	0·0	—
	5·75	—	5·66	—	−1·5	—
Factor = 0·1314	8·21	—	8·03	—	−2·2	—
	7·80	—	7·88	—	+1·0	—
	—	5·24	—	5·19	—	−0·9
$(C_{26}H_{30}O_2N_4{\cdot}H)_2IrCl_6$	—	10·48	—	10·14	—	−3·2
	—	13·10	—	13·13	—	+0·2
Factor = 0·1523	—	8·52	—	8·68	—	+1·9
	—	6·55	—	6·55	—	0·0

Extractive Separation of Iridium and Rhodium, Platinum and Rhodium, and Palladium and Rhodium by means of Diantipyrylpropylmethane

The difference in extractability of iridium(IV), platinum(IV), palladium(II) and rhodium(III) has permitted the development of an extraction method for separating small amounts (6–10 mg) of rhodium and iridium, rhodium and platinum, and rhodium and palladium with the aid of diantipyrylpropylmethane.

Before separation, the solution containing the platinum metals was evaporated three times with concentrated hydrochloric acid, sodium chloride and hydrogen peroxide, to convert the platinum metals to the chloride complexes. During the extraction, part of the quadrivalent iridium may be reduced to the tervalent state, so that this operation of evaporating the solution must be repeated before each successive extraction. Moreover, it has been found that the extraction of the chloride complex of rhodium is irreversible, *i.e.*, when the extract is shaken with 1*M* hydrochloric acid no appreciable amounts of rhodium pass into the aqueous phase. To re-extract the rhodium from the organic phase, the extract was shaken with a 25% solution of nitric acid (under these conditions, platinum, palladium and iridium are also re-extracted). The re-extract was then treated with concentrated hydrochloric acid and sodium chloride to reconvert the platinum metals to the chlorides.

The separation was carried out in separating funnels by Bush and Densen's scheme (Fig. 8).[41] A 1% solution of diantipyrylpropylmethane in dichloroethane was used for the extraction. The volume of the organic phase was 10 ml and that of the aqueous phase 20 ml, and the over-all concentration of hydrochloric acid in the aqueous phase was 1*M*. The results obtained are given in Table IX.

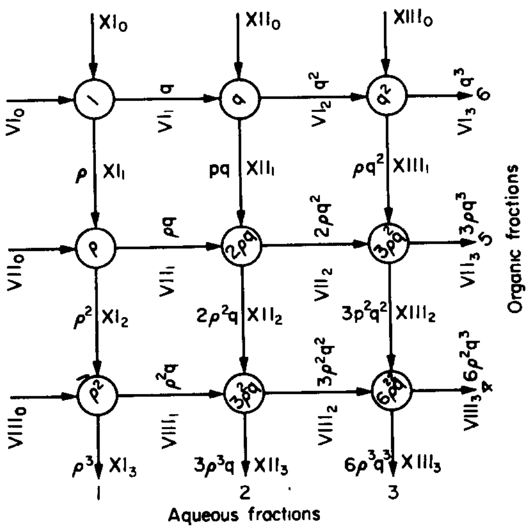


FIG. 8—Scheme of extractive separation.

TABLE IX.—SEPARATION OF RHODIUM AND IRIDIUM, RHODIUM AND PLATINUM, AND RHODIUM AND PALLADIUM

Fraction no.	Metal found,[a] *mg*					
	Rh	Ir	Rh	Pt	Rh	Pd
1	7·60	0·00	7·60	0·00	7·70	0·00
2	2·11	0·00	2·18	0·00	2·12	0·00
3	0·30	0·00	0·18	0·00	0·22	0·00
4	traces	0·000	traces	0·00	traces	0·00
5	0·00	0·33	0·00	traces	0·00	0·32
6	0·00	6·22	0·00	6·50	0·00	7·45

[a] Amounts taken were 9·88 mg of Rh, 6·55 mg of Ir, 6·60 mg of Pt and 7·80 mg of Pd.

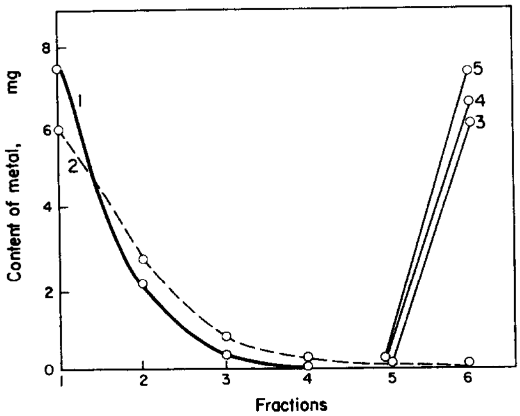


FIG. 9.—Experimental curves of the distribution of rhodium (1), iridium (3), platinum (4) and palladium (5), and theoretical curves of the separation of rhodium (2) and iridium (practically coinciding with the experimental curve).

The experimental distribution curves (Fig. 9) of rhodium and iridium proved to be close to those calculated from the formula

$$p = \frac{K.V_x}{K.V_x + V_y}$$

where p is the fraction of the metal remaining in the aqueous phase after the first extraction, V_x and V_y are the volumes of the aqueous and organic phases, respectively, and $K = \frac{1}{D}$ where D is the distribution coefficient. After a 9-stage extraction separation, about 80% of the original amount of rhodium taken was obtained in the first fraction, which was spectroscopically free from iridium, platinum and palladium. However, to obtain samples of iridium, platinum and palladium spectroscopically free from rhodium it was necessary to carry out the separation with a greater number of extraction stages.

The method developed has been used to purify metallic rhodium from trace amounts of platinum, iridium and palladium.

It is also possible to use diantipyrylpropylmethane for the extractive separation of platinum, palladium, iridium, osmium and ruthenium from other elements, *e.g.* from nickel and selenium, which are not extracted by dichloroethane in the presence of diantipyrylpropylmethane.

Zusammenfassung—Die Reaktion von vierwertigem Osmium und Iridium mit Antipyrin und einigen seiner Derivate wurde untersucht und es wurde gezeigt, daß in sauren Lösungen Verbindugnen vom Typ $(RH)_2MeX_6$ gebildet werden. Die Extraktion von Halogenokomplexen von Osmium, Iridium, Ruthenium, Rhodium, Platin und Palladium mittels Diantipyryl-propylmethan in Dichloräthan wurde geprüft. Eine extraktiv-photometrische Methode wird vorgeschlagen für die Bestimmung von 2–20 μg/ml Osmium neben 50 mg Ruthenium und von 4–40 μg/ml Iridium neben 4 mg Rhodium mittels Diantipyryl-propylmethan. Der Fehler der Bestimmung ist ±10%. Eine gravimetrische Methode zur Osmium- und Iridiumbestimmung, in Mengen von 5–13 mg, mittels Diantipyryl-propylmethan und Diantipyryl-methan wird vorgeschlagen. Die Möglichkeit selektiver Extraktion kleiner Mengen Iridium und Rhodium, Platin und Rhodium und Palladium und Rhodium mittels Diantipyryl-propylmethan wird gezeigt.

Résumé—On a étudié la réaction de l'osmium tétravalent et de l'iridium avec l'antipyrine et quelques-une de ses dérivés, et l'on a montré qu'en solutions acides, il se forme des composés $(RH)_2MeX_6$. On a examiné l'extraction des complexes halogénés d'osmium, iridium, ruthénium, rhodium, platine et palladium au moyen de diantipyryl-propylméthane en dichloréthane. On propose une méthode photométrique par extraction pour le dosage de 2–20 μg/ml d'osmium en présence de 40 mg de ruthénium, et de 4–40 μg/ml d'iridium en présence de 4 mg de rhodium, au moyen de diantipyrylpropyl méthane. L'erreur du dosage est ±10%. On propose une méthode gravimétrique pour le dosage de 5–13 mg d'osmium et d'iridium au moyen de diantipyrylpropylméthane et diantipyrylméthane. L'erreur du dosage est ±3%. On montre la possibilité d'extraire séparément des petites quantités d'iridium et rhodium, platine et rhodium, et palladium et rhodium, à l'aide du diantipyrylpropylméthane.

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NOTICES

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UNITED KINGDOM

Wednesday 2 *December* 1964: Meeting on **Solvent Extraction:** *Society for Analytical Chemistry.* Wellcome Building, Euston Road, London N.W.1, 3.00 p.m.

Friday 4 *December* 1964: **Scientific Examination of Documents,** C. L. WILSON: *Chemical Society; Society for Analytical Chemistry, Scottish Section* and *Royal Institute of Chemistry.* University of Strathclyde, Glasgow, 6.00 p.m.

Tuesday 8 *December* 1964: **Experience in U.S.A. on Boilers,** D. H. JOHNS; **Principles of Chemical Control of High Pressure Boilers,** E. C. POTTER: *Society for Analytical Chemistry, Midlands Section.* University of Birmingham, Edgbaston, Birmingham 15, 6.30 p.m.

Wednesday 9 *December* 1964: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Thursday 10 *December* 1964: **Annual General Meeting** followed by **Discussion Meeting:** *Society for Analytical Chemistry, Biological Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Friday 11 *December* 1964: **Some Aspects of Polarography,** M. L. RICHARDSON: Society for *Analytical Chemistry, North of England Section* and *Special Techniques Group.* Great Northern Hotel, Leeds, 7.30 p.m.

Friday 11 *December* 1964: **Thin-Layer Chromatography,** E. V. TRUTER: *Society for Analytical Chemistry, Western Section* and *Royal Institute of Chemistry, Cardiff and District Section.* University College, Cardiff, 6.30 p.m.

Tuesday 15 *December* 1964: **Annual General Meeting** followed by Discussion Meeting on **Special Assemblies and Adaption of Atomic-Absorption Apparatus:** *Society for Analytical Chemistry, Atomic-Absorption Spectroscopy Group.* Burlington House, London W.1, 6.30 p.m.

ERRATA—Volume 10

Page 1088, Table I: Compound XIII under the heading Ar should read $3—MeO—4—OH—C_6H_3$ instead of $3—Me—4—OH—C_6H_3$

Page 1088, Table I: For compound *XIII* read *XIV*; for compound *XIV* read *XV*; for compound *XV* read *XIII*

ERRATA—Volume 11

Page 998, Fig. 5: This should read

Curve I ——— 10·8 mg of boron, 216 mA; Curve III —·—·— 0·50 mg of boron, 19 mA;
Curve II - - - - 1·08 mg of boron, 19 mA; Curve IV —··— ·— 0·10 mg of boron, 4·5 mA.

Page 998, Fig. 6: This should read

Curve I —·—·— 10·8 mg of boron, 216 mA; Curve II — — — 1·08 mg of boron, 19 mA.

Page 999, Fig. 7: This should read

Curve I ——— 10·8 mg of boron, 216 mA;
Curve II — — — 1·08 mg of boron, 19 mA;
Curve III —·—·— 0·50 mg of boron, 19 mA.

Page 999, line 5 under Table II: This should read . . . . .0·1 mg of boron.

Page 1314, line 4: For UO_2^{2-} read UO_2^{2+}

Page 1317, Table I: In the first column read UO_2^{2-} for UO_2^{2-}

Page 1406, Table I: The headings for columns two, three and four should read

Cu^{2+} taken, *mmole/100 ml*	HEDTA taken, *mmole/100 ml*	Resin, *g*

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OBITUARY

ELEMÉR SCHULEK

It is with regret that we announce the sudden death on Wednesday, 14th October, 1964, at the age of 71, of ELEMÉR SCHULEK. Professor Schulek, Member of the Hungarian Academy of Sciences and Head of the Institute of Inorganic and Analytical Chemistry of the L. Eötvös University of Budapest, had been a Member of the Advisory Board of *Talanta* since its inception in 1958. A review of his career and his scientific work was published in *Talanta*, 1963, **10**, 429.

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NOTICES

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BUNDESREPUBLIK DEUTSCHLAND

1.–2. *April* 1964: *GDCh-Fachgruppe "Kern-, Radio und Strahlenchemie"*: Symposium über *Methoden zur Messung weicher β-Strahler:* Karlsruhe.

CZECHOSLOVAKIA

Tuesday 29 *September–Friday* 2 *October* 1964: **Third National Radiochemical Conference:** *Czechoslovak Chemical Society, Nuclear Chemistry Section:* Scientific House, Liblice by Praha.

The following topics are proposed for the Conference:

1. Separation methods in radiochemistry.
2. Radioisotopes in chemical analysis.
3. Hot atom chemistry.
4. Radioisotopes in chemistry and industrial research.
5. Production of radioisotopes.

Original papers are invited. Two copies of a brief abstract (150 words) with names of authors and their address should be sent, not later than 1 May, 1964, to Jaremír Růžička C. Sc., Faculty of Technical and Nuclear Physics, Praha 1, Břehovà 7. Other correspondence and the full text of papers should be sent to Miroslav Křivànek C. Sc., Institute of Nuclear Research ČSAV, Rež by Praha.

DEUTSCHE DEMEKRATISCHE REPUBLIK

14.–17. *April* 1964: **Moderne elektrochemische Analysenmethoden:** Eisenach (Die Hauptvorträge sind in *Talanta*, 1963, **10**, December, i, schon angedeutet worden).

SWEDEN

Monday–Saturday 14–19 *September* 1964: **Third International Measurement Conference and Sixth International Instruments and Measurements Conference:** The Congress halls at *Felkets Hus*, Stockholm.

Approximately 120 papers have been submitted by scientific and technical societies participating in the organisation of the Conference. Topics of general character will be discussed in the Plenary Sessions and in Sections, whereas new methods for measuring specific physical or chemical quantities are to be handled in the Specialised Sections. New developments in the border fields of measurement and automation will again be discussed in a Section organised jointly with the Technical Committee on Components of the International Federation for Automatic Control. The number of papers has been limited so as to secure time for personal discussions, visits to institutes and plants, excursions, etc.

Correspondence regarding registration, accommodation, *etc.*, should be addressed to RESO Congress Service, Stockholm 1, Sweden. Enquiries regarding the scientific programme should be directed to IMEKO Secretariat, Budapest 5, P.O.B. 3, Hungary. Information regarding the Commercial Exhibition may be obtained from the Exhibition Management, AB Anders Beckman, Birger Jarlsgatan 13, Stockholm C, Sweden.

UNITED KINGDOM

Thursday 2 *April* 1964: Contributions from Research Workers in Universities and Colleges of Advanced Technology: *Society for Analytical Chemistry:* University College, Gower Street, London W.C.1.

Monday–Thursday 6–9 *April* 1964: **Anniversary Meetings:** *Chemical Society:* University, Edgbaston, Birmingham 15.

This will include a Symposium on **New Methods of Organic Analysis** the programme for which is as follows:

Wednesday 8 April, Afternoon	
Qualitative organic analysis.	F. Feigl
Determination of organic functional groups.	F. E. Critchfield
Some instrumental methods in organic anlaysis.	J. R. Majer
Thursday 9 April, Afternoon	
General developments in organic analysis.	R. Belcher
Analysis of organic compounds by titration in non-aqueous media.	E. A. M. F. Dahmen
Organic polarography.	P. Zuman

Further information may be obtained from The Chemical Society, Burlington House, London W.1.

Friday 17 *April* 1964: **Fluorine and Teeth Decay** G. N. JENKINS: **Chemical Additives in Foods** J. MARKLAND: *Society for Analytical Chemistry, North of England Section* and *Scottish Section*: Central Hotel, Victoria Viaduct, Carlisle. 7.15 p.m.

Wednesday 22 *April* 1964: **Analytical Chemistry, Chemical Analysis and the Analyst,** R. C. CHIRNSIDE: *Society for Analytical Chemistry, Midlands Section* and *Royal Institute of Chemistry, Lea Valley Section:* Luton.

Wednesday 29 *April* 1964: Meeting on **Immunological Assay of Hormones:** P. G. H. GELL and A. J. FULTHORPE: *Society for Analytical Chemistry, Biological Methods Group:* Burlington House, London W.1. 7.00 p.m.

Sunday–Saturday 6–12 *September* 1964: **Summer School in Organic Spectroscopy:** *Royal Institute of Chemistry* in collaboration with *Society for Analytical Chemistry:* School of Pharmacy, Brunswick Square, London W.C.1.

The Summer School will provide an organised and concise presentation of infrared and nuclear magnetic resonance spectroscopy in terms of organic structures. Emphasis will be placed on fundamental principles and basic techniques. There will be morning lectures and small seminar discussion groups each afternoon. Laboratory sessions will also be provided.

Further information may be obtained from the Summer School Secretary: Mr. G. D. CHISMAN, Royal Institute of Chemistry, 30 Russell Square, London W.C.1.

At the **Ninth Annual General Meeting** of the *Western Section* of the *Society for Analytical Chemistry* held on *Friday*, 10 *January*, 1964, the following Officers were elected for the forthcoming year:

Chairman: E. A. HONTOIR
Vice-Chairman: L. E. COLES
Secretary/Treasurer: T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

At the **Twenty-Ninth Annual General Meeting** of the *Scottish Section* of the *Society for Analytical Chemistry* held on *Friday*, 24 *January*, 1964, the following Officers were elected for the forthcoming year:

Chairman: R. A. CHALMERS
Vice-Chariman: J. K. McLELLAN
Secretary/Treasurer: J. W. MURFIN, Boots Pure Drug Co. Ltd., Motherwell Street, Aidrie, Lanarkshire.

UNITED STATES OF AMERICA

Sunday–Friday 5–10 *April* 1964: **147th National Meeting:** *American Chemical Society:* Philadelphia. This includes Symposia on *Chromatography and Electrophoresis* and on *Chemical Analysis through Systems Control.*

Tuesday 7 *April* 1964: **Applications of High Resolution NMR to Determination of Organic Structures** J. L. HOLCOMB: *Society for Applied Spectroscopy, New York Section:* Hotel Manhattan, 8th and 44th Street.

Thursday–Saturday 16–18 *April* 1964: Course on **Evaluation and Interpretation of Physical and Chemical Testing Methods:** *American Society for Quality Control* and *American Chemical Society, Joliet Section:* Kankakee, Ill.

Sunday–Tuesday 19–21 *April* 1964: **Second Annual Oak Ridge Radioisotope Conference:** Gatlinburg, Tenn.

Wednesday–Saturday 22–25 *April* 1964: **Fourth Rare Earth Research Conference:** Camelback Inn, Pheonix, Ariz.

Wednesday–Friday 11–13 *November* 1964: **Sixth Eastern Analytical Symposium:** *Analytical Groups* of *New York and North Jersey Sections* of *American Chemical Society, American Microchemical Society,* and *Baltimore-Washington, Delaware Valley, New England* and *New York Sections* of *Society for Applied Spectroscopy:* Statler-Hilton Hotel, New York.

Following the successful pattern of previous years, the technical programme will consist of selected invited papers on topics of current interest in chemical analysis and closely related fields. Suggestions for programme topics and speakers are invited from all interested persons, These should be submitted to the Programme Chairman: Dr. LEO SAFRANSKI, E. I. du PONT de Nemours and Co., Plastics Department, Experimental Station, Wilmington 98, Delaware.

American Society for Testing and Materials has announced that the following publications in the field of spectroscopy are now available:
First Supplement to the Molecular Formula List of Compounds, Names and References to Published Infrared Spectra: STP 331-A (Price $4.50; $3.15 to ASTM members).
Index of Mass Spectral Data: STP 356 (Price $18.50; $13.00 to ASTM members).
Molecular Formula List of Compound Names and References to Published Ultraviolet and Visible Spectra: STP 357 (Price $6.00; $4.20 to ASTM members).
Serial Number List of Compound Names and References to Published Infrared Spectra: STP 358 (Price $12.00; $8.40 to ASTM members).

Copies may be obtained from ASTM, 1916 Race Street, Philadelphia, Pa.

ERRATUM—Volume 11

Page 2, *line* 7: this should read *Methods have previously been described . . .*

Page 16, *line* 2 *above formula* XIX: this should read *In order to study the formation of complexes by arsenazo . . . .*

Page 18, *line* 4 *of Synthesis:* this should read *excess of nitrous acid . . .*

Page 5, *insert after Zusammenfassung*

Résumé—L'utilité analytique particulière de l'Arsenazo-III est due à sa capacité de former des complexes spécialement stables avec certains elements. Ceci permet le dosage en milieu acide fort (HCl, 10 M ou SO_4H_2) des éléments penta- ou quadrivalents: Pa, Np^{IV}, Th, Zr, Hf, U^{IV}; la reproductibilité est bonne, la manipulation facile et l'on ne note que de petites interférences dûes aux anions. La grande sensibilité (0,1–0,01 μg/ml, coefficient d'absorption molaire 50–150 × 10^3) est due au grand effet de contraste de la réaction (changement de coloration durose au vert émeraude, déplacement du maximum d'absorption de 125 mμ), nature de spectre, et enfin possibilité d'atteindre des dilutions extremes sans dissociation des complexes.

Page 41, *insert after Zusammenfassung*

Résumé—Les mélanges formés d'orthophosphate, de ses polymères linéaires supérieurs jusqu'au tridécaphosphate compris et trois polymères cycliques ont pu être séparés par chromatographie d'échange ionique. L'un des polymères cycliques (recontré dans les verres de polyphosphate . . . est probablement le pentamétaphosphate. Sa nature cyclique a été démontrée par dosage des groupes terminaux et chromatographie sur papier, mais les tentatives de dénombrement des atomes de phosphore du noyau ont échouées à cause de la très faible quantité de produit disponible. Évidence est presentée a l'appui de la supposition courante que les phosphates linéaires supérieurs sont élués suivant leur degré de polymérisation.

Page 46, *insert after Zusammenfassung*

Résumé—Une méthode pour le dosage des trimétaphosphates en présence d'oligophosphates linéaires supérieurs au trimère est developpée. Il a été démontré que l'ortho-, lt pyro-, at le triphosphate ne sent pas complètement précipitéspar l'ion baryum, tandis que les phosphates oligomères linéaires de type supérieur sont précipités quantitativement. Ces derniers sont isolés des mélanges de phosphates par chromatographie d'échange d'anions, mélangés avec des quantités connues de phosphates cycliques, at précipités par l'ion baryum. Une erreur moyenne de +0,8 et un écart standard de ±3 micromoles de phosphore de l'ion cyclique a été mise en évidence dans les mélanges contenant de 0 à 203 micromoles de phosphore sous forme de trimétaphosphate en présence de 0 à 81 micromoles de phosphare sous forme de polymères linéaires,

Page 49, *line* 1: this should read *using barium diphenylamine . . .*

Page 57, *line* 1: this should read *between ammonium ion and chloramine-T . . .*

Page 57, *insert after Zusammenfassung*

Résumé—La chloramine-T oxyde quantitativement la thiourée en urée et l'ion sulfate en milieu neutre et en milieu basique. L'oxydation est totale en 2 minutes même en présence d'un léger excès d'oxydant. L'uree et l'ion ammonium ne sont pas gênants si l'oxydation est effectuée en milieu alcalin.

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NOTICES

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CZECHOSLOVAKIA

At the **National Meeting on Activation Analysis** at Modrá from 4 to 7 November, 1963, 20 papers were presented. The subjects included instrumental activation analysis, neutron sources, methods of counting and gamma spectrometry. Substoichiometry, especially its use for determination of traces of elements by activation analysis, was discussed. The meeting was sponsored by the Scientific and Technical Society in collaboration with the Department of Radiochemistry and Radiation Chemistry, Faculty of Chemistry Bratislava Kollárovo nám. 2. Abstracts of the papers are available from the above address.

III. Internationaler Polarographischer Kursus

In der Zeit vom 31.8. bis 12.9.1964 veranstaltet das Institut für Physikalische Chemie der Karls Universität und das Polarographische Institut der Tschechoslowakischen Akademie der Wissenschaften einen Lehrgang in Polarographie. Dieser Kursus besteht aus Vorlesungen über die Grundlagen der Polarographie, die in deutscher Sprache abgehalten werden, und einen entsprechenden Praktikum. Der Lehrgang ist für Hochschulabsolventen gedacht, spezielle Vorkenntnisse der Polarographie sind jedoch nicht Bedingung. Die Zahl der Teilnehmer wird auf 20 begrenzt. Dieser Lehrgang wird vorbereitet unter Schirmherrschaft von Professor Dr. J. HEYROVSKÝ, die Vorlesungen und das Praktikum liegen in den Händen von Fachkräften der Karls-Universität und des Polarographischen Instituts. Die Teilnahmegebühr beträgt Kčs 300.-einschliesslich eines Ausfluges in die Umgebung Prags und eines gemeinsamen Abendessens am Abschlusstage des Lehrganges. Eine Unterbringung in Studentenheimen zu mässigen Preisen bzw. auf besonderen Wunsch im Hotel, wird gewährleistet.

Vorläufige Anmeldungen mit Angabe von Titel, Name und Adresse sind an das Institut für Physikalische Chemie der Karls-Universität, Prag 2, Albertov 2030, bis spätestens 15. Mai 1964 zu richten.

UNITED KINGDOM

Wednesday 5 *February* 1964: Brains Trust Evening entitled **High Purity Chemicals**: E. F. HERSANT, B. ILLINGWORTH and F. H. LEVER: *Society for Analytical Chemistry, Midlands Section:* University, Edgbaston, Birmingham 15: 6.30 p.m.

Friday 14 *February* 1964: **Hydrolytic Studies of Phosphorus Compounds using Chromatographic Methods**: F. H. POLLARD: *Society for Analytical Chemistry, North of England Section* and *Leeds University Chemical Society:* University, Leeds: 6.00 p.m.

Friday 21 *February* 1964: **Annual General Meeting** followed by **Ordinary Meeting**: *Society for Analytical Chemistry, Microchemistry Group:* Burlington House, London W.1.

Tuesday 25 *February* 1964: Meeting on **Atomic Absorption Spectroscopy**: **Chemistry of Flames,** T. M. SUGDEN: **Review of Progress in Field of Atomic Absorption Spectroscopy**: J. B. DAWSON: *Society for Analytical Chemistry, Midlands Section* and *Physical Methods Group* with *Royal Institute of Chemistry, East Midlands Section* and *Leicester University Chemical Society:* University, Leicester: 7.00 p.m.

Friday 28 *February* 1964: Meeting on **Qualitative Analysis**: W. MOSER and E. H. REID: *Society for Analytical Chemistry, Scottish Section:* Paisley College of Technology: 7.15 p.m.

A **Conference of the Society for Analytical Chemistry** will be held at Nottingham University between 19 and 23 July, 1965.

The scientific programme, which will consist of original papers on all aspects of analytical chemistry, is to be organised by the Programmes Committee of the Society, and the responsibility for refereeing of papers will be in the hands of *The Analyst* Editorial Committee. A Trade Exhibition (Secretary, Mr. N. Mix, Standards Department, Boots Pure Drug Co. Ltd., Nottingham) and a programme of social functions will also be arranged.

Preliminary enquiries should be addressed to Mr. C. A. Johnson, Honorary Secretary, SAC Conference 1965, 14 Belgrave Square, London S.W.1.

At the **Nineteenth Annual General Meeting** of the *Physical Methods Group* of the *Society for Analytical Chemistry* held on Tuesday, 26 November, 1963, the following Officers were elected for the forthcoming year:

Chairman: L. Brealey
Vice-Chairman: G. F. Reynolds
Secretary and Treasurer: T. L. Parkinson, Product Research Department, Beecham Food and Drink Division Ltd., Harpenden Rise, Harpenden, Herts.

At the **Nineteenth Annual General Meeting** of the *Biological Methods Group* of the *Society for Analytical Chemistry* held on Thursday, 12 December, 1963, the following Officers were elected for the forthcoming year:

Chairman: W. A. Broom
Vice-Chairman: M. W. Parkes
Secretary and Treasurer: K. L. Smith, Standards Department, Boots Pure Drug Co. Ltd., Pennyfoot Street, Nottingham.

UNITED STATES OF AMERICA

Monday–Tuesday 3–4 *February* 1964: Research Conference on **Progress in Gas Chromatography:** University of California, Los Angeles, Calif.

The programme is as follows:

Monday, February, 3

Preparative Gas Chromatography	J. Howard
Mixed Bed Columns	C. N. Reilley

Tuesday, February 4

Improvements in Detectors and Readout	J. C. Sternberg
Gas Chromatography of Steroids and Related Substances	E. C. Horning

The Conference will be followed by an intensive basic **Three-Day Chromatography Course** (5–7 February) of lectures and laboratory work for those with a limited amount of experience in gas chromatography, as well as those who are new to the field.

Monday–Thursday 3–6 *February* 1964: **International Conference on Materials:** *American Society for Testing and Materials:* Sheraton Hotel, Philadelphia, Pa.

The following items from the programme may be of interest to analytical chemists:

Monday, 3 *February: Application of Advanced and Nuclear Physics to Testing Materials*

Application of Microwave Spectroscopy in Non-destructive Testing	A. Watson
X-Ray Fluorescence Analysis of Materials	B. L. Bean and W. Mulligan
Use of Neutron Diffraction in Study of Properties of Matter	E. Ligrand
Non-destructive Estimation of Cement Content of Finished Concrete	E. Yaltkaya, S. Urkan, S. Sentürk, K. Köksal and B. V. Enüstün.
Impact of Nuclear Technology on Highway Engineering	P. L. Blackwell
Measurement of Moisture Content in Brick Walls by a Neutron-Scattering Technique	B. Rossinski, T. Przedecki and Z. Stacmonwicz

Tuesday, 4 *February*

Influences of Modern Physics on Properties of Wood and their Evaluation	R. L. Youngs
Applications of Centimetric Radio Waves in Non-destructive Testing	R. W. Nurse
Microwave and X-Ray Diffraction Studies of Swelling of Baked Clays by Radioisotope Techniques	J. Brocard, C. DaWance, R. LaChaud and J. Paquet

Wednesday, 5 February: Impact of Physics on Analysis and Testing of Materials

Electron Beam Microprobe as a Tool in Materials Engineering	F. P. Landis, R. W. Merchant and P. D. Zemany
Progress in Field Ion Microscopy	E. W. Mueller
Nuclear Magnetic Resonance in Materials Analysis and Testing	C. M. Huggins
Modern Solid-State Mass Spectroscopy as a Tool for Standardisation in Analysis of Nuclear Materials	T. L. Collins, Jr.

Thursday, 6 February: Modern Physics and New Materials

Lasers and Laser Materials	K. Nassau

Monday–Friday 3–7 *February* 1964: **Winter Gordon Research Conference on Electrochemistry: Electrode Reactions:** Miramar Hotel, Santa Barbara, California [see *Talanta*, 1963, **10** (December), Notices p. ii].

Tuesday 4 *February* 1964: Panel Discussion on **Emission Spectroscopy Techniques:** E. Jaycox, T. Sheehy and C. Albright: *Society for Applied Spectroscopy, New York Section:* Hotel Manhattan, 8th Avenue and 44th Street, New York: 8.00 p.m.

Thursday–Saturday 27–29 *February* 1964: **Fifth Omnibus Conference on Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy:** Mellon Institute, Pittsburgh, Pa.

National Bureau of Standards has announced the availability of a new nitrogen-bearing and two new precipitation-hardening stainless steel standards. NBS Standard Sample No. 343 is intended for calibrating procedures for determining nitrogen and the precipitation-hardening standards, Nos. 344 and 345, for controlling the composition of these stainless steels.

In addition, nine other standard materials, previously available but recently out of stock, have been renewed. Of these, No. 158a is a standard copper alloy (silicon bronze), No. 3a is a standard white iron in chip form, Nos. 83c and 84g are standards of purity (arsenious oxide and acid potassium phthalate, respectively) and the remaining five are rubber or rubber-compounding standards (sulphur: 371d; stearic acid: 372e; benzothiazyl disulphide: 373e; oil furnace black: 378a; styrene-butadiene, type 1500: 386d).

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NOTICES

(Material for this section should be sent directly to the Associate Editor)

Guides to Guides to Scientific Literature

About 40% of the references to Scientific literature are obtained from abstracting and indexing periodicals. There are now about 2,000 of these. Two useful guides to abstracting and indexing publications exist. They are

A Guide to the World's Abstracting and Indexing Services in Science and Technology: National Federation of Science Abstracting and Indexing Services, Washington, D.C., 1963 ($5.00)

obtainable from:

National Federation of Science Abstracting and Indexing Services, 324 East Capitol Street, Washington, 3 D.C., U.S.A.

and

Index Bibliographies, 4th Edition, Vol. 1: *Science and Technology:* Federation Internationale de Documentation, The Hague, 1959

obtainable from:

Federation Internationale de Documentation,
6 Willem Witsenplein, The Hague, Netherlands.

