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PRESSUROMETRIC TITRATIONS WITH XENON TRIOXIDE AS OXIDANT

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Summary—The reaction of XeO_3 with thirteen reducing agents was studied qualitatively. From these, Fe(II) and Ti(III) were chosen for direct titration with XeO_3 with pressurometric end-point detection. The precision was a few parts per thousand. Evidence was found for the production of oxygen during both titrations, and of hydrogen peroxide formation during the Ti(III) reaction. The Ti(III)/Xe reacting ratio was independent of the amount of Ti(III) from 35.5 to 87.7 μmole and was 5.93 ± 0.03 instead of the expected 6.00. The ratio for the Fe(II) reaction varied from 5.85 to 5.95 over the Fe(II) range from 10.05 to 78.7 μmole. The stoichiometric ratio for the iodometric standardization of XeO_3 solutions was confirmed as 6.00.

Pressure transducers offer a convenient way to follow gas-evolution or gas-absorption reactions and their use for titrimetric end-point detection has been reviewed by Curran.[1] The reaction of xenon trioxide with reducing agents liberates xenon and pressurometric measurements would seem to be ideally suited for the study of XeO_3 as an oxidant. Approximate values for the oxidation potentials have been obtained by O'Hare, Johnson and Appelman[2] from calorimetric measurements:

$$XeO_3 + 6H^+ + 6e^- \rightarrow Xe(g) + 3H_2O; \quad E^\circ = 2.10 \pm 0.01\ V$$

$$HXeO_4^- + 3H_2O + 6e^- \rightarrow Xe(g) + 7OH^-; \quad E^\circ = 1.24 \pm 0.01\ V$$

These potentials indicate that XeO_3 is a very strong oxidant. However, the half-reactions are irreversible and many reactions with reducing agents are slow. A review of XeO_3 chemistry is available.[3] Analytical applications fall into two categories: titrimetric methods and kinetic methods. There is an induction period when alcohols are added to a solution of XeO_3, and Kreuger, Vas and Jaselskis have utilized the initiation time to determine as little as 22 μg of tert.-butyl alcohol.[4] Primary and secondary alcohols may catalyse this reaction and methanol, ethanol and propan-2-ol were determined on this basis. Nearly all titrimetric procedures involve reaction with an excess of XeO_3 followed by iodometric determination of the excess. Alcohols,[5–7] carboxylic acids,[8] and hydrogen peroxide[9] have been determined in this way. The only direct titration appears to be the spectrophotometric titration of hydrogen peroxide.[9]

In the present work, a number of reductants were surveyed qualitatively for possible direct titration with XeO_3, and two were studied in detail: Fe(II) and Ti(III). Reaction with the former was known to be fast[10] but reaction with the latter had not been previously reported. Precision of a few parts per thousand in the titration of mg amounts of both Fe(II) and Ti(III) was achieved but an empirical factor is necessary. Evidence showing the correctness of the iodometric standardization of XeO_3 solutions was obtained.

EXPERIMENTAL

Apparatus

The pressure-transducer system has already been described.[1,11,12] A Datametrics Series 511-10, 0–10 Thor Barocel Pressure Sensor was used (Datametrics Inc., Wilmington, Mass. 01887). Figure 1 shows the titration apparatus developed for this work. Two flasks, F and G, were made by joining 1/2-in. (bore) glass pipe connections (Fischer-Porter 670-000) to 25-ml Erlenmeyer flasks. Cell F serves as a reference vessel and cell G as a titration or reaction vessel. They are fastened to the rest of the apparatus at joints K which are also 1/2-in. glass pipe connectors, with spring-loaded pinch clamps. A 5/8-in. O-ring, L, is used to provide a pressure-tight seal. The micrometer-driven microburettes, D and E, (type S-3100, Roger Gilmont Instrumentation Inc., 161 Great Neck, N.Y.) have a capacity of 0.25 ml with vernier reading to 0.00001 ml and a specified precision of 0.02–0.04%. Burette E was used to deliver titrant and D to compensate for the volume change produced by delivery of titrant. The glass stems of the burettes were ring-sealed to the inner section of an 18/9 ₸ spherical ground-glass joint, which allowed the burettes to be connected to the system through joints Q. Stop-cocks A, B and C permit the reference and reactor gas phases to be connected to each other, to the atmosphere, or to be isolated. With all stop-cocks open, gas may be swept through the apparatus. The shape of the reactor vessel and proper positioning of the burette tip H allow very vigorous stirring to be used without significant loss of solution by splashing. The joints R were used to connect the reaction flasks to the pressure-transducing system.

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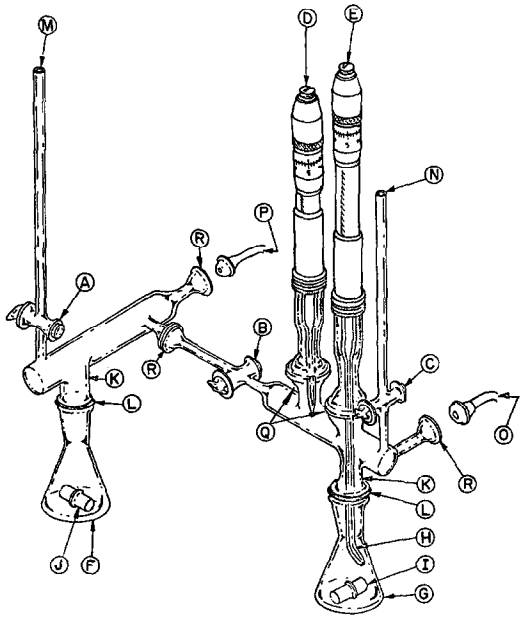


Fig. 1. Apparatus for pressurometric titrations. A, B, C, 2 stop-cocks; D, volume-compensating microburette, 0.25-ml capacity; E, titrant delivery microburette, 0.25-ml capacity; F, reference vessel; G, working vessel; H, tip of titrant delivery burette; I, J, Teflon-coated magnetic stirring bars; K, pipe joints, 1/2-in. i.d.; L, rubber O-rings; M, N, side-arms leading to reference and working vessels respectively; O, tubing leading to the working port of the pressure transducer; P, tubing leading to the reference port of the pressure transducer; Q, 18/9 ball and socket joints; R, 12/5 ball and socket joints.

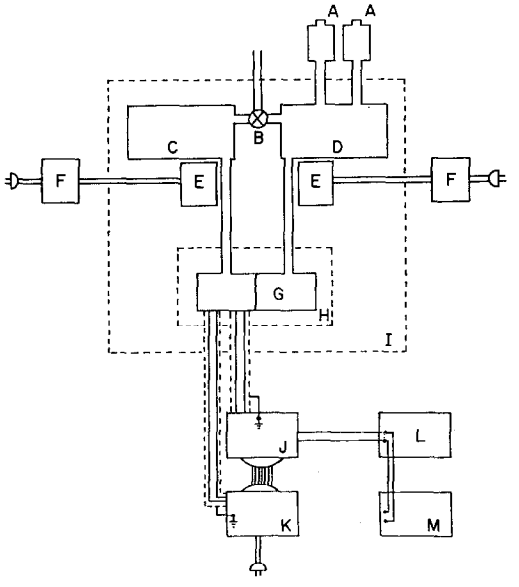


Fig. 2. Schematic diagram of pressurometric titration equipment. A, microburettes; B, 2 stop-cock; C, reference vessel; D, working vessel; E, Tri-R Model MS-7 submersible magnetic stirring motors; F, Tri-R motor controls; G, Datametrics Inc. Series 511-10 Barocel Pressure Sensor; H, watertight box enclosing the pressure sensor; I, constant-temperature bath; J, Datametrics Type 1015 signal conditioner; K, Datametrics Type 700 power supply; L, potentiometer; M, recorder.