BUNDESREPUBLIK DEUTSCHLAND

6. *Juni* bis 2 *Juli* 1964: **Deutschsprachige Spektrometer-Tagung:** Frankfurt/Main.

Die Fachgruppe "Analytische" der Geselleschaft Deutscher Chemicker, der Deutsche Arbeitskreis für Spektroskopie, die Arbeitsgruppe Massenspektrometrie der Deutschen Physikalischen Gesellschaft und die Chemikerausschüsse der Gesellschaft Deutscher Metallhütten- und Bergleute, des Steinkohlenbergbauvereins und des Vereins Deutscher Eisenhüttenleute veranstalten gemeinsamam eine Tagung über "Moderne Methoden der anorganischen Analyse". Diese Tagung soll vom 5. –7. Oktober 1964 in Düsseldorf stattfinden.

Es sind folgende Hauptthemen für die Tagung vorgesehen:

1. Nichtmetalle in Metallen.
2. Analyse von Verbindungsformen und ihre Verteilung im festen Zustand
3. Probenahme
4. Erfassen und Verwerten analyrischen Zahlenmaterials.

Zu diesen Themen werden Hauptvorträge von folgenden Kollegen gehalten:

Prof. Dr. J. FISCHER, Frankfurt (Gruppe 1)
Prof. Dr. W. KOCH, Duisburg (Gruppe 2)
Dr. ZETTLER, Hamburg, und
Dipl.-Ing. SPORBECK, Essen (Gruppe 3)
N.N. Gruppe 4)

FRANCE

La **Commission Internationale d'Essais** "C.I.E." du **COMITE INTERNATIONAL DE LA DETERGENCE** (C.I.D.) a tenu, sous la présidence du Dr. GÖTTE (Allemagne), sa session annuelle les 23 et 24 Mars 1964 à Düsseldorf, sur aimable invitation du Deutscher Ausschuss für Grenzflächenaktive Stoffe.

C'est la 7ème fois que les pays membres de cette Commission sont appelés ainsi à se réunir depuis sa fondation, et 10 pays ont répondu à cette invitation: Allemagne, Autriche, Belgique, Espagne, France, Italie, Pays-Bas, Portugal, Royaume Uni et Suisse. L'INTERNATIONAL ORGANIZATION FOR STANDARDIZATION "I.S.O.", qui suit tous les travaux du C.I.D., avait délégué un de ses collaborateurs.

Les travaux de la C.I.E. étant considérés comme suffisamment avancés sur un certain numbre de sujets, il a été décidé que 5 projets de normes pouvaient être adoptés définitivement et seraient présentés dans le courant de l'année au Comité Technique ISO/TC-91 "Agents de Surface" pour homologation sur le plan international. Il s'agit des normes suivantes:

Stabilité des agents de surface à l'eau dure,
Eau distillée (conditions requises pour essais physicochimiques relatifs aux agents de surface),
Eau dure (définition et propriétés),
Masse volumique apparente des pâtes,
Point de trouble des agents de surface non-ioniques selon la méthode au butyldiglycol.

Le nombre des travaux soumis à l'ISO/TC-91 par la C.I.E. se trouvera ainsi porté à 9.

Par ailleurs, les membres de la C.I.E. effectueront des essais inter-laboratoires dans leurs pays, pour améliorer ou vérifier certaines études actuellement au stade expérimental:

Solubilité des agents de surface,
Pouvoir protecteur vis-à-vis des savons calcaires, en utilisant un savon préparé à l'avance,
Tension superficielle selon une méthode dite "de la bulle par pression", pur laquelle un appareil nouveau a été mis au point en Allemagne. Les mesures seront comparées à celles du pouvoir mouillant sur coton.
Viscosité des agents de surface sur appareils Roto-Visco et Rhéomat,
Stabilité des solutions d'agents de surface, en utilisant la chromatographie par couche mince,
Mesure de la couleur par comparaison de différentes échelles colorimétriques,
Contrôle du lessivage à l'aide de bandes-témoins non souillées; un groupe de travail a été spécialement créé à cet effet et fait appel au concours de techniciens du lavage.

Enfin, un travail bibliographique et documentaire sera entrepris pour différentes questions nécessitant encore de longues études, telles que les pouvoirs détergent, dispersant, émulsionnant et la stabilité des émulsions, la concentration critique de micelles, l'action des oxydants et leur influence sur les taches, la préparation des détergents en pastille, le dish washing test et al tension d'adhésion.

Ce programme de travail est important et nécessite, de la part des laboratoires, de longues et patientes recherches mais leurs efforts s'avèrent, de par les résultats déjà obtenus, particulièrement fructueux et appréciés sur le plan international.

Rappelons que le but de la Commission Internationale d'Essais est de mettre au point des méthodes d'essais facilement reproductibles et utilisables de par le monde. C'est pourquoi elles sont établies selon un schéma uniformisé et recommandent des appareillages connus de tous les techniciens.

La prochaine session de la C.I.E. aura lieu en Mars 1965, sur invitation du British National Committee on Surface Active Agents, et elle se déroulera à Londres.

UNITED KINGDOM

Thursday-Saturday 2–4 *July* 1964: **Symposium on Pollution:** *Society for Analytical Chemistry, Western Section:* University College, Singleton Park, Swansea.

The programme is as follows:

Thursday, 2 July: Morning	
Opening Address—Environmental pollution.	D. T. Lewis
The effects on industry of recent legislation on the discharge of trade effluent.	A. I. Biggs
Thursday, 2 July: Afternoon	
Water pollution with respect to sewage.	S. H. Jenkins
Water pollution of all kinds.	L. Klein
Friday, 3 July: Morning	
Atmospheric pollution.	S. G. Burgess
Effects of pollution on vegetation.	J. Webber
Friday, 3 July: Afternoon	
Lecture and visit to the Lower Swansea Valley Project.	
Saturday, 4 July: Morning	
Biological effects of pollution.	R. D. Brinkhurst
Tidal pollution.	P. N. J. Chipperfield

Further information may be obtained from Dr. T. G. Morris, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

Thursday-Friday 2–3 July 1964: Summer Meeting on **Limitations of Detection in Spectrochemical Analysis:** *Institute of Physics and Physical Society, Spectroscopic Group:* University of Exeter (see *Talanta*, 1964, **11,** April, vi).

Sunday-Saturday 19–25 *July* 1964: **Third International Congress for Polarography:** *Polarographic Society:* University of Southampton.

Tuesday 28 *July* 1964: Lecture by W. Kemula: *Society for Analytical Chemistry* and *Polarographic Society:* Burlington House, London W.1.

British Standards Institution has announced the following *New British Standard:*
B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 13: 1964: *Method for the determination of titanium in aluminium and aluminium alloys (absorptiometric chromtropic acid method).* This specifies reagents required, recommended methods of sampling and analytical procedure for the determination of titanium in alloys having a titanium content between 0·005 and 0·3%. (*Price* 4s.)

The following *Amendment Slip* has also been announced:
B.S. 1016: *Methods for the analysis and testing of coal and coke: Part* 1: 1957: *Total moisture of coal. Amendment No.* 1: *PD* 5146.

UNITED STATES OF AMERICA

Tuesday–Thursday 6–8 *October* 1964: **Eighth Conference on Analytical Chemistry in Nuclear Technology:** *Analytical Chemistry Division of Oak Ridge National Laboratory:* Mountain View Hotel, Gatlinburg, Tennessee.

The subject will be **Determination of Interstitials and Trace Constituents in Reactor Materials and Products.** The Conference will be composed of six sessions embracing the following subtitles:

1. *Spectrochemical and X-ray Methods of Analysis.*
2. *Mass Spectrometric Methods of Analysis.*
3. *Nuclear Methods of Analysis.*
4. *Gas Chromatographic Methods of Analysis.*
5. *Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals.*
6. *Determination of Trace Constituents by Diverse Methods.*

Participation in the Conference will be on the basis of invited contributions. However, a limited number of papers, up to 25 min in length, are solicited and will be accepted provided the subject matter of such contributions fits in with the over-all objectives of the Conference and meets with the approval of the Programme Committee.

Those who wish to make contributions are requested to submit an abstract of 200–500 words not later than 10 July, giving the name of the intended speaker and the amount of time that will be required for the presentation. Abstracts of papers and any enquiries concerning the Conference should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee.

Monday–Thursday 19–22 *October* 1964: **78th Annual Meeting of Association of Official Agricultural Chemists:** Marriott Motor Hotel, Twin Bridges, Washington D.C. 20044.

The programme will have almost 300 scientific papers on analysis of foods, drugs, cosmetics, food and colour additives, beverages, pesticides, extraneous materials in foods and drugs, fertilisers, feeds, and many other commodities important to agriculture and public health. In addition, six outstanding European scientists will present key addresses to general sessions on such topics as drugs, pesticides, food laws, chromatography detectors, food additives and fish composition. The six invited speakers are: J. A. LOVERN (Scotland); J. F. REITH (Netherlands); D. C. GARRATT, A. T. JAMES (England); H. CHEFTEL (France) and FINN BRO-RASMUSSEN (Denmark). Dr. D. T. LEWIS, Head, Laboratory of the Government Chemist, England, will keynote the Monday evening banquet with his address, *The Changing Environment of Mankind.* Another feature of the banquet will be honoring the winner of the Harvey W. Wiley Award for notable contributions to analytical methodology.

The meeting will include about 30 exhibits of the latest equipment and supplies for analytical chemists. Other information is available from LUTHER G. ENSMINGER, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, U.S.A.

The **ORNL Master Analysis Manual** is a collection of the analytical methods developed and used in the Analytical Chemistry Division of Oak Ridge National Laboratory. The manual was begun in 1963, but includes methods used earlier. In 1957, the Office of Technical Services of the U.S. Department of Commerce reprinted the unclassified sections of the manual for public sale and since then has issued annual supplements that contain reprints of new or revised methods. These reprinted parts are designated TID-7015.

The Oak Ridge National Laboratory has now published a paperbound volume which consists of a key word index composed from method titles, a bibliographic index that is equivalent to a table of contents for the manual, an author index, and method-number cross indexes. The bibliographic index gives the complete history and current status of every method. The titles entered in this publication are those of all unclassified methods included in the manual from 1953 through 1962.

The indexes will be brought up-to-date annually. This publication, TID-7015 (Indexes), is available from the U.S. Department of Commerce, Office of Technical Services, Washington, D.C. 20230 ($2.50).

The publication of **Nuclear Magnetic Resonance Abstracts** has been announced. This is intended to include the total world literature on all aspects of nuclear magnetic resonance; theoretical and applied papers in both high resolution and broad line areas, techniques, apparatus, *etc.*, will be covered. The abstracts will be in English. Further information is available from Preston Technical Abstracts Co., 1718 Sherman Avenue, Evanston, Ill. 60201.

The **American Society for Testing and Materials** has announced the publication of *Report on Available Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analysis* (1963): STP 58-E. This provides an up-to-date reference to the availability and sources of 5050 samples and materials. The introduction presents the scope and form of the report and a discussion of definitions and nomenclature.

The following parts of the 1964 *Book of ASTM Standards* are now available: *Part* 30: *General Testing Methods; Quality Control; Appearance Tests; Temperature Measurements; Effects of Temperature* (Price $11.00; $7.70 to ASTM members).
Part 31: *Metallurgy; Nondestructive Testing; Radioisotopes and Radiation Effects; Industrial Chemicals; Emission, Absorption and Mass Spectrometry* (Price $12.00; $8.40 to ASTM members).
Part 32: *Chemical Analysis of Metals* (Price $14.00; $9.80 to ASTM members).

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NOTICES

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The **Fifth Report on Reagents and Reactions for Qualitative Inorganic Analysis,** prepared by the *Commission on Analytical Reactions* of the *Analytical Chemistry Division of I.U.P.A.C.* has now been published (*Pure and Applied Chemistry*, 1964, **8,** No. 1).

CANADA

Monday–Wednesday 1–3 *June* 1964: **47th Annual Meeting of Chemical Institute of Canada:** Kingston, Ontario.

The programme for the **Analytical Chemistry Division** is as follows. It should be noted that Sessions I and II on 1 June will be concurrent.

Monday, 1 *June Morning—Professional development seminar statistics*

Statistics applied to production.	R. Vance Ward
Designed experiments.	N. Sawyer
Evolutionary operation.	B. Bonner

Monday, 1 *June, Afternoon*

Session I

A definition of the chemical sampling and smoothing problem.	G. A. Coulman
Statistical evaluation of routine test methods.	A. G. Wood and M. L. Yeo
Using statistical inference in development of analytical methods	C. G. Miller
Qualitative aspects of surface chemistry in polarographic maxima suppression.	R. G. Barradas and F. M. Kimmerle

Session II

Process analysers: Philosophy and experiences.	R. O. Clark
Conductometric determination of salt in crude oils.	R. E. Borup
Some analytical applications of vacuum spark mass spectrography.	E. R. Blosser
Analytical instruments in Shell's Oakville refinery.	L. Korchinski
Carboxyl group response in flame ionisation detectors.	R. G. Ackman
Determination of ethanol and some other volatiles in blood, urine and tissue by gas-liquid chromatography.	B. B. Coldwell and G. L. Grant

Tuesday, 2 *June, Morning—Quality control and laboratory administration*

Quality control and laboratory administration.	S. Siggia
Minimising the risk concept in laboratory safety.	E. A. Crockett
A format for writing analytical test methods.	J. Russel
Administration of a modern centralised petrochemical analytical laboratory.	W. H. Webster
Use of spectrophotometry in inspection services.	M. T. Antoniades

Tuesday, 2 *June, Afternoon—Panel discussion: Management assays the image of the analytical chemist*

Personnel director: D. S. Kirkbridge
Management consultant: G. M. Currie
Industrialist: J. C. Langford
Director of quality control: D. S. Jackson

Wednesday 3 *June, Morning—Panel discussion: Application of instruments to analytical chemistry*

Mass spectrometry: R. T. Moir
Spectrophotometry: M. M. Antoniades
Emission spectroscopy: D. Bender
High resolution NMR: J. F. Hanlan
Infrared spectroscopy: R. M. B. Small

FEDERAL GERMAN REPUBLIC

Friday–Saturday 19–27 *June* 1964: **European Convention of Chemical Engineering 1964,** including **1964 ACHEMA Congress:** Frankfurt am Main (see *Talanta*, 1964, **11**, February, i).

UNITED KINGDOM

Tuesday, 9 *June* 1964: **Galvanic Analysis:** P. HERSCH: *Society for Analytical Chemistry, Midlands Section* with *Royal Institute of Chemistry, Birmingham and Midlands Section* and *Polarographic Society* and *Guild of Associates of Birmingham College of Advanced Technology:* University, Edgbaston, Birmingham 15: 6.30 p.m.

Wednesday 17 *June* 1964: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group: The Feathers*, Tudor Street, London E.C.4: 6.30 p.m.

Thursday–Friday 27–28 *August* 1964: **Conference on Recent Advances in Activation Analysis:** University of Glasgow.

The Conference will be conducted under the following general themes:

(a) *Instrumentation and techniques*
(b) *Biological and medical applications*
(c) *Industrial applications*
(d) *Future trends.*

Further information can be obtained from Dr. J. M. A. LENIHAN, Regional Physics Department, Western Regional Hospital Board, 9–13 Graham Street, Glasgow C.4.

Monday–Tuesday 14–15 *September* 1964: **First European Colloquium on Electron-Probe X-Ray Microanalysis:** *Institute of Physics and Physical Society, Electron Microscopy and Analysis Group* and *Sous-Commission Microsonde of France:* Delft, Holland.

The Colloquium will be divided into three main sessions: instrumentation, quantitative microanalysis and applications. An invited survey will precede each of the main sessions. Advance registration is necessary and application forms and further details are available from Administration Assistant, Institute of Physics and Physical Society, 47 Belgtave Square, London S.W.1, England.

British Standards Institution has announced the following *New British Standard: B.S.* 1748*: Methods for the analysis of copper alloys: Parts* 11–12*:* 1964: *The determination of copper and lead in leaded-bronze alloys.* Part 11 specifies reagents required, recommended methods of sampling and test procedure for the determination of copper in copper alloys containing lead in the range 7–25%. The method is applicable to copper contents in the range 70–90%. Part 12 specifies reagents required, recommended methods of sampling and test procedure for the determination of lead in copper alloys containing lead in the range 7–25%. (*Price* 4s.)

UNITED STATES OF AMERICA

Monday–Wednesday 1–3 *June* 1964: **10th National ISA Analysis Instrumentation Symposium;** *Instrument Society of America, N. California Section:* Sheraton-Palace Hotel, San Francisco, California.

The advance programme is as follows:

Monday morning, June 1	
A systematic review of the research programme for Instrumental Analysis at the Technical University in Eindhoven, Holland.	A. I. M. KEULEMANS
Analysis instrumentation in the petrochemical industry.	THEODORE W. EVANS
Monday afternoon, June 1: *AIR POLLUTION*	
The phenomena of light scattering by fine particles in relation to air-pollution instruments.	J. RAYMOND HODKINSON
Exhaust inspection instrumentation.	CHARLES HEINEN
Collecting representative exhaust gas samples.	RICHARD W. HURN, JAMES O. CHASE and RALPH D. FLEMING
Instrumental measurement of contamination in clean rooms for proposed federal standard 209.	PAUL L. MAGILL

Monday afternoon, June 1: ELECTROCHEMICAL AND CHEMICAL METHODS OF ANALYSIS

Electrochemical transducers for water quality.	Curtis E. Borchers, R. W. Raible M. K. Testerman and R. W. Romine
Analogue simulation design of a highly-dynamic pH control system.	Robert M. Green
Membraneless potentiometric analysis of dissolved oxygen in process streams.	Kenneth K. Konrad
Process polarograph for measuring PPM H_2S.	Bernard L. Connelly
A new process analyser for hydrogen.	James J. McKinley and Edward A. Hinkle

Tuesday morning, June 2: LABORATORY METHODS OF ANALYSIS—I

Determination of molecular weights of high melting point polymers.	Harry C. Ehrmantraut and Leon E. Hiam
Role of EPR in free radical chemistry.	Lawrence H. Piette
Present status of high resolution NMR spectroscopy.	James N. Shoolery and Leroy F. Johnson

Tuesday morning, June 2: RADIATION METHODS OF ANALYSIS

Radiation gauging breakthrough.	Charles O. Badgett
Application of actuation analysis in the petroleum and chemical industries.	Frank A. Iddings

Tuesday morning, June 2

Maintenance Workshop (morning session)
Discussion of Plant Analysers

Tuesday afternoon, June 2: LABORATORY METHODS OF ANALYSIS—II

Preparative GC for analytical purposes.	Roy Teranishi
Modern electroanalytical techniques.	Richard Pierson Buck
A mathematical procedure for referral of day-to-day analytical data to an original working curve, with emphasis on X-ray emission techniques.	William F. Loranger

Tuesday afternoon, June 2: PHYSICAL PROPERTIES ANALYSIS

Automatic pour point testers.	W. V. Cropper and G. L. Hammond
Haze point analyser.	D. J. Geniesse
Design and performance of the piezoelectric sorption hygrometer.	W. H. King, Jr., H. M. Crawford T. J. Mesh and J. J. Heigl

Tuesday afternoon, June 2

Maintenance Workshop (afternoon session)
Panel on instrument maintenance

Wednesday morning, June 3: GAS CHROMATOGRAPHY—I: PROCESS

Simultaneous analysis and BTU determination of natural gas.	Bryan Thompson and Richard C. Cavenah
New detectors for gas chromatography.	D. M. Coulson
Liquid chromatography.	L. E. Maley

Wednesday morning, June 3: OPTICAL METHODS OF ANALYSIS

A versatile process polarimeter.	Robert S. Saltzman
Flame photometry instrumentation at Indian Point nuclear power plant.	W. A. Crandall
Film coating monitoring by non-dispersive infrared.	Robert L. Chapman and William P. Houben

Wednesday morning, June 3: LABORATORY METHODS OF ANALYSIS—III

A closed-loop laboratory liquid feeder.	Lewis Fowler and Walter N. Trump

Advances in analytical emission flame spectrophotometry.	PAUL T. GILBERT, JR.
Atomic absorption spectrophotometry.	WALTER SLAVIN

Wednesday afternoon, June 3: *GAS CHROMATOGRAPHY—II: LABORATORY*

A programmed attenuator for laboratory gas chromatography.	LEWIS FOWLER, R. L. MCKINLEY and W. N. TRUMP
Generalisations of gas chromatography to study vapour—solid and vapour liquid equilibrium in multicomponent mixtures at elevated pressures.	R. KOBAYASHI
A simple apparatus for reproducibly packing gas chromatographic columns.	R. VILLALOBOS and G. R. NUSS
Application of switching valves in laboratory gas chromatography.	C. B. MCKINNEY and D. CARLE

Wednesday afternoon, June 3: *USE OF PROCESS STREAM ANALYSERS IN ON-LINE COMPUTER SYSTEMS*

Instream analysers aid in computer control.	J. C. RHODES and B. A. RITZENTHALER
Gas stream analysers in computer process control.	JOSEPH C. LANDWEHR, LLOYD J. BOESCH and EVERETT M. WOLVERTON
Chromatographs mated to digital computer implement process Studies.	W. H. WILLIAMS and M. C. BURK

Tuesday–Friday 2–5 *June* 1964: **15th Annual Mid-America Symposium on Spectroscopy:** Sheraton-Chicago Hotel, Chicago, Illinois.

Sunday–Friday 7–12 *June* 1964: **12th Annual Conference on Mass Spectrometry and Allied Topics:** *ASTM Committee E*-14: Sheraton-Mt. Royal Hotel, Montreal, Canada.

Monday–Friday 15–19 *June* 1964: **Symposium on Molecular Structure and Spectroscopy:** Department pf Physics, Ohio State University.

Sunday–Friday 21–26 *June* 1964: **Annual Meeting of ASTM and 16th Materials Testing Exhibit:** Conrad Hilton Hotel, Chicago, Illinois.

Wednesday–Friday 24–26 *June* 1964: Summer Symposium on **Recent Developments in Structure Determination:** *American Chemical Society, Division of Analytical Chemistry:* Cornell University, Ithaca, N.Y.: (see *Talanta*, 1964, 11, April vii).

Wednesday 30 *September–Thursday* 2 *October* 1964: **11th National Vacuum Symposium:** *American Vacuum Society:* Pick Congress Hotel, Chicago, Illinois.

The Programme Committee solicits the submission of contributed papers from those who have new and original work to report. Abstracts (150 words, in triplicate) should be submitted by 1st July to G. H. BANCROFT, Bendix-Balzers Vacuum, Inc., 1645 St. Paul Street, Rochester, New York.

Wednesday–Friday 21–23 *October* 1964: **12th Anachem Conference and Instrument Exhibit:** *Association of Analytical Chemists* (an affiliate of *ACS Detroit Section*) in collaboration with *Optical Society of America, Detroit Section:* McGregor Memorial Conference Center, Wayne State University, Detroit, Michigan.

It will feature symposia in many fields of interest, including thermal methods of analysis, organic functional group analysis, micro analysis, spectroscopy (emission, absorption, X-ray), *etc.*, and automation in analytical chemistry.

Further information can be obtained from C. M. GAMBRILL, Co-Chairman of the Publicity Committee, Ethyl Corporation, 1600 West 8 Mile Road, Detroit 20, Michigan.

Talanta, 1964, Vol. 11, pp. i to ix. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Division of Analytical Chemistry
Commission on Microchemical Techniques

International Investigation into Errors in Elementary Organic Microanalysis

The deadline for this investigation (see *Talanta*, 1964, **11**, April, i) has been extended until 1st September, 1964.

BELGIUM

Monday–Saturday 7–12 *September* 1964: **Fourth International Congress on Surface-Active Substances**; *Comité International de la Détergence*: Université Libre de Bruxelles, 48 Avenue Franklin Roosevelt, Bruxelles 5.

The scientific meetings are divided into three sections, of which Section A is on *Chemistry of Surface-Active Substances.* The provisional papers in Group A/IV, *Analytical Methods*, are as follows:

Analysis of fatty alcohol and alkyl phenol ethylene oxide condensation products.	P. Voogt
Direct determination of anionics in the anionics-ampholytics-nonionics ternary system.	Y. Izawa, Y. Ogata and W. Kimura
Separation and determination of nonionics in anionics-ampholytics-nonionics ternary mixtures.	W. Kimura and Y. Izawa
Development of an analytical method for determination of alkyl benzenesulphonate in surface waters and sewage.	Y. Dessouky
Determination of alkyl napthalenesulphonate in tomato products.	Y. Dessouky
Méthodes d'analyse des esters de saccharose et des sucroglycérides.	M. Roussos
Contribution à l'analyse des Polyéthylèneglycols et de leurs monoéthers, par chromatographie sur papier de leurs esters 3,5-*dinitrobenzoïques.*	H. Gauthier et M. G. Mangeney
Analyse des poloxyéthylèneglycols commerciaux par chromatographie en phase gazeuse de leurs dérivés diméthylés et dichlorés.	R. Celades et C. Paquot
Novel methods of isolation and identification of odiferous compounds in polypropylenebenzenesulphonate.	W. K. Seifert
Etude sur l'application de la technique chromatographique sur couches minces à l'analyse des mélanges des agents de surface (note III° des recherches sur la chimie analytique des agents de surface).	A. Arpino et V. De Rosa
Recherches sur le fractionnement et la composition de la fraction non sulphonée dans une pâte alkylarene-sulfonates.	A. Arpino, V. De Rosa et G. Jacini
Untersuchungen der in der Textilindustrie angewendeten Makromolekularen oberflächenaktiver Stoffe mittels der polarographischen Maximadämpfungen bzw. der oszillo-polarographischen kapazitiven Ströme.	A. Gergely
Estimation of alkyl phenol ethylene oxide adducts in soil.	B. Weibull

Verteilung zwischen Wasser und Chllroform von den Verbindungen aus n-Nonylbenzolsulfonat und einige n-Alkyltrimethylammoniumbromiden.	M. Hellsten

Further information is available from the General Secretariat of the Congress, 49 Square Marie-Louise, Bruxelles 4.

Monday–Tuesday 14–15 *September* 1964: **Third International Symposium on Chromatography;** *Belgian Society of Pharmaceutical Sciences*: Universite Libre de Bruxelles, Faculte de Medecine, 115 boulevard de Waterloo, Bruxelles 1.

Papers will be presented on theoretical aspects and practical applications in the following fields: *Biological Analytical Chemistry, Photochemistry, Analysis of Medicaments, Food Chemistry, Toxicology Industrial Chemistry and Synthetic Products, Radioisotopes—Tracers, Techniques, Apparatus, Solvents, Reagents.* The following Plenary Lectures will be given:

Détermination de la nature de la liaison mucopolyoside-protéine dans les glucoprotéides.	J. Montreuil
Chromatography in toxicological analysis.	A. S. Curry
Sur l'identification des composés dans la chromatographie en phase gazeuse.	A. I. Keulemans
Neue techniken und fortschrifte auf dem gebiet der dunnschikt-Chromatographie.	E. Stahl

Further information is available from the Secretariat of the Belgian Society for Pharmaceutical Sciences, 11 rue Archimede, Brussels 4.

CZECHOSLOVAKIA

Wednesday 26 *August–Friday* 4 *September* 1964: **Third European Regional Conference on Electron Microscopy;** Prague.

FRANCE

Monday–Friday 14–18 *September* 1964: **International Conference on Mass Spectrometry;** *Committee E-*14 *American Society for Testing and Materials, Groupement pour l'Avancement des Méthodes Spectrographiques, Institute of Petroleum:* Salle La Rochefoucauld-Liancourt, 9 bis, Avenue d'Iéna, Paris 16^e.

The programme is as follows:

Monday, 14 *September, Morning*

Détermination précise des masses atomiques.	J. Mattauch

Instrumentation and Advanced Techniques

Production of field ionisation mass spectra with a sharp edge.	A. J. B. Robertson and B. W. Viney
Progress of experimental techniques, applications and theory of field ion mass spectrometry.	H. D. Beckey
Mass spectrometric studies of the species of particles leaving a monocrystalline target in a charged or uncharged state under high-energy ion bombardment.	M. Kaminskny
Microanalyse par émission ionique secondaire.	R. Castaing et G. Slodzian

Monday, 14 *September, Afternoon—Analysis of Solids*

Analysis of solids by mass spectrometry.	R. E. Honig
Essai d'analyse absolue par spectrométrie de masse à étincelles.	M. Desjardins, R. Stefani, R. Bourguillot et A. Cornu
Qualitative analysis by spark source mass spectrometry.	J. S. Halliday, P. Swift and W. A. Wolstenholme
Contribution to the investigation of background effects in spark source mass spectrography.	H. Mai

Tuesday, 15 *September, Morning—Ion Collisions*

Ion-molecular reactions.	V. Talrose
Ionisation efficiency measurements by the retarding potential difference method.	S. Tsuda and W. H. Hamill
Appearance potentials obtained from a study of organic chlorides.	M. Baldwin, A. Maccoll and S. I. Miller

Positive and negative ion mass spectra of phosphorus compounds.	H. Halmann and Y. Klein
Ionisation cross-section measurements for 0·5–20 keV *electrons in atomic and molecular gases.*	B. L. Schram, A. J. H. Boerboom, M. J. v.d. Wiel and F. J. de Heer
A new type of formation of secondary negative ions in a mass spectrometer.	A. Henglein and G. Jacobs
Studies of atomic impact phenomena on metal surfaces with a pulsed molecular-beam mass spectrometer.	M. Kaminsky

Tuesday, 15 *September*, *Afternoon*

Ion molecular reaction cross sections.	C. F. Giese
The "stripping" and "inelastic complex" model in ion-molecule reactions.	A. Henglein, K. Lachmann and G. Jacobs
Réactions molecule-ion dans le cyanogène et l'acide cyanhydrique.	M. Inoue et M. Cottin
A high pressure mass spectrometric study of neopentane.	M. J. Henchman, H. T. Othwinowska and F. H. Field
Study of unimolecular and bimolecular reactions of ions using a pulsed ion source.	A. G. Harrison, T. W. Shannon and F. Meyer
Charge transfer collisions by ground state ions.	J. T. Scott and J. B. Hasted
Effect of excitation energy on charge transfer reactions.	F. W. Lampe
Charge transfer and atom transfer in ion-molecule interactions studied by a time-of-flight mass spectrometer.	J. B. Homer, R. S. Lehrle, J. C. Robb and D. W. Thomas

Wednesday, 16 *September*, *Morning—Theory of Mass Spectra*

Mass spectra theory of small molecules.	H. M. Rosenstock
Structure électronique des alkanes ionisés.	J. C. Lorquet
Unimolecular ion decompositions.	F. W. McLafferty
Etude par la méthode de déviation des distributions d'énergie cinétique d'ions formés par impact électrique.	J. Durup, J. Appell et F. Heitz
Mass spectrometric study of photoionisation of small molecules.	V. H. Dibeler and R. M. Reese
Effets isotopiques dans la dissociation par impact électronique des molécules triatomiques deutérées.	F. Fiquet-Fayard et P. M. Guyon
Study of fragment-ions formation in mass spectra of 1-*butyne*, 1-*pentyne*, 1-*hexyne*, 1-*heptine*, 1-*octyne*.	Z. Dolejsek, V. Hanus and K. Vokac

Thursday, 17 *September*, *Morning—Measurements of Isotopic Abundances*

Precise atomic abundance measurements.	H. Hintenberger
Mesure de l'abondance relative et absolue des isotopes de lithium produits dans des réactions nucléaires à haute énergie sur des cibles métalliques.	E. Alorent, R. Klapisch, E. Gradsztajn, F. Yiou, M. Épherre et R. Bernas
Tandem mass spectrometer for precise analysis.	L. G. Ridley
Abundance of vanadium isotopes in well-characterised sources of geochemical interest.	G. D. Flesch, J. Capellen and H. J. Svec
Preliminary report on half-life of tellurium-130 *double β-decay.*	K. Ogata, J. Okano and N. Takaoka
Etude par spectrométrie de masse des réactions du type La(p, 3p × n)Cs.	Nguyen Long-Den
Analyse de bore par dilution isotopique au spectromètre de masse.	M. Chemla et M. Périe
Isotopic analysis of boron as trimethyl borate by mass spectrometry.	H. Sanz Garcia

Thursday, 17 *September*, *Afternoon—High Resolution Mass Spectrometry*

Use of mass spectrometry in conjunction with other analytical techniques.	H. Powell
Distinction entre pics moléculaires et pics de fragmentation du spectre de masse d'un mélange complexe.	J. Champy et A. Cornu

Mass spectrometric investigation of di- and oligosaccharides and acylated peptides containing trifunctional amino acids.	H. Scharmann, K. Heyns and H. Fr. Gutzmacher
Mass spectrometry in natural product chemistry.	M. Barber, T. Bryce, E. Clayton, H. C. Hill, A. McCormick and R. I. Reed
Mass spectra of saturated cyclic nitrogen compounds.	A. E. Williams
Application of high-resolution mass spectrometry in molecular structure studies.	A. L. Burlingame
High resolution mass spectrometry of some large molecules.	M. Barber, R. M. Elliott and T. O. Merren
Combination of high resolution and low ionising voltages in determination of hydrocarbon and sulphur compound types in petroleum fractions using mass spectrometry.	W. K. Reid, W. L. Mead and K. M. Bowen

Friday, 18 *September, Morning—Instrumentation and Advanced Techniques*

Some problems relating to thermal emission of ions in mass spectrometric determination of isotopic abundances for neutron cross section measurements.	R. Baldock
Influence of oxygen on surface ionisation of some rare earth metals on tungsten and rhenium.	W. Weierhausen
Thermal ionisation of elements of high ionisation potential.	D. A. Crouch
Problèmes liés a l'obtention de réponses rapides em spectrométrie de masse.	J. Vastrel et J. Duroux
Sector-type double focussing mass spectrometer.	M. Sakai and M. Goto
Application à grande échelle d'analyse chimique industrielle par spectrométrie de masse: Digitalisation des informations en spectrométrie de masse.	P. Dard, J. Guiborg, J. C. Merlivat et G. Bernard
Results of a new time-of-flight mass spectrometer developed at the reactor centre Seibersdorf.	M. J. Higatsberger, F. Rudenauer, F. P. Viehbock and F. Butschbeck
Mass spectrometric sampling and detection of intermediates for gaseous reactions.	J. Cuthbert
Mass spectrometric sampling of high pressure high temperature sources.	F. T. Greene and T. A. Milne

Friday, 18 *September, Afternoon—Mass Spectrometry in General Chemical Research and in the Field of High Temperature Chemistry*

Review paper.	P. Le Goff et P. Goldfinger
Etude de l'oxydation du tantale et du tungstène: Etude thermodynamique du système uranium-dioxyde.	J. Drowart, F. De Greve, D. Detry et A. Pattoret
Equilibres thermodynamiques dans le système Sb–O *déterminés avec le spectromètre de masse.*	A. J. H. Boerboom et J. Kistemaker
Etude thermodynamique de l'hémioxyde de soufre (S_2O) *par spectrométrie de masse.*	R. Hagemann, R. Botter, G. Nief et E. Roth
A new-type of flow reactor for measurements of fast thermal reactions.	I. P. Fischer, J. B. Homer, B. Roberts and F. P. Lossing
Etude par spectrométrie de masse de la pyrolyse de quelques composés organiques.	E. Collin
Mass spectrometric investigation of reactions involving free radicals.	V. Talrose
Application of high temperature mass spectrometry to study of composition function of thermodynamic properties in non-stoichiometric compounds.	K. A. Gingerich

Further information may be obtained from Secretariat du G.A.M.S., 1 rue Gaston-Boissier, Paris 15^{e}, France.

UNITED KINGDOM

Sunday–Saturday 19–25 *July* 1964: **Third International Congress of Polarography;** *Polarographic Society*: University of Southampton.

The following papers will be presented:

Polarography in organic solvents (Presidential Address).	I. M. Kolthoff

SECTION 1.—*Theory, Methods and Instrumentation*

Role of polarography in study of rapid electrode processes.	G. C. Barker
Prospective developments in d.c. polarography and tensammetry.	B. Breyer
Determination of fast reaction processes at the dropping mercury electrode.	M. Fleischmann
Temperature coefficients of the electric tension (electrode potential) of individual electrodes.	G. Milazzo
Recent developments in d.c. polarography.	D. J. Fisher, W. L. Belew and M. T. Kelley
Complex plane analysis of cell impedances.	M. Sluyters-Rehback, D. J. Kooijman and J. H. Sluyters
Determination of rate constants for dissociation and recombination of weak acids by High Level Faradaic Rectification.	H. W. Nurnberg
Shielding effect of the capillary tip and its influence on RF current distribution.	A. W. Gardner
Recent studies in high-resistance polarography.	W. B. Schaap and P. S. McKinney
Diffusion-controlled electrolysis with gas injection through the porous electrode.	D. B. Spalding and P. L. Duffield
Multi-sweep oscillographic polarography: Theory, instrumentation and applications in analytical chemistry.	H. A. Glastonbury
Square wave d.c. bridge polarograph.	E. Niki
Alternating current polarography at stationary electrodes.	Yu. S. Lyalikov, V. I. Bodyu and L. G. Madan
Studies in subtractive and continuous polarography.	K. G. Powell and G. F. Reynolds
An oscillopolarography using a magnetic deflecting cathode-ray tube.	Y. Yasumori
Application of transistors to polarographic instrumentation.	C. L. Roughton
Graphite indicating electrodes: Theory, methodology and applicability.	P. J. Elving and I. Fried
Moglichkeiten und Grenzen einer Strömungsapparatur mit Polarographischer Registrierung.	E. Bauer and H. Berg
Influence of salting-out effect on polarographic behaviour of pyridine.	C. Pécasee and L. Gierst
Study of return of polarographic maxima in the function of the base electrolyte.	I. Rusznak, A. Gergely, I. Kralik and V. Komiszar
Reduction of hydrogen ions at the dropping mercury electrode.	O. H. Müller
An interpretation of differential electrolytic potentiometers as a linear diffusion process.	E. Bishop and G. D. Short
Auto-inhibition phenomena in polarography.	E. Laviron and Ch. Degrand
Kapazitäts und Inhibitions-Untersuchungen mit der Wechselstrompolarographie.	H. Jehring
Investigation of adsorption phenomena occurring at the dropping mercury electrode.	F. Peter
Application of cyclic chronopotentiometry to study of electrode reaction mechanisms.	A. J. Bard and H. B. Herman
Study of chronopotentiometric curves in current scanning polarography.	E. Laviron
Fortschritte der Photo-polarographie.	H. Berg

SECTION 2.—*Study and Analysis of Inorganic Systems*

Polarography and mechanism of electroreduction of carbon dioxide.	P. T. Smith

Polarographic studies of carbonate complexes of some metal ions.	S. Misume and Y. Masuda
Reduction, oxidation and disproportionation of uranium ions in sodium carbonate solutions.	M. Branica and V. Pravdić
Influence of pH and of the double layer on rate constants of reduction of oxygen on the dropping mercury electrode.	J. Kuta and J. Koryta
A study of the polarographic behaviour of the system O_2Pb^{II}.	A. Arevalo and A. Bazo
Polarography of sulphide-ion.	S. Zhdanov and B. Kiselev
Polarographic determination of sulphur in organic compounds.	G. Russell
La polarographie de la réaction de l'activation de quelques ions complexes diacidotétrammino Co^{III}.	R. Ralea, G. Burlacu et D. Giurgiu
La radio-polarographie des maximas obtenues par la réduction de l'arsenic cataliseé par le cobalt et le fer.	R. Ralea et A. Cecal
Polarographic investigation of metal acetylacetones—II: Cupric acetylacetonates.	M. Petek, L. Jeftić and M. Brancia
Polarography of pentacyano-, tetracyano- and dicyano-cobalt(III) complexes: Electron-transfer mechanism of the electrode reaction.	N. Maki
Polarographic studies of zirconium with Solochrome Violet RS in various supporting electrolytes.	D. S. Turnham
Polarographic behaviour of tervalent lanthanide ions in aquo-alcoholic media.	V. A. Huertas, J. A. Huertas and J. S. Gomez
Polarographic study of dibromotetraquochromium(III) ion hydrolysis.	J. Ibarz, A. M. Calvo and J. M. Costa
Determination of composition and stability constants of mercury(II)—thioacetamide complexes.	T. D. Seth and R. C. Kapoor
Polarographic behaviour of metal ions in aged KOH solutions.	P. Bersier and F. V. Sturm
Polarographic studies of ion binding: Zinc Polystyrene Sulphonate.	S. Lapanje and S. Oman
Polarographic determination of traces of molybdenum.	H. Woggon
Polarographic determination of mercury distribution in mercuric chloride catalyst supported by activated carbon granules.	F. Zilio-Grandi, A. M. Perazzolo and L. Fornasiero
Determination of trace metal impurities in zinc oxide and zinc salts.	R. J. Browning and G. F. Reynolds
Polarographic investigations in acidic fluoride solutions.	J. B. Headridge, A. G. Hamza, D. P. Hubbard and M. S. Taylor
Some uses of solvent extraction in polarographic analysis.	R. C. Rooney and D. L. Jones
Application of single-sweep polarography to analysis of trace elements in sea-water.	G. Whitnack
Continuous multipotential polarography in strong gamma-radiation field.	Z. P. Zagórski

SECTION 3.—*Study and Analysis of Organic Systems*

Recent trends in organic polarography.	P. Zuman
Oscillopolarographic study of reductions at high negative potentials.	R. Kalvoda
Formation of surface film by cyclohexane on mercury cathode.	K. Tsuji
Effect of composition of aqueous-organic solvents on polarographic behaviour of organic compounds.	S. Mairanovskii
*Polarographic investigation of indandione-*1,3 *and related compounds.*	J. Stradins, I. Tutane and G. Vanags
Some observations about the connection between structure and adsorption at the DME of some aromatic sulphonic acids.	G. Palyi
Polarography of sulphilimines.	M. Vajda and F. Ruff

Polarography of some α-halogen substituted aldehydes in dimethylformamide.	N. Moe
Polarographische untersuchung und Bestimmung von Krotonaldehyd im Technischen n-butylalkohol.	J. Pasciak
Polarography of tropon and 2,3-*dimethyl*-7-*benzotropon.*	A. Pozdeeva and S. Zhdanov
Controlled potential electrolytic reduction of polycyclic aromatic hydrocarbons, and concurrent polarography and spectrophotometry of the reduction products.	I. Bergman
Contribution a l'etude polarographique de quelques aci-reductones.	P. Souchay, M. Fleury and D. Fleury
Polarographie et electrolyse a potentiel controlé de derives aliphatiques gem-halogenonitres, gem-halogenonitrosés et gemnitrosonitrés.	P. Souchay, J. Armand and S. Deswarte
Role of surface active cations in electrode reaction mechanism of catalytic currents caused by organic compounds containing nitrogen.	E. Pungor
Über reversibilität und reversibilitätsgrenzen von Azo-/Hydrazo-Redoxreaktionen an der Hg-Tropfelektrode.	L. Holleck
Polarographic reversibility of the azobenzene-hydrazobenzene system with special reference to an absorption mechanism.	B. Nygård
Properties electrochimiques de l'hydrazo-9 *acridine et de l'azo*-9 *acridine en milieu non-aqueux*: *Deux radicaux libres intermediares.*	C. Cauquis and G. Fauvelot
Polarographic reduction of 4-*methylimidazol*-2-*ylthiosulphuric acid.*	R. A. F. Bullerwell
Polarographische Untersuchungen der Kinetik und Mechanismus der Azomethinreaktionen.	M. Deželić
Polarographic behaviour of 1-*oxy*-1,2,3,4-*tetrahydroisoquinoline.*	K. Gyorbiro
Development of polarographic activity in some cyostatic agents containing nitrogen.	T. Horvath and J. K. Pauncz
Determination of residual fumaric and maleic esters in copolymer emulsions.	J. S. Double, C. E. R. Jones and G. E. J. Reynolds

SECTION 4.—*Study and Analysis of Biological Systems*

New contributions to palladium polarography and their application to carbon monoxide determination in blood.	R. Portillo, P. Sanz Pedrero and P. Ramos
Polarographische Sauerstoffmessungen mit der Quecksilbertropfelektrode and Festelektroden in Mikrobenkulturen und ihr Vergleich mit Redoxpotentialmessungen.	G. Horn and H. E. Jacob
Tissue pO_2 *measurement with a miniaturized Clark-type electrode.*	R. Penneys
Controlled potential electrolytic reduction of diphosphopyridine nucleotide and a number of model compounds: *Polarography of oxidised and reduced forms.*	I. Bergman
The Brdicka serum filtrate reaction applied to normal and cancerous menstrual fluids.	R. Rappolt
Polarographic study of effect of gamma radiation on 1-*ascorbic acid.*	R. P. Lansky

SECTION 5.—*Study of Non-aqueous Systems*

Die polarographische Bestimmung kleinster Mehgun von Wasser und Stoffen mit aktivem Wasserstoff.	H. Dehn, V. Gutmann and G. Schober
Complex formation in polarography of aromatic compounds in organic solvents.	M. E. Peover and J. D. Davies

Voltammetric oxidation of aromatic compounds in acetonitrile.	T. A. Gough and M. E. Peover
Polarographic studies in acetonitrile and dimethylformamide: Behaviour of triphenylphosphine and related compounds.	S. Wawzonek and J. H. Wagenknecht
A simple quasi reference electrode: Applications in controlled potential polarography and voltammetry and in chronopotentiometry.	D. J. Fisher, W. L. Belew and M. T. Kelley
A reference electrode for polarography in organic solvents.	G. P. Kumar and D. A. Pantony
Electrochemistry in acetic anhydride: Behaviour of silver, mercury, gold and platinum electrodes and oxidation-reduction systems of iodine.	V. Plichon and J. Badoz-Lambling
Etude des domaines d'electroactivité a une electrode de platine poli de quelques ammoniacates liquids.	J Badoz-Lambling and M. Herlem
Polarography in the eutectic aluminium chloride-sodium chloride potassium chloride.	R. M. de Fremont, R. Rosset and M. Leroy
Polarography in molten fluorides.	D. L. Manning and J. W. Dale
Oscillographic polarography in molten nitrates II° Association constants determination.	M. F. Francini and S. Martini

Further information may be obtained from Dr. D. A. Pantony, Department of Metallurgy, Royal School of Mines, London S.W. 7, England.

Thursday–Friday 27–28 *August* 1964: **Conference on Recent Advances in Activation Analysis;** University of Glasgow (see *Talanta*, 1964, **11**, May, ii)

Tuesday–Wednesday 13–14 *April* 1965: **Symposium on Thermal Analysis;** Northern Polytechnic, London

The programme will include main lectures on various aspects of thermogravimetric and differential thermal analysis to be given by distinguished visitors from Europe and U.S.A. Contributed papers are also invited. Further information is available from Dr. B. R. Currell, Northern Polytechnic, Holoway Road, London N.7.

British Standards Institution has announced the following *New British Standard*:

B.S. 3727: *Methods for the analysis of nickel for use in electronic tubes and valves* (Price of Parts: 3s. each).

Part 4: 1964: *Determination of chromium*, 0·002–0·010% (*photometric method*).
Part 5: 1964: *Determination of cobalt*, 0·01–1·0% (*photometric method*).
Part 6: 1964: *Determination of copper*, 0·002–0·20% (*photometric method*).
Part 7: 1964: *Determination of iron*, 0·03–0·25% (*photometric method*).
Part 8: 1964: *Determination of manganese*, 0·005–0·025% (*photometric method*).
Part 10: 1964: *Determination of silicon*, 0·020–0·25% (*photometric method*).
Part 14: 1964: *Determination of tungsten, up to* 5% (*gravimetric method*).

UNITED STATES OF AMERICA

Monday–Tuesday 10–11 *August* 1964: **Seventh Annual Rocky Mountain Spectroscopy Conference;** *Society for Applied Spectroscopy, Rocky Mountain Section*: Albany Hotel, Denver, Colorado.

Wednesday–Friday 12–14 *August* 1964: **Thirteenth Annual Conference on Application of X-Ray Analysis;** Albany Hotel, Denver, Colorado.

Monday–Thursday 17–20 *August* 1964: **Sixteenth Annual Meeting of American Association of Clinical Chemists;** Hotel Statler-Hilton, Boston, Mass.

Monday–Friday 17–21 *August* 1964: **Gordon Research Conference on Analytical Chemistry;** New Hampton School, New Hampton, New Hampshire (see *Talanta*, 1964, **11**, April, viii).

Sunday 30 *August–Friday* 4 *September* 1964: **148th National Meeting of American Chemical Society;** Chicago, Ill.

Monday–Thursday 19–22 *April* 1965: **International Conference on Modern Trends in Activation Analysis;** *International Atomic Energy Agency, Division of Isotopes Development of U.S. Atomic Energy Commission* and *Activation Analysis Research Laboratory of Texas A and M University*: Texas A and M University, College Station, Texas.

Reports of new activation analysis developments in the following categories are invited:

1. *Radiochemical Methods*
2. *Instrumental Methods*
3. *Data Processing*
4. *Detector Developments*
5. *Sources*
6. *Nuclear Reactions*
7. *Statistical Considerations*
8. *Applications*

A technical abstract (250–500 words) should be submitted, not later than 1 August, 1964, to Dr. R. E. WAINERDI, Activation Analysis Research Laboratory, Texas A and M University, College Station, Texas, U.S.A. Authors will be notified of the decisions of the selection committee before 1 October, 1964. Abstracts should describe new, unpublished work of substantial interest. Those papers which indicate trends and new approaches are especially encouraged. Abstracts and papers should be submitted in English, which will be the official language of the Conference.

Sunday–Friday 22–27 *August* 1965: **International Symposium on Microchemical Techniques**—1965; *American Microchemical Society* with sponsorship of *I.U.P.A.C.*: Pennsylvania State University, Pa.

A call is now being made for research papers directed towards small-scale operations, techniques and methods in all phases of chemistry, including clinical chemistry and biochemistry. Papers centered on history, speculation or review will not be considered. It is hoped to have sessions on the following subjects:

1. *Micro methods in structural elucidation.*
2. *Micro techniques in peptide studies.*
3. *Clinical and forensic analysis.*
4. *Novel micro and ultramicro approaches in organic elemental analysis.*
5. *Micro techniques with high-energy materials.*
6. *Novel micro separation methods.*
7. *Inorganic microanalysis and trace analysis.*
8. *Micro methods in air and water pollution studies.*
9. *Determination of physical properties with small samples.*
10. *Education for instrumentation.*
11. *General papers.*

Further information, including regulations governing papers, may be obtained from Mr. H. FRANCIS, JR., Vice-Chairman, Intern. Sym. Microchem. Techniques—1965, c/o Pennsalt Chemicals Corp., 900 First Ave., King of Prussia, Pennsylvania, U.S.A. A descriptive title and abstract for a paper must be received by 31 January, 1965, and the text of the paper by 31 April, 1965.

American Society for Testing and Materials has announced the availability of the following publication:

ASTM Standards on Methods for Emission Spectrochemical Analysis (1963): E-2 (Price $16.00; $11.20 to ASTM members). This compilation, now in its fourth edition, contains all spectrochemical practices and methods published by the Society, as well as excerpts from ASTM methods or practices. The scope, limitations, precision and accuracy of the methods have been recorded to the extent of data available so that the methods can be compared and evaluated with respect to other analytical methods. The table of contents lists those methods and practices which have been discontinued or replaced since the previous edition.

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NOTICES

(Material for this section should be sent directly to the Associate Editor)

UNITED KINGDOM

Wednesday 4 *November* 1964: Afternoon and evening meeting on **Toxic Substances in Air:** Society for Analytical Chemistry. Wellcome Building, Euston Road, London N.W.1, 3.00 p.m.

Friday–Saturday 12–13 *November* 1964: Conference on **Accuracy in X-Ray Analysis:** *Institute of Physics and Physical Society, X-Ray Analysis Group.* Institution of Mechanical Engineers, London S.W.1 (see *Talanta*, 1964, **11**, August, ii).

Thursday 19 *November* 1964: **Photometric Titrations:** J. B. HEADRIDGE: *Society for Analytical Chemistry, Midlands Section.* Lanchester College of Technology, Priory Street, Coventry, 7.00 p.m.

Friday 20 *November* 1964: **High Resolution Mass Spectrometry:** W. SNEDDON: *Society for Analytical Chemistry, North of England Section* and *Special Techniques Group.* The Blossoms Hotel, Chester, 6.00 p.m.

Tuesday 24 *November* 1964: **Annual General Meeting** followed by Film Show: *Society for Analytical Chemistry, Special Techniques Group.* Burlington House, London W.1, 7.00 p.m.

Friday 27 *November* 1964: **Some Aspects of Chemical Toxicological Analysis:** H. V. STREET: *Society for Analytical Chemistry, Scottish Section.* University of Strathclyde, Glasgow, 7.15 p.m.

Friday 27 *November* 1964: **Recent Advances in Analytical Chemistry:** T. S. WEST: *Society for Analytical Chemistry, Western Section* and *Royal Institute of Chemistry, Cardiff and District Section.* College of Technology, Newport, 6.30 p.m.

British Standards Institution has announced the following **New British Standards:**

B.S. 3599/6–15: 1964: *Organic pigments for paints.* C.I. Pigment Red 12 (Bordeaux F2R), C.I Pigment Red 112 (Red FGR), C.I. Pigment Red 10 (Red FRL), C.I. Pigment Red 7 (Red F4RH), C.I. Pigment Red 9 (Red FRLL), C.I. Pigment 5 (Carmine FB), C.I. Pigment Green 7 (Polychlorocopper phthalocyanine), C.I. Pigment Blue 15 (Copper phthalocyanine), C.I. Pigment Green 10 (Nickel azo yellow), C.I. Pigment Yellow 12 (Benzidine yellow).

Residue on sieve, sulphated ash, matter volatile at 100°, matter soluble in water and pH of aqueous extract, oil absorption value, colour, staining power and colour on reduction, fastness to light, bleeding, heat stability and resistance to acids and alkalis, determination of copper content. Stability of C.I. Pigment Blue 15. (*Price:* 17s. 6d.)

B.S. 3762: 1964: *Methods of sampling and testing detergents.*

Part 1, two sampling methods for powders from packets;
Part 2, analytical methods in four sections; A: two qualitative test methods; B: seventeen methods for schematic examination of active matter; C: nine other methods for analysis of active matter; D: fourteen methods for determination of constituents other than active matter.
Part 3, nine test methods for physical properties and performance.
Appendices: special reagents, three methods of preparation and one specification. (*Price* £2. 2s.)

The following *Revised British Standards* have been announced:

B.S. 903: *Methods of testing vulcanized rubber: Part B*14: 1964: *Determination of carbon black* (*replacing Part* 7 *of B.S.* 903: 1950). This covers three methods of determining carbon black with details of reagents, apparatus and procedure. (*Price:* 10s.)

B.S. 2690: *Methods of testing water used in industry: Part* 1: 1964: *Copper and iron. This details three methods for copper and two methods for iron.* (*Price:* 6s.)

The following *Amendment Slips* have been announced:

B.S. 1728: *Methods for the analysis of aluminium and aluminium alloys: Part* 5: 1953: *Copper (absorptiometric method). Amendment No.* 1: *PD* 5267.

B.S. 2782: *Methods of testing plastics. Part* 4: *Analytical methods and viscosity in solution. Amendment No.* 10: *Methods* 405 and 406: *PD* 5283. (*Price:* 10s.)

UNITED STATES OF AMERICA

Wednesday–Friday 21–23 *October* 1964: **Twelfth Detroit Anachem Conference.** McGregor Memorial Conference Centre, Wayne State University, Detroit, Michigan.

The programme is as follows:

Wednesday Morning, October 21: *Significance of Spectroscopic Methods to Clinical and Biological Research*

Interpretation of analytical data in clinical and biological research.	H. MITCHELL PERRY, JR.
Standardisation problems in analysis of biological samples for trace elements.	C. L. GRANT
Spectrographic determination of beryllium in air, biological materials and ores using the sustaining a.c. arc.	R. G. KEENAN and J. L. HOLTZ
The place of atomic absorption in tissue analysis.	C. FELDMAN
Lasers in emission for clinical research.	F. BRECH
Light-induced absorption changes in photosynthetic bacterial preparations.	H. E. BALES

Symposium on Thermal Methods of Analysis

New developments in "solution enthalpimetry".	J. JORDAN and P. T-S PEI
A critical evaluation of experimental variables in DTA.	J. R. SCHEMPF, F. M. ANGELONI and F. E. FREEBERG
Evaluation of solid state phase transformations by DTA and dilatometry.	S. GORDON
Improved resolution of differential thermal analyses through use of pressure effects.	P. D. GARN
A thermoanalytical study of pyrotechnic coloured smoke compositions.	C. CAMPBELL, G. WEINGARTEN and D. ANDERSON
Thermoparticulate analysis.	F. W. VAN LUIK, JR. and C. B. MURPHY
Thermal analysis in phase purifications of polymorphic solids.	A. R. GLASGOW, JR.
Product control by differential scanning calorimetry.	J. L. JUSTIN and N. BRENNER

Wednesday Afternoon, October 21: *Significance of Spectroscopic Methods in Clinical and Biological Research*

The analytical problems in biology and medicine.	W. B. MASON
Chemical enrichment methods in spectrographic analysis.	E. E. PICKETT
X-Ray methods of elemental analysis.	T. HALL
Breath analysis: Key to diagnosis of vapour exposure.	R. D. STEWART

Symposium on Microanalysis

Microchemistry: Implications and current trends.	T. S. MA
A rapid Pregl combustion carbon-hydrogen determination.	C. E. CHILDS and E. E. MEYER
Chemical analysis of thin films.	K. L. CHENG
Role of the electron probe microanalyser in microanalytical chemistry.	A. C. OTTOLINI and T. P. SCHREIBER

Analytical Chemistry—General

Determination of trace amounts of vanadium in steels and cast irons by amperometric titration.	F. P. VALENTE and G. H. CAREY
Cumulative coulographic titrimetry—I: Principles—II: Some new light on mercury catalysis in halogenation of unsaturated compounds: Titrations with electrogenerated bromine monochloride.	S. T. HIROZAWA

Reactions in concentrated lithium chloride solutions: Determination of free acid and hydrolysable metal.	H. Kubota
Radio-release methods for evaluation of atmospheric pollution.	H. H. Ross

Thursday Morning, October 22: Symposium on Polarography

Recent developments in stripping analysis.	I. Shain
Application of derivative techniques to anodic stripping voltametry.	S. P. Perone and J. R. Birk
Stripping and voltammetric determination of manganese via manganese dioxide.	C. Huber
Second derivative d.c.-polarography as a technique in quantitative polarographic measurements.	W. L. Belew, J. D. Fisher and M. T. Kelley
Pulse polarography.	E. P. Parry, R. A. Osteryoung and H. Schlein
Recent developments in lanthanide ion polarography.	A. Timnick, R. F. Large and R. O'Donnell
Polarographic reduction of pyridinium ion in pyridine: Application to determination of Bronsted and Lewis acids.	M. S. Spritzer, J. M. Coste and P. J. Elving
Electro-oxidation of tetraphenylborate ion at the pyrolytic graphite electrode.	W. R. Turner and P. J. Elving
Polarographic behaviour of molybdenum(VI) in acidic chloride media.	G. A. Rechnitz and J. Wittick

Symposium on Organic Functional Group Analysis

New dimensions in organic functional group analysis.	S. Siggia
Recent advances in redox methods.	K. G. Stone
Reagents for hyroxyl group analysis.	G. H. Schenk
Potentiometric determination of acid groups in acrylic polymers and fibers.	J. R. Kirby and A. J. Baldwin
Colorimetric determination of tertiary aromatic amines in primary and secondary amines using tetracyanoethylene.	P. O. Warner and G. H. Schenk
Determination of 18 *to* 22 *mole ethoxymers in* 9 *mole ethylene oxide adduct of p-nonylphenol.*	N. E. Skelly and W. B. Commett

Thursday Afternoon, October 22: Anachem Award Symposium

Anachem Address: *The challenge of analytical chemistry.*	L. T. Hallet
Trends and problems in the literature of analytical chemistry.	W. D. Cooke
The information explosion myth.	H. S. Nutting

Thursday Evening, October 22: Conference Address

Alpha particle analysis of surfaces: Plans for lunar missions.	A. Turkevich

Friday Morning, October 23: Clinical and Biochemistry Symposium

A study of determination of phosphorus in blood serum and urine.	R. E. Mosher
Colorimetric estimation of urinary iron by a non-ashing technique.	J. F. Goodwin
Spectrophotometric determination of p-hydroxyphenylpyruvic acid in human urine.	I. J. Holcomb and A. J. Boyle
Photosynthetic nucleotide coenzyme analyses.	W. L. Ogren
A study of the Liberman colorimetric determination of serum cholesterol.	J. Caruso and G. H. Schenk
Measurement of serum cholesterol synthesis employing deuterium.	C. B. Taylor, B. Mikkelson, J. A. Anderson and D. T. Forman
Nature of lactic dehydrogenase isoenzymes.	N. Ressler, U. Cook, E. Olivero and R. Joseph
New applications of Starch gel electrophoresis to study of complex molecules.	A. L. Koen
Determination of acid mucopolysaccharides in tissue culture.	Y. Shimizu and D. Francis

Chromatography

Application of gas chromatography to determination of carbonate carbon in sodium metal.	H. Bradley, J. Ferguson and S. A. Meacham

A modified high temperature combustion technique for determination of carbon in sodium.	E. J. Havlena and H. V. Myers Jr.
Separation of methyl and propyl esters of p-hydroxybenzoic acid by gas chromatography and their determination by ultraviolet spectroscopy.	S. J. Donato
New correlations between physical properties and gas chromatographic retention times for members of various homologous series of organic compounds.	B. J. Gudzinowicz
Identification of polymeric materials using two new instrument attachments.	K. A. Hutchinson
Rapid quantitative determination of long chain tertiary amines by thin layer chromatography.	J. R. Pelka and L. D. Metcalfe
Column, paper and thin-layer chromatographic characterisation methods for aromatic compounds and their application to air pollution.	E. Sawicki, H. Johnson and T. W. Stanley
Column chromatographic separation of basic polynuclear aromatic compounds from complex mixtures.	E. Sawicki, J. E. Meeker and M. Morgan

Spectrophotometry

Precision analysis of high purity gallium by indirect spectrophotometry.	R. Bastian, R. S. Kelly and E. W. Lanning
Simultaneous determination of trace amounts of titanium and zirconium.	J. O. Hibbits, A. F. Rosenburg and R. T. Williams
Improved spectrophotometric method for determination of organo aluminium compounds.	S. R. Henderson, T. G. Mungall and J. H. Mitchen
Indirect spectrophotometric determination of chlorine dioxide.	J. A. Howell, G. E. Linnington and D. F. Boltz
Spectrophotometric determination of antimony.	J. C. Guyon and R. M. Matulis
Determination of oxides of nitrogen in effluent of an inert gas generator.	D. M. Zall
Method for sampling and analysis of nitrogen in potassium.	H. Kirtchik
Determination of fluorine in organic compounds.	M. Brandt and D. G. Cobb

Friday Afternoon, October 23: Symposium on Automation in Analytical Chemistry

Automation in analytical chemistry.	B. Klein
Automated determination of proteins.	E. S. Baginski and B. Zak
Automated determination of iron.	B. Zak
Kinetic measurements in the clinical laboratory.	D. G. Remp
Automatic, real time digital integration of amino acid peaks.	D. W. Spence and H. J. Jones
Automatic potentiometric EDTA and redox titrations of nonstoichiometric compounds.	M. C. Gardels and J. C. Cornwell
Automated system for rapid and precise neutron activation analysis.	J. R. Vogt and W. D. Ehmann

Industrial Application of Optical Methods of Analysis

Refinement of spectrochemical procedures.	J. K. Hurwitz
Spectrographic determination of impurities in beryllium.	E. S. Melick, L. Bunck and E. Peterson
Industrial applications of atomic absorption spectroscopy.	R. E. Mansell
Vacuum ultraviolet instrumentation and development and manufacture of a double beam monochromator for ultraviolet region.	P. M. McPherson
Vacuum ultraviolet and soft X-radiation detection.	C. F. Hendee
A precise recording absolute spectroflurometer.	G. K. Turner and R. E. Phillips
Optical emission spectrographic method for determination of chloride ion in chromium plating baths.	W. Edgar and N. B. Parseghian
Spectrochemical determination of microgram amounts of tantalum, niobium, titanium and hafnium in U_3O_8.	J. E. Scott and E. R. Shuster, Jr.

Wednesday–Friday 4–6 *November* 1964: **Annual Pittsburgh Diffraction Conference.** Mellon Institute, Pittsburgh, Pa.