A block diagram is shown in Fig. 2. Two submersible stirring motors, E, were operated by motor controls, F. The pressure-transducing system was modular and consisted of sensor G in a water-tight Lucite box H, signal conditioner J, and power supply K. The system output was measured either with potentiometer M, or recorder L, selected by a switch (not shown). The Lucite box was fitted with an 1/8-in. thick aluminium lid fastened with 8 bolts. Stop-cock grease and a rubber gasket were used to produce a seal. The lid provided good heat-transfer between the bath and the pressure transducer.

The titration apparatus, stirring motors and transducer, mounted in the box, were placed on a ring stand so that the entire unit could be submerged in the bath up to the metal parts of the burettes. The bath was regulated at $26 \pm 0.001°$ with a Tronac Temperature Controller, model PTC-1000.

A Perkin-Elmer Model 900 Gas Chromatograph was used with an 18-in. aluminium column, 1/4 in. in diameter, packed with Linde 5A molecular sieve (baked out in vacuum at 200° for 4–5 hr before packing). Reactors were constructed for studying the production of oxygen during XeO_3 reactions and had the following features: inert-gas flow (He), trapped inert atmosphere, septum for introducing XeO_3 solutions and sampling of reactor gases, and magnetic stirring.

Amperometric titrations were done in a 30-ml beaker fitted with a three-hole rubber stopper, a Sargent Model P Ampot being used; a potential of 200 mV was impressed across two identical 2-cm^2 platinum flag electrodes.

Visible spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer, operating on fast scan at a slit-width of 25 μm.

For spectrophotometric titrations of Ti(III) with XeO_3 a Heath Model EU-701C recording spectrophotometer was used. The expanded scale was used and a special stand and cell were constructed which provided magnetic stirring, use of the Gilmont microburette for titrant delivery, introduction of a nitrogen atmosphere and reduction of stray light. Titrations were performed at a wavelength of 520 nm.

Thiosulphate solutions were standardized coulometrically by use of a Sargent Model IV Coulometric Current Source with a 2-cm^2 platinum flag generator electrode. A starch end-point was used.

A 250-μl pipette was silaned and calibrated. The result of 5 determinations was $0.2494 \pm 0.0002_4$ ml delivered.

Reagents and solutions

All solutions were prepared from laboratory-distilled water redistilled from alkaline permanganate. Reagent-grade chemicals were used unless otherwise stated. Potassium azide, hydrazine sulphate and hydroquinone were Eastman "white label" and used as received. Xenon trioxide solutions were obtained from Matheson, Coleman and Bell or the Argonne National Laboratory. Sulphur dioxide was 99.9% pure (Union Carbide-Linde). The nitrogen used was Airco prepurified and was scrubbed first with chromous solution and then with solvent.

Solutions of Fe(II) were prepared by dissolving accurately weighed amounts of ferrous ammonium sulphate hexahydrate in appropriate sulphuric acid solutions in standard flasks. The concentration of Fe(II) was calculated from the weight taken and in some cases was checked by titration with Ce(IV) (ferroin as indicator). The results agreed within 0.1–0.2%. Air oxidation of Fe(II) is known to be slow, but pressurometric titrations were performed on deaerated Fe(II) solutions under an atmosphere of nitrogen. Stock solutions of Ti(IV) were obtained by dissolving TiO_2 in a mixture of concentrated sulphuric acid and ammonium sulphate, and then diluted with water. More dilute Ti(IV) solutions were prepared from aliquots of the stock solutions. Ti(III) was prepared from the Ti(IV)

solutions by reduction with liquid zinc amalgam in a nitrogen atmosphere. About 1 hr was sufficient for complete reduction, but generally 2 hr or more were allowed. Ti(III) solutions were standardized by adding an aliquot to excess of Fe(III) and titrating the resultant Fe(II) with Ce(IV) (ferroin as indicator).

Procedures

Procedures for using the pressure-transducing system have been described.[11,13] Reactions were judged to be over when the system pressure reached a steady value. Reaction times include the time for the gas to be partitioned between the liquid and gas phases (1–3 min) by vigorous stirring. Stringent measures were taken to minimize contact of Fe(II), Ti(III) and other air-sensitive solutions with the atmosphere. The reactor shown in Fig. 1 was flushed with nitrogen before a sample was placed in it. The pipettes used for transfer were flushed with nitrogen just before use. Nitrogen was passed over the titrant until the vessel was connected to the apparatus, and all solutions were deaerated with nitrogen. Titrations were normally done under nitrogen.

RESULTS AND DISCUSSION

Survey of reactions

Qualitative studies of a number of XeO_3 reactions not previously reported are summarized in Table 1. It was possible, on the basis of the predicted increase in pressure, to estimate the reaction stoichiometry. Although As(III) and Sb(III) did not appear to react with XeO_3 alone, gas evolution did occur when a trace of iodide was present, more so in the case of As(III), and a few experiments were done to determine the effect of iodide concentration and acidity. Table 2 shows that the acidity is the main factor. The nature of this reaction remains unknown. On the basis of the survey and earlier reports in the literature, Fe(II) and Ti(III) were chosen for further study.

Iodometric standardization of XeO_3 solutions

Templeton *et al.*,[14] Williamson and Koch[15] and Appelton and Malm[16] have found I/Xe reacting ratios of 6.06, 6.06 and 6.09 respectively, for the reaction of XeO_3 with an excess of iodide in acidic solution. The procedure involves thiosulphate back-titration of the iodine produced. It is not clear whether the discrepancies from the theoretical stoichiometry are simply due to experimental error. However, the iodometric procedure appears to be the accepted method for the standardization of XeO_3 solutions. It has been suggested by Appelman[17] and Krueger *et al.*[9] that intermediate oxides of xenon produced during chemical reduction of XeO_3, such as XeO_2 or XeO, can either decompose into xenon and oxygen, or oxidize water to H_2O_2, which can then be further oxidized to oxygen. Williamson and Koch[15] cite evidence that no oxygen is liberated when solid potassium iodide is added to an acidic solution of XeO_3. Gas-chromatograph experiments performed

Table 1. Survey of some xenon trioxide reactions

Reactant	Product	Reactant concentration, $10^{-3}M$	XeO_3 concentration $10^{-4}M$	Solution conditions	Procedure*	Apparent reaction time, *sec*
Ti(III)	Ti(IV)	33	0.51	$0.13M$ H_2SO_4	S	30
V(IV)	V(V)	57	120	$0.1M$ H_2SO_4	C	600–900
		27	70	$0.4M$ NaOH	C	2–3
		14	36	pH = 8	C	2–3
Fe(II)	Fe(III)	0.11	0.043	$0.05M$ H_2SO_4	P	90
		3.1	0.93	$1.0M$ H_2SO_4	P	90
Mo(V)	?†	0.50	0.34	$0.008M$ H_2SO_4	P	⩾1200
		0.50	0.34	$0.25M$ H_2SO_4	P	90–120
		0.50	0.34	$0.5M$ H_2SO_4	P	120–150
		0.50	0.34	$1.5M$ H_2SO_4	P	300
As(III)	—	0.41	0.55	$0.05M$ H_2SO_4	P	NR§
	—	0.73	0.34	$1.5M$ H_2SO_4	P	NR
Sb(III)	—	0.5	0.34	$0.5M$ H_2SO_4	P	NR
	—	0.25	0.34	$4.5M$ H_2SO_4	P	NR
	Sb(V)	0.25	0.34	$4.5M$ H_2SO_4 $1.5 \times 10^{-5}M$ KI	P	>600
Sn(II)	Sn(IV)	0.80	0.34	$0.05M$ H_2SO_4	P	120–180
		0.26	0.51	$1.0M$ H_2SO_4	P	>>1500
Cl^-	—	50	0.34	$0.5M$ H_2SO_4	P	NR
NH_4^+	—	0.17	0.13	$0.05M$ H_2SO_4	I	NR
N_2H_4	?	0.24	0.34	pH = 7.3	P	120–180
N_3^-	—	0.46	0.28	$0.05M$ H_2SO_4	P	NR
SCN^-	?	1500	92	$0.01M$ H_2SO_4	I	Slow
Hydro-quinone	?	0.46	0.34	neutral	P	⩾1500
	?	0.46	0.34	pH = 8.5	P	120

* S, spectrophotometric at 520 nm; C, colour change of the solution observed visually; P, reaction monitored pressurometrically; I, XeO_3 determined iodometrically to measure the extent of reaction.