Monday 30 *November-Friday* 4 *December* 1964: **Short Course on Gas Chromatography:** *Instrument Society of America.* Carnegie Institute of Technology, Pittsburgh, Pa. (see *Talanta*, 1964, **11**, August iii).

New standard samples for four groups of copper-base alloys have been issued by the **National Bureau of Standards Institute for Materials Research**. Several samples, which vary in composition, are available for each of the alloys—free-cutting brass, gilding metal, commercial bronze and aluminium brass. These standards have been prepared primarily for optical-emission and X-ray spectrochemical analysis calibrations and are in a form convenient for such use.

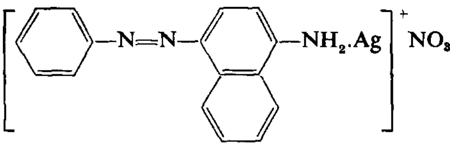
American Society for Testing and Materials has compiled the *Wyandotte-ASTM Punched Card Index* for finding and correlating infrared spectral absorption data using programmed tapes for computers. These tapes are used in connection with the Codes and Instructions for the Wyandotte-ASTM Punched Card System. This system facilitates the sorting of spectral data in matching spectrograms in qualitative analysis. Further information is available from Dr. L. E. KUENTZEL, ASTM, 1916 Race Street, Philadelphia, Pa. 19103.

American Society for Testing and Materials has announced the availability of the following publication:

ASTM Standards for Industrial Water and Atmospheric Analysis: Part 23 *of* 1964 *Book of ASTM Standards* (*Price* $13.00; $9.10 *to ASTM members*). This contains 98 standards of which 58 are new or have been revised since the publication of the 1960 edition of *Manual on Industrial Water-D*-19, which it replaces. The contents include industrial water—sampling and analytical methods, corros-tests, methods of reporting; atmospheric analysis.

ERRATA—Volume 11

Page 1098: The structural formula for compound III should be



Page 1121: The title should read *Colorimetric determination of cobalt*[11]
Page 1136, Table I: the second entry in the last column should read 0·511 *MeV*
Page 1137, Table II: The entries in the third column should read 0·511 *MeV* and 1·04 *MeV*
Page 1177: This paper should read *Eingegangen am* 15. *Februar* 1964
Page 1200, Table III: The heading to the fifth column should read *Found*, 0·05*M*, *ml*
Page 1203: This paper should read *Received* 10 *February* 1964
Page 1239: This paper should read *Received* 18 *March* 1964
Page 1249: This paper should read *Received* 9 *April* 1964
Page 1275: This letter should be dated 26 *March* 1964
Page 1284, Fig. 5: This should read $\gamma_0 = 0{\cdot}06$, etc.
Page 1313, line 4 of Experimental: This should read 1,2-*diaminocyclohexanetetra-*
Page 1314, line 2 of *Apparatus:* This should read *photoelectric attachment*
Page 1314, line 8 under Results and Discussion: This should read *a molar ratio of* 1:1, *V*:(*XO*),
Page 1325, second footnote to page: Delete *Preparation:*
Page 1329: This should read *Table I*
Page 1350, line 14 of Results and Discussion: This should read *measured in* 1-*ml cells*
Page 1355, reference 6: The journal should read simply *Japan Analyst*
Page 1366, line 3 above *Procedure:* This should read (1 *ml* $\equiv$ 100 μg *of cadmium*)
Page 1367, line 7 from bottom of page: This should read *chromium*(*VI*), *remaining after volatilisation, to chromium*(*III*)
Page 1377, line 2 under *Calculations:* This should read 6–7 *MeV*

Talanta, 1964, Vol. 11, pp. i to vii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

BUNDESREPUBLIK DEUTSCHLAND

"Moderne Methoden der anorganischen Analyse": Vortragstagung veranstaltet von der Fachgruppe "Analytische Chemie" in der Gesellschaft Deutscher Chemiker in Zusammenarbeit mit den Chemikerausschüssen der Gesellschaft Deutscher Metallhütten- und Bergleute des Steinkohlenbergbauvereins und des Vereins Deutscher Eisenhüttenleute sowie dem Deutschen Arbeitskreis für Spektroskopie und der Deutschen Arbeitsgruppe Massenspektrometrie der Deutschen Physikalischen Gesellschaft: Düsseldorf 5.-7. Oktober 1964.

Vortragsprogramm

Montag, 5. Oktober: Nichtmetalle in Metallen

Nichtmetalle in Metallen.	J. Fischer
Die Bestimmung kleiner Gehalte Selen in Kupfer mit Röntgenfluoreszenz-Spektralanalyse	G. Maassen
Nachweis und Analyse kleinster Gasmengen in Metallen mit Massenfilter.	H. Böhm, K. G. Günther und W. Kuhl
Eine γ.γ-Koinzidenz-Anordnung zur aktivierungsanalytischen Bestimmung der Spurenghalte Ir, Se etc. in Platinmetallen und in Nickeleisen.	W. Herr und R. Wolfle
Massenspektroskopische Analyse von Nichtmetallen in Metallen.	H. Hintenberger
Bestimmung von Sauerstoff in Kupfer und Blei.	A. Olofsson
Nichtdispersive Spektralanalyse der Gase aus der Hekissextraktion.	W. Baum und S. Eckhard
Schnellbestimmung des Stickstoffs in Stahl nach dem Schmelzextraktionsverfahren in Trägergasstrom. Weiterentwicklung und statische Bewertung.	H. Lemm
Gefügeuntersuchungen von Erzen und Schlacken mit dem Mikroanalysator.	P. Dickens, P. König und P. Jaensch
Die Sauerstoffbestimmung in Urancarbiden durch Heissextraktion.	H. Nickel und J. Rottmann
Fortschritte bei der Bestimmung des Sauerstoffs, Wasserstoffs und Stickstoffs in Metallen.	Th. Krays
Beitrag zur Bestimmung von Spurenverunreinigungen in hochreinem Germanium(IV)-chlorid und Germanium(IV)-oxid.	E. Wunderlich

Mitgliederversammlung des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute

Dienstag, 6. Oktober: Erfassen und Verwerten analytischen Zahlenmaterials

Mathematisch-statische Grundlagen des Auswertens von analytischem Zahlenmaterial.	R. Wartmann
Erfassen und Verwerten chemischer Daten.	F. A. Pohl
Zur Problematik der Nachweisgrenzen.	H. Kaiser
Die Anwendung des Streudiagramms am Beispiel der Spektralanalyse.	G. Holdt

Probenahme

Probenahme.	H. Zettler
Technische Hilfsmittel der Probenahme und Probenvorbereitung.	H. Sporbeck

Ein Metall-Aufschluss und -Umschmelzverfahren zur Herstellung von Proben für die Spektralanalyse.	P. Holler
Zur Probenahme von Schwefelkiesabbränden.	H. Spitzer
Probenahme von Fe- und Mn-Erzen, gegenwärtrige Situation bei der ISO-Normung.	K. E. Stumpf
Auswirkungen theoretischer Überlegungen bei der Probenahme von Kohlen.	F. Finze

Mitgliederversammlung der GDCh-Fachruppe "Analytische Chemie"
Mitgliederversammlung des Deutschen Arbeitskreises für Spektroskopie

Mittwock, 7 Oktober: Analyse von Verbindungsformen und ihre Verteilung im festen Zustand

Analyse von Verbindungsformen und ihre Verteilung im festen Zustand.	W. Koch
Die Reaktionen des Mangans in Kohlenstoffstählen, untersucht durch electrolytisches Isolieren.	W. Koch und H. Keller
Bestimmung von metallischem und Oxidischem Nickel in Hüttenprodukten.	G. Kraft
Strukturen und chemische Eigenschaften verschiedener Nitride in ternären Eisenlegierungen.	W. Koch und K.-H. Sauer
Zusammenhänge zwischen Raumgewicht, Grobkorntitration und chemischer Analyse bei gebranntem kalk.	S. Eckhard
Einsatz der Autoradiographie zur Untersuchung der Verteilung von Verunreinigungen in Elektrolytniederschlägen.	Ch. Fischer-Bartelk

Spektrochemische Analyse

Lösungsspektralanalyse von Edelmetallen.	W. Diehl
Quantitative Analyse von Metallspuren mit Hilfe der Flammenphotometrie (Atom-Absorption).	(G. Nonnenmacher und F. H. Schleser
Untersuchungen zur Anwendung des Eichzusatzverfahrens.	G. Ehrlich und R. Gerbatsch
Die Verwendung radioaktiver Nuklide zur Untersuchung physikalisch-chemischer Vorgange in Graphitelektroden bei Lichtbogenanregung.	H. Nickel
Die röntgenspektrometrische Bestimmung von Metallspuren mit Hilfe einer speziellen Methode des inneren Standards	E. Bankmann
Fällungsoperationen durch Dekomplexierungen.	Sw. Pajakoff

Das 3. **International Fluorsymposium** findet vom. 30. August bis 2. September 1965 in München statt und wird von der Gesellschaft Deutscher Chemiker organisiert. Der wissenschaftlische Teil wird von Herrn. Prof. Dr. F. Weygand, Technische Hochschule München, bearbeitet.

Anmeldeformulare für die Teilnahme und zur Vorankündigung von Diskussionsvorträgen können bei der

GDCh-Geschäftsstelle
6000 Frankfurt/Main, Postfach 9075

angefordert werden. Dabie ist zu bemerken, daß diese Voranmeldungen bis zum 30. September 1964 bei der GDCh-Geschäftsstelle eingegangen sein müssen.

CZECHOSLOVAKIA

Tuesday 29 *September-Friday* 2 *October* 1964: **Third National Radiochemical Conference:** *Czechoslovak Chemical Society, Nuclear Chemistry Section:* Scientific House, Liblice by Prague (see *Talanta*, 1964, **11**, March, i).

UNITED KINGDOM

Friday-Saturday 25–26 *September* 1964: Meeting on **Automatic Methods of Analysis:** *Society for Analytical Chemistry, Microchemistry Group and Scottish Section:* University of Aberdeen, Old Aberdeen.

The following papers will be presented and discussed on the Friday evening:

Nomenclature.	T. R. Fennel
Process gas chromatography.	C. S. F. Pine
Automation in clinical chemistry.	C. F. M. Rose
Differential thermal analysis.	R. C. MacKenzie

On the Saturday evening there will be a discussion meeting on *Automatic Techniques.*

Thursday 1 *October* 1964: **Solvent Extraction,** D. Betteridge: *Society for Analytical Chemistry, Midlands Section: Spread Eagle Hotel,* Shakespeare Street, Nottingham. 7.00 p.m.

Monday-Wednesday 12–14 *October* 1964: **Technicon 26th Anniversary International Symposium on Automated Analytical Chemistry:** Royal College of Surgeons, Lincoln's Inn Fields, London W.C.2.

Papers will be presented under the following headings:

Monday, 12 *October:* Pollution Analyses; Power Station Chemistry; Chemical Process Control; Soils, Rocks and Fertilisers; Pharmaceutical Assays; Food Chemistry; New Methods.

Tuesday, 13 *October:* Chromatography; Lipid Analyses; Enzyme Analyses; Cell Physiology; Electrophoresis; Elemental Analysis; Haematology; Haemagglutination Procedures; New Methods.

Wednesday, 14 *October:* Multiple Analytical Techniques and Health Screening Procedures; Gynaecological Cancer; *In Vivo* Techniques; Electrophoresis; New Methods.

Wednesday 14 *October* 1964: Symposium on **Thin-Layer Chromatography:** *Society for Analytical Chemistry, Midlands Section and Thin-Layer Chromatography Panel* with *Royal Institute of Chemistry, Birmingham and Midlands Section:* University, Edgbaston, Birmingham 15 (see *Talanta*, 1964, 11, August): 1.30 p.m.

British Standards Institution has announced the following *New British Standards:*

B.S. 1428: *Microchemical apparatus: Part B*3: 1964: *Nitrogen determination apparatus (non-transference micro-Kjeldahl).* This includes the components for the digestion apparatus and distillation apparatus used in the micro-determination of nitrogen by the Kjeldahl method without transference of the digestion mixture; alternative types of components where appropriate; notes on the method of use of the apparatus; and dimensioned drawings. (*Price:* 5s)

B.S. 1673: *Methods of testing raw rubber and unvulcanized compounded rubber: Part* 5/5.2-4: 1964: *Analysis of styrene butadiene copolymers (SBR).* This gives methods for determination of moisture, solvent extraction and total ash. (*Price:* 4s. 6d.)

The following *Revised British Standards* have also been announced:

B.S. 1428: *Microchemical apparatus: Part B*1: 1964: *Nitrogen determination apparatus (micro-Kjeldahl).* This includes components for the digestion apparatus and Parnar-Wagner type distillation apparatus used in the micro-Kjeldahl method; alternative types of components where appropriate; notes on method of use of the apparatus; and dimensioned drawings. (*Price:* 5s.)

B.S. 1902: *Methods of testing refractory materials: Part* 2*A*: 1964: *Chemical analysis of high silica and aluminosilicate materials.* This details the reagents required for analysis, determination of blanks; preparation of sample, loss on ignition. For high silica materials: determination of silica, ferric oxide, titania, phosphorus pentoxide, alumina, lime, magnesia and alkali metals. For aluminosilicates: determination of manganese oxide plus above-mentioned constituents. Method for the direct determination of alumina. (*Price:* 10s.)

UNITED STATES OF AMERICA

Monday 28 *September-Friday* 2 *October* 1964: **Third National Meeting:** *Society for Applied Spectroscopy:* Sheraton-Cleveland Hotel, Cleveland, Ohio.

Monday-Thursday 5–8 *October* 1964: **Fourteenth Annual Instrument Symposium and Research Equipment Exhibit:** National Institutes of Health, Bethesda, Md.

Tuesday-Thursday 6–8 *October* 1964: **Eighth Conference on Analytical Chemistry in Nuclear Technology:** *Analytical Chemistry Division of Oak Ridge National Laboratory:* Mountain View Hotel, Gatlinburg, Tennessee (see *Talanta*, 1964, 11, **June**, iii).

The preliminary programme is a follows:

Tuesday Morning, 6 October: Nuclear Methods of Analysis

Application of a Potentiostatic Electrodeposition Technique to Ultra-trace Analysis by Neutron-Activation Methods.	Harry B. Mark, Jr. and Francis J. Berlandi
Determination of Trace Elements in Wool	L. C. Bates and W. B. Healy
Photon Activation Analysis of Caesium.	Jacob Spira, Robert Bastian and Carmine Persiani
Precision of Activation Analysis of Short-Lived Nuclides.	F. F. Dyer and J. F. Emery
Determination of Attogram Quantities of ^{3}H *and* ^{3}He *Produced by Photonuclear Reactions.*	L. A. Currie
Reactions Observed with 14-*MeV Neutrons.*	W. J. Ross and J. E. Strain

Determination of Trace Constituents in Alkali Metals

Rapid Determination of Low Concentrations of Oxygen and Hydrogen in Alkali Metals by a Modified Amalgamation Technique.	Gerald Goldberg
Precise Determination of Oxygen in Alkali Metals by Neutron-Activation Analysis.	E. L. Steele
Determination of Oxygen in Metallic Sodium.	K. S. Bergstresser, G. R. Waterbury and C. F. Metz
Determination of Oxygen in Rubidium and Caesium.	Sheridan Rogers and Fred Tepper
Determination of Total Carbon in Sodium Metal by High-Temperature Combustion.	Harold Bradley and S. A. Meacham
Determination of Total Carbon in Sodium.	D. Dutina, W. W. Sabol, D. E. Rey and J. L. Simpson
Methods of Analysing Sodium Metal at Culcheth Laboratory, U.K.A.E.A.	W. T. Edwards

Tuesday Afternoon, 6 October: Burnup Analysis

Technetium-99 *as a Burnup Monitor for Fast and Thermal Reactors.*	R. J. Meyer, R. D. Oldham, R. J. Popek and R. P. Larsen
Lanthanum-139 *as a Burnup Monitor- a Mass Spectrometric Method.*	E. R. Ebersole, R. P. Larsen, M. T. Laug and J. J. McCown
Uranium-235 *Thermal Fission Yields of Caesium*-133 *and* -137.	R. P. Larsen, R. J. Meyer, M. T. Laug and G. W. Smith
Determination of Nuclear Fuel Burnup: Status of Development Programme.	James E. Rein
Proposed Determination of Nuclear Fuel Burnup Based on Ratio of two Stable Fission Products of same Element.	William J. Maeck
Flame Photometric Determination of Lithium Produced by B-10(*N, a*)*Li*-7 *Reaction to Measure Boron*-10 *Burnup in Reactors Utilising Chemical Shim Control.*	B. D. LaMont and W. D. Fletcher

Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals

Determination of Gases in Plutonium Nitride and Carbide, and in Plutonium Metal.	Manley W. Mallett
Manometric Measurement of Nitrogen, Oxygen, and Hydrogen Extracted from Plutonium Materials by Inert Gas Fusion.	Ben D. Holt and Harvey T. Goodspeed
Determination of Oxygen in Pyrolytic-Carbon-Coated Uranium Dicarbide Beads.	M. E. Smith, J. M. Hansel and G. R. Waterbury
Oxygen and Nitrogen Determination in Columbium and Tantalum by Inert Gas Fusion Employing Chromatographic Detection.	W. C. Gannon and F. T. Coyle
An Automatic Spectrographic Method for Determination of Oxygen in Steel.	M. S. W. Webb and R. J. Webb
Comparative Studies on Determination of Oxygen, Nitrogen and Hydrogen in Rare-Earth Metals, and of Oxygen in Thorium.	Wayne E. Dallman, Velmer A. Fassell, C. Clifton Hill and Royce K. Winge
Analysis of Zirconium Metal and Alloys for Hydrogen, Carbon and Oxygen.	H. R. Weiler, Jr.

Spectrochemical and X-ray Methods of Analysis

Wednesday Morning, 7 October:

Influence of Interaction of Plasma Components on Spectroscopic Analysis.	Wilhelm H. Tappe
Spectrographic Determination of Chlorine in Refractory Materials.	G. Baudin
Effect of Electrode Dimensions in Carrier Distillation Procedure for Spectrochemical Analysis.	H. R. Mullins and R. L. Graff
Determination of Uranium Isotopes by Atomic Absorption Spectrophotometry.	Joseph A. Goleb
Use of Computers in Spectrochemical Analysis	Isabel H. Tipton, Fred W. Roberts and Jane J. Shafer
Far Ultraviolet Flame Emission Lines of Cobalt	John A. Dean and J. E. Adkins
Chemical Isolation and Flame Photometric Determination of Barium.	Cyrus Feldham, T. C. Rains and N. Marion Ferguson

Mass Spectrometric Methods of Analysis

Commentary on Spark Source Mass Spectrograph.	W. Fletcher
Commentary on O.R.N.L., Double-Magnet Mass Spectrometer.	A. E. Cameron
Determination of Hydrogen in Zirconium Alloys by Isotopic Equilibration.	R. W. Ashley and A. S. Denovan

Gas Chromatographic Methods of Analysis

Adaptation of the Chromatograph for Analysis of Corrosive Gases.	E. L. Williamson
Determination of Trace Impurities in Helium.	E. G. H. Romberg

Special Methods of Separation and Determination

Wednesday Afternoon, 7 October:

A Specific Method for Determination of Titanium.	J. O. Hibbits and Silve Kallmann, William Giustetti and Hans K. Oberthin
Microdetermination of Ruthenium in Uranium Compounds.	O. A. Vita and C. F. Trivisonno
An Infrared Method for Determining Variations in Deuterium Content of Natural Water.	W. H. Stevens, J. G. Bayly and W. M. Thurston
Separation of Americium from Lower Transuranics: Extraction with Quaternary Ammonium Salts.	William J. Maeck, Maxine E. Kussy and James E. Rein
Separation of Europium from Fission Product Samples by Reduction with Lithium Amalgam.	J. Bubernak, M. Lew and G. M. Matlack
Reversed-Phase Partition Chromatographic Separation of the Lanthanides with Paper Impregnated with Bis-(Di-N-Hexylphosphinyl) Methane.	George J. Kamin, Jerome W. O'Laughlin and Charles V. Banks
Analysis of High Purity Materials in Nuclear Energy Research: A Short General Survey of Methods.	A. A. Smales

Thursday Morning, 8 October: Radiochemistry

Radiochemical Techniques in Fission Gas Mobility Studies of Hydride Systems.	Alfred J. Moses
Analytical Determination of Uranium-232 and Uranium-233 in Irradiated Thorium.	M. R. Weiler and W. Y. Matsumoto
Non-Destructive Determination of Uranium-232 and Thorium-228 by Gamma Spectrometry.	S. A. Reynolds
Determination of Nuclide Concentrations in Solutions Containing Low Levels of Radioactivity by Least-Squares Resolution of Gamma-Ray Spectra.	Ernest Schonfeld, Arlene H. Kibbey and Wallace Davis, Jr.

Liquid Scintillation Counting

Determination of Radioactive Noble Gases with a Liquid Scintillator.	Donald L. Horrocks and Martin H. Studier

Liquid Alpha-Gamma Counter for Simultaneous Determination of Plutonium and Americium.	K. I. Hawkins and C. R. Forrey
Absolute Counting of Beta-Emitters by Liquid Scintillation Method.	Gerald Goldstein

Spectrochemical and X-Ray Methods of Analysis

Application of Anion Exchange-Partition Chromatography to Trace Impurity Analysis of Thorium-Uranium and Plutonium-Thorium-Uranium Alloys.	Edmund A. Huff
Determination of Plutonium in Irradiated Uranium Dioxide Fuel Pellets by X-Ray Fluorescence Spectrometry.	B. D. LaMont, J. D. Johnson and J. A. McSorley
Applications of Electron Probe Microanalyzer to the Determination of Trace Constituents in Reactor Materials.	E. A. Hakkila, G. R. Waterbury and C. F. Metz

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Monday-Thursday 12–15 *October* 1964: **Ninteenth Annual Instrument-Automation Conference and Exhibit:** *Instrument Society of America:* New York City.

The following lectures may be of interest to analytical chemists:

Monday, 12 *October: Primary Elements (Transducers)I*

Design of pH Control Systems.	H. S. Wilson and W. J. Wylupek

Tuesday, 13 *October: Process Simulation by Analogue Method*

A pH Control System Implemented from a Simulated Design.	William B. Field and Robert M. Green

Tuesday 13 *October: Fluorescence Instrumentation*

A Precision Recording Absolute Spectrofluorometer.	G. K. Turner and R. E. Phillips
Design of a Fluorescence Spectrometer.	John U. White
Construction and Calibration of a Spectro-radiometer-Fluorimeter for Fluorescence Quantum Yield Studies.	B. G. Roberts and R. C. Hirt
Modifications of Existing Instruments for Fluorescence Measurements.	L. A. Hurlbut and E. F. Gillette

Tuesday, 13 *October: Laboratory Instrumentation*

Internal Reflection Spectroscopy.	N. J. Harrick

Wednesday, 14 *October: Radiation Methods of Analysis*

Moisture Measurement with Radio-Frequency Techniques.	Fred W. Truxall
Computer-Integrated Activation Analyses.	John W. Nostrand, Jr. and Henry H. Kramer

Thursday, 15 *October: Chemical and Instrumental Methods of Analysis*

Spectroscopic Methods to Detect Water in Salts (Alkali Halides).	J. Greenberg
Preparation of Mercury/Mercurous Sulphate Reference Electrode for Halide Titrations.	Richard A. Murie and A. C. Eckert
An Improved Cell for Analysis of Impurities in Liquid Chlorine Using Infrared Spectroscopy.	David L. Hammitt
Continuous Process Stream Analyser for Determination of Aluminium Alkyl Concentration.	R. J. Fanning
A Recording Electrolytic Titrator.	Dr. Austin

Thursday, 15 *October: Introduction to Thermoanalysis: Methods and Applications*

Differential Thermal Analysis-Principles and Applications.	Saul Gordon
Automatic Recording Thermo Balances.	H. Vaughan
DTA Variables.	I. M. Sarasohn
Theory and Application of Thermogravimetry.	A. E. Newkirk
Quantative Dynamic Calorimeter.	E. L. Dosch

Tuesday-Friday 13–16 *October* 1964: **Annual Meeting:** *Electron Microscopy Society of America:* Detroit Hilton Hotel, Detroit, Mich.

Wednesday-Friday 14–16 *October* 1964: **Third Annual Gas Chromatography Symposium:** *A.S.T.M. Committee E*-19: Sheraton-Lincoln Hotel, Houston, Texas.

Thursday-Saturday 15–17 *October* 1964: **South-East Regional Meeting:** *American Chemical Society:* Charleston, W. Va.

Monday-Thursday 19–22 *October* 1964: **78th Annual Meeting:** *Association of Official Agricultural Chemists:* Marriott Motor Hotel, Twin Bridges, Washington D.C. 20044 (see *Talanta,* 1964, **11,** June, iii).

Wednesday-Friday 21–23 *October* 1964: **Twelfth Anachem Conference and Instrument Exhibit:** *Association of Analytical Chemists* in collaboration with *Optical Society of America, Detroit Section:* McGreggor Memorial Conference Center, Wayne State University, Detroit, Mich. (see *Talanta,* 1964, **11,** May, iv).

Wednesday-Friday 21–23 *October* 1964: **Conference on Spectroscopy, Instrumentation and Chemistry:** Jack Tar Hotel, San Francisco, Calif.

ERRATUM—Volume 11

Page 891: The first author of the paper should read *Farhataziz*
Page 905: line 1 of Résumé: For *sodage* read *dosage*
Page 905: line 3 of Résumé: For *volumé-triquement* read *volumétriquement*
Page 905: last line of Résumé: For *direct* read *directe*
Page 953: line 4 of Résumé: For *effect* read *effet*
Page 964: line 12 of Résumé: For 24 *hau moirs* read 24 *h au moins*
Page 972: line 3 of Résumé: For *vagurs* read *vagues*
Page 975: line 3 of Résumé: For *delle* read *celle*
Page 975: line 7 of Résumé: For *peurvent* read *peuvent*
Page 975: line 8 of Résumé: For *ses* read *ces*
Page 982: line 1 of Résumé: For *résponse* read *réponse*

Talanta, 1964, Vol. 11, pp. i to viii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

(Material for this section should be sent directly to the Associate Editor)

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Division of Analytical Chemistry
Commission on Microchemical Techniques

International Investigation into Errors in Elementary Organic Microanalysis*

The obsrevations, findings and effects governing the microanalytical errors encountered by every microanalyst in the course of his daily work only add to his special knowledge or that of his close collaborators. In order to go beyond the limits of the individual laboratory, the Commission on Microchemical Techniques has set up a Study Group on Errors in Elementary Organic Microanalysis, which is intended to centralise, classify and publish these findings in generally workable form for the benefit of all.

The study Group on Errors in Elementary Organic Microanalysis invites microanalysts of all countries, either personally or as representatives of their laboratories, to collaborate in this collective international task by communicating in the form of a report the results of their experiences.

In practice, it is desriable that each report conform to the outlines given below:

1. It must be drafted in either German, English, French or Russian.
2. It must be divided into as many separate parts as the errors under examination.
3. Each part must follow the headings of the following outline.

Outline

1. Element(s), amount(s)
2. Microanalytical range (milligram, decimilligram, centrmilligram)
3. Microanalytical balance employed (principle, model, installation, with or without air-conditioning *etc.*); standard deviation of weights
4. Method employed—principle of mineralisation (combustion), principle of the determination, apparatus, reagents, method of operation, *etc.*
5. Type of error studied—systematic or uncertain errors affecting the accuracy or precision of the results
6. Order of algebraic magnitude of the systematic error, standard deviation or possible limits of the uncertain errors (errors of chance)
7. Sources of error, real or apparent. All of the factors of error must be retained, especially those which appear in the following unlimited list:
    Order of magnitude of the contents to be determined
    Physical properties of the compounds analysed (condition, vapour pressure, hygroscopicity, triboelectricity (static electricity) *etc.*)
    Structures of the compounds analysed
    Presence of interfering elements
    Presence of interfering functional groups
    Principle of the method of mineralisation (combustion) employed
    Principle of determining the end product
    Reagents employed (nature, degree of purity, source)
    Other chemical products employed
    Small apparatus and various material employed (joints, stoppers, glass, silica, plastic materials, metals, *etc.*)
    Manual or automatic apparatus employed for the mineralisation (combustion)
    Apparatus employed for the measurements (balances, burettes, colorimeters, spectrophotometers, potentiometers, coulometric, conductometeric, or thermal-conductometric set-ups, recorders, integrators, *etc.*). Possible influence of automation

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* The present investigation does not include trace analysis.

Operative parameters (temperature, rate of gas flow, pressure, *etc.*)
Environment parameters (temperature, relative humidity, atmospheric pressure, air pollution, vibrations, situation and exposure of the laboratory, place or position of installation in the laboratory, *etc.*)
Subject parameters (manipulations, lectures, observations)
Operative methods and techniques

8. Means employed for characterising the source of error (if possible)
9. Modifications eventually used with the intention of diminishing or eliminating the error
10. Suggestions
11. Specific questions

The preceding outline must be considered as a simple, helpful memorandum. The errors reported need not necessarily be "originals"; they may have been cited in publications from which they have been noted.

The present investigation is already in progress; consequently, the reports, depending upon the geographic location or the language used, can be addressed without delay to the following members of the Study Group on Errors in Elementary Organic Analysis:

a. American reports in the English language (U.S.A., Canada, *etc.*) to:

Dr. Al Steyermark, Chairman
Commission on Microchemical Techniques
Hoffmann-La Roche Inc.
Nutley 10, New Jersey
U.S.A.

b. European reports in the German or Slavic languages (with the exception of Russian) to:

Dr. Wolfgang Schöniger, Secretary
Commission on Microchemical Techniques
Department of Pharmaceutical Chemistry
Sandoz, Ltd.
Basle 13, Switzerland

c. Reports originating in Russia to:

Dr. N. E. Gel'man, Associate Member
Commission on Microchemical Techniques
Institute on Elemental Organic Compounds
Academy of Sciences
Moscow, Russia

c. Reports in the English, French, or German languages which originate in coutries other than those listed in a, b, and c, to:

Dr. Roger Lévy, Titular Member
Commission on Microchemical Techniques
Chairman, Study Group on Errors in
Elementary Organic Analysis
Central Department of Microanalysis
of the National Center of Scientific Research
39 bis, rue de Dantzig
Paris 15, France

In order to speed up the study, the Study Group would like to receive reports on errors which will eventually be part of a published report, even though the main portion is not ready for publication.

The deadline for this material will be 1st, July 1964.

BUNDESREPUBLIK DEUTSCHLAND

1. *und* 2. *April* 1964: Symposium **Methoden zur Messung weicher β-Strahler** veranstaltet von der *Fachgruppe Kern-, Radio- und Strahlenchemie* der *Gesellschaft Deutscher Chemiker* und der *Gesellschaft fur Kernforschung mbH*, Karlsruhe-Leopoldshafen.

Programm

Mittwoch, 1. *April*

Hauptvortrag

Übersicht über die Methoden zur Messung weicher β-Strahler — H. KIEFER

Diskussionsvorträge

Erfahrungen mit einen Gaszählrohr für die Serienmessung von Kohlendioxyd. — E. BRODA und B. KALAB

Nominierung der Meßbedingungen bei der Routinebestimmung von Tritium und ^{14}C im Proportionalzählrohr.	P. Jordan
Bestimmung niederer spezifischer Aktivitäten von ^{45}Ca durch flüssige Szintillationszählung	H. Vemmer und J. O. Gütte
Donnerstag, 2. April	
Hauptvortrag	
Gas Radio Chromatography.	A. T. James
Diskussionsvorträge	
Einige Ergahrungen über Radiogaschromatographie ^{14}C- oder T-markierter Verbindungen mit Proportional-Gaszählrohren und Ionisationskammern.	H. Simon und R. Medina
Neuere Anwendungen der Radio-Dünnschicht-Chromatographie.	M. Wenzel P. E. Schulze
Messung niederenergetischer β-Strahler in heterogener Phase mit Flüssigszintillatoren.	W. Hoffmann
Kontinuierliche Messung von ^{14}C-markeirten Aminosäuregemischen nach der Trennung an Ionenautasschersäulen mit Hilfe von Szintillatorschlauch.	H.-J. Stan

NETHERLANDS

Wednesday–Saturday 20–23 *May* 1964: Symposium on **Modern Methods of Analysis of Organic Compounds:** *Fachgruppe Analytische Chemie* of *Gesellschaft Deutscher Chemiker* and *Sectie voor Analytische Chemie* of *Koninklijke Nederlandse Chemische Vereniging:* Eindhoven.

The Symposium represents a continuation of the meeting on the same subject at Munich in 1960 and has the following programme:

Wednesday, 20 *May*

Plenary Lectures:	
Die Bedeutung der Analyse für die Organische Chemie	J. F. Arens
Derzeitiger Stand der organischen Mikroelementaranalyse.	W. Schöniger
Gruppenreaktionen in der organischen Analyse.	S. Veibel
Discussion Lectures:	
I. *Elemental Analysis*	
A six minute C—H-determination with titrimetric finish.	L. Blom
Ein Schnellverbrennungsapparat mit elektrischer Endpunktsanzeige zur Bestimmung von Kohlenstoff und Wasserstoff in organischen Substanzen.	F. Salzer
Three Decimal Place Hydrogen and Carbon Determination in Mineral Oil Samples.	P. Gouverneur
Zweijährige Erfahrungen in der Routine-analyse mit einem CNH-Automaten,	H. Weitkamp
Ultramikroelementaranalyse organischer Stoffe mit Substanzmengen von 1–20 µg.	G. Tölg
A Colorimetric Method for the Sub-micro Determination of Bromine in Organic Compounds.	T. R. F. W. Fennell
II. *Massspectrometry*	
Jetziger Stand der Massenspektrometrie in der organischen Analyse.	E. Stenhagen
Anwendung eines hochauflösenden Massenspektrometers in der organischen Analyse.	D. Henneberg
III. *X-ray Analysis*	
Structure Determination of Organic Compounds by X-ray Analysis.	J. D. Dunitz
Wege zur automatisierten Strukturanalyse.	W. Hoppe
Über ein neues Gerät zur automatischen Messung der Intensität von Einkristallreflexen.	E. Mayer

Thursday, 21 *May*

Plenary Lectures:	
Moderne Analysenverfahren, besonders Gaschromatographie, bei stereoisomeren alicyclischen Verbindungen.	W. Hückel
Spektrochemische Verfahren zur Konstitutionsermittlung.	G. Kresze
Analytical Separation Techniques.	A. J. P. Martin

Discussion Lectures:	
IV. *Constitution determination via mol spectrometry*	
Applications of Proton Magnetic Resonance to Functional Group Analysis.	N. van Meurs
Die Kernresonanzspektren von Steroiden in polaren Lösungsmitteln.	B. Hampel
Konformationsanalyse von Nitrosteroiden mit Hilfe des Circulardichroismus.	G. Snatzke
Präzisionsanalyse von Mehrkomponentengemischen in Quarzspektrophotometergebiet.	I. S. Herschberg
Bestimmung der Geschwindigkeitskonstanten der Dissoziation und Rekombination organischer Säuren mit der Methode der "High Level Faradaic Rectification."	H. W. Nürnberg
V. *Separation Techniques, part I*	
Über ein neues Verfahren der Flüssigkeits-Chromatographie.	E. Bayer
Die Anwendung einer neuen Arbeitsweise in der Flüssig-fest- bzw. Flüssig-flüssig-Chromatographie.	D. Jentzsch
Permanente Kolonnen für Flüssigkeitsverteilungschromatographie.	R. Dijkstra
Automatische Kopplung der Dünnschicht-Chromatographie an temperaturprogrammierten Gas-Chromatographen als stoffspezifische Detektion und Analysenkontrolle.	R. Kaiser
Möglichkeiten und Grenzen der Identifizierung von Stoffen aus ihrem Verhalten bei der isothermen Eluierungsgaschromatographie.	J. F. K. Huber
Some Rapid Identification Methods in Gas Chromatography.	F. H. Huyten
Friday, 22 May	
Plenary Lectures:	
Analysis in Polymer Research.	P. W. D. Wijga
Aminosäuren und Peptide.	F. Weygand
New Developments in Clinical Analysis.	E. J. van Kampen
Discussion Lectures:	
VI. *Separation techniques, part II*	
Auswahl der stationären Phase für die Dünnschicht-Chromatographie.	P. J. Schorn
The Mechanism of Peak Broadening in Paper Chromatography.	C. L. de Ligny
Quantitative Analyse von Polyphenylgemischen mit der Dünnschichtchromatographie.	F. J. Ritter
Verwendung Silbernitrat-imprägnierter Silicagel-Dünnschichten.	F. C. den Boer
Separation of Sterol Acetates by Thin-layer Chromatography in Reversed-phase Systems and on Silicagel G-silver Nitrate Plates.	J. W. Copius Peereboom
R_f-Werte und Annellierung kondensierter polycyclischer aromatischer Kohlenwasserstoffe.	S. Laufer
VII. *Analysis of high polymers*	
Pyrolysis Gas Chromatography with Programmed Temperature and Capillary Columns.	L. S. Ettre
Infrared Determination of Unsaturation in Polyethylene.	R. J. de Kock
Saturday, 23 May	
Discussion Lectures:	
VIII. *Clinical Analysis, Analysis of Natural products*	
Präparative dünnschichtchromatographische Trennung von Phosphatiden und dünnschichtchromatographischer Nachweis ihrer Hydrolyseprodukte.	O. W. Thiele
Eine verbesserte Methode zur quantitativen Elektrophorese in Agar-Agar-Schichten.	K. Dose
Über die Reaktion von Diazoniumsalzen mit Nukleotiden und Nukleinsäuren und ihre mögliche Anwendung zur Sequenzanalyse.	H. Kössel

Acetessigsäurebestimmung in 0,1 *ml Blut. Die Abtrennung des Acetons durch wärmebeschleunigte Mikrodiffusion und seine Bestimmung mit Salicylaldehyd.*	F. Bahner
Die Bestimmung von Aminosäuren durch Messung der elektrischen Leitfähigkeit.	A. Niemann
Verbesserung und Automation der Kreatininbestimmung.	K. Beyermann
Ein Beitrag zur Analytik der Tropan-Alkaloide.	H. Frauendorf
Die Analyse von Arzneistoffen in biologischen Flüssigkeiten mit der Tropäolinmethode.	P. Hajdu

Further information can be obtained from the GDCh-Geschäftstelle, 6000 Frankfurt (Main), Postfach 9075.

ÖSTERREICH

Tagung der Österr. Gesellschaft für Mikrochemie und Analtyische Chemie in Bad Hall

Die Österr. Gesellschaft für Mikrochemie und analytische Chemie im Verein der österr. Chemiker hielt am 28. und 29. Februar 1964 in Bad Hall, 0.Ö., seine 17. ordentliche Jahreshauptversammlung ab.

Vor etwa 80 Fachkollegen aus Industrie und Wissenschaft aus Österreich, Deutschland und der Schweiz wurde zunächst im Rahmen der Geschäftssitzungen der Fritz-Feigl-Preis 1964 an den Oberass. der Techn. Hochschule Wien, Dr. L. J. Ottendorfer, für seine Arbeiten auf dem Gebiet der Mikrochemie, insbesondere über den Nachweis kleinster Mengen radioaktiver Stoffe verliehen.

Im wissenschaftlichen Teil dieser Tagung wurde eine Reihe von Fragen über moderne Analysenmethoden besprochen, die für die Industrie und das Hüttenwesen von besonderem Interesse sind.

Im ersten Vortrag sprach Univ.-Prof. Dr. W. Leithe (Österr. Stickstoffwerke, Linz) über Gaschromatographie in der Industrie, wobei er die wichtigsten Anwendungsmöglichkeiten dieser vielseitigen Methode erläuterte.

Anschließend berichtete Frau Dpl. Ing. H. Selzer (Österr. Mineralöl-verwaltung, Raffinerie Schwechat) über die speziellen Probleme der Gaschromatographie in der Mineralölindustrie und anschließend berichtete Herr Dr. Bayzer (Österr. Stickstoffwerke, Linz) über Trennung und Nachweis der Aminosäuren.

Ein gemeinsamenes Abendessen im Kurhotel Landes-Sanatorium gab den Teilnehmern Gelegenheit, bei zwanglosem Beisammensein über ihre Erfahrungen zu diskutieren.

Am Samstag, 29. Februar, vormittags, fanden Vorträge von Herrn Doz. Dr. Zitter (Gebr. Böhler AG., Kapfenberg) über die derzeit aktuellen Fragen der Gasbestimmung in Eisenlegierungen und Dr. E. Lassner (Metallwerke Plansee, Reutte/Tirol) über die Bestimmung von Sauerstoff in hochschmelzenden Metallen wie Molybdän und Wolfram statt. Der letzte Vortrag der Tagung wurde von Dr. Breit (Vereinigte Metallwerke, Ranshofen-Berndorf) beigesteuert, der über die analytischen Fragen bei der Erzeugung und Verarbeitung von Aluminium berichtete.

UNITED KINGDOM

Wednesday 29 *April* 1964: Meeting on **Immunoassay of Hormones**: *Society for Analytical Chemistry, Biological Methods Group*: Burlington House, Piccadilly, London W.1: 7.00 p.m.

The programme is as follows:

Outline of principles and methods available.	P. G. H. Gell
Immunoassay of chorionic conadotrophin.	A. J. Fulthorpe
Immunoassay of insulin.	C. N. Hales

Thursday 2 *April* 1964: Meeting consisting of **Contributions from Research Workers in Universities and Colleges of Advanced Technology**: *Society for Analytical Chemistry*: University College, Gower Street, London W.C.1.

Afternoon Session—2.30 p.m.

The automation of anion-exchange chromatography of phosphorous anions.	G. Nickless and D. Rogers
Kinetic studies in bromate titrimetry.	J. M. Ottaway
Use of liquid anion exhangers in analytical chemistry.	A. D. Damodaran

Evening Session—5.15 p.m.

Some applications of thermogravimetric analysis.	A. W. Coats
Spectrographic determination of beryllium in fluorite minerals.	D. N. Waters
Gravimetric determination of iron by the homogeneous precipitation of tris(2-thiopyridine-N-oxide)iron^{III}.	J. A. W. Dalzeil and M. Thompson

Friday 1 *May* 1964: **Physical Methods of Moisture Determination:** *Society for Analytical Chemistry, Physical Methods Group* and *Midlands Section,* and *Royal Institute of Chemistry, East Anglia Section*: Levington Research Station, Ipswich, Suffolk: 6.00 p.m.

Review of methods determining moisture in paper.	L. A. Kirk
An introduction to microwaves moisture measurement.	H. B. Taylor
Application of nuclear magnetic resonance to measurement of mositure content of coals and cokes.	W. R. Ladner

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Friday 8 *May* 1964: Meeting of *Microchemistry Group, Society for Analytical Chemistry*: Royal College of Advanced Technology, Salford 5, Lancs.

Thursday–Friday 2–3 *July* 1964: Summer Meeting on **Limitations of Detection in Spectrochemical Analysis.** *Institute of Physics and Physical Society, Spectroscopy Group*: University of Exeter.

The main subjects and speakers are as follows:

Introduction and principles.	F. W. J. Garton and R. J. Webb
Emission spectroscopy	
(*a*) *Instrumental factors*	A. C. Menzies
(*b*) *Metallurgical samples*	W. Ramsden
(*c*) *Non-metallurgical samples, e.g., silicates and plant residues.*	R. L. Mitchell and R. O. Scott
X-ray fluorescence.	R. Jenkins
Atomic absorption.	J. A. F. Gidley
Mass spectroscopy.	R. A. Saunders
Comparison of emission, X-ray and mass spectroscopy.	N. W. H. Addink

Further details can be obtained from the Spectroscopy Group Secretary: Dr. L. Bovey, Building 329, A.E.R.E. Harwell, Nr. Didcott, Berks.

Monday–Saturday 12–17 *July* 1965: **XII International Spectroscopy Colloquium:** British *Spectroscopist Co-ordinating Committee* in collaboration with *Institute of Physics and Physical Society*: University of Exeter.

The subjects to be dealt with are concerned primarily with analytical applications of spectroscopy. The principal topics will be optical emission, absorption, X-ray and mass spectroscopy and special attention will be given to chemical, metallurgical, medical and biological applications. Continuous process control, the detection of non-metallic impurities in metals and a study of the limitations to detection in analysis will be some of the subjects of discussion. The official languages of the Colloquium will be English, French, German and Russian: simultaneous interpretation will be available. Some 6 invited papers are being arranged on leading topics of interest in the field of spectroscopy and also some open discussions on current trends. There will also be an opportunity for about 70 original contributed papers which should be submitted for consideration before the end of this year.

All enquiries should be addressed to the Colliquium Secretary: Mrs. C. E. Arregger, 1 Lowther Gardens, Prince Consort Road, London S.W.7.

At the **Annual General Meeting** of the *Society for Analytical Chemistry*, held on Wednesday, 4 March, 1964, the following were ellected Officers and Members of Council for the forthcoming year:

President: D. C. Garratt

Past Presidents serving on Council: A. J. Amos, R. C. Chirnside, J. H. Hamence, K. A. Williams.

Vice-Presidents: S. G. Burgess, A. A. Smales, R. E. Stuckey.

Hon. Treasurer: D. T. Lewis

Hon. Secretary: S. A. Price

Hon. Assistant Sectetaries: B. S. Cooper, D. W. Wilson.

Ordinary Members of Council: A. S. Beidas, E. Bishop, L. Brealey, H. J. Cluley, C. A. Johnston, A. G. Jones, E. Q. Laws, G. W. C. Milner, F. H. Pollard, F. C. J. Poulton, S. G. E. Stevens, C. Whalley.

Ex-Offico Members of Council: C. J. House, R. A. Chalmers, E. A. Hontoir, W. H. Stephenson, D. W. Wilson, L. Brealey, W. A. Broom.

At the **Twentieth Annual General Meeting** of the *Microchemistry Group* of the *Society for Analytical Chemistry*, held on Friday, 21 February, 1964, the following Officers were elected for the forthcoming year:

Chairman: D. W. Wilson
Vice-Chariman: R. Goulden
Treasurer: G. Ingram
Secretary: Mrs. D. E. Butterworth, National Chemical Laboratory, Teddington Middlesex.

At the **Ninth Annual General Meeting** of the *Midlands Section* of the *Society for Analytical Chemistry*, held on Wednesday, 11 March, 1964, the following Officers were elected for the forthcoming year:

Chariman: W. H. Stepenson
Vice-Chariman: W. T. Elwell
Treasurer: J. Blenkin
Secretary: M. L. Richardson, John and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham 30.
Asst. Sectetary: R. Adkins

British Standards Institution has announced the following new *British Standard*: *B.S.* 3703: 1964: *Method for the quantitative chemical analysis of binary mixtures of wool and certain regenerated protein fibres.* This provides a method for determining the proportions of fibre in binary mixtures of wool and certain proprietary regenerated protein fibres. It is suitable for application to fibres in any textile form with the exception of high density felts. (*Price* 3*s*.)

UNITED STATES OF AMERICA

Thursday–Friday 7–8 *May* 1964: **Fourth Informal Conference on Vacuum Microbalance Techniques:** Mellon Institute Auditorium, 4400 Fifth Avenue, Pittsburgh, Pennsylvania (see *Talanta*, 1963, **10**, *October*, iii).

Tuesday 12 *May* 1964: **Spectroscopic measurements from above the atmosphere:** D. Morton: *Society for Applied Spectroscopy, New York Section*: Hotel Manhattan, 8th Avenue and 44th Street: 8.00 p.m.

Wednesday–Friday 24–26 *June* 1964: Summer Symposium on **Recent Developments in Structure Determination:** *American Chemical Society, Division of Analytical Chemistry*: Cornell University, Ithaca, N.Y.

The programme is as follows.

Wednesday, 24 *June*

NMR of heavier nucleii and structure determination.	W. G. Schneider
Application of NMR to problems in stereochemistry.	A. D. Cross
Homonuclear and heteronuclear spin-decoupling: Application to high-resolution NMR	H. Agahigian
Electron paramagentic resonance.	W. Landgraf
Electron spin resonance of randomly orientated triplets.	E. Wasserman

Thurdsay, 25 *June*

Mass spectrometry.	F. W. McLafferty
High resolution mass spectra of organic compounds.	K. Biemann
Combining separation and instrumental techniques.	W. R. Moore
Chemical exploitation of the Mössbauer effect.	R. H. Herber
X-ray diffraction.	R. F. Bryan

Friday, 26 *June*

Molecular structure determinations by microwave spectroscopy.	R. D. Lide, Jr.
Raman spectroscopy.	J. C. Evans
Opitcal rotatory dispersion and circular dichroism.	U. Weiss
Microscopy.	W. C. McCrone

Further infromation may be obtained from Dr. F. W. McLafferty, The Dow Chemical Company, Eastern Research Laboratory, Framingham, Massachussetts, U.S.A.

Wednesday–Friday 12–14 *August* 1964: **Thirteenth Annual Conference on Applications of X-ray Analysis:** *Metallurgy Division, Denver Research Institute, University of Denver*: Albany Hotel Denver, Colorado.

There will be sessions on X-ray diffraction, emission spectroscopy, microprobe, absorption and microscopy, and instrumentation.

Monday–Friday 17–21 *August* 1964: **Gordon Research Conference on Analytical Chemistry:** New Hampton School, New Hampton, New Hampshire.

The programme is as follows:

Monday, 17 *August*	
Thermochemical titrations.	J. JORDON
pH measurements in amphiprotic solvents.	R. F. BATES
Problems in potentiometric measurements: pH, pNa and pM.	J. E. LEONARD
Tuesday, 18 *August*	
Principles and applications of spectrofluorimetry.	D. M. HERCULES
Laser principles and materials.	R. PASTOR
Laser excited emission spectroscopy: Current and potential capabilities.	F. BRECH
Wednesday, 19 *August*	
Photoluminescence and the triplet state.	C. A. PARKER
Modern methods of microanalysis.	G. SLODZIAN
Thursday, 20 *August*	
Nuclear magnetic resonance studies of metal chelates.	D. T. SAWYER
(to be announced)	C. N. REILLEY
Open discussion	
Friday, 21 *August*	
Recent advances in gas chromatography and their practical significance.	B. O. AYRES.

Further information may be obtained from Dr. W. GEORGE PARKS, Director of Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island.

April 1965: **1965 International Conference on Modern Trends in Activation Analysis:** *International Atomic Energy Commission*, and *Activation Analysis Research Laboratory, Texas A and M University*: Texas A and M University, College Station, Texas.

For information contact either Dr. RICHARD E. WAINERDI, Activation Analysis Research Laboratory, Texas A and M University, College Station, Texas, U.S.A., or Dr. DEREK GIBBONS, Wantage Research Laboratory, U.K.A.E.A., Wantage, Berkshire, England.

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NOTICES

(*Material for this section should be sent directly to the Associate Editor*)

FEDERAL GERMAN REPUBLIC

Friday–Saturday 19–27 *June* 1964: **European Convention of Chemical Engineering 1964:** Frankfurt am Main

This will include the **1964 ACHEMA Congress**, of which the following parts of the programme may be of interest to analytical chemists

Friday, 19 *June Measurement and measured-value transformation in chemical technology*

Intermittierende elektrochemische Sauerstoffmessungen in verungreinigten Gewässern.	F. Tödt
Neue elektrochemische Meßanordnungen zur Kontrole von Spurenkonzentrationen reduzierender Stoffe in Gasen und Flussigkeiten	G. Teske
Volltransistorisierter Gleichspannungsverstarker fur pH-Messungen.	P. Wunderer
Durchflußmessung von aggressiven und mit Festoffen versetzten Flüssigkeiten.	H. Engelhardt
Ein neuer Meßplatz zur Bestimmung der Stoffkonstanten E_r und tan δ von Proben mit weitgehend beliebigen Formen bei 3000 *MHz.*	G. Schilling
Emploi du chromatographe automatique à l'usine de Lacq	R. Caboz
Die Flammenionisation zur kontinuierlichen Bestimmung von Qualitätsgrößen	G Steinmuller

Saturday, 20 *June*

Szintillationsspektrometrie von α und β-Strahlung mit Cäsiumjodid.	K. H. König
Neuere Entwicklung bei der Meßwertgebung mit Radioisotopen.	A. Trost
Isotopenanwendung in der chemischen Industrie	K. Czeija
Kontinuierliche Dichtemessung in Industriebetrieben	H. Krech
Überwachung der Äthylenproduktion mit dem Massenspektrometer.	H. G Lossau
The infrared analyser—a powerful analytical tool for on-line chemical analysis.	E. G. Meyer
Neue Erfahrungen bei der kontinuierlichen Überwachung der Viskositat.	H. Kühlewein

Tuesday, 23 *June: New physical methods of chemical analysis, especially methods of trace analysis*

Brennstoffzellen als Spurenmeßgerate.	P. Hersch
Fortschritte in der Entwicklung der Analyse mit Hochfrequenz.	K. Cruse
Impurity analysis in high polymers by the pulse dielectric method	P. Hedvig
Ein neues Gerat für Elektronenbeugung im Ultravakuum.	M. Gribi und L. Wegmann
Neuere Entwicklungstendenzen in der EPR-Spektrometrie.	H. G. Thom
Ein Universalgerät fur Kernresonanzuntersuchungen.	F. Furrer
High precision comparative polarography	H. M Davis
Some analytical applications of differential cathode ray polarography.	R. C. Rooney
Coulo-Halometrie mit galvanischen Zellen	P. Hersch

Wednesday, 24 *June*

Dreidimensionale Dünnschicht-Chromatographie bei tieferen Temperaturen	E. Stahl
New developments in column technology in gas chromatography	L. S Ettre

Arbeitsmethoden der Gaschromatographie	E Rodel
Erfahrungen auf dem Gebiet der gaschromatographischen Spurenanalyse mit neuen hochempfindlichen Detektoren.	E. Thom
Separation of multicomponent mixtures by continuous gas-liquid chromatography	P E Barker
Applications of duel channel gas chromatography	J Amy, K P Dimick and T Z Chu
Thermische Fragmentierung und Strukturbestimmung organischer Verbindungen	W. Simon
Versuche zur Spurenanalyse von Kohlenwasserstoffgasen	M Freund, L Szepesy und F Simon
Die Anwendung der Gas-Chromatographie in der CHN-Analyse.	K. Derge

Thursday, 25 *June*

Die Bedeutung einer Erweiterung des Spektralbereiches in der Infrarot-Spektroskopie.	G. Kemmner und F Brunner
Automatisierte Röntgenfluoreszenz-Analyse.	H Neff
Röntgenmikroanalyse elektronenmikroskopischer Praparate.	K.-H. Herrmann und H Neff
Ölverschmutzung in Wasser und Gewässern. Nachweis und quantitative Bestimmung mit dem IR-Spektrophotometer	W Fastabend
Eine neue Apparatur zur Prüfung der Lichtund Wetterechtheit von Farbungen auf dem Textilgebeit, von Kunststoffen, Lackanstrichen und Gumm.	E O Seitz
Flammenspektrometrische Möglichkeiten zur Bestimmung von Phosphor in phosphororganischen Verbindungen.	W Schmidt
Strahlenquellen für die atomare Absorptionsspektroskopie.	K Osterhammel
A new instrument for analytical atomic absorption spectrophotometry.	W J Price
Eine neue Geräteserie selbstkompensierender Analysenautomaten fur die Spurenmessung.	H Fuhrmann
Kontinuierliches Meßverfahren zur Überwachung von MAK-Werten	W Gey und K Schuster

Friday, 26 *June*

Submicro methods of organic analysis.	R Belcher
Eine neue Vakuumthermowaage.	H G. Wiedemann
Eine neue Dosierungsmethode zur Durchfuhrung von Mikroreaktionen.	H. Straubel
Neue Verfahren auf dem Gebiet der thermometrischen Titration	H Knauer
Polymer molecular weight analysis by gel permeation chromatography.	L. E Maley
Neue Anwendungsgebeite des Verfahrens der Gel-Filtration durch die Entwicklung neuer Dextrangele	B Gelotte
Die Endpunktbestimmung in der analytischen Chemie.	H Jucker
Neue Laborwaagen mit Vorrichtungen zur Bedienungserleichterung.	H Hartwig
Gravimetrische Sondergeräte für physikalischchemische Untersuchungen.	B. Kassner

The **Deutsches Atomforum e. V.** is organising for the first time a series of lectures within the framework of the Convention on 25 June, entitled *Nuclear Radiations in Science and Industry*. The following of the lectures may be of interest to analytical chemists

Aktivierungsanalyse und Erzeugung kurzlebiger Isotope in Chemie und Technik in kleinen Reaktoren.	A. Thiel
Das kontinuierliche Beta-Gamma-Photometer als Hilfsmittel bei der Uberwachung und seine Grenzen.	K. H. Waechter
Sunnschichtmelzen mit radioaktiven Stoffen. Dünnschichtchromatographie mittels Radionukliden	G. Boucke
Zonenschmelzen mit radioaktiven Stoffen	H. Schildknecht
Bremsstrahlen-Fluoreszenzanalyse.	W. Kuhn
Verweilzeit-Messungen mittels radioaktiver Indikatoren	D. Schulz-Pillot

Further information can be obtained from DECHEMA, 6 Frankfurt (Main) 7, Postfach 7746, Bundesrepublik Deutschland.

FRANCE

La **Commission Internationale d'Analyse "C I A."** du **Comité Internationale de la Détergence** "C.I D" a tenu sa 7ème session les 24 et 25 Octobre 1963 à Saint-Gall, sur invitation du Comité Suisse de la Détergence, sous la présidence du Prof JACINI (Italie)

Apres avoir entendu un rapport sur l'activite generale, depuis un an, du C.I.D par son Secrétaire Géneral, M. DE WIT et sur l'organisation du 4eme *Congres International de la Détergence* qui doit avoir lieu a Bruxelles du 7 au 12 Septembre 1964, les membres de la C I A discutèrent les résultats des differentes analyses circulaires effectuees en 1963, concernant notamment

—analyse des alkylsulfonates de sodium,
—analyse de melanges d'alkylsulfates primaires et d'alkylarènesulfonates,
—analyse de mélanges de non-ioniques, d'alkylarènesulfonates et de savon,

toutes réalisées a l'aide de méthodes récemment mises au point par les pays appartenant à la Commission et basees sur l'emploi des échangeurs d'ions Ces travaux seront repris au cours de l'année prochaine en vue de leur apporter certaines améliorations avant de les faire homolguer sur le plan international

Les discussions sur l'analyse des non-ioniques ont occupé une grande partie de la session. L'étude de méthodes reproductibles a été confiee, il y a deux ans, à un Groupe de Travail, dont les travaux avancent rapidement puisqu'il a pu soumettre à ses collègues de la C.I.A , qui les ont acceptées, des propositions pour les déterminations titrimétriques et celles de l'eau et des cendres, qui seront presentées incessamment, pour homologation, à l'Organisation Internationale de Normalisation "I S.O."

Le programme futur de ce Groupe de Travail comprendra la poursuite des recherches sur la détermination de l'oxyde d'éthylène, de l'indice d'hydroxyle, des polyglycols libres, et des alkylphénols libres dans les alkylphénols oxyéthylenes D'autres Commissions devant s'attacher plus particulièrement à la séparation des hydrocarbures non sulfonés et à la détermination des polyoxyéthyles sulfatés

Il est à noter que les méthodes d'analyse déjà soumises a l'I.S O. semblent devoir être adoptées sans difficulté par les membres de cette Organisation, ce qui est un grand encouragement pour la C.I.A

POLAND

Tuesday–Saturday 15–19 *September* 1964· **XXXVth International Congress of Industrial Chemistry:** Varsovie.

Among the many sections of the Congress, one is devoted to *Analytical Chemistry*. Further information can be obtained from the Scientific Committee of the XXXVth International Congress of Industrial Chemistry, Warsaw 86, skr. poczt 26, Poland

UNITED KINGDOM

Wednesday 4 *March* 1964: **Annual General Meeting** followed by **Bernard Dyer Memorial Lecture:** *Society for Analytical Chemistry.* Burlington House, London W 1: 3.00 p m

Wednesday 11 *March* 1964. **Annual General Meeting** followed by **Analysis of Peroxygen Compounds:** C. WHALLEY: *Society for Analytical Chemistry, Midlands Section* University, Edgbaston, Birmingham 15: 6.30 p.m

Saturday 14 *March* 1964: **Biochemistry of Quinones:** R. A MORTON: *Society for Analytical Chemistry, North of England Section* City Laboratories, Mount Pleasant, Liverpool: 2.15 p m

Wednesday 18 *March* 1964· **Discussion Meeting:** *Society for Analytical Chemistry, Microchemistry Group· The Feathers,* Tudor Street, London E C 4· 6 30 p m

Friday 20 *March* 1964· **Organic Analytical Reagents—A Survey of Some New Work:** W. I. STEPHEN· *Society for Analytical Chemistry, Scottish Section* Queen's College, Dundee· 7.15 p.m.

Tuesday 24 *March* 1964: **The Work of a Public Analyst:** R A DALLEY· *Society for Analytical Chemistry, Midlands Section·* Nottingham and District Technical College: 7 00 p m.

Tuesday 24 *March* 1964: **Physical Methods Applied to Examination of Archaeological Remains:** E. T. HALL and A. E. A WERNER: *Society for Analytical Chemistry, Physical Methods Group* Burlington House, London W.1· 6.30 p.m

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Wednesday 14 *October* 1964: Symposium on **Thin-Layer Chromatography:** *Society for Analytical Chemistry, Thin-Layer Chromatography Panel* and *Midlands Section* with *Royal Institute of Chemistry, Birmingham and Midlands Section* University, Edgbaston, Birmingham 15.

The programme will consist of a Plenary Lecture by Professor Dr. E. STAHL and the following lectures:

Thin-Layer Chromatography in Biosynthetic Studies	T. W GOODWIN
Recent Developments in Thin-Layer Chromatographic Equipment	R. P. HIRSCH

Thin-layer Chromatography on Ion-Exchange Media. C. S KNIGHT
Thin-Layer Chromatography in Clinical Chemistry. J G. LINES
Exploitation of Thin-Layer Chromatography in Plant Chemistry. E J SHELLARD

Further information can be obtained from Mr. M L. RICHARDSON, John and E. Sturge, Lifford Lane, Kings Norton, Birmingham 30.

At the **First Annual General Meeting** of the *Atomic Absorption Spectroscopy Discussion Panel* of the *Physical Methods Group* of the *Society for Analytical Chemistry*, held on Tuesday, 3 December, 1963, the following Officers were elected for the forthcoming year —

Chairman· W T ELWELL

Secretary: D. MOORE, 98 St. Pancras Way, Camden Road, London N W.1

British Standards Institution has announced the following *New British Standards*:—

B S 2649: *Methods for the analysis of glass: Part* 4: 1963: *Recommended procedure for the analysis of fluoride-opal glasses.* This recommends detailed analytical procedures for determining all of the important constituents of the so-called 'fluoride-opal' glasses based on investigations carried out by the Society of Glass Technology. (*Price* 6s.)

B S 3406: *Methods for the determination of particle size of powders. Part* 2: 1963: *Liquid sedimentation methods.* This describes methods of determination of the size distribution of particles in those fractions of powders which pass a 75 μ British Standard test sieve, using the principle of liquid sedimentation Four methods are described, *viz.* the fixed depth pipette, the fixed position pipette, the liquid column method with sedimentation accumulation and the liquid column method with sediment extraction. The basic principle (Stokes's law) is described in the foreward. An appendix advises on liquid suspended media and dispersing agents, providing a list of suitable suspended media for many materials. Other appendices describe methods of evaluating a size analysis instrument and the correlation of results from different methods of size determination. (*Price* 15s.)

Part 4: *Optical microscope method* This describes a method of determination of the size distribution of particles in those fractions of powders which pass through a 75 μ British Standard test sieve A representative sample of powder to be sized is dispersed and placed on a glass slide and the particles are viewed through a microscope by means of transmitted light. The areas of the magnified images of the particles are compared with the areas of reference circles of known size inscribed on a graticule and simultaneously visible The relative numbers of particles in each of a series of size classes are determined. These numbers, expressed as percentages, constitute the size distribution by number From the relative numbers in the size classes it is possible to calculate the size distribution by weight, provided it is assumed that particles of all sizes have the same shape in the sense that the square root of the projected area of a particle stands in a constant ratio to the cube root of the volume of the particle, and that all of the particles have the same density. (*Price* 20s.)

B.S 3681: 1963. *Methods for the sampling and testing of lightweight aggregates for concrete* This describes methods for sampling and testing of lightweight aggregates for concrete. The tests cover bulk density, sieve analysis, apparent specific gravity, sulphate content, volatile matter, loss-on-ignition, carbon content and soundness. (*Price* 7s. 6d.)