† Only half of the expected pressure change for the production of Mo(VI) was observed.

§ NR = no reaction.

Table 2. Effect of iodide on the As(III)–XeO_3 reaction

As(III), $10^{-4}M$	XeO_3, $10^{-5}M$	Iodide, $10^{-6}M$	H_2SO_4, M	Time for complete reaction, *min*
4.1	5.5	0	0.05	NR*
7.3	3.4	0	1.5	NR
5.8	3.4	0.75	0.025	NR
7.1	3.3	15	0.5	⩾30
7.1	3.3	15	1.5	25–30
5.3	3.9	41	1.5	15–20
7.3	3.4	0.75	3.0	25–30
7.1	3.3	15	3.0	6–7
7.2	3.4	3.7	4.5	4–5

* NR = no reaction.

Table 4. Gas chromatographic evidence for oxygen production during the Fe(II) reaction

Time of sampling, *min*	Gas sample volume, *μl*	Peak height† O_2	Peak height† N_2	O_2/N_2	Oxygen, *μeq*
15	100	24.3	42.4	0.573	0.1
24	100	16.1	21.0	0.767	0.7
30	100	26.2	35.8	0.732	1.0
41	200	50.6	69.9	0.724	1.0
49	400	182.0	278.8	0.653	1.1
blank	100	17.6	31.4	0.561	—
blank	100	26.3	49.2	0.535	—

* 0.017M XeO_3 was added to 96 μmole of Fe(II) as follows: 0.50 ml at "zero" time, 0.70 ml at 18 min.
† Recorder divisions.

in this work confirm this finding. The gas phase of a closed reactor was sampled before and after addition of XeO_3 solution to potassium iodide solutions in 0.025M sulphuric acid. A helium atmosphere was maintained throughout, but residual air could not be entirely eliminated. The ratio of the oxygen peak to the nitrogen peak for a blank, along with a calibration factor determined from air-injections, was used to correct the data for residual air. No evidence for oxygen production was found when XeO_3 was added in excess. With iodide in excess, there was a slight enhancement of the oxygen/nitrogen ratio, but this would correspond to less than 0.1% loss of XeO_3 by oxygen production.

Another possible source of error could be air-oxidation of iodide. Starch indicator showed that no iodine was present after a solution of 0.5M potassium iodide in 0.025M sulphuric acid had stood in contact with air for 20 min. Iodometric determinations of XeO_3, done in an atmosphere of air, oxygen or nitrogen, produced results which agreed to within 1 part per thousand.

Loss of iodine by volatilization would produce an error leading to a low I/Xe ratio for titrations done in open beakers. The usual remedy for this is to have sufficient iodide present to convert most of the iodine into tri-iodide. To evaluate the extent of iodine volatilization, the oxidizing power of 0.2494-ml portions of 0.016M XeO_3 solution was determined as a function of the iodide level. The volume of iodide solution in all cases was 2.00 ml and the sulphuric acid concentration was 0.025M. The results, shown in Table 3, indicate that the loss of iodine decreases as the iodide concentration increases. With 0.5M potassium iodide the normality of an XeO_3 solution remained the same when the amount of xenon trioxide reacted was doubled. We conclude that there is no significant loss of iodine by volatilization when 25 μeq or less of XeO_3 are reacted under these conditions if the potassium iodide concentration is 0.5M or greater.

Table 3. Loss of iodine by volatilization

Initial concentration of I^-, M	No of detns.	Thiosulphate consumed, *ml*
0.050	3	0.1923
0.125	1	0.1942
0.24	1	0.1952
0.50	4	0.1958

Fe(II) and Ti(III) titrations

With the exception of the reaction with iodide, no titration reactions of XeO_3 reported in the literature have exhibited the theoretical stoichiometric ratio. The presence of trace impurities[3,5,8,9] and reactive intermediate oxidation states of xenon[3,5,9,18] have been offered as explanations for non-stoichiometric ratios. Mechanisms proposed always invoke the production of H_2O_2 through oxidation of water by lower oxidation states of xenon and the production of oxygen from H_2O_2 and/or species such as XeO_2 and XeO. Gas-chromatography experiments performed in this work confirmed the production of oxygen during the titration of both Fe(II) and Ti(III). Results are shown in Table 4 for the Fe(II) reaction. Amounts

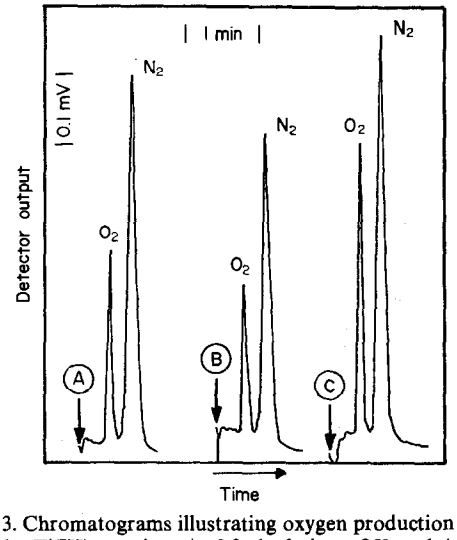


Fig. 3. Chromatograms illustrating oxygen production during the Ti(III) reaction. A: 2.0 μl of air at 25° and 1 atm; B: 100 μl of reactor gas before the addition of XeO_3; C: 200 μl of reactor gas after addition of 1.1 ml of 0.017M XeO_3 to 25.0 ml of 3.61mM Ti(III) in 0.12M H_2SO_4.

Table 5. Dependence of the pressurometric end-point on the titration procedure

Procedure	No. of detns.	XeO_3 consumed, μmole	Std. devn., μmole	Fe(II)/Xe
*a**	3	13.29	0.03	5.91
b†	3	13.38	0.02	5.87

* Procedure *a*: Fe(II) taken = 78.5_2 μmole; titrant volumes added (μl): 60, 90, 120, 150, 180, 210, 220, 230, 240, 250; elapsed titration time: 5.0 sec per μl of titrant.
† Procedure *b*: As for *a* except that the volumes added were 30, 60, 90, 120, 150, 210, 220, 230, 240, 250 μl.

of oxygen larger than those shown in Table 4 were generated if an excess of XeO_3 was added all at once to the Fe(II) solution. The reaction of Ti(III) with oxygen is known to be much faster than that of Fe(II), but it was still possible to demonstrate that oxygen is produced during the Ti(III) reaction, as shown by the chromatograms in Fig. 3. The oxygen peak is clearly enhanced for chromatogram C. Evidence to support the idea of H_2O_2 production was also obtained during the experiments with Ti(III). Hydrogen peroxide and Ti(IV) are known to form a yellow complex. During the gas-chromatography studies, a very faint yellow colour was observed when a slight excess of XeO_3 was added to a Ti(III) solution. The colour was more easily seen when some of the solution was transferred to an 18-cm long glass tube. The colour disappeared on standing for 10–15 min. Addition of a larger excess of XeO_3 in one portion to the Ti(III) solution produced a more intense yellow colour. These visual observations were confirmed by spectrophotometric measurements.

A blank was run on 20 ml of 0.05*M* sulphuric acid. The addition of 2.00 μl of 0.4163*N* XeO_3 produced no pressure change observable on the ×0.03 range of the pressure-transducer system. This indicates the absence of impurities which could react with XeO_3, but does not rule out the presence of impurities which might react with highly reactive intermediates produced during the titration reactions.