The following *Revised British Standards* have also been announced:—

B S 1428: *Microchemical apparatus. Part* 11: 1963: *Combustion boats and sheath for microchemical analysis.* This specifies the following apparatus designed to fit the microcombustion tubes specified in other parts of B.S 1428: one size of platinum combustion boat and a sheath to fit it and three sizes of porcelain combustion boat It includes dimensional drawings as well as appropriate requirements for material, weight and marking, and for constancy of weight of the platinum boat or sheath or ignition It also gives desirable limits for constancy of weight of porcelain boats on ignition or heating with acid, but these are not a mandatory part of the specification. (*Price* 4s 6d)

B S 1747 *Methods for the measurement of air pollution Part* 4: 1963: *The lead dioxide method* This covers the construction and use of apparatus for the lead dioxide method of measuring the reactivity of atmospheric sulphur compounds. (*Price* 5s)

B S 1016: *Methods for the analysis and testing of coal and coke Part* 14: 1963: *Analysis of coal ash and coke ash* This deals with the determination by chemical analysis of the major constituents in samples of coal ash or coke ash An appendix describes a spectrographic method by which certain constituents can be determined speedily and with sufficient precision for most purposes. (*Price* 10s)

B S 1715: 1963· *Methods of analysis of soaps and soap powders.* This describes methods of sampling and the preparation of the sample for analysis, and the following determinations: total fatty matter, alkali combined as soap, total alkali, titre, matter insoluble in ethanol, matter insoluble in water, free alkali, free fatty acids, unsaponifiable matter and unsaponified fat, chlorides, silica, phosphate, per-salts, rosin, glycerol, loss on drying at 100–105° and water. (*Price* 16s.)

B.S. 1756: *Methods for the sampling and analysis of flue gases. Part* 5: 1963: *Semi-routine analyses.* This describes semi-routine methods for the determination of carbon dioxide, carbon monoxide and total oxides of sulphur, mainly employed for the assessment of the combustion performance of domestic gas appliances. (*Price* 6s.)

UNITED STATES OF AMERICA

Monday–Friday 2–6 *March* 1964: **15th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy:** *Analytical Chemistry Group, Pittsburgh Section ACS and Spectroscopy Society of Pittsburgh.* Penn-Sheraton Hotel, Pittsburgh, Pa.

The programme is as follows.—

Monday, 2 March. Morning

Gas Chromatography—Detectors

Characteristics of a sensitive and absolute ultrasonic detector for gas chromatography.	F. W. Noble and K. Abel
Response of hotwire thermal conductivity cell.	D. W Robinson and D. M. Rosie
Electron drift-velocity detector for gas chromatography.	V. N. Smith and J. F. Fidiam
Piezoelectric sorption detector.	W. H. King, Jr
A high temperature hydrogen flame ionisation detector. A critical evaluation of design and operating characteristics.	A C Seibel
A rapid-scan far UV spectrophotometer for monitoring gas chromatograph effluent	W. Kaye and F Waska
A preliminary study of the characteristics of a photoionisation detector for gas chromatography.	J F Roesler

Instruments for Analysis

A fully automated analytical balance.	L Cahn and H. Schultz
A versatile sorption hygrometer	J. Kertzman
Electrodeless conductance measurements	D. E. Burge and T A. Olson
Galvanic determination of strong acids.	P. Hersch and C. Sambucett
Electronic potentiometer defines new standard in pH instrumentation	D. C. Douglass and E. F. Blondfield
A convenient solution calorimeter	E M Arnett, J. J. Burke and L. V. Guild
Oxygen gauge.	W. M Hickam
Instrument cloud point determinations.	J. L. Williams and N Stein

Symposium on High Resolution NMR of Oriented Molecules

NMR in liquid crystals: PMR spectrum of benzene in a nematic solution.	A. Saupe
PMR investigations on oriented molecules.	G Englert
Some studies of ordered nematic phases from highly resolved dipole-dipole splittings	W. D. Phillips, J C. Rowell and L R. Melby
NMR spectra in single crystals.	P. C Lauterbur

Monday, 2 March: Afternoon

Gas Chromatography—General

GLC studies of bile acid esters.	L I. Braddock, J. J Kelly and L. V Hook
Analyses of chloraniline isomers by gas chromatography.	K J. Bombaugh
Gas chromatography of water in hygroscopic liquids	S Ahuja, G D. Chase and J G Nikelly
Analysis of diluted auto exhaust with a multi-columned gas chromatograph.	T. A. Bellar, M. L. Bellar and E. Sigsby, Jr
Use of polymers as liquid phase in gas chromatographic analysis of high boiling-point compounds.	P Shapras and G. C Claver
Behaviour of phosphate pesticides in electron affinity detectors.	G E. Cook, C W. Stanley and J. E. Barney II

A microvapour-phase hydrogenation accessory for gas chromatographic analysis of glyceride oils.	T. L. Mounts and H. J. Dutton
Correlations between electron capturing ability and structure.	W. E. Baitinger and J. W. Amy

Spectrophotometric Methods of Analysis

Determination of microgram quantities of non-radioactive caesium in uranium and its compounds.	L. Silverman and R. S. Dunn
Determination of phosphorus in alloy steels.	G. A. Bauer
Automated procedures for spectrophotometric determination of silicon, phosphorus and manganese in steel.	P. H. Scholes and C. Thulbourne
Spectrophotometric determination of antimony in gold.	B. Yurash
Simultaneous spectrophotometric determination of calcium and magnesium with chlorophosphonazo III.	J. W. Ferguson, J. J. Richard J. W. O'Laughlin and C. V. Banks
Use of the molybdenum blue reaction in spectrophotometric determination of thallium.	L. Hargis and D. F. Boltz
An improved chloanilate method for determination of boron.	D. R. Peterson and J. R. Hayes
Precision analysis of highly pure bismuth telluride by differential spectrophotometry.	A. Eldridge, R. S. Kelly and R. Bastian
Indirect UV spectrophotometric determination of ammonia.	J. Howell and D. F. Boltz
New technique for study of photometric precision.	D. C. Nelson and R. C. Hawes
A study of a new spectrophotometric data acquisition system.	R. N. Rand and B. Helm

Symposium on High Resolution NMR of Oriented Molecules

NMR of polar molecules in an external electric field.	J. S. Waugh and J. D. Macomber
High resolution NMR spectra of molecules in an applied electric field	K. A. McLauchlan

NMR and ESR Spectroscopy

Conformation of sugars and glucose polymers by PMR.	C. A. Glass
A nuclear resonance study of equilibria in the system boron trifluoride-methanol.	S. Brownstein
NMR study of isomeric pentadienes.	P. W. Flanagan and H. F. Smith
Proton and carbon-13 NMR of coal derivatives and other carbonaceous materials	H. L. Retcofsky and R. A. Friedel
End-group analysis and number average MW determination of some polyalkylene glycols and their esters using NMR spectroscopy	T. F. Page, Jr. and W. E. Bresler
A new type of spectrometer.	M. Takeuchi and T. Miyamae
ESR observations of oxidation-reduction process in some viscera.	T. Okabe and P. Y. Sakagishi

Tuesday, 3 March Morning

Analysis of Inserstitial Elements in Metals

Co-operative testing programmes on gases in metals.	T. D. McKinley
Separation and identification of impurities in hydrided uranium-zirconium alloy.	L. Silverman and D. J Klein
Rapid determination of nitrogen in refractory borides and nitrides.	J. W. Tereshko
Simultaneous determination of oxygen and nitrogen in refractory metals by d.c. carbon arc-gas chromatographic technique.	R. K. Winge and V. A. Fassel
Rapid determination of low concentrations of oxygen in potassium and NaK by a modified amalgamation technique.	G. Goldberg
Determination of carbon and carbon compounds in alkali metals.	J. C. Gerken, S. J. Rodgers and J. W. Mausteller
Rapid method for determination of micro amounts of sulphur in selenium.	L. Acs and S. Barabas
A recording linear-response gauge for vacuum fusion analysis.	H. F. Waldron

Liquid and Gas Chromatography

Improved techniques in liquid column chromatography.	L E. Maley and J. L. Waters
Advantages and limitations of gel permeation chromatography.	L. E. Maley, G. E. Stackhouse and J. L. Waters
Thin-layer chromatography of organic phosphorus compounds.	C. W. Stanley
Quantitative analysis of mixtures separated on thin-layer chromatographic plates.	R D. Spencer and B H. Beggs
A method for recording elution curves on liquid column chromatography.	T. Naono
Effect of column shape on efficiency in gas chromatography preparative separations.	E. M. Taft, J. E. Booker and K. P. Dimick
Effect of injection port temperature on peak broadening in gas chromatography.	T. Haruki, T. Morii and K. Sato
Injection and vapourisation of samples in gas chromatography.	T. Johns and B. Thompson
Polymer analysis by pyrolysis-gas chromatography.	B. Groten

Polarography and Coulometric Analysis

A versatile polarographic analyser incorporating facilities for conventional d.c., rapid d.c., anodic stripping and a.c. polarography	R. Kopp
Polarographic determination of mercury, tellurium and cadmium in HgTe and CdTe alloys.	M. C. Gardels and J. C. Cornwell
Polarographic determination of cadmium in stainless steel.	H. S. Karp and G. Krapf
Dissolved oxygen measurement by constant-potential continuous coulometry.	E. L. Eckfeldt and E. W. Shaffer
Chromatographic separation and coulometric determination of magnesium, calcium and strontium.	J. W. O'Laughlin, G. J. Kamin and C. V. Banks
Controlled potential coulometric studies of oxidation state ratios of trace elements.	B. W. Conroy and O Menis
Application of controlled-potential coulometry to study of redox reactions in solution. The iridium^{III} *chlorate system.*	J. McClure and G A Rechnitz
A continuous automatic coulometric titrator.	P. Johnson, J K. Jacobsen and R. J. Drago
An advanced automatic microcoulometer for trace sulphur and halogen analysis.	J. A. McNulty and A. R Myers

Tuesday, 3 *March: Afternoon*

Symposium on Analysis of Gases and Non-Metallic Inclusions in Metals

Basic concepts of quantitative separation of alloy phases.	W. Koch
Neutron-activation analysis of metals for nitrogen, oxygen, silicon, phosphorus and sulphur.	V. P. Guinn
Analysis for non-metallic elements in metals by vacuum spark mass spectrography.	W. M. Henry and E. Blosser
Separation of oxide inclusions and nitrides.	W. Koch

Gas Chromatography—General

An ultra pure hydrogen generator for gas chromatography.	J. K. Jacobsen
Construction and performance of an IR chromatographic fraction analyser.	R. Brown and P. A. Wilks, Jr.
Design and performance of a portable ionisation chromatograph.	B. H. Andreen and D. V. Kniebes
Design considerations for an over-all high performance gas chromatograph.	M. R. Burnell
Pyrolysis gas chromatography with programmed temperature and capillary columns.	E. W. Cieplinski and L S. Ettre
A continuous extractor for analysis of trace gases in liquids.	H. L. Ashmead, B. D. Crouch and J. A. Schmit
Minimising the time for the chromatographic analysis of complex mixtures.	T. B. Rooney and W. Aznavourian

An analogue bleed line compensation system	E J Levy, D G Paul and L Mikkelson
Multiple column compensation in process gas chromatographs	E L Szonntagh and T A Gray

General Analytical Methods

Radio-release determination of vanadium	A S Gillespie, Jr. and H G Richter
Rapid radiochemical determination of americium^{III}	M H Campbell
Determination of nickel by magnetic susceptibility	J F Reed
A rapid and simple mass spectrometric procedure for detection and determination of boron	K F Sporek and R A Duvall
Indirect determination of fluorides by EDTA titration of samarium	H F. Combs and E L. Grove
Determination of ferrous oxide in ferrites	K L Cheng
Analysis of vanadium-gallium alloys based on displacement of vanadium^{V} *from its EDTA complex*	M C Gardels
Determination of silica in presence of phosphate and fluoride	F W Czech, T P Hrycyshyn and R J Fuchs
Determination of nitrate plus nitrite with special reference to air pollution	N A Huey, C C Golden and R E Boone
Precise method for assay of potassium iodate by comparison with (primary standard) arsenic trioxide	S M Tuthill, R S Sprague and W C Stoecker
Very accurately defined gas mixtures for use as primary standards	H G Guillaume and G Kanter
Use of cylinder gas mixtures to check moisture analysis instruments	H G Guillaume

Wednesday, 4 March Morning

Symposium on Chemical Applications of Far Infrared Spectroscopy

Recent developments in far infrared spectroscopy	R C Lord
Interferometrics spectrometers Their use as a practical laboratory tool	A Maki, L R Blaine and R Nelson
Far infrared interferometer for the region 20–1000 micron	J Tadayon and J N. A Ridyard
Torsional vibrations in the far infrared spectrum	W G Fateley, R K Harris, F A Miller and R E Witkowski
Hydrogen bond studies in the far infrared	R J Jacobsen and J W Brasch
On the lattice spectrum of HI	D W Robinson
Some infrared absorption studies in the 350–100 cm^{-1} *region*	F F Bentley, N T McDevitt and A Rozek

Analysis of Organic and Biological Material

Polymer MW determination by high temperature vapour pressure osmometry	J P Burger
Ion-exchange separation of acetamide from ammonium acetate and its determination	P King and J R Simmler
Polarographic determination of aldehydes and acetals in alcohols	C C Budke, D K Banerjee and F J. Miller
Polarographic determination of microgram amounts of selenium in biological material	G D. Christian and W C Purdy
Determination of dl and meso dibromosuccinic acids in aqueous solutions	R Annino and D. J Manzo
A new spectrofluorophotometer and its application to determination of biological substances	K Iwai, S. Kazawa and T Haruki
Determination of phenyl-β-naphthylamine in polyurethane	D W. Chambers, D. M. Knight and J L Myers
A study of the pi complexes of trinitrofluorenone Determination of amines, phenols and aromatic hydrocarbons	G H. Schenk, P. Wines and C Mojzis
A new automated apparatus for determination of oxygen in organic compounds	M. E Ebeling and D W Marcinkus

Thermal Analysis and Potentiometric Analysis

Differential thermal analysis using self-generated atmospheres at supra-ambient pressures	P D Garn
Application of differential thermal analysis to quantitative analysis	J Justin and N Brenner
A semi-micro thermogravimetric analyser	R W Tabeling
Determination of fluosulphonic acid in solutions containing large amounts of hydrofluoric, sulphuric and fluosulphonic acids	W E Skillmann and S A Ashworth
Differential potentiometric determination of palladium in presence of platinum	S Barabas and J Vinaric
Comparison of methanol with water as solvent in potentiometric titration of halides	H T Havacek and W B Swann

Symposium on Chemical Applications of Far Infrared Spectroscopy

The cooled germanium bolometer as a far infrared detector	C E Jones, Jr, R Hilton, J B Damrel Jr, and C C Helms
A comparison of the Golay cell and the thermocouple as far infrared detectors	G L Carlson
Far-infrared instrumentation Second generation	G T Keahl, H J Sloane and M Lu
Special sampling system for far infrared	A J Russo and E H Siegler, Jr
Low frequency infrared spectrum and vibrational assignment of glyoxal	R K Harris
Infrared absorption study of some metal oxides in the region 350 to 70 cm^{-1}	N T McDevitt, W L Baun and F F Bentley
Far infrared spectra of DL-leucine and DL-2-methylleucine	L May and M St L Eaton

Infrared Sampling and ATR

Arsenic trichloride as a solvent for NMR and IR spectroscopy	H Szymanski, A Bluemle, D Bakalik and J LaFanora
Design and application of a high temperature IR gas cell	R W Rinehart, G E Bronson and A W Crowley
Soldering non-metals to metals for construction of improved IR absorption cells	J S Ard
New IR absorption cells for macro to ultramicro quantities, utilising soldered seals of windows to metals	J S Ard
Microsampling techniques in the IR	R C Gore
ATR and specular reflectance measurements in the IR	D E McCarthy
Evaluation of some factors affecting reproducibility of ATR spectra	R L Harris
Analysis of suspended particulates with membrane filters and ATR	R W Hannah and J L Dwyer
ATR analysis of the non-volatile vehicle in unseparated paint	R J McGowan

Apparatus and Equipment for X-Ray Spectrographic Analysis

Effects of X-ray tube parameters on fluoresence analysis	H T Dryer
Effect of excitation on X-ray emission intensities	F Bernstein
Description of an automatic "twin path" X-ray fluorescent spectrometer and its applications to process control	C C Pyne
Multilayer soap films as analysing crystals in X-ray spectrometry	A J Mabis and K T Knapp
Components for X-fluorescence spectroscopy in the 5–65 Å wavelength region	J A Dunne
X-radiation analysers Some advantages and disadvantages of various operating techniques	R Torkildsen
Automatic analysis of X-ray spectrographic data	R. W Deichert
A new simultaneous spectrometer for analysis of the light and heavy elements in static and dynamic samples	J F Croke and W J Pfoser

Thursday, 5 March Morning

Instrumentation for Molecular Spectroscopy

A new routine spectrophotometer	J. J J Staunton and R. E Boostrom
An across-the-counter double beam microscope spectrophotometer	H C Duecker and E R Lippincott

Performance of the model 350 recording spectrophotometer in the far UV region.	T. J. Porro, H. T. Morse and E. S. Gillette
An improved method for measuring optical rotatory dispersion	G. R Thiel and D. C. Demoth
A precision recording absolute spectrofluorimeter.	G. K. Turner
Raman spectra of small solid samples including lattice vibrations.	D. C. Nelson and W. N. Mitchell
A near IR spectrophotometer for physical measurements.	R. C. Hawes, J. R. Eno and K. A. Wickersheim
Design development of a new filter-grating IR spectrophotometer.	C. W. Warren, A. E Chapple and R. P. Bauman
Construction and performance of a frustrated multiple internal reflectance IR spectrophotometer.	P. A. Wilks, Jr
Continuous IR instrumentation in packaging converting operations	I. L. Brazier

Emission Spectroscopy—Excitation Techniques

New studies with gas-controlled arc sources	M. Margoshes
The hollow cathode tube as a source for optical emission spectroscopy.	J. E. Paterson
A year of progress in laser excited spectroscopy	F. Brech
Characteristics of the laser source for spectral excitation	S. D. Rasberry, B. F. Scribner and M. Margoshes
The laser as a direct excitation source in analytical emission spectroscopy.	R. L. Rupp and R. Bastian
On the spectral excitation mechanism and properties of high frequency plasma-flames and d.c. plasma-jets	J. van Calker and W. Tappe

Infrared

Vibrational spectra of hexafluoroacetone.	C. V. Berney
Infrared and Raman spectrum of methyl isocyanate	R. E. Witkowski and W. G. Fateley
Asymmetric rotor band contours.	S. C. Wait
Infrared stretching frequency of Si—F bond	G. W. Miller, R. Gagne and J. Vanek
Infrared spectral studies of sulphones in the 2000–250 cm^{-1} *region.*	W. R. Feairheller, J. E. Katon and F. F. Bentley
Infrared spectra of organophosphate and organophosphorothioate pesticides.	L. Kahn and C. H. Wayman
Infrared studies of water of hydration in inorganic acetates.	S. E. Wiberley and K. J. Eisentraut
Infrared spectra of condensed thiophenes and their alkyl derivatives.	F. R. McDonald and G. L Cook

Thursday, 5 March: Afternoon

Coblentz Memorial Symposium

Coblentz memorial lecture.	G. B. B. M. Sutherland
Development of vibrational spectroscopy of high polymers	S. Krimm
Electronic spectra of polyatomic molecules.	D. A. Ramsay

Emission and Mass Spectroscopy—Instrumentation

Sensitivity and accuracy of analysis by spark source mass spectrometry.	J. S. Halliday, W. A. Wolstenholme and J. D. Waldron
Discussion of an interference spectrometer with resolution in excess of 10^6	J. O. Crote and D. C. Damoth
The lazyprobe, a device for sampling large objects non-destructively for emission spectrochemical analysis	A. Arrak, G. Chaplenko and D. O. Landon
A new visual spectroscope and its application to metal analyses.	Y. Tachibana and K. Kobayashi

Minimisation of spectral background influence and results of its automatic removal in direct reading instrumentation for stainless steels.	W. R. Kennedy
Multichannel spectrophotometer	C. Iida, K. Fuwa and B. L. Vallee
Automatic readout system for a spectrometer.	H. R. Gram, Jr.

Atomic Absorption Spectroscopy

Simultaneous multi-channel analysis by atomic absorption spectroscopy.	A. Strasheim and L. R. P. Butler
Hollow cathode lamps for atomic absorption spectroscopy.	C. Sebens, D. C. Manning and W. Slavin
Relation between the Ca-resonance line profile of the hollow cathode lamp or flame and absorption intensity in atomic absorption.	K. Yasudo and S. Matsudaira
Determination of selenium and tellurium in copper by atomic absorption spectrophotometry.	S. Sprague, D. C. Manning and W. Slavin

Friday, 6 March Morning

Symposium on Application and Instrumentation for Electron Probe Analysis

Application of electron probe to determination of concentration gradients and dispersed phase compositions.	D. M. Koffman
Electron probe and metallographic characterisation of an NBS spectrometric low alloy steel standard.	R. E. Michaelis, H. Yakowitz and G. A. Moore
Recent advances in application and instrumentation of electron probe microanalysis.	D. A. Melford
Application of the Zeibold-Ogilvie empirical quantitative calculation method to electron beam microanalysis.	S. H. Moll
Quantitative microanalysis using the A.E.I. scanning electron probe microanalyser.	P. W. Wright
Progress in design of equipment for electron probe analysis.	E. Davidson, W. E. Fowler, H. Neuhaus and W. G. Shequen
On the backscattered electron image by silicon P-N junction through the electron probe X-ray microanalyser.	S. Kimoto and H Hashimoto

Symposium on Spectra of Adsorbed Molecules

Application of ESR to study of heterogeneous catalysis.	R. J. Kokes
IR spectroscopy in study of adsorption at non-metallic surfaces.	R. S. McDonald
Application of IR spectroscopy to study of adsorption on metal surfaces.	J. W. Ward
Electronic spectra of adsorbed molecules.	H. P. Leftin
Hydrogen chemisorbed in silicon	W. A. Pliskin

Emission Spectroscopy—Applications

Spectrographic determination of silicon, phosphorus and nickel in copper-germanium alloys.	A M. Liebman, R J. Carver, L A. Tissot and J. R. Zuber
Quantitative analysis of major and minor constituents of silicate rocks and minerals by means of direct reading spectroscopy.	H. Schwander and J. B. Marling
Element calibrations by plasma jet solution spectrography.	E. H. Sirois
Methanol as a diluent for gas stabilised arc sources.	J. D. Nohe
Use of a nitrogen atmosphere to reduce matrix effects in analysis of aluminium alloys using point-to-plane spark excitation.	C. K. Matocha, J Petit and W. H. Tingle
Spectrochemical determination of cobalt, nickel, aluminium and boron in commercial acid gold baths by solution technique.	E. F. McLain and W H Wade
A direct reading spectrochemical procedure for measurement of 19 minor elements in natural water.	J. F. Kopp and R C. Kroner
Spectrochemical determination of microgram amounts of tantalum, niobium, titanium and hafnium in U_3O_8.	J. E. Scott and E. R. Shuster, Jr
Multi-element spectrographic impurity analysis of graphite.	O. V. Coble and F. V. Fair

Friday 6 March Afternoon

Electron Diffraction and Applied X-Ray Spectrography

A new high vacuum unit for electron diffraction combined with surface electron microscopy	M GRIBI, L WEGMANN and L M MOUNTFORD
X-ray fluorescent determination of cobalt, zinc and iron in organic matrices	S A BARTKIEWICZ and E A HAMMATT
Internal standard X-ray spectrographic procedure for determination of calcium, barium, zinc and lead in hydrocarbons	W E BURKE L S HINDS, G E DEODATO, E D SAGER, JR and R E BORUP
X-ray spectrographic determination of trace thorium in U_3O_8	J E. SCOTT and E R SHUSTER, JR
X-ray emission analysis of solders by solution technique	W T BARNES and D E WILSON
Combined X-ray spectrometric and IR method for determining sulphonate and sulphate concentration of detergent range alkylbenzene solutions	S D. KULLBOM, W K POLLARD and H F SMITH
Digital programming applied to steel analysis	P BRECKHEIMER and W E FOWLER

Analyses by Microwave and Infrared, Fluoresence

Microwave spectroscopy for compound identification	W O SWAN, G F CRABLE and J C WAHR
Quantitative analysis by microwave spectroscopy	G. F. CRABLE, W O. SWAN J C WAHR
Analytical applications of IR spectroscopy with gratings	G KEMMNER
Analysis of detergents in aqueous solutions using IR spectrometry	G JENKINS and D ELLIS
Chemical nature of plastic film surfaces	M W LONG, JR. and J G COBLER
Butadiene-styrene copolymer ratio by IR spectrometry	A. S WEXLER
Quantitative determination of polychloroprene microstructures by IR and NMR spectroscopy	R. C FERGUSON
Fluorescence of aromatic hydrocarbon-1,3,7,9-*tetramethyluric acid complexes in the solid state*	B L VAN DUUREN and C. E BARDI
Polarization of steroid fluoresence	H S STRICKLER and R C. GRAUER

Infrared-Spectra and Miscellaneous

Computor handling of spectra—III —Programmes for evaluation of spectrophotometer performance	A SAVITZKY and J M ROCHE
Identification of IR spectra by computor techniques	P SADTLER and J BIRKENSTOCK
A computor analysis of carbon-hydrogen stretching bands in the IR spectra of hydrocarbons.	A S. ROSENBERG and H F. SMITH
Vibrational and NMR spectra of some methyl derivatives of the guanidinium ion.	J U. LOWE, A S TOMPA and G B WILMOT
IR study of the asymmetric methylene stretching band of alkanes, alkenes, alcohols, phenylalkanes and chloro-, bromo- and iodo-alkanes	A S. ROSENBERG and H. F SMITH
New group frequency assignments	H. SZYMANSKI
An IR study of keto-enol tautomerism as a function of sample preparation.	R T CONLEY and J A CORRIGAN
Low frequency O—H . . O bond vibrations in hydrogen bonded crystals	V ANANTHANARAYANAN

Further information can be obtained from R. B. FRICIONI, Allegheny Ludlum Steel Corporation, Brackenbridge Works, River Road, Brackenbridge, Pa , U S.A

Monday-Thursday 23–26 *March* 1964. **Second International Symposium on Advances in Gas Chromatography**: Sheraton-Lincoln Hotel, Houston, Texas

The programme is as follows —

Monday, 23 *March*. *Morning*

Cross-section ionization	J. E. LOVELOCK
Concentration and mass flow sensitive detectors in gas chromatography	I. HALASZ
Specific detection of halogens by flame ionisation	A. KARMEN

Monday, 23 March Afternoon

How to obtain maximum information from a chromatogram Identification in particular	A I M Keulemans
Gas chromatographic characterisation of organic substances in the retention index system	E Kovats
The specific retentions of monofunctional organic solutes in monofunctional hexadecyl derivatives.	A B Littlewood
Pressure volume changes in a gas chromatographic column	R P W Scott

Tuesday, 24 March Morning

Gas chromatographic analysis of urinary oestrogens.	H H. Wotiz
Gas-liquid chromatography of carbohydrates and related compounds	C C Sweeley
Characterisation and estimation of organic amines of biological interest	E C. Horning
Gas Chromatographic analysis of catechol amines	C J W Brooks
A new type of liquid–liquid and liquid–solid chromatography	E Bayer

Tuesday, 24 March Afternoon

Performance of argon detectors in the field intensified current region	J Z. Knapp
Measurement and interpretation of the C terms of gas chromatography	J C Giddings
Temperature limitations of stationary phases in gas chromatography	S. J. Hawkes
A new method of measuring the diffusivity in the gas phase and the obstruction factor	J. H Knox
Effect of particle-to-column diameter ratio on band spreading.	J. C Sternberg

Wednesday, 25 March Morning

Analysis of flavours by gas chromatography	A I M. Keulemans
Analysis of sulphur compounds with electron capture/flame dual channel gas chromatography.	K. P Dimick
Thermoramic programmed gas chromatography in the separation of very complex mixtures	C Merritt, Jr
Capillary column gas chromatography Mass spectral analyses of volatiles from orange oil	R. Teranishi

Wednesday, 25 March Afternoon

Preparative columns	C. Y. Sacodynsky
Simulated distillation by gas chromatography.	L E. Green
Automatic capillary gas chromatography and sampling of distillation products	D. W. Grant
Air pollution measurements by gas chromatography and flame ionisation detection	J. L. Monkman

Thursday, 26 March Morning

Gas chromatographic study of influence of geometry and chemistry of silica surfaces on their separating and adsorption properties	A V. Kiselev
Gas chromatography using solid adsorbents	L B. Rogers
Applications of isotopic exchange in gas chromatography.	J Tadmor
Some properties of graphited black and stationary phases in gas chromatography	I. Halasz

Further information and registration forms are available from Dr A. Zlatkis, Chemistry Department, University of Houston, Houston, Texas, U.S.A.

Monday-Thursday 12-15 *October* 1964 **19th Annual International Instrument-Automation and Exhibit of Instrument Society of America:** New York City

Papers are now invited for the above meeting Individuals active in all major areas of instrumentation, including measurement, information processing and automatic control, should submit abstracts to H TYLER MARCY, Vice President-Development, General Products Division, International Business Machines Corporation, White Plains, New York, U S A (deadline 31 March) The theme of the meeting is **World Frontiers in Instrumentation.**

The **American Society for Testing and Materials** has announced the availability of the 32-volume 1964 *Book of ASTM Standards* This reflects the entire span of today's knowledge of materials and materials testing Each volume covers a specific field of interest and includes a detailed index, table of contents and numeric list of standards. Beginning with the 1964 edition, the book will be brought up to date and published annually with the various parts available on the same scheduled date each year There will no longer be supplements

PAPERS RECEIVED

Chelating radiometric titrations by ion exchange for determination of traces of metals: JIŘI STARY JAROMÍR RŮŽIČKA and ADOLF ZEMAN (29 *July* 1963).

Chromatography of p'-substituted-p-hydroxyazobenzenes on alumina-impregnated papers: R J T GRAHAM and C W STONE (9 *November* 1963)

4,5-Diamino-6-thiopyrimidine as a reagent for the spectrophotometric determination of selenium: FRANK L. CHAN (2 *December* 1963)

Rapid determination of boron in iron and steel by pyrohydrolysis and constant-current coulometry: TAKAYOSHI YOSHIMORI, TOMOO MIWA and TSUGIO TAKEUCHI. (2 *December* 1963)

Contributions to the basic problems of complexometry—XIV: Determination of zirconium, thorium and titanium in the presence of each other: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (2 *December* 1963)

New trace analysis using radioactive isotope: NOBUO SUZUKI (2 *December* 1963)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—III: Titrimetric determination of cerium: G GOPALA RAO, P KANTA RAO and S BHANOJEE RAO (4 *December* 1963)

Precipitation of metal 8-hydroxyquinolates from homogeneous solution—VII: Indium and gallium· J P JONES, O E. HILEMAN, JR., A. TOWNSHEND and LOUIS GORDON (9 *December* 1963)

Precipitation of indium 8-hydroxyquinaldate from homogeneous solution: J PAUL JONES, ORVILLE E HILEMAN, JR , and LOUIS GORDON (9 *December* 1963)

Use of "dead stop" indication of the end-point in chelometric titrations: F VYDRA and J VORLICEK. (10 *December* 1963).

The use of a high frequency Tesla discharge tube for the determination of nitrogen and oxygen in helium: P ELMOTT and R E. WILSON. (13 *December* 1963)

Silver^{II} in aqueous perchlorate solutions: GARRY A RECHNITZ and SIDNEY B ZAMOCHNICK (24 *December* 1963)

Absorptiometric study of ammonium aurintricarboxylate as a reagent for palladium^{II}: KAILASH N MUNSHI and ARUN K. DEY (24 *December* 1963)

Colorimetric determination of cobalt^{II} by a specific spot reaction: M H HASHMI, A A AYAZ and ABDUR RASHID. (30 *December* 1963)

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following review published in Talanta are available from Journals Department, Pergamon Press Ltd , Headington Hill Hall, Oxford, England, at 7s or $1 per copy, on a cash with order basis only

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H Firsching

Talanta, 1964, Vol. 11, p. ii. Pergamon Press Ltd Printed in Northern Ireland

PAPERS RECEIVED

Zur Entmischung der Lösungsmittel bei der chromatographischen Trennung-III: Einfluss des Alkohol-Wasser-Verhaltnisses auf den Sorptionsvorgang: Jan Michal und Gerhard Ackermann. (7 *September* 1964)

A method for increasing the reproducibility of chromatographic parameters in thin-layer chromatography: L. S. Bark, R. J. T. Graham and D. McCormick. (8 *September* 1964)

The determination of beryllium by means of hexamminecobalt(III) carbonatoberyllate: R. G. Monk and K. A. Exelby. (8 *September* 1964).