In view of the results above, the oxidation of Fe(II) and Ti(III) by XeO_3 evidently proceeds in a manner analogous to that of previously reported reactions with the side-production of oxygen, probably through H_2O_2 as intermediate. It might be expected that the procedure used for the titrations would have an effect

Table 6. Pressurometric titrations of Fe(II)

Fe(II) taken, μmole	XeO_3 consumed, μmole	Std. devn., μmole	Fe(II/Xe
78.7_2	13.22	±0.01*	5.95
40.3_8	6.81	±0.01†	5.93
21.20	3.58_3	$\pm0.00_6$*	5.91
10.05	1.716	$\pm0.00_9$†	5.85

* 5 trials.
† 6 trials.

on the stoichiometric ratios observed. This was found to be the case, the change in the ratio being less than 2%. For example, 78.5 μmole of Fe(II) were titrated by two procedures which differed only in the volume of the initial increment of titrant. Results are found in Table 5. When the first volume increment of titrant is larger, and therefore the measurements are made closer to the equivalence point, the observed ratio is closer to the theoretical stoichiometry. Similarly, for the titration of 87.7 μmole of Ti(III), a ratio of 5.83 was found, but this increased to 5.93 when a larger initial increment of titrant was added. Consequently, in further titrations the measurements were made over the range corresponding to 65–140% titration for samples containing 10–80 μmole of Fe(II) or 35–90 μmole of Ti(III). Titrations were run in 20 ml of sulphuric acid which was 0.05*M* for iron and 0.09–0.16*M* for titanium. The pressure increases linearly up to the end-point and then becomes constant. The results of these titrations are shown in Tables 6 and 7. The stoichiometric ratio appears to be independent of the amount of Ti(III) taken, but decreases from 5.95 to 5.85 as the initial amount of Fe(II) decreases. A plot of the data in Table 6 [μmole of XeO_3 consumed *vs.* μmole of Fe(II) taken] gave a straight line. A least-squares regression analysis gave a slope of 0.1674 mole of XeO_3 per mole of Fe(II), with an absolute standard deviation of ±0.0001 and an intercept of 0.035 ± 0.004 μmole of XeO_3. The difference between experimental and theoretical slopes is only 0.4%. The intercept accounts for the apparent change in stoichiometry with decrease in the amount of Fe(II) titrated. An intercept of 0.035 μmole of XeO_3 amounts to 2.0% of the amount of XeO_3 consumed for the lower level of 10.05 μmole of Fe(II) taken. The total deviation of the observed stoichiometric ratio from the theoretical is, therefore, 2.4%. Most of this error is due to the

Table 7. Pressurometric titrations of Ti(III)

Ti(III) taken, μmole	Concentration of H_2SO_4, *M*	XeO_3 consumed, μmole	Std.* devn., μmole	Ti(III)/Xe
87.7	0.16*M*	14.79	±0.03	5.93
71.8	0.16*M*	12.18	±0.04	5.89
53.3	0.16*M*	8.96	±0.03	5.95
35.5	0.09*M*	5.97	±0.01	5.95
				Average 5.93 ±0.03

* 5 trials.

intercept. On the other hand, the intercept plays a smaller role for larger amounts of Fe(II), the error approaching the 0.4% due to the error in the slope. The precision in all cases is quite good and accurate results can be obtained by the use of such an empirical working curve.

The results of the pressurometric titrations of Fe(II) were confirmed by a second titration method. Biamperometric titration of Fe(II) solutions yielded the expected titration curve shape for a system involving a reversible titrand reaction and an irreversible titrant reaction. The average stoichiometric ratio for 4 titrations of 3.5-mg samples of Fe(II) was 5.96 (±0.2%). However, the XeO_3 used in these titrations was standardized in the presence of an insufficient excess of potassium iodide. The error due to volatilization was estimated experimentally to be −0.6%. Correcting the ratio for this error gives a result of 5.92, in excellent agreement with the ratio found in the pressurometric experiments.

The titanium titration is more complicated than that of Fe(II), because any oxygen produced in side-reactions is more likely to react with Ti(III) and the net consumption of titrant may or may not correspond to the correct stoichiometry. The precision of the results shown in Table 7 is satisfactory and the use of an empirical stoichiometric ratio would lead to accurate results for pressurometric titrations. Despite the precautions taken to eliminate air, some concern remained about possible loss of Ti(III) because of residual air in the apparatus. Samples of Ti(III) were treated according to the titration procedure, except that no titrant was added. After the time normally required to complete the titration had elapsed, the amount of Ti(III) present was determined by adding an excess of deaerated Fe(III) solution, adjusting the sulphuric acid concentration to 1*M* and titrating the resultant under nitrogen with Ce(IV) to a ferroin end-point. An aliquot of the original Ti(III) solution was back-titrated in the same fashion but with no waiting period. Any difference between the results was attributed to oxidation of Ti(III) by residual air in the apparatus. The results are presented in Table 8. An average of 0.4 μmole appears to be lost for both concentrations studied. However, the results are regarded as inconclusive since the precision is not high enough to guarantee that the difference is due to loss of Ti(III). These experiments cannot exactly simulate an actual titration and a maximum loss of 1% may occur.

Table 8. Loss of Ti(III) due to residual air

Ti(III) taken, *μmole*	Ti(III) lost, *μmole*	Devn., *μmole*
88.7	0.9	+0.5
88.7	0.2	−0.2
88.7	0.1	−0.3
	Average 0.4 ± 0.4	
35.5	0.5	+0.1
35.5	0.5	+0.1
35.5	0.1	−0.3
	Average 0.4 ± 0.2	

The Ti(III) was also titrated spectrophotometrically. The absorbance did not change linearly except near the end-point. It was observed in this work and by Goroshchenko and Godneva[19] and by Shenk[20] that the addition of Ti(IV) to Ti(III) in sulphuric acid solution causes the colour of the solution to deepen. The absorption maximum of this solution occurs at a shorter wavelength than that of a Ti(III) solution and the molar absorptivity is higher. Nevertheless, a linear extrapolation near the end-point is quite feasible. The results for titrations carried out in air and under nitrogen are shown in Table 9. These are very close to the theoretical stoichiometry and differ from those shown in Table 7. Whether or not the reaction between Ti(III) and oxygen will compensate for the loss of XeO_3 to side-reactions will depend on the rate of partition of the oxygen and the volume of the gas phase but it can affect only the reaction ratio; there will be a negative error in the amount of Ti found. Conditions were more favourable for compensation in the case of the spectrophotometric titrations, but the precision was not as good.

Table 9. Spectrophotometric titrations of Ti(III)*

Atmosphere	Ti(III) taken, *μmole*	End-point volume, *μl*	XeO_3 consumed, *μmole*	Ti(III)/Xe
Air	87.3	212.8	14.76	5.92
Air	88.5	211.2	14.65	6.04
Air	88.5	220.5	15.30	5.78
				Average 5.91 ±0.16
Nitrogen	88.5	214.3	14.87	5.95
Nitrogen	88.5	211.3	14.66	6.04
Nitrogen	88.5	210.7	14.62	6.05
				Average 6.01 ±0.06

* Titrant, 0.416_3N XeO_3; Ti(III) taken, 2.010 ml of 0.440_2N solution except for trial 1, where 2.005 ml of 0.0435_5N Ti(III) was taken.

This work, and previous work reported in the literature, demonstrates that excess of XeO_3 is consumed in titrimetric reactions with reducing agents. In the case of Fe(II) and Ti(III), the deviation from theoretical stoichiometry is slight but significant. Nevertheless, XeO_3 is an excellent titrant for pressurometric titrations. Fairly precise results have been obtained and good accuracy can be achieved by the use of an empirical stoichiometric ratio.