Determination of sulphite and sulphurous acid by permanganate using iodine monochloride: H. G. S. Sengar and Y. K. Gupta. (8 *September* 1964).

New analytical methods based on the principle of quantitative isotope dilution and their application to radioactivation analysis: Nobuo Suzuki. (8 *September* 1964).

A coulometric titrator using potentiometric end-point determination: Gillis Johansson. (9 *September* 1964).

The EDTA titration of iron(III) in the presence of high concentrations of bismuth: H. Flaschka and J. Garrett. (15 *September* 1964).

Tetraethylenepentamine-$N,N,N',N'',N''',N'''',N''''$-hepta-acetic acid as a titrimetric reagent: Rudolf Přibil and Vladimir Veselý. (16 *September* 1964).

Amperometry with two polarisable electrodes-III: Chelometric determination of iron(III) using the indication system of two carbon electrodes: J. Vorlíček and F. Vydra. (21 *September* 1964).

Precipitation of zirconium tetramandelate from homogeneous solution: John C. Rowe, Louis Gordon and William G. Jackson. (22 *September* 1964).

Analytical applications of Solochrome Azurine B.S: New method for the specific detection of copper: Uma Tandon, S. N. Tandon and S. S. Katiyar. (26 *September* 1964).

The reflectance spectra of two solvated uranium 8-hydroxyquinolates: R. J. Magee and Louis Gordon. (26 *September* 1964).

The infrared spectra of chelate compounds-IV: A study of the uranyl chelates of 8-hydroxyquinoline in the region 5000 cm^{-1} to 250 cm^{-1}: R. J. Magee and Louis Gordon. (26 *September* 1964).

Study of zirconium reaction with arsenazo-III by means of zirconium radioactive tracer: P. Pištěk, J. Rais and M. Kyrš. (28 *September* 1964).

Talanta, 1964, Vol. 11, pp. i to iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Monday 8 *February* 1965: **First Toronto Symposium on Thermal Analysis.** Seaway Towers Hotel, Toronto, Ontario.

The programme will include a technical session, instrument exhibit, dinner and an evening panel discussion between speakers and audience. Papers to be presented will be

Experimental practices and considerations in differential thermal analysis.	P. D. Garn
Dynamic thermogravimetry.	A. E. Newkirk
Quantitative information from DTA.	R. L. Bohon
Making decomposition rate measurements on simple inorganic chemical powders by TGA.	T. R. Ingraham
Simultaneous thermal methods.	W. W. Wendlandt
Applications of thermal analysis to the study of polymers.	H. W. Holden
Application of DTA to evaluation and testing of catalysts.	W. M. Keely
Applications of DTA to petroleum chemistry.	L. Weber

Further details and registration forms may be obtained from Dr. H. G. McAdie, Ontario Research Foundation, 43 Queen's Park Cresent East, Toronto 5, Ontario.

DEUTSCHE DEMOKRATISCHE REPUBLIK

Die Unterkommission für Gas-Chromatographie bei der Sektion Chemie der Deutschen Akademie der Wissenschaften zu Berlin (Sekretariat, Leipzig 0 5, Permoserstraße 15) veranstaltet

vom 11. bis 14. *Mai* 1965 in Berlin
das
V. Symposium über Gas-Chromatographie
in der Deutschen Demokratischen Republik

Es sind Vorträge zur Methodik und Theorie der Gas-Chromatographie, zu vielfältigen anwendungstechnischen und zu apparativen Fragen vorgesehen. In den Nebenräumen des Konferenzsaales wird eine Ausstellung mit kommerziellen Geräten und Zubehör für die Gas-Chromatographie gezeigt werden.

FRANCE

Vendredi 15-1-1965: **Les développements récents de l'électrochimie organique,** par M. G. Cauquis, à 17 h 30, à l'Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre Curie, Paris 5^{e}.

UNITED KINGDOM

Friday 8 *January* 1965: **Annual General Meeting** followed by **Editing a Scientific Journal,** J. B. Attrill: *Society for Analytical Chemistry, Western Section.* College of Advanced Technology, Bristol, 6.30 p.m.

Tuesday 19 *January* 1965: Discussion Meeting on **Analysis of Polyester Resins,** C. H. Hughes: *Society for Analytical Chemistry, Midlands Section.* University of Birmingham, Edgbaston, Birmingham 15, 7.00 p.m.

Friday 22 *January* 1965: **Annual General Meeting:** *Society for Analytical Chemistry, Scottish Section. More's Hotel,* Glasgow, 1.45 p.m.

Wednesday 27 *January* 1965: **Discussion Meeting:** *Society for Analytical Chemistry, Microchemical Methods Group. The Feathers,* Tudor Street, London E.C.4, 6.30 p.m.

Saturday 30 *January* 1965: **Annual General Meeting** followed by address of Retiring Chairman, C. J. House: *Society for Analytical Chemistry, North of England Section. Old Nags Head Hotel,* Lloyd Street, Manchester, 2.15 p.m.

At the *Twentieth Annual General Meeting* of the **Special Techniques Group** of the **Society for Analytical Chemistry** held on Tuesday, 24 November, 1964, the following Officers were elected for the forthcoming year:

Chairman: L. Brealey
Vice-Chairman: G. F. Reynolds
Secretary and Treasurer: T. L. Parkinson, Product Research Department, Beecham Food and Drink Division Ltd., Harpenden Rise, Harpenden, Herts.

British Standards Institution has announced the following *New British Standard: B.S. 1747: Methods for the measurement of air pollution: Part 2: 1964: Determination of concentration of suspended matter.* This covers the construction and use of apparatus for the determination of fine suspended particles (smoke) in the atmosphere, both by comparison with an arbitrary standard and by an absolute (weighing) method. (*Price:* 6s.)

UNITED STATES OF AMERICA

Friday-Saturday 22–23 *January* 1965: **Symposium on Hydrocarbon Analysis—Future Development and Applications:** *American Society for Testing and Materials, Committee D-2 on Petroleum Products and Lubricants.* Sheraton-Lincoln Hotel, Houston, Texas.

The following papers will be presented:

Friday Afternoon, 22 January—Where we are and a look ahead

The basis for future developments of hydrocarbon analysis.	S. S. Kurtz, Jr.
Current and future applications of hydrocarbon analysis in quality control.	L. C. Dawson

Potential analytical developments

Mass spectrometric analysis of hydrocarbons.	R. A. Brown and R. F. Stubbeman
NMR analysis of hydrocarbons and related molecules.	J. R. Zimmerman
Absorption spectroscopy of hydrocarbons.	R. L. LeTourneau
Applications of gas chromatography to hydrocarbon analysis.	J. M. Dietz

Saturday Morning, 23 January—Integrated methods approach

Gasoline and blended fuels.	D. M. G. Lawrey
Analysis of kerosine and gas-oil fractions.	R. E. Farrell, A. J. Ehrler, I. M. Nawrocka and N. M. Ingber
Aromatic hydrocarbons in high-boiling fractions.	B. J. Mair
The molecular complex comprising heavy petroleum fractions.	J. G. Erdman

Hydrocarbon and non-hydrocarbon impurities

Trace impurities in hydrocarbons used as raw materials.	R. A. Klett, L. R. Korous, R. W. King and R. W. Warren
Sulphur compounds in petroleum.	C. J. Thompson, H. J. Coleman, R. L. Hopkins and H. T. Hall
Basic nitrogen compounds in petroleum.	D. M. Jewell, R. E. Snyder and J. P. Yevich
Non-basic nitrogen compounds in petroleum.	D. R. Latham, I. Okuno and W. E. Haines
Aspects of linear elution adsorption chromatography for extraneous materials.	L. R. Snyder
Research Division IV of Committee D-2 leadership: Past, present and future	J. F. Hickerson

Further information may be obtained from R. R. Wright, A.S.T.M., 1916 Race Street, Philadelphia, Pa. 19103.

Sunday-Friday 16–21 *May* 1965: **13th Annual Conference on Mass Spectrometry and Allied Topics:** *American Society for Testing and Materials, Committee E-14 on Mass Spectrometry.* Sheraton-Jefferson Hotel, St. Louis, Missouri.

In addition to contributed papers, the Conference will include four one-half day symposia in which invited speakers will discuss particular topics. It is expected that over 100 technical papers will be presented during the five day Conference. The general subjects to be covered by the symposia, together with those individuals responsible for their arrangement, are as follows:

Photoionisation and electron impact phenomena:	V. H. Diebler
Isotope abundance and atomic weights:	A. E. Cameron
High resolution mass spectroscopy in organic analysis:	F. W. Lafferty
Instrumentation developments:	W. M. Brubaker

Contributed papers are solicited in research and development topics pertinent to mass spectrometry and ionisation phenomena. The deadline for submitted abstracts is 15 February, 1965. Contributed papers and correspondence should be sent to Dr. H. M. Rosenstock, National Bureau of Standards, Washington, D.C. 20234.

ERRATA—Volume 11

Page 438: The equations should be numbered (1) and (2) and not (2) and (3).
Page 438: In equation (2) [incorrectly numbered (3)] the term $2OH^{-}$ is unnecessary.
Page 1498, line 2 of the procedure: This should read ..... *peroxytitanate, Add potassium*.......
Page 1550, line 10 from bottom of page: For *silver-III* read *silver*-111.

Talanta, 1964, Vol. 11, p. iii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Structure Elucidation of Natural Products by Mass Spectrometry: Volume 1: Alkaloids: HERBERT BUDZIKIEWICZ, CARL DJERASSI and DUDLEY H. WILLIAMS. Holden-Day, Inc., San Francisco, U.S.A., 1964. Pp. xi + 233, $10.50.

Introduction: Deuterium labelling: Simple indole alkaloids: Iboga and voacanga alkaloids: Tetrahydro-β-carboline alkaloids: Eburnamine and related indole alkaloids: Aspidospermine and related alkaloids: Akuammicine and related alkaloids: Oxindole and pseudoindoxyl alkaloids: Physostigmine and related alkaloids: Isoquinoline alkaloids: Emetine and related alkaloids: Colchicine and related alkaloids: Lycopodium alkaloids: Quinazolone and purine alkaloids: Miscellaneous classes of alkaloids: Index.

Water and Solute-Water Interactions: J. LEE KAVANAU. Holden-Day, Inc., San Francisco, U.S.A., 1964. Pp. 101, $5.50.

The structure of ice. The "vacant-lattice-point" model: The "flickering-cluster" model: The "water-hydrate" model: The "distorted-bond" model: Liquid deuterium oxide.

Alteration of liquid-water parameters. Frank-Evans icebergs: Soft ice: Ion-dipole oriented water; Hydrogen-bonded and dipole-dipole oriented water: Proton mobility: Mobility of protons in water and ice: Mobility of protons relative to binding sites: The effects of ions on water structure; The ion-water interaction; Shortcomings of electrostatic models and recent alternative considerations; Consequence for proton exchanges.

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Author and subject indexes.

Bibliography No. 7: Spectroscopy and Spectrophotometry. The Documentation and Supply Centre of Robert Maxwell and Co. Ltd., Oxford, England: The Documentation and Procurement Center, Manwell Scientific International Inc., Long Island City 1, N.Y., U.S.A., 1964, pp. 15 + ii. Available free-of-charge.

An international Bibliography of Spectroscopy and Spectrometry, including spectral analysis, spectrochemistry, but excluding spectral theory. Period covered 1960–1963. 131 entries.

Selected References to Tracer Techniques: The Radiochemical Centre, Amersham, Buckinghamshire, England, 1964, pp. 12, free on application.

General Texts (11): Labelled Compounds—Preparation (23): Applications of Tracers (30): Measurement; General (25); Scintillation counting (40); Gas counters and ion chambers (12); Photographic methods (8): Safety Precautions (16).

American Society for Testing and Materials has announced that the following publications in the field of spectroscopy are now available:
First Supplement to the Molecular Formula List of Compounds, Names and References to Published Infrared Spectra: STP 331-A (Price $4.50; $3.15 to ASTM members).
Index of Mass Spectral Data: STP 356 (Price $18.50; $13.00 to ASTM members).
Molecular Formula List of Compound Names and References to Published Ultraviolet and Visible Spectra: STP 357 (Price $6.00; $4.20 to ASTM members).
Serial Number List of Compound Names and References to Published Infrared Spectra: STP 358 (Price $12.00; $8.40 to ASTM members).

Copies may be obtained from ASTM, 1916 Race Street, Philadelphia, Pa.

ERRATUM—Volume 11

Page 2, *line* 7: this should read *Methods have previously been described . . .*

Page 16, *line* 2 *above formula* XIX: this should read *In order to study the formation of complexes by arsenazo . . . .*

Page 18, *line* 4 *of Synthesis:* this should read *excess of nitrous acid . . .*

Page 5, *insert after Zusammenfassung*

Résumé—L'utilité analytique particulière de l'Arsenazo-III est due à sa capacité de former des complexes spécialement stables avec certains elements. Ceci permet le dosage en milieu acide fort (HCl, 10 M ou SO_4H_2) des éléments penta- ou quadrivalents: Pa, Np^{IV}, Th, Zr, Hf, U^{IV}; la reproductibilité est bonne, la manipulation facile et l'on ne note que de petites interférences dûes aux anions. La grande sensibilité (0,1–0,01 μg/ml, coefficient d'absorption molaire 50–150 × 10^3) est due au grand effet de contraste de la réaction (changement de coloration durose au vert émeraude, déplacement du maximum d'absorption de 125 mμ), nature de spectre, et enfin possibilité d'atteindre des dilutions extremes sans dissociation des complexes.

Page 41, *insert after Zusammenfassung*

Résumé—Les mélanges formés d'orthophosphate, de ses polymères linéaires supérieurs jusqu'au tridécaphosphate compris et trois polymères cycliques ont pu être séparés par chromatographie d'échange ionique. L'un des polymères cycliques (recontré dans les verres de polyphosphate . . . est probablement le pentamétaphosphate. Sa nature cyclique a été démontrée par dosage des groupes terminaux et chromatographie sur papier, mais les tentatives de dénombrement des atomes de phosphore du noyau ont échouées à cause de la très faible quantité de produit disponible. Évidence est presentée a l'appui de la supposition courante que les phosphates linéaires supérieurs sont élués suivant leur degré de polymérisation.

Page 46, *insert after Zusammenfassung*

Résumé—Une méthode pour le dosage des trimétaphosphates en présence d'oligophosphates linéaires supérieurs au trimère est developpée. Il a été démontré que l'ortho-, lt pyro-, at le triphosphate ne sent pas complètement précipitéspar l'ion baryum, tandis que les phosphates oligomères linéaires de type supérieur sont précipités quantitativement. Ces derniers sont isolés des mélanges de phosphates par chromatographie d'échange d'anions, mélangés avec des quantités connues de phosphates cycliques, at précipités par l'ion baryum. Une erreur moyenne de +0,8 et un écart standard de ±3 micromoles de phosphore de l'ion cyclique a été mise en évidence dans les mélanges contenant de 0 à 203 micromoles de phosphore sous forme de trimétaphosphate en présence de 0 à 81 micromoles de phosphare sous forme de polymères linéaires,

Page 49, *line* 1: this should read *using barium diphenylamine . . .*

Page 57, *line* 1: this should read *between ammonium ion and chloramine-T . . .*

Page 57, *insert after Zusammenfassung*

Résumé—La chloramine-T oxyde quantitativement la thiourée en urée et l'ion sulfate en milieu neutre et en milieu basique. L'oxydation est totale en 2 minutes même en présence d'un léger excès d'oxydant. L'uree et l'ion ammonium ne sont pas gênants si l'oxydation est effectuée en milieu alcalin.

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Frontal solubilisation chromatography: HARVEY D. SPITZ, HERBERT L. ROTHBART and WM. RIEMAN III. (8 *October* 1964)

Simultaneous colorimetric determination of thallium^{III} and thallium^{V}: M. H. HASHMI, ABDUR RASHID, HAMID AHMAD and A. A. AYAZ. (14 *October* 1964)

Polarographic study of the uranyl-pyrophosphate complex in the presence of various surface-active substances: TSAI-TEH LAI and SONG-JEY WEY. (16 *October* 1964)

Contributions to the basic problems of complexometry-XVIII: Masking of iron with fluoride: R. PŘIBIL and V. VESELÝ. (16 *October* 1964)

Synthesis of nitrosotirone and the use of some of its colour reactions in analytical chemistry: M. BERAN and S. HAVELKA. (16 *October* 1964)

Photometric determination of niobium with 4-(2-thiazolylazo)resorcinol: VĚNCESLAV PATROVSKÝ. (16 *October* 1964)

The determination of sulphate with barium chloranilate: J. E. BARNEY II. (16 *October* 1964)

Applications of nuclear and electron magnetic resonance in analytical chemistry: A review: B. D. FLOCKHART and R. C. PINK. (19 *October* 1964)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium-IV: Titrimetric determination of vanadium^{IV} and cerium^{III} alone and in mixtures of iron^{II} with photometric end-points: G. GOPALA RAO and P. KANTA RAO. (19 *October* 1964)

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Determination of potassium by a titrimetric method: TADASHI IWACHIDO. (27 *October* 1964)

Chelating resins—their analytical properties and applications: A review: G. SCHMUCKLER. (28 *October* 1964)

Amperometrische Bestimmungsmethode des Thioacetamid (TTA): MARIA PRYSZCZEWSKA. (30 *October* 1964)

Investigation of the behaviour of molybdenum(VI) in formic acid solutions of ion-exchange resins: D. A. SHISHKOV and E. G. KOLEVA. (4 *November* 1964)

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Investigation of the cation-exchange behaviour of molybdenum(VI) in hydrochloric alcohol solutions: D. A. SHISHKOV and L. G. SHISHKOVA. (4 *November* 1964)

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"**Recent Developments in the Ring Oven Technique**" by H. Weisz.

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"**Radiometric Titrations**" by T. Braun and J. Tölgyessy.

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Application of the measurement of thermoelectric tension in chemical analysis—I: Determination of silicon in cast iron: A. Krajina and J. Dolezal. (19 *December* 1963)

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Correction for the separation of hydrogen isotopes during distillation in the determination of tritium: C. J. Riley and H. Brooks. (2 *January* 1964).

A new spot test for titanium with resacetophenone-oxime: S. G. Kadarmandalgi. (2 *January* 1964).

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Theorie und Praxis der gravimetrischen Analyse: László Erdey. Band I, Theoretischer Teil, S. 382, \$9.00: Band II, Bestimmung der Kationen, S. 802, \$18.00: Band III, Bestimmung der Anionen, S. 340, \$13.00. Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences), Budapest, V, Alkotmány utca 21, Hungary, 1964.

Band I: Einleitung: Qualitative und quantitative Analyse; Die Bedeutung der quantitativen Analyse; Die Eigenart der quantitativen Analyse; Methoden der quantitativen Analyse; Die Menge der analytischen Probe; Das Ziel einer wissenschaftlichen Analyse; Das Ziel der technischen Analysen; Verfahren der Gewichtsanalyse; Fällungsverfahren der Gewichtsanalyse.

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Tabellen (Löslichkeitsprodukte der wichtigeren analytischen Niederschläge bei Zimmertemperatur; Stöchiometrische Facktoren; Gekürtze Fünfstellige Logarithmentafel: Interpolationsdiagramm).

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The Determination of Sterols: Society for Analytical Chemistry Monograph No. 2. The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1, 1964, pp. 72, 15s: \$2.00.

Six papers originally presented at a Meeting of the Society held on May 2nd 1962.

G. S. Boyd: Determination of cholesterol for clinical purposes. J. Glover: Determination of cholesterol and 7-dehydrosterols. C. J. W. Brooks: Gas-chromatographic examination of sterols. J. H. Recourt and R. K. Beerthus: The detection of animal fats in vegetable fats by gas-chromatographic analysis. W. E. Davies, T. W. Goodwin and E. I. Mercer: The identification and determination of plant sterols. E. V. Truter and B. Bush: Determination of sterols (of wool wax) by the Liebermann-Burchardt reaction. Discussion.

Monday 30 *November–Friday* 4 *December* 1964: **Short Course on Gas Chromatography:** *Instrument Society of America.* Carnegie Institute of Technology, Pittsburgh, Pa. (see *Talanta*, 1964, **11,** August iii).

New standard samples for four groups of copper-base alloys have been issued by the **National Bureau of Standards Institute for Materials Research.** Several samples, which vary in composition, are available for each of the alloys—free-cutting brass, gilding metal, commercial bronze and aluminium brass. These standards have been prepared primarily for optical-emission and X-ray spectrochemical analysis calibrations and are in a form convenient for such use.

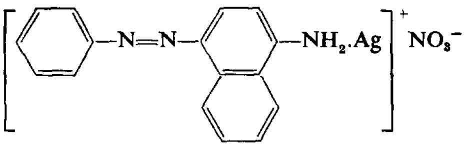
American Society for Testing and Materials has compiled the *Wyandotte-ASTM Punched Card Index* for finding and correlating infrared spectral absorption data using programmed tapes for computers. These tapes are used in connection with the Codes and Instructions for the Wyandotte-ASTM Punched Card System. This system facilitates the sorting of spectral data in matching spectrograms in qualitative analysis. Further information is available from Dr. L. E. KUENTZEL, ASTM, 1916 Race Street, Philadelphia, Pa. 19103.

American Society for Testing and Materials has announced the availability of the following publication:

ASTM Standards for Industrial Water and Atmospheric Analysis: Part 23 *of* 1964 *Book of ASTM Standards* (*Price* $13.00; $9.10 *to ASTM members*). This contains 98 standards of which 58 are new or have been revised since the publication of the 1960 edition of *Manual on Industrial Water-D*-19, which it replaces. The contents include industrial water—sampling and analytical methods, corrostests, methods of reporting; atmospheric analysis.

ERRATA—Volume 11

Page 1098: The structural formula for compound III should be



Page 1121: The title should read *Colorimetric determination of cobalt*[11]
Page 1136, Table I: the second entry in the last column should read 0·511 *MeV*
Page 1137, Table II: The entries in the third column should read 0·511 *MeV* and 1·04 *MeV*
Page 1177: This paper should read *Eingegangen am* 15. *Februar* 1964
Page 1200, Table III: The heading to the fifth column should read *Found,* 0·05*M*, *ml*
Page 1203: This paper should read *Received* 10 *February* 1964
Page 1239: This paper should read *Received* 18 *March* 1964
Page 1249: This paper should read *Received* 9 *April* 1964
Page 1275: This letter should be dated 26 *March* 1964
Page 1284, Fig. 5: This should read $\gamma_0 = 0{\cdot}06$, etc.
Page 1313, line 4 of Experimental: This should read 1,2-*diaminocyclohexanetetra-*
Page 1314, line 2 of *Apparatus:* This should read *photoelectric attachment*
Page 1314, line 8 under Results and Discussion: This should read *a molar ratio of* 1:1, *V*:(*XO*),
Page 1325, second footnote to page: Delete *Preparation:*
Page 1329: This should read *Table I*
Page 1350, line 14 of Results and Discussion: This should read *measured in* 1-*ml cells*
Page 1355, reference 6: The journal should read simply *Japan Analyst*
Page 1366, line 3 above *Procedure:* This should read (1 *ml* ≡ 100 *μg of cadmium*)
Page 1367, line 7 from bottom of page: This should read *chromium*(*VI*), *remaining after volatilisation, to chromium*(*III*)
Page 1377, line 2 under *Calculations:* This should read 6–7 *MeV*

Talanta, 1964, Vol. 11, p. v. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Direct titrimetric determination of iron with disodium cyclohexanediamine tetra-acetate: L. W. Marple, (2 *April* 1964).

Extraction and spectrophotometric determination of microamounts of aluminium, chromium, copper, iron, manganese, molybdenum and nickel in pure water: Use of 8-hydroxyquinaldine and dimethylglyoxime as reagents: Kenji Motojima znd Nasumi Ishiwatari. (3 *April* 1964).

Determination of scandium, yttrium, samarium and lanthanium in standard silicate rocks G-1 and W-1 by neutron-activation analysis: H. B. Desai, R. Krishnamoorthy Iyer and M. Sankar Das. (9 *April* 1964).

The determination of phosphate in the presence of calcium by the vanadomolybdate method: M. L. Richardson. (9 *April* 1964).

Successive determination of thorium and rare earths by complexometric titrations: Asim K. Gupta and Jack E. Powell. (10 *April* 1964).

Ammonium hexanitratocerate(IV) as an oxidising agent-IV: Titration of hydrazine and isonicotinic acid hydrazide at room temperature: G. Gopala Rao and P. V. Krishna Rao. (13 *April* 1964).

A study of the oxidation of manganese(II) and chromium(III) ions by silver(II) oxide: C. P. Lloyd and W. F. Pickering. (14 *April* 1964).

Some problems in the analysis of gaseous decomposition products: Pauz D. Garn. (15 *April* 1964).

Miniature magnetic stirring motor for student or analytical-control laboratories: G. Frederick Smith and A. H. Smith. (17 *April* 1964).

Ultraviolet spectra of piaselenol derivatives: Masako Toto and Kyoji Toei. (17 *April* 1964).

Mesityl oxide as an extracting agent: S. M. Khopkar. (21 *April* 1964).

Spectrophotometric determination of small amounts of tellurium with diphenylthiourea: H. Yoshida and S. Hikime. (22 *April* 1964).

An examination of the atomic absorption spectroscopy of silver: R. Belcher, R. M. Dagnall and T. S. West. (22 *April* 1964).

Systematic titration errors I: General considerations and neutralisation titrations: U. A. Th. Brinkman. (24 *April* 1964).

Rapid iodometric determination of copper in alloys with tin, antimony and other metals: J. Agterdenbos. (28 *April* 1964).

The preparation of ceric hydroxide from ammonium hexa-nitratocerate (IV) by employing kinetically controlled precipitation through urea dissociation: G. Frederick Smith. (28 *April* 1964).

Separation of bismuth from lead, copper and other elements by means of anion exchange: F. Feik and J. Korkisch. (30 *April* 1964).

A Spectrophotometric study of the complexes formed between uranyl and oxalate ions in water and water-dioxan solvents: Carz L. Griffis, Nirmal K. Shastri and Edward S. Amis. (1 *May* 1964).

A thermogravimetric pyrolysis study of the interaction of di(1,2,3-benzotriazolatium) hexacyanoosamat (IV) with certain organic amines: Ray F. Wilson and Phillip Merchant, Jr. (5 *May* 1964).

Extraction and spectrophotometric determination of rhenium(VIII) with 2-thenoyltrifluoroacetone: Anil K. De and M. Syedur Rahaman. (6 *May* 1964).

Use of masking agents in chelatometric titrations-IV: Dimercaptosuccinic acid: Tôru Mekada, Kôichi Yamaguchi and Keihei Ueno. (6 *May* 1964).

ERRATA

Page 105, line 18 of Summary: this should read *Cerfak* [*sodium naphthalene.*
Page 105, line 6 from bottom of page: this should read [*sodium naphthalene.*
Page 271, line 4 of Summary: this should read
by the equations $\log k = -11{\cdot}372 + 0{\cdot}0128t$ and $\gamma = 45{\cdot}5 - 0{\cdot}182t$.
Page 288, line 1: this should read $\bar{X} = \Sigma X_i/n$.
Page 288, line 2: should read *standard error of* $Y_i = \log K_{H_i}$.
Page 290, Fig. 4: this should read ◑ – K_D in D_2O.
Page 292, line 4: this should read *than for* D_2O.
Page 292, line 10: this should read *than for* H_2O,[13].
Page 292, line 23: for *liberation* read *libration.*
Page 292, line 25: for *liberational* read *librational.*
Page 340, Table III: the units in the headings to columns 6, 7 and 8 should read *V* and not *v*.

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:

A. I. Busev	N. Tanaka
L. B. Rogers	D. W. Wilson

Also, they would like to record their sincere thanks for the help given by

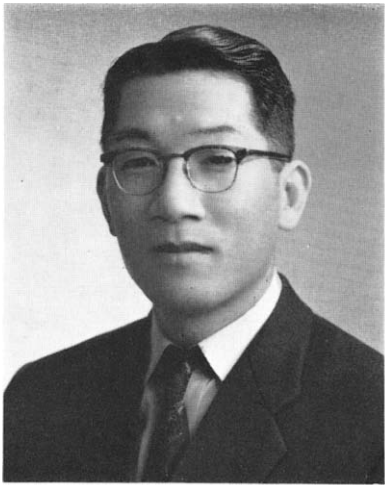
C. E. Crouthamel

who retires from the Advisory Board.

Aleksei Ivanovich Busev (U.S.S.R.) was born in 1919. He defended a thesis for the degree of Candidate in Chemistry in 1946 and a thesis for the degree of Doctor in Chemistry in 1952. From 1953 to 1955 he worked as Lecturer and subsequently as Professor in the Chair of Analytical Chemistry, M.V. Lomonosov State University, Moscow. Since 1953 he has been a member of the Commission on Analytical Chemistry of the Academy of Sciences of the U.S.S.R. Professor Busev's most important work has been on organic analytical reagents and the analytical chemistry of the rarer metals. He has published a number of monographs on these metals.

Born in 1917, LOCKHART B. ROGERS (U.S.A.) studied at Wesleyan University for his B.A. (1939) and Princeton University for his Ph.D. (1942). Thereafter he held various positions before moving to Massachusetts Institute of Technology in 1948. In 1961 he was appointed Professor and Head of the Analytical Chemistry Division at Purdue University. He is a past Secretary-Treasurer and past Chairman of the Division of Analytical Chemistry of the American Chemical Society. His main research interests are in analytical separations (electroanalytical, gas chromatographic) and trace analysis (polarography, coulometry and fluorimetry).

NOBUYUKI TANAKA (Japan) was born in 1920 and educated at University of Tokyo, where he received his B.S. (1941). He was appointed Assistant Professor at University of Tokyo in 1947 and obtained his Dr.S. there in 1948. From 1952 to 1954 he worked as a Research Fellow with Professor I. M. Kolthoff at University of Minnesota (U.S.A.). Since 1955 he has been Professor of the Department of Chemistry at Tohoku University, Sendai. His fields of research include co-ordination chemistry, electrode kinetics and electroanalytical chemistry.



DAVID W. WILSON (U.K.) graduated at Queen's University of Belfast, and obtained his M.Sc. there, having been on the Lecturing Staff for a short time before World War II. After a period in the Armaments Research Department of the Ministry of Supply, followed by a year on the Staff of the Northampton Polytechnic in London, he moved to Sir John Cass College where he eventually became Head of the Chemistry Department in 1962. He is associated with his brother, the Editor-in-Chief of TALANTA, as joint editor of the multi-volume work *Comprehensive Analytical Chemistry*. He is closely connected with the Society for Analytical Chemistry, being a past Secretary and now Chairman of its Microchemistry Group, and also an Assistant Secretary of the Society.

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"**Precipitation of Metal Chelates from Homogeneous Solution**" by F. H. Firsching.

"**Recent Developments in the Ring Oven Technique**" by H. Weisz.

"**Absorption Indicators in Precipitation Titrations**" by R. C. Mehrotra and K. N. Tandon.

"**Radiometric Titrations**" by T. Braun and J. Tölgyessy.

"**Recent Uses of Liquid Ion Exchanges in Inorganic Analysis**" by H. Green.