Acknowledgements—We express our appreciation to E. Appelman and the Argonne National Laboratory for supplying some of the XeO_3 solution used in this work. Partial financial support by the National Institutes of Health, under Grant GM-12284, is acknowledged.

REFERENCES

1. D. J. Curran, In *New Developments in Titrimetry*, J. Jordan, ed., Vol. 2, p. 91. Dekker, New York, 1974.
2. P. A. G. O'Hare, G. K. Johnson and E. H. Appelman, *Inorg. Chem.*, 1970, **9**, 332.
3. B. Jaselskis, *Record Chem. Progr.*, 1970, **31**, 103.
4. R. H. Krueger, S. Vas and B. Jaselskis, *Talanta*, 1971, **18**, 116.
5. B. Jaselskis and J. P. Warriner, *Anal. Chem.*, 1966, **38**, 563.
6. H. J. Rhodes and M. I. Blake, *J. Pharm. Sci.*, 1967, **56**, 1352.
7. H. J. Rhodes, R. P. Shiau and M. I. Blake, *ibid.*, 1968, **57**, 1706.
8. B. Jaselskis and R. H. Krueger, *Talanta*, 1966, **13**, 945.
9. P. H. Krueger, J. P. Warriner and B. Jaselskis, *ibid.*, 1968, **15**, 741.
10. S. M. Williamson and C. W. Koch, *Noble Gas Compounds*, p. 158. University of Chicago Press, Chicago, 1963.
11. D. J. Curran and J. L. Driscoll, *Anal. Chem.*, 1966, **38**, 1746.
12. D. J. Curran, *J. Chem. Educ.*, 1969, **41**, A465.
13. D. J. Curran and J. E. Curley, *Anal. Chem.*, 1970, **42**, 373.
14. D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson, *J. Am. Chem. Soc.*, 1963, **85**, 817.
15. S. M. Williamson and C. W. Koch, *Science*, 1963, **139**, 1046.
16. E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, 1964, **86**, 2141.
17. E. H. Appelman, *Inorg. Chem.*, 1967, **6**, 1305.
18. R. P. Shiau, *Dissertation Abstr. Int. B.*, 1971, 2571.
19. Ya. G. Goroshchenko and M. M. Godneva, *Russ. J. Inorg. Chem.*, 1961, **6**, 744.
20. M. Shenk, *Helv. Chim. Acta*, 1936, **19**, 4.

Talanta, Vol. 25, pp. 9–14. Pergamon Press, 1978. Printed in Great Britain.

CONDUCTOMETRIC TITRATION WITH INDICATING RESISTANCE—IV*

THE USE OF MEMBRANES WITH SOME ORGANIC AND INORGANIC ACIDS AS ACTIVE COMPONENTS, FOR HCl TITRATION IN A HIGHLY CONDUCTING MEDIUM

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Summary—Membranes consisting of a methyl polymethacrylate or collodion support containing sparingly soluble inorganic or organic acids can be used for end-point detection in acid–base titrations in high-conductivity media. The collodion + $Na_3[As(Mo_3O_{10})_4].nH_2O$ + Na-Alassion CS membrane is a very good conductometric sensor if given preliminary treatment to form molybdic acid. The conductivity jump with this membrane starts at pH ~7 and permits titration of strong acid down to $10^{-4}M$ concentration in highly conducting medium. Similar membranes containing some organic acids such as benzoic, *o*-chlorobenzoic, and *o*-phthalic also behave as conductometric sensors, giving a conductivity change at a pH which depends on the dissociation constant of the organic acid used and on the way it interacts with the support and the conducting medium used.

The determination of the equivalence point in acid–base conductometric titrations in highly conducting solutions has been solved by introducing some indicating membrane between the two electrodes of the conductivity cell.[1,2] The study of the functional mechanism of the membrane PVC + Alassion CS (cation-exchanger) + dioctylphthalate (plasticizer)[3] proved that in the process of membrane preparation, as a result of the sulphonic acid groups on the cation-exchanger, the dioctyl phthalate decomposes to form phthalic acid which dissolves in the PVC membrane. The carboxylic groups of the phthalic acid present in the membrane, on neutralization, cause a sudden change in the conductivity of the membrane, corresponding to the equivalence point at pH ~7.

Taking into account that the active element of the indicating resistance is a sparingly soluble acid, we have studied some membranes containing different sparingly soluble inorganic and organic acids.

The method of preparation of the methyl polymethacrylate (MPMA) membranes is based on production of a homogeneous monomer/inorganic or organic acid mixture to which Na-Alassion CS can be added in order to raise the conductivity. The mixture is laid on a glass plate and kept under ultraviolet radiation for 5 min for polymerization. The resultant film is then carefully removed from the glass plate. Collodion membranes are obtained in the same way: a thin layer of collodion and heteropoly acid mixture is spread on a glass plate and left to dry at room temperature.

MPMA was chosen as support for the following reasons: (*a*) the polymerization can be performed at 70° or less, which makes it possible to use acids with a relatively low melting point; (*b*) the membrane is strong; (*c*) most of the organic acids used are soluble in the monomer as well as in the polymer, giving homogeneous membranes.

The membranes are characterized by their conductivity K_m, which is found from two consecutive measurements of either conductivity or resistance, with the membrane present for the first and absent for the second. The conductivity is calculated according to the formula:

$$K_m = \frac{R_s/a_s}{R_m/a_m} K_s$$

where R_s stands for the resistance of the solution, a_s for the distance between the electrodes, R_m for the membrane resistance, a_m for the thickness of the membrane and K_s for the conductivity of the solution in which the measurements are made (5*M* sodium chloride).

The conductivity "jump" for titrations giving a reversal of the direction of change in conductivity is assessed from the change in slope of the two branches of the titration curve. Where there is no change in the sign of the slope, the "jump" is calculated by performing an extrapolation of the type shown in Fig. 1 and expressing the change in conductivity at the equivalence point as a percentage of the mean value of the observed and extrapolated conductivities.

To obtain the data a conductivity cell, with cell constant $C = 1.91 \times 10^{-2}$ m^{-1} (Fig. 2) was used, as well as a Radelkis instrument with an alternating current of 80 Hz for conductances less than 1.5×10^{-4} $\Omega^{-1}.m^{-1}$ and 3000 Hz for the higher conductances. The titrations in the presence of the membrane were

* Part III, *Talanta*, 1972, **19**, 980.

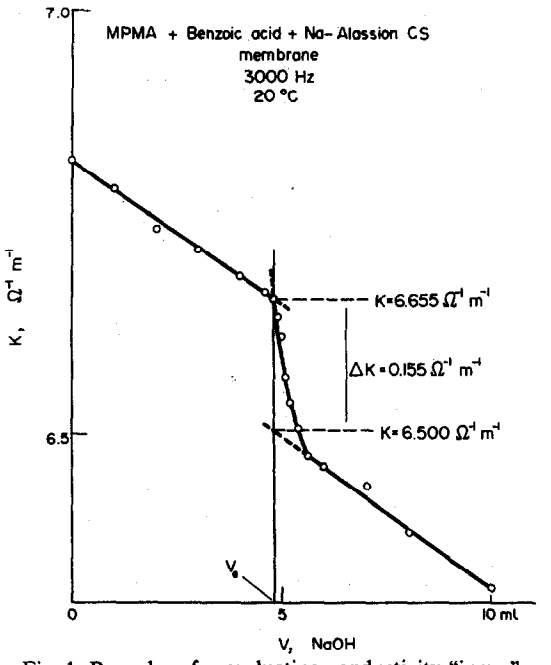


Fig. 1. Procedure for evaluating conductivity "jump."

performed in both compartments of the cell under equilibrium conditions.

Inorganic acid membranes

The following titrations were performed at 20°: hydrochloric acid of different concentrations (10^{-1}, 10^{-2}, 10^{-3} and $10^{-4}M$) in $5M$ sodium chloride medium with sodium hydroxide solution ten times as concentrated as the acid (~ 1, $\sim 10^{-1}$, $\sim 10^{-2}$ and $\sim 10^{-3}M$, respectively).

Table 1 shows the characteristics of the membranes with MPMA and collodion support.

Tungstic acid membrane. With any MPMA membrane + tungstic acid + Na-Alassion CS, the endpoint is sharp only for 10^{-1} and $10^{-2}M$ hydrochloric acid (Fig. 3, curves *c* and *b*). The increase in conductivity starts at pH 10.65, and for this reason the error is $\pm 1\%$ even with high acid concentrations ($>10^{-1}M$). The tungstic acid in the membrane reacts with the sodium hydroxide at high pH, and that is why the characteristic conductivity jump does not occur in the titration of $10^{-3}M$ hydrochloric acid. This membrane, like the corresponding molybdic acid membrane, can be used only once, because the formation of sodium tungstate in alkaline medium removes the tungstic acid from the membrane.

Collodion membrane with sodium arsenomolybdate. Sodium arsenomolybdate is used to produce molybdic acid directly in the membrane. It is added as a powder to the collodion membrane, because of its insolubility in nitrocellulose, thus the resulting membrane is heterogeneous; the collodion fully protects the active substance. It is possible to perform several titrations (5–10) with the same membrane if care is taken to avoid keeping it in alkaline medium (pH > 12) for long periods.

This membrane acquires indicator properties only after preliminary treatment with sodium hydroxide at pH 11.5–12 for 1–2 hr and then with $10^{-2}M$ hydrochloric acid for ~ 1 hr. The alkaline solution converts part of the arsenomolybdate into free molybdate, which then yields molybdic acid in acid solution. When acids of concentration $>10^{-3}M$ are titrated, some of the sodium molybdate formed after the equivalence point dissolves, increasing the conductivity jump. The conductivity jump is particularly large for titration of $10^{-1}M$ hydrochloric acid, and serviceable even for the $10^{-4}M$ acid titration (Fig. 4).

Organic acid membranes

Table 2 shows the characteristics of these membranes.

Benzoic acid membranes. Two membranes were prepared with benzoic acid: MPMA + benzoic acid and MPMA + benzoic acid + Na-Alassion CS. The presence of the Na-Alassion CS, a conducting component in the membrane, improves the titration curves (Fig. 5). The conductivity jump becomes 4–5 times bigger and takes place at pH 9.70. The membrane with the Na-Alassion CS present gives an error of $\pm 1\%$ or less if the hydrochloric acid concentration is $>10^{-2}M$. A disadvantage is that the membrane can be used only a few times because of the gradual loss of the benzoic acid by dissolution (Fig. 4, curves *b* and *c*).

o-*Chlorobenzoic acid membranes.* The MPMA membrane containing *o*-chlorobenzoic acid and Na-Alassion CS (Table 2) gives a negative conductivity jump at pH 3.27 (Fig. 6). The membrane gives an error of 1% or less only for titration of $>10^{-1}M$ hydrochloric acid. The gradual dissolution of the *o*-chlorobenzoic acid affects this membrane also.

o-*Phthalic acid membranes.* *o*-Phthalic acid is used in MPMA with and without Na-Alassion CS. The titration curves (Fig. 7) differ for the two types of membrane. Two jumps are observed when there is no Na-Alassion CS present, one being negative (pH 9.95) and the other positive (pH 10.86), and they result from neutralization of the two carboxylic groups of

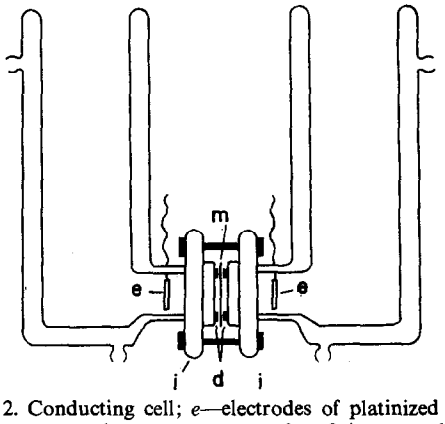


Fig. 2. Conducting cell; *e*—electrodes of platinized platinum; *m*—membrane; *i*—system for fixing membrane; *d*—rubber seals.

Table 1. Membrane conductometric sensors for acid–base titration in 5*M* NaCl

Active component (*A*)	Support (*B*)	Conductive component (*C*)	Membrane *A*:*B*:*C*	Method of forming	Form in which active component is added	Membrane thickness *mm*	K_m in 5*M* NaCl $\Omega^{-1}.m^{-1}$	Titrimetric characteristics [HCl], *M*	pH at "jump"	"Jump"*
Tungstic acid	MPMA	Na-Alassion CS	3:3:2	polymerization	powder	0.07	3.97 ± 10^{-3}	10^{-1}	10.65	$\Delta S + 0.08$
$Na_3[As(Mo_3O_{10})_4]$	collodion	—	1:1:0	evaporation	powder	0.07	4.73 ± 10^{-3}	10^{-4}	7	$\Delta S + 1.54$
Molybdic acid	MPMA	Na-Alassion CS	12:20:10	polymerization	powder	0.08	3.81×10^{-3}	10^{-2}	4.25	$\Delta A + 5.6$
Phosphomolybdic acid	collodion	—	1:1:0	evaporation	dissolved	0.02	4.09×10^{-1}	10^{-1}	3.55	$\Delta S + 0.2$
Phosphotungstic acid	collodion	—	1:1:0	evaporation	dissolved	0.02	3.69×10^{-1}	10^{-2}	9.5	$\Delta A + 0.7$

* For titration of 0.01*M* HCl.

Table 2. Membrane conductometric sensors for acid–base titration in 5*M* NaCl

		Membrane characteristics					Titrimetric characteristics		
Active component (*A*)	Support (*B*)	Conductive component (*C*)	*A*:*B*:*C*	Form in which active component is added*	Thickness of membrane, *mm*	K_m in 5*M* NaCl, $\Omega^{-1}.m^{-1}$	[HCl], *M*	pH at "jump"	"Jump"†
Benzoic acid	MPMA	Na-Alassion CS	2:3:2	d	0.09	2.32×10^{-2}	0.01	9.73	−2.4
Benzoic acid	MPMA	—	2:3:0		0.04	2.29×10^{-5}	0.01	11.10	−0.3
o-Chlorobenzoic acid	MPMA	Na-Alassion CS	1:2:1	d	0.08	9.7×10^{-4}	0.1	3.26	−12.1
o-Chlorobenzoic acid	MPMA	—	1:2:0	d	0.045	2.24×10^{-5}	0.1	3.26	−4.0
o-Phthalic acid	MPMA	—	1:2:0	d	0.07	2.98×10^{-4}	0.1	9.95	−2.9
								10.86	+4.4
o-Phthalic acid	MPMA	Na-Alassion CS	1:2:1	d	0.09	3.03×10^{-3}	0.1	10.43	−12.7
o-Salicylic acid	MPMA	—	1:2:0	d	0.04	5.08×10^{-6}	0.1	2.52	
								3.56	−2.5
								11.80	−5.4
o-Salicylic acid	MPMA	Na-Alassion CS	1:2:1	d	0.08	3.49×10^{-2}	0.1	3.90	−1.6
								11.58	−0.7
Gallic acid	MPMA	—	1:2:2		0.07	1.49×10^{-3}	0.1	3.56	−6.6
								11.71	+0.9
Gallic acid	MPMA	Na-Alassion CS	6:10:5	p	0.08	1.40×10^{-2}			

* All membranes were made by polymerization: d = dissolved; p = powder.
† ΔA, % (see Table 1, footnote).