Talanta, 1964, Vol. 11, p. vi. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Analysis of ores containing lead, copper and zinc by anion-exchange chromatography and complexometry: D. Sen Gupta and R. N. Sen Sarma. (7 *August* 1964)

Remote simultaneous titration of free acid and metal ions in irradiated fuel re-processing solutions: H. H. Ph. Moeken, H. Keese and W. Heinz. (10 *August* 1964)

The methoxyl content of *Acacia* gum exudates: D. M. W. Anderson, G. M. Cree, M. A. Herbich, K. A. Karmalla and J. F. Stoddart. (10 *August* 1964)

Precipitation of copper 8-hydroxyquinaldate from homogeneous solution: R. P. Graham, E. J. Billo and J. A. Thomson. (14 *August* 1964)

Selektive Trennung von Selen(IV) durch Extraktion mit Methyläthylketon: N. Jordanov und L. Futekov. (17 *August* 1964)

Spectrophotometric investigation of the nature and stability of silver(II) in acidic sulphate media: G. A. Rechnitz and S. B. Zamochnick. (17 *August* 1964)

Applications of precipitate membranes in analytical chemistry: T. Braun and J. Tölgyessy. (18 *August* 1964)

Complexes of 3-methylgalangin with uranyl and thorium ions: Mohan Katyal and R. P. Singh. (19 *August* 1964)

Theoretical considerations in the zone melting of organic substances: Paul J. Jannke and Robert Friedenberg. (21 *August* 1964)

Selective retention of alkali metals on cation-exchange resin: Rapid separation of alkali metals from other metals: Eugene D. Olsen and Harold R. Sobel. (17 *August* 1964)

Relation between the shapes of titration curves of a dibasic acid and of a mixture of two monobasic acids with equal concentrations: A. A. Bugaevsky. (22 *August* 1964)

Spectrophotometric study of the iron(III) reaction with 3,5-di-iodine-salicylic acid and its utilisation in iron determination: I. C. Ciurea, Gr. Popa and C. Lazar. (1 *September* 1964)

Selective spot tests for glyoxal, pyruvic and lactic acid: F. Feigl and S. Yariv. (2 *September* 1964)

Application of steady-state controlled-potential coulometry to the study of homogeneous solution reactions: G. A. Rechnitz and J. E. McClure. (2 *September* 1964)

Eine Analysemethode des nichtwassrigen Medium: Die Bestimmung von aromatischen Aminen: László Légrâdi. (2 *September* 1964)

Talanta, 1964, Vol. 11, p. vi. Pergamon Press Ltd.

PAPERS RECEIVED

Radiometric titrations—I: Automatic titrimeter for titrations based on precipitate formation: J. Tölgyessy, V. Jeszenák, T. Braun and M. Hradil. (4 *March* 1964)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—V: Potentiometric determination of uranium^{VI}: Reduction with excess of iron^{II} in a strong phosphoric acid medium and titration with potassium dichromate: G. Gopala Rao, P. Kanta Rao and M. A. Rahman. (10 *March* 1964).

Determination of rare earths by neutron activation with the aid of ion-exchange chromatography: Analysis of spectrally pure erbium oxide: Jerzy Minczewski and Rajmund Dybczynski. (14 *March* 1964)

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"Deionized" or "deioned": Rudolph Alexander Geitz. (26 *March* 1964)

Extraction and spectrophotometric determination of micro amounts of aluminium, chromium, copper, iron, manganese, molybdenum and nickel in pure water: Use of 8-quinolinol, 8-hydroxyquinaldine and dimethylglyoxime as reagents: Kenji Motojima and Masumi Ishiwatari. (3 *April* 1964)

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Talanta, 1964, Vol. 11, pp. vii to viii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Chromatographie Symposium II, 1962: Société Belge des Sciences Pharmaceutiques, Rue Archimède, 11, Bruxelles 4, Belgium. 1963, pp. 310. 150 B.F.

Papers presented at the Second Symposium on Chromatography, held in Brussels 14–15 September, 1962 by the Belgian Society of Pharmaceutical Sciences.

Conferences: Chromatographie sur papier et en couche mince des alcaloïdes et des flavonoïdes: Récentes acquisitions sur l'identification chromatographique des oses et oligosaccharides: Polyamidchromatographie: Gas-liquid chromatography: a compact gas-radio chromatogram.

Communications: Les procédés d'étude de la structure des glycoprotéides: Sur la séparation chromatographique sur papier des ions; magnésium, calcium, sodium et potassium; applications aux eaux minérales: Dünnschicht-verteilungschromatographie der Plastidenpigmente: Concernant la séparation des amino-acides par chromatographie en phase gazense: Chromatographie des acides désoxyribonucléiques sur papier de diéthylaminoéthyl-cellulose: Chromatography and electrochromatography of gastric and duodenal extracts: The detection of lipoproteins after electrochromatography: Étude chromatographique de dérivés substitués du lysozyme: Étude comparative des hémoglobines humaine, de lapin et de poule: Fractionnement des protéines soluble du jaune d'oeuf de poule: Dünnschichtchromatographie von Tricarbonsäurezyklus-substraten mit Autoradiographie: Radiochromatographie sur Dowex des acides aminés iodés du sérum: Chromatographic separation of the components of staphylomycin: Considérations sur l'analyse chromatographique des sulphamides: Papierchromatographische Trennung der gebraüchlichen Kationen: Chromatography of Doriden (α-phenyl-α-ethyl glutarimide) in postmortem material on coated glass sheets: Die Dünnschicht-Chromatographie als Analysenmethode zur Untersuchung lipophiler sekundärer Pflanzeninhaltsstoffe unter besonderer Berücksichtigung der Harze und Balsame: Récherches chromatographiques sur les acides aminés libres des vins naturels: Chromatographie de flavonoïdes sur échangeurs d'ions: Dünnschichtchromatographie von Phosphatiden, Glykolipiden und Ubicenonen: Chromatographie sur verre sablé et muni de couches minces: Utilisation de la poudre de verre en chromatographie sur couche mince: The Unikit: an apparatus and Manual for the teaching of chromatography and electrophoresis on paper: The adsorption system in column and thin-layer chromatography; recent results: Les applications de l'automation à la séparaton chromatographique et au dosage des acides aminés, peptides et protéines: Spectrofluorimetric identification of chromatographically separated plastid pigments: Les cétoses de l'urine: Chromatographie des protéines urinaires: Fractionnement chromatographique des hétérosaccharides du colostrum humain: The biosynthesis of unsaturated fatty acids in plant systems: Dünnschichtchromatographie von Phloroglucinbutanonen:

Immunochemistry: Vol. I, No. 1, April 1964. Regional Editors: Dan H. Campbell, Alain Bussard, Henri Isliker, Fred Karush. Pergamon Press, Oxford, London, New York, Paris, quarterly, pp. 63. Annual subscription rates: (A) For libraries, government establishments, research institutions, *etc.*, £15 ($40.00): (B) For individuals who place their orders directly with the publisher and certify that the Journal is for their personal use, £5 ($15.00).

J. F. Gerstein, L. Levine and H. Van Vunakis: Altered antigenicity of pepsinogen and pepsin as an index of conformational change: effect of urea and reducing agents. S. J. Singer: On the heterogeneity of anti-hapten antibodies. M. Eichlin, M. Hoy and L. Levine: Antibodies to human A_1 hemoglobin and their reaction with A_2, S, C, and H hemoglobins. J. L. Groff and F. Haurowitz: Comparison of the peptide maps of antibodies against an acidic and basic determinant group. P. J. Lachmann and C. B. Richards: Some molecular parameters of borine conglutinin. L. Gyenes and A. H. Sehon: The use of toly-lene-2,4-diisocyanate as a coupling reagent in the passive hemagglutination reaction. F. Franěk and I. Řiha: Purification and structural characterization of 5 S γ-globulin in new-born pigs.

Application of Distillation Techniques to Radiochemical Separations: James R. DeVoe, National Academy of Sciences, National Research Council, Nuclear Science Series, Radiochemical Techniques. NAS-NS 3108, Aug., 1962. Pp. 29, $0.50. (Available from the Office of Technical Services, Department of Commerce, Washington, 25, D.C., U.S.A.)

Introduction: The Distillation Process for Radiochemical Separations: Radiochemical Distillation Procedures; Hydrogen; Rare Gases; Carbon, Nitrogen and Oxygen; Halogens; Alkali Metals; Silicon; Phosphorus; Sulfur; Alkaline Earths, Rare Earths and Yttrium; Vanadium; Chromium; Manganese; Germanium, Arsenic, Antimony and Tin; Selenium and Tellurium; Ruthenium, Osmium, Technetium, Rhenium; Rhodium and Silver; Cadmium; Indium; Gold; Mercury; Lead; Bismuth; Polonium; Astatine; Uranium: References (66).

Interpretation of Mass Spectra of Organic Compounds: HERBERT BUDZIKIEWICZ, CARL DJERASSI and DUDLEY H. WILLIAMS. Holden-Day, Inc., San Francisco, U.S.A., pp. xiii + 271, 1964, $8.75.
Aliphatic and monocyclic carbonyl compounds: Alcohols: Ethers, thioethers and mercaptans: Amines and amides: Cyclic amines: Aliphatic cyanides and isothiocyanates: Alkyl halides: Bicyclic ketones: Aromatic hydrocarbons and functional derivatives: Tropones and tropolones: Aromatic heterocyclics: Index.

Controlled Potential Analysis: GARRY A. RECHNITZ. International Series of Monographs on Analytical Chemistry, Volume 13. Pergamon Press. Ltd., Oxford, London, New York, 1963, pp. 85, 35s.
Introduction: Theory: Apparatus and Techniques: Analytical Applications: Author Index: Subject Index.

Titrimetric Organic Analysis, Part I: Direct Methods. M. R. F. ASHWORTH. (Chemical Analysis, Volume 15, Editors, P. J. ELVING and I. M. KOLTHOFF.) Interscience Publishers (John Wiley and Sons) New York, London, Sydney, Pp. xx + 501, 132s.
Introduction: *Section* 1; Titration Procedure; Physical properties and measurements in end-point determination: (A) Light absorption, (B) Electrical properties, (C) Temperature, (D) Other physical properties; Automatic titration; Reactions used in the direct titration of organic compounds; Examples of direct titration of organic compounds: *Section* 2; Reagents (117 categories) used in direct titration of organic compounds: *Section* 3; Index to functional groups and compound classes (105 entries): Indexes.

Handbuch der Kolorimetrie, Band II: Kolorimetrie in der Pharmazie: BOHUMIL KAKÀČ and ZDENĚK J. VEJDĚLEK. Übersetz von E. HACHOVÁ. VEB Gustav Fischer Verlag, Jena, DDR., 1963, pp. xv + 1128, £7 1s. 0d.
I. Synthetische Verbindungen: *Acyclische Verbindungen*; Kohlenwasserstoffe und Derivate, Oxyverbindungen, Oxoverbingungen, Säuren und ihre Funktionsderivate, Amine, Aminoalkohole: *Isocyclische Verbindungen*; Oxyverbindungen, Oxoverbindungen, Säuren und ihre Funktionsderivate, Sulfonsäuren und ihre Funktionsderivate, Amine, C-As und C-Hg-Verbindungen: *Heterocyclische Verbindungen*; 10, 1N, 2N, 3 und mehr N, 10(S) + 1N, 10(S) + 2N.
II. Organopräparate
III. Steroïde
IV. Einige anorganische anionen.
Monographienverzeichniss (1 S.): Autorenregister (41 S.): Synonymregister (34 S.): Sachregister (48 S).

Radioactive Isotope Dilution Analysis: The Radiochemical Centre, Amersham, Buckinghamshire, England, 1964, pp. 12, free on application.
Introduction: Laboratory and material requirements: Principle: Developments in dilution analysis; derivative dilution; saturation analysis: Inorganic applications: Conclusion: References (25).

Practical Optical Crystallography: N. H. HARTSHORNE and A. STUART. Edward Arnold (Publishers) Ltd., London, England, 1964, pp. vii + 326, 40s.
The morphology of crystals: The optical properties of crystals: The polarising microscope: The microscopic examination of crystals; A. Orthoscopic observations ("parallel" light); B. Conoscopic observations ("convergent" light): The stereographic projection: Preparation, mounting and manipulation of material: Determining optical crystallographic properties; some practical examples: Appendix I; Books recommended for further reading: Appendix II; Tables and collection of optical crystallographic data: Appendix III; Sources of certain material mentioned in the text: Index: Folding chart; nomogram for determination of refractive indices.

Talanta, 1964, Vol. 11, p. x. Pergamon Press Ltd. Printed in Northern Ireland

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A review of recent uses of liquid ion exchangers in inorganic analysis: H. GREEN. (27 *June* 1964).

Coprecipitation kinetics—I: Coprecipitation of lead with barium sulphate; DAVID H. KLEIN and BERNARDO FONTAL. (6 *July* 1964).

5,5′-Thiodisalicyclic acid as an analytical reagent: MARY L. GOOD and SURESH C. SRIVASTAVA. (16 *July* 1964).

Reaction of boric acid with pyrocatecholphthalein: VENCESLAV PATROVSKY. (20 *July* 1964).

The determination of copper in sea water by atomic-absorption spectroscopy: ROBERT J. MAGEE and A. K. MATIOR RAHMAN. (21 *July* 1964).

An investigation of complex formation reactions and their analytical applicability—I: Evaluation of constants of equilibria involved in sparingly soluble complex formation: A. DUTTA AHMED. (22 *July* 1964).

Precipitation of zinc sulphide from ammoniacal solutions by thioacetamide: DAVID H. KLEIN and ERNEST H. SWIFT. (23 *July* 1964).

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Jodgravimetrische Methoden in der organischen Elementaranalyse—I: Ein neues Reagenz zur quantitativen Umsetzung von Chlor und Brom in Jod im Verbrennungsrohr: E. KOZLOWSKI. (5 *August* 1964).

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Talanta, 1964, Vol. 11, p. x. Pergamon Press Ltd. Printed in Northern Ireland

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Spectrophotometric determination of fluorine in silicate rocks: LEE C. PECK and VERTIE C. SMITH. (4 *May* 1964).

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Nucleation and precipitation of silver chloride solutions: C. E. MELLISH. (14 *May* 1964).

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The accuracy of copper determinations by atomic absorption methods: H. KHALIFA, L. ERDEY and G. SVEHLA. (19 *May* 1964).

The determination of titanium, tantalum and niobium by precipitation from homogeneous solution: R. DAMS and J. HOSTE. (23 *May* 1964).

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Colour reagents for the spectrophotometric determination of rare earth elements in the presence of traces of thorium: SHIGERU KATSUMATA. (4 *June* 1964).

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ERRATUM—Volume 11

Page 7, line 2 from bottom: for *TR* read *rare earths*
Page 295, line 1 of Summary: this should read *Equilibrium constants of the principal reactions*
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Page 295, line 3 of Reagents: this should read *photometrically at 520* $m\mu$, *was*
Page 297, line 5: this should read *cyanide-ammonium sulphite mixture*
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Page 299, equation (4c): this should read

$$k_3 = \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]}$$

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$$\Sigma[Pb] = [Pb^{2+}] + [PbOH^+] + \ldots . [PbHDz^+] + \ldots [PbX^+] + \ldots$$

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Page 302, line 16: for *nitrate* read *citrate*
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$$[Pb^{2+}][HDz^-]^2 = 3 \times 10^{-4} \times 7 \times 10^{-16} = 2 \times 10^{-24}$$

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Page 306, line 11: for *electrode* read *glass electrode*
Page 306, line 2 above Fig. 5: for *Fig. 4* read *Fig. 5*
Page 311, Fig. 8: this should read

□—*Reversion method*: *10 ml of aqueous phase*

Page 312, equation in mid-page: this should read

$$[Pb(HDz)_2]_0 = \frac{(\Sigma[Pb] - \Sigma[S] \pm \{(\Sigma[Pb] - \Sigma[S])^2 + 4 \times 5{\cdot}6 \times 10^{-5}[H_2Hz]_0^{\,2}\}^{1/2}}{2}$$

Page 313, line 1: for *Proctor* read *Procter*
Page 313, reference 2: for *S. Vallenga* read *S. Vellenga*
Page 421, line 21: for *molydbenum* read *molybdenum*
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Page 474, line 9 from bottom: for *0·2 ml of arsenious acid* read *2·0 ml of arsenious acid*
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Page 475, line 9: this should read . . . . . *for amines Nos. 1, 5, 6, 7 and 10* (*Table III*)
Page 479, reference 15: this should read . . . . . *Carcinogenic and Chronic Toxic Hazards of Aromatic Amines* . . . .
Page 499, line 17: this should read . . . . *by a 130-ml fraction* . . . .
Page 534, line 12 from bottom: this should read

$$\ldots\ldots K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}\Big).$$

Page 563, line 2 under Fig. 11: for *450°* read *540°*
Page 563, line 3 under Fig. 11: for *140°* read *150°*
Page 581, line 4 under Apparatus: for *precede* read *preceed*
Page 595, line 17: this should read *Weisse*,[26] . . . . . .
Page 599, reference 18: this should read *F. Haber u. Z. Klemensiewicz*, ...
Page 599, reference 23: this should read *F. Crotogino*, ...

Page 618, Table I: for *mv* in heading to column 3 read *mV*
Page 623, Table II: for 0·065 absorbance in bromine water (1·0 ppm of cyanide, 30 min after mixing) read 1·065
Page 625, Fig. 2: for (*c*) both in the figure and caption read (*d*)
Page 740, line 16 from bottom: for *nagatively* read *negatively*
Page 760, reference 5: this should read . . . .*ibid.*, 1964, **11**, 667.
Page 801, line 14: for *iridium*$^{(III)}$ read *iridium*^{III}
Page 801, line 15: for *iridium*$^{(IV)}$ read *iridium*^{IV}
Page 807, line under Table VI: this should read . . . . . *then cooled and weighed. At most*
Page 837, reference 29: this should read . . . . . *Talanta*, 1964, *11*, 703.
Page 842, Table I: the second and third entries in column (1) of the R$_f$ values should read *0·13*^{a} and *0·08*^{a}
Page 871, Fig. 1: the second line of the caption should read . . . . . . *Duyckaerts, Drèze and Simon*[14]:

AUTHOR INDEX

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

"Recent Developments in the Ring oven Technique" by H. Weisz.

Monday-Thursday 12-15 *October* 1964 **19th Annual International Instrument-Automation and Exhibit of Instrument Society of America:** New York City

Papers are now invited for the above meeting Individuals active in all major areas of instrumentation, including measurement, information processing and automatic control, should submit abstracts to H TYLER MARCY, Vice President-Development, General Products Division, International Business Machines Corporation, White Plains, New York, U S A (deadline 31 March) The theme of the meeting is **World Frontiers in Instrumentation.**

The **American Society for Testing and Materials** has announced the availability of the 32-volume 1964 *Book of ASTM Standards* This reflects the entire span of today's knowledge of materials and materials testing Each volume covers a specific field of interest and includes a detailed index, table of contents and numeric list of standards. Beginning with the 1964 edition, the book will be brought up to date and published annually with the various parts available on the same scheduled date each year There will no longer be supplements

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ERRATA

Volume 10

Page 1088, Table I: For Compound XIII, under the heading *Ar* for *3-Me-4-OH-*C_6H_3 read *3-MeO-4-OH-*C_6H_3.
Page 1088, Table I: For compound *XIII* read *XIV*; for compound *XIV* read *XV*; for compound *XV* read *XIII.*

Volume 11

Page 2, line 7: This should read *Methods have previously been described . . .*
Page 5: Insert after Zusammenfassung

Résumé—L'utilité analytique particulière de l'Arsenazo-III est due à sa capacité de former des complexes spécialement stables avec certains éléments. Ceci permet le dosage en milieu acide fort (HCl, 10 M ou SO_4H_2) des éléments penta- ou quadrivalents: Pa, Np^{IV}, Th, Zr, Hf, U^{IV}; la reproductibilité est bonne, la manipulation facile et l'on ne note que de petites interférence dûes aux anions. La grande sensibilité (0,1–0,01 μg/ml, coefficient d'absorption molaire 50–150 × 10^3) est due au grand effet de contraste de la réaction (changement de coloration du rose au vert émeraude, déplacement du maximum d'absorption de 125 mμ), nature de spectre, et enfin possibilité d'atteindre des dilutions extremes sans dissociation des complexes.

Page 7, line 2 from bottom: For *TR* read *rare earths.*
Page 16, line 2 above formula XIX: This should read *In order to study the formation of complexes by arsenazo III . . . .*
Page 18, line 4 of Synthesis: This should read *excess of nitrous acid . . .*
Page 41: Insert after Zusammenfassung

Résumé—Les mélanges formés d'orthophosphate, de ses polymères linéares supérieurs jusqu'au tridécaphosphate compris et trois polymères cycliques ont pu être séparés par chromatographie d'échange ionique. L'un des polymères cycliques (recontré dans les verres de polyphosphate . . . est probablement le pentamétaphosphate. Sa nature cyclique a été démontrée par dosage des groupes terminaux et chromatographie sur papier, mais les tentatives de dénombrement des atomes de phosphore du noyau ont échouées à cause de la très faible quantité de produit disponsible. Évidence est presentée a l'appui de la supposition courante que les phosphates linéaries supérieurs sont élués suivant leur degré de polymérisation.

Page 46: Insert after Zusammenfassung

Résumé—Une méthode pour le dosage des trimétaphosphates en présence d'oligophosphates linéares supérieurs au trimère est developpée. Il a été démontré que l'ortho-, le pyro-, at le triphosphate ne sont pas complètement précipités par l'ion baryum, tandis que les phosphates oligomères linéares de type supérieur sont précipités quantitativement. Ces derniers sont isolés des mélanges de phosphates par chromatographie d'échange d'anions, mélangés avec des quantités connues de phosphates cycliques, et précipités par l'ion baryum. Une erreur moyenne de + 0,8 et un écart standard de ±3 micromoles de phosphore de l'ion cyclique a été mise en évidence dans les mélanges contenant de 0 à 203 micromoles de phosphore sous forme de trimétaphosphate en présence de 0 à 81 micromoles de phosphore sous forme de polymères linéares,

Page 49, line 1: This should read *using barium diphenylamine . . .*
Page 57, line 1: This should read *between ammonium ion and chloramine-T . . .*
Page 57: Insert after Zusammenfassung

Résumé—La chloramine-T oxyde quantitativement la thiourée en urée et l'ion sulfate en milieu neutre et en millieu basique. L'oxydation est totale en 2 minutes même en présence d'un léger excès d'oxydant. L'urée et l'ion ammonium ne sont pas gênants si l'oxydation est effectuée en milieu alcalin.

Page 105, line 18 of Summary: This should read *Cerfak* [*sodium naphthalene . . . .*
Page 105, line 6 from bottom of page: This should read [*sodium naphthalene . . . .*
Page 271, line 4 of Summary: This should read

$$\textit{by the equations} \qquad \log k = -11{\cdot}372 + 0{\cdot}0128t \qquad \textit{and } \gamma = 45{\cdot}5 - 0{\cdot}182t.$$

Page 288, line 1: This should read $\bar{X} = \Sigma X_i/n$.
Page 288, line 2: This should read *standard error of* $Y_t = \log K_{H_i}$ . . . .
Page 290, Fig. 4: This should read ◑ − K_D *in* D_2O.
Page 292, line 4: This should read *than for* D_2O.

Page 292, line 10: This should read *than for* H_2O,[13].

Page 292, line 23: For *liberation* read *libration.*

Page 292, line 25: For *liberational* read *librational.*

Page 295, line 1 of Summary: This should read *Equilibrium constants of the principal reactions* . . . .

Page 295, penultimate line of Summary: this should read *A variation of ca. 0·2 pH unit* . . .

Page 295, line 3 of Reagents: This should read *photometrically at 520 mμ, was* . . .

Page 297, line 5: This should read *cyanide-ammonium sulphite mixture* . . .

Page 299, line under equation (1): This should read Pb^{2+} *and* $Pb(HDz)_2$ . . .

Page 299, equation (4c): This should read

$$k_3 = \frac{[HPbO_2^-](aH^+)^3}{[Pb^{2+}]}$$

Page 300, line 2: This should read

$$\Sigma[Pb] = [Pb^{2+}] + [PbOH^+] + \ldots [PbHDz^+] + \ldots [PbX^+] + \ldots$$

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Page 302, line 16: For *nitrate* read *citrate.*

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$$[Pb^{2+}][HDz^-]^2 = 3 \times 10^{-4} \times 7 \times 10^{-16} = 2 \times 10^{-24}$$

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Page 306, line 11: For *electrode* read *glass electrode.*

Page 306, line 2 above Fig. 5: For *Fig. 4* read *Fig. 5.*

Page 311, Fig. 8: This should read

□—*Reversion method: 10 ml of aqueous phase*, . . .

Page 312, equation in mid-page: This should read

$$[Pb(HDz)_2]_0 = \frac{(\Sigma[Pb] - \Sigma[S] \pm \{(\Sigma[Pb] - \Sigma[S])^2 + 4 \times 5{\cdot}6 \times 10^{-5}[H_2Hz]_0^{\,2}\}^{1/2}}{2}$$

Page 313, line 1: For *Proctor* read *Procter.*

Page 313, reference 2: For *S. Vallenga* read *S. Vellenga.*

Page 340, Table III: The units in the headings to columns 6, 7 and 8 should read *V* and not *v.*

Page 421, line 21: For *molydbenum* read *molybdenum.*

Page 438: The equations should be numbered (*1*) and (*2*) and not (*2*) and (*3*).

Page 438: In equation (2) [incorrectly numbered (3)] the term $2OH^-$ is unnecessary.

Page 474, line 18 from bottom: This should read (*4-aminophenyl*)*morpholine and N*-(*4-aminophenyl*)-*piperazine.*

Page 474, line 12 from bottom: This should read . . . *and* (*vi*) *2·0 μg of* CN^-/*ml of the final solution tested.*

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Page 474, line 9 from bottom: For *0·2 ml of arsenious acid* read *2·0 ml of arsenious acid.*

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Page 475, line 9: This should read . . . *for amines Nos. 1, 5, 6, 7 and 10* (*Table III*).

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Page 534, line 12 from bottom: This should read

$$\ldots K = \frac{C_{\text{solid phase}}}{C_{\text{solution}}}\Big).$$

Page 553, caption to Fig. 4: For *390°* read *340°*.

Page 563, line 2 under Fig. 11: For *450°* read *540°*.

Page 563, line 3 under Fig. 11: For *140°* read *150°*.

Page 581, line 4 under Apparatus: For *precede* read *preceed.*

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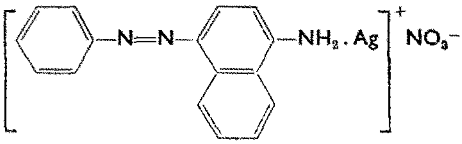
Page 599, reference 18: This should read *F. Haber u. Z. Klemensiewicz*, ...

Page 599, reference 23: This should read *F. Crotogino*, ...

Page 618, Table I: For *mv* in heading to column 3 read *mV.*

Page 623, Table II: For *0·065* absorbance in bromine water (1.0 ppm of cyanide, 30 min after mixing) read *1·065.*

Page 625, Fig. 2: For (*c*) both in the figure and caption read (*d*).
Page 740, line 16 from bottom: For *nagatively* read *negatively.*
Page 760, reference 5: This should read . . . *ibid., 1964, 11, 667.*
Page 801, line 14: For *iridium*^{IV} read *iridium*^{III}.
Page 801, line 15: For *iridium*^{III} read *iridium*^{IV}.
Page 807, line under Table VI: This should read . . . *then cooled and weighed. At most* . . .
Page 837, reference 29: This should read . . . *Talanta, 1964, 11, 703.*
Page 842, Table I: The second and third entries in column (1) of the R_f values should read $0{\cdot}13^d$ and $0{\cdot}08^d$.
Page 871, Fig. 1: The second line of the caption should read . . . *Duyckaerts, Drèze and Simon.*[14]
Page 887, line 30 of main text: This should read . . . Tiron forms with iron . . .
Page 891, The first author of the paper should read *Farhataziz.*
Page 905, line 1 of Résumé: For *sodage* read *dosage.*
Page 905, line 3 of Résumé: For *volumé-triquement* read *volumétriquement.*
Page 905, last line of Résumé: For *direct* read *directe.*
Page 908, Table I: The R_f value for Th should read *In Front 2* (*R_f value in relation to Front I is 0·9*).
Page 908, Table I: The R_f value for U should read *In Front 2* (*R_f value in relation to Front I is 0·9*).
Page 927, equation above Fig. 13: For NH_4NO_3 read NH_4VO_3.
Page 948, line 13: For *Erió* read *Erić.*
Page 953, line 4 of Résumé: For *effect* read *effet.*
Page 964, line 12 of Résumé: For *24 hau moirs* read *24 h au moins.*
Page 972, line 3 of Résumé: For *vagurs* read *vagues.*
Page 973, last line: For *ternary* read *binary.*
Page 973, last line: For *is* read *are.*
Page 975, line 3 of Résumé: For *delle* read *celle.*
Page 975, line 7 of Résumé: For *peurvent* read *peuvent.*
Page 975, line 8 of Résumé: For *ses* read *ces.*
Page 982, line 4 of Summary: This should read *is proved to result from* . . .
Page 982, line 1 of Résumé: For *résponse* read *réponse.*
Page 997, line 13 from bottom of page: This should read *mannitol, a coulometric titration* . . . .
Page 998, Fig. 5: This should read
Curve I ———— 10·8 mg of boron, 216 mA;
Curve II - - - - - - - 1·08 mg of boron, 19 mA;
Curve III — · — · — 0·50 mg of boron, 19 mA;
Curve IV — ·· — ·· — 0·10 mg of boron, 4·5 mA.
Page 998, Fig. 6: This should read
Curve I ———— 10·8 mg of boron, 216 mA;
Curve II - - - - - - - 1·08 mg of boron, 19 mA.
Page 999, Fig. 7: This should read
Curve I ———— 10·8 mg of boron, 216 mA;
Curve II - - - - - - - 1·08 mg of boron, 19 mA;
Curve III — · — · — 0·50 mg of boron, 19 mA.
Page 999, line 5 under Table II: This should read . . . *0·1 mg of boron.*
Page 1026, caption to Table III: This should read *Effect of diverse ions on the determination of selenium*[a] (*20 ml of final solution contains 30 μg of selenium*^{IV}).
Page 1036, footnote to Table II: For *Mohrs* read *Mohr's.*
Page 1036, footnote to Table II: For *pocassium* read *potassium.*
Page 1060, reference 74: The author should read *J. E. Barney, II.*
Page 1064, line above Conclusion: This should read . . . *charge:metal ion radius.*[2]
Page 1098: The structural formula for compound III should be



Page 1121: The title should read *Colorimetric determination of cobalt*^{II} . . .
Page 1136, Table I: the first entry in the last column should read *0·511 MeV.*
Page 1137, Table II: The entries in the third column should read *0·511 MeV* and *1·04 MeV.*
Page 1141, line 13: This should read *The investment cost is estimated to be $20,000 for each fully automatic measuring device. The requirement of a generator* . . .
Page 1177: This paper should read *Eingegangen am 15. Februar 1964.*
Page 1200, Table III: The heading to the fifth column should read *Found, 0·05M, ml.*
Page 1203: This paper should read *Received 10 February 1964.*

Page 1239: This paper should read *Received 18 March 1964.*
Page 1249: This paper should read *Received 9 April 1964.*
Page 1275: This letter should be dated *26 March 1964.*
Page 1284, Fig. 5: This should read $\gamma_0 = 0{\cdot}06$, *etc.*
Page 1307, line 2: For *though* read *through.*
Page 1311, reference 46: This should read . . . *1963,* ***18****, 18.*
Page 1313, line 4 of Experimental: This should read . . . *1,2-diaminocyclohexanetetra-acetic.*
Page 1314, line 2 of Apparatus: This should read . . . *photoelectric attachment* . . .
Page 1314, line 4: For UO_2^{2-} read UO_2^{2+}.
Page 1314, line 8 under Results and Discussion: This should read . . . *a molar ratio of 1:1, V:(XO)*, . . .
Page 1317, Table I: In the first column read UO_2^{2+} for UO_2^{2-}.
Page 1325, second footnote to page: Delete *Preparation*:
Page 1329: For *Table 1* read *Table I.*
Page 1350, line 14 of Results and Discussion: This should read . . . *measured in 1-ml cells* . . .
Page 1355, reference 5: The journal should read simply *Japan Analyst.*
Page 1366, line 3 above Procedure: This should read *(1 ml ≡ 100 μg of cadmium).*
Page 1367, line 7 from bottom of page: This should read . . . *chromium(VI), remaining after volatilisation, to chromium(III)* . . . .
Page 1377, line 2 under Calculations: For *MEV* read *MeV.*
Page 1406, Table I: The headings for columns two, three and four should read

Cu^{2+} taken, *mmole/100 ml*	HEDTA taken, *mmole/100 ml*	Resin, *g*

Page 1498, line 2 under the heading *Precipitation of Titanium from Homogeneous Solution:* This should read . . . *peroxytitanate. Add potassium* . . . .
Page 1550, line 10 from bottom of page: For *silver-III* read *silver-111.*
Page 1607, line 8: This should read *hydriodic acid and stannic tetra-iodide* . . . .