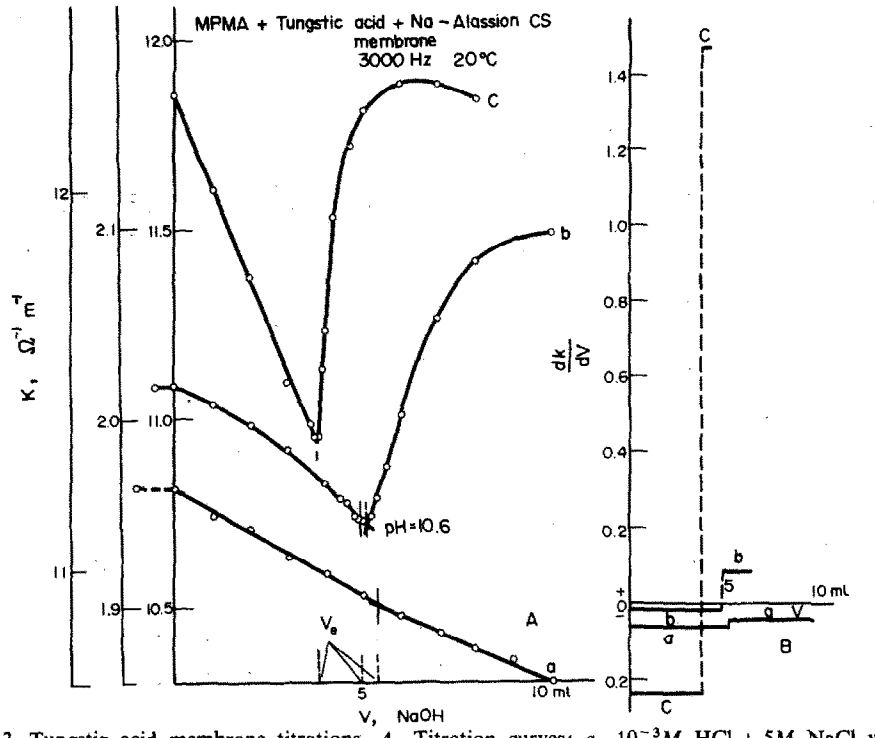


Fig. 3. Tungstic acid membrane titrations. *A*—Titration curves: *a*—$10^{-3}M$ HCl + $5M$ NaCl with $10^{-3}M$ NaOH; *b*—$10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH; *c*—$10^{-1}M$ HCl + $5M$ NaCl with $1M$ NaOH. *B*—Evaluation of conductivity jumps for linear part of curves.

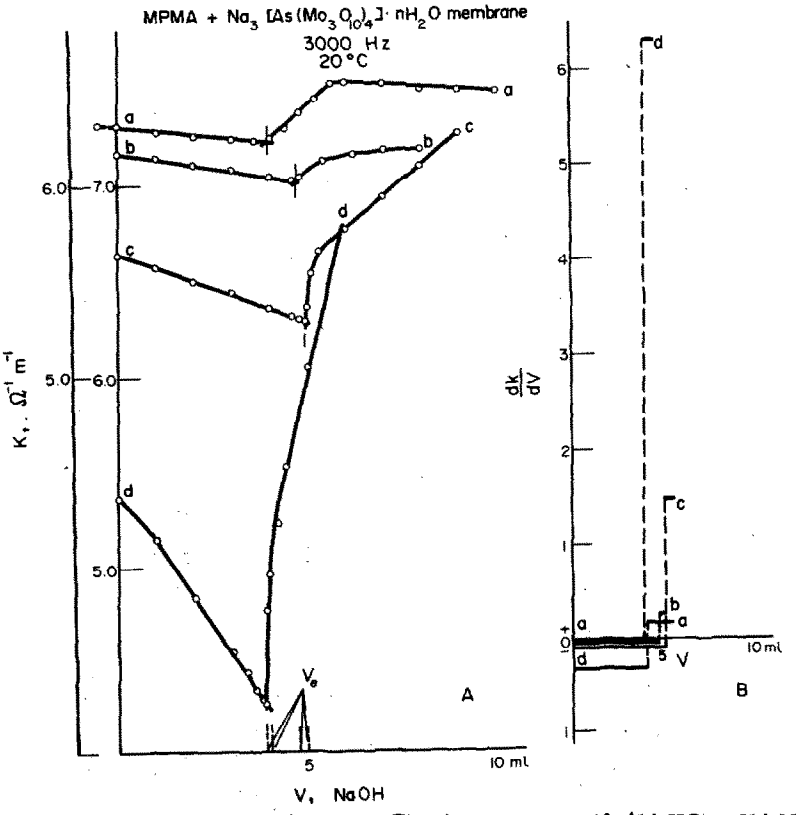


Fig. 4. Sodium arsenomolybdate membrane. *A*—Titration curves: *a*—$10^{-4}M$ HCl + $5M$ NaCl with $10^{-3}M$ NaOH; *b*—$10^{-3}M$ HCl + $5M$ NaCl with $10^{-2}M$ NaOH; *c*—$10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH; *d*—$10^{-1}M$ HCl + $5M$ NaCl with $1M$ NaOH. *B*—Evaluation of conductivity jumps for linear part of curves.

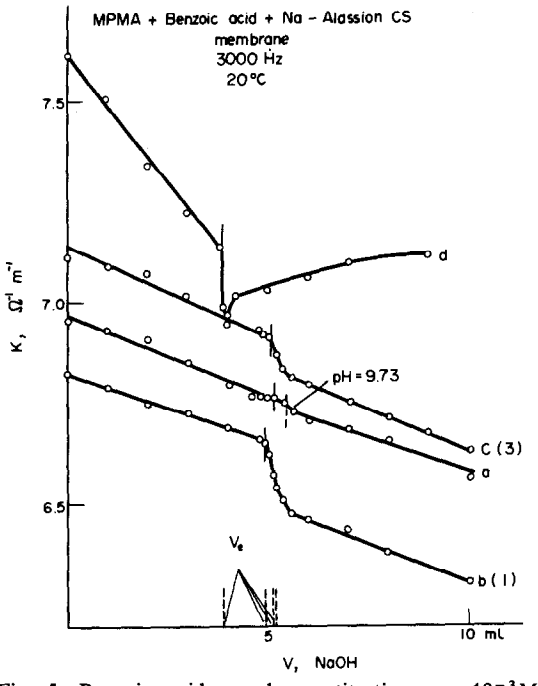


Fig. 5. Benzoic acid membrane titrations. *a*—$10^{-3}M$ HCl + $5M$ NaCl with $10^{-2}M$ NaOH; *b* and *c*—$10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH; *d*—$10^{-1}M$ HCl + $5M$ NaCl with $1M$ NaOH. The figures in brackets give the serial number of the determination in a set with the same membrane.

the phthalic acid. Addition of Na-Alassion CS to the membrane enhances the second dissociation of *o*-phthalic acid, giving a more extensive negative jump at the equivalence point (at pH 10.43). The error is

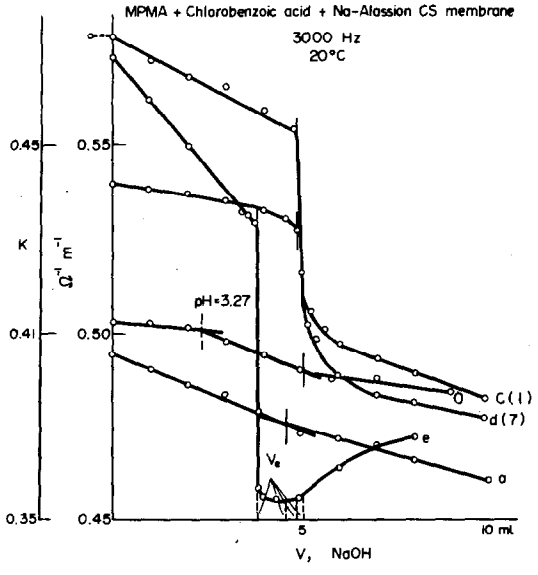


Fig. 6. *o*-Chlorobenzoic acid membrane titrations. *a*—$10^{-4}M$ HCl + $5M$ NaCl with $10^{-3}M$ NaOH; *b*—$10^{-3}M$ HCl + $5M$ NaCl with $10^{-2}M$ NaOH; *c* and *d*—$10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH; *e*—$10^{-1}M$ HCl + $5M$ NaCl with $1M$ NaOH. The figures in brackets give the serial number of the determination in a set with the same membrane.

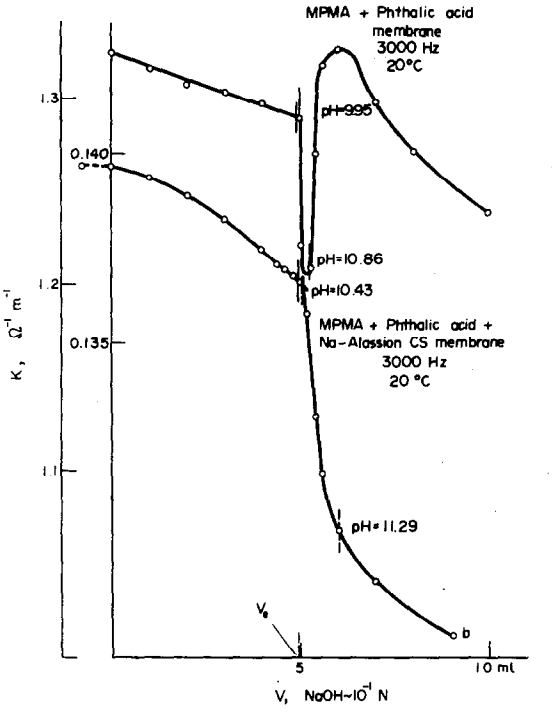


Fig. 7. Phthalic acid membranes: conductometric titration curves of $10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH.

$\pm 1\%$ or less only for hydrochloric acid concentrations $> 10^{-1}M$.

Conclusions

The inclusion of molybdic or tungstic acid in the membrane, or producing them directly in the membrane by decomposition of a heteropoly acid, produces positive conductivity jumps at the end-points. These jumps are caused by the fact that the equilibrium

$$(HA)_m + Na^+ \rightleftharpoons (Na^+ + A^-)_m + H^+$$

shifts to the right, with dissociation of the salt into $Na^+ + A^-$ in the membrane body. The increasing conductivity of the solution-membrane system is also due to dissolution of this salt after the active component has been neutralized.

The collodion + $Na_3[As(Mo_3O_{10})_4].nH_2O$ + Na-Alassion CS membrane is a very good indicator for acid–base conductometric titration if it is given the preliminary treatment necessary for the formation of molybdic acid. The conductivity jump with this membrane starts at pH 7 and permits titration of down to $10^{-4}M$ hydrochloric acid in highly conducting medium.

The conductivity jump for titrations done with the aid of the membranes with sparingly soluble organic acids takes place in a pH-region which evidently depends on the dissociation constant of the organic acid included and on the way the acid interacts with the support and with the conductivity component used (Na-Alassion CS).

REFERENCES

1. C. Liteanu and E. Hopîrtean, *Rev. Roumaine Chim.*, 1967, **12**, 517.
2. C. Liteanu and L. Ghergariu-Mîrza, *ibid.*, 1970, **15**, 1871.
3. *Idem*, *Talanta*, 1972, **19**, 980.
4. C. Liteanu and E. Hopîrtean, *Studia Univ. Babes-Bolyai Series Chemie*, 1966, **11**, 135.

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DIFFERENTIAL DETERMINATION OF SELENIUM(IV) AND SELENIUM(VI) WITH SODIUM DIETHYLDITHIOCARBAMATE, AMMONIUM PYRROLIDINEDITHIOCARBAMATE AND DITHIZONE BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY WITH A CARBON-TUBE ATOMIZER

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Summary—The extraction behaviour of selenium(IV) and selenium(VI) with sodium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate and dithizone in organic solvents has been investigated by means of flameless atomic-absorption spectrophotometry with a carbon-tube atomizer. The selective extraction of selenium(IV) and differential determination of selenium(IV) and selenium(VI) have been developed. With sodium diethyldithiocarbamate and carbon tetrachloride, when the aqueous phase/organic solvent volume ratio is 5 and the injection volume in the carbon tube is 20 μl, the sensitivity for selenium is 0.4 ng/ml for 1% absorption. The relative standard deviations are *ca.* 3%. Interference by many metal ions can be prevented by masking with EDTA. The proposed methods have been applied satisfactorily to determination of Se(IV) and Se(VI) in various types of water.

Viewed for decades as a toxin, and as a pollutant in the geochemical environment, selenium may now be viewed as a critical nutrient. The discovery that selenium may be nature's antidote to heavy metal toxicities (Cd^{2+}, Hg^{2+}, Cu^{2+} and others) has attracted much interest. In previous papers the differential determination of arsenic(III) and (V), and antimony(III) and (V) by solvent extraction combined with atomic-absorption spectrophotometry by means of a carbon-tube atomizer has been described.[1,2] For selenium determination in aqueous samples atomic-absorption techniques based on the hydride[3,4] and a carbon-tube method[5–7] have been developed, enhancing the sensitivity. For differential estimation of selenium(IV) and (VI) the hydride method has been used in combination with selective reduction of selenium(VI) with iodide.[8]

In this paper, we extend to selenium determination the techniques used for arsenic[1] and antimony.[2]

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard selenium(IV) solution, 1000 ppm. Prepared by dissolving 1.405 g of selenium dioxide and diluting to 1000 ml with water. Diluted with water to give a concentration of 0.4 ppm before use.

Standard selenium(VI) solution, 1000 ppm. Prepared by dissolving 2.801 g of potassium selenate and diluting to 1000 ml with water. Diluted with water to give a concentration of 0.4 ppm before use.

Selenium(IV)-75m solution. Prepared by diluting 1 mCi of the radioisotope selenium(IV)-75m (selenious acid in 1*M* hydrochloric acid) to a suitable concentration, with addition of inactive selenium(IV) as carrier.

Buffer solution, pH 4. Prepared by mixing 1*M* acetic acid and 1*M* sodium acetate in a suitable ratio.

Apparatus

The apparatus was that described before,[1] except for the light-source, a Westinghouse selenium hollow-cathode lamp.

Recommended general procedure

Selenium(IV) determination. Take an aliquot of a sample solution containing not more than 2 μg of selenium(IV), in a separatory funnel. Add 5 ml of 5% EDTA solution. Add 2 ml of 1% sodium diethyldithiocarbamate (DDTC) solution and 5 ml of acetate buffer, and dilute to 25 ml with water. Shake the solution for 2–5 min with 10 ml of carbon tetrachloride. Let stand for 20–30 min and separate the organic phase. Inject 20 μl of the organic phase by micropipette into the carbon tube. Pass argon through the furnace at a flow-rate of 3 l./min, and then atomize the sample by the following heating sequence: drying for 30 sec at 20 A (*ca.* 200°), ashing for 120 sec at 60 A (*ca.* 900°), and atomization for 7 sec at 230 A (*ca.* 2400°). Record the absorption signal at 1961 Å. Run a reagent blank at the same instrumental settings and subtract it from the analytical value.

Total selenium determination. Take an aliquot of sample solution containing not more than 2 μg of selenium, in a beaker. Add hydrochloric acid to adjust the acidity of the solution to *ca.* 4*M*. Heat in a boiling water-bath or a steam-bath for 20 min. Cool, add 5 ml of 5% EDTA solution, 2 drops of Methyl Orange solution and neutralize with ammonia. Add 2 ml of 1% DDTC solution, adjust the pH to 3.5–4.5 with 5 ml of buffer, transfer the mixture to a separatory funnel and adjust the volume to 25 ml with washings from the beaker. Extract and measure the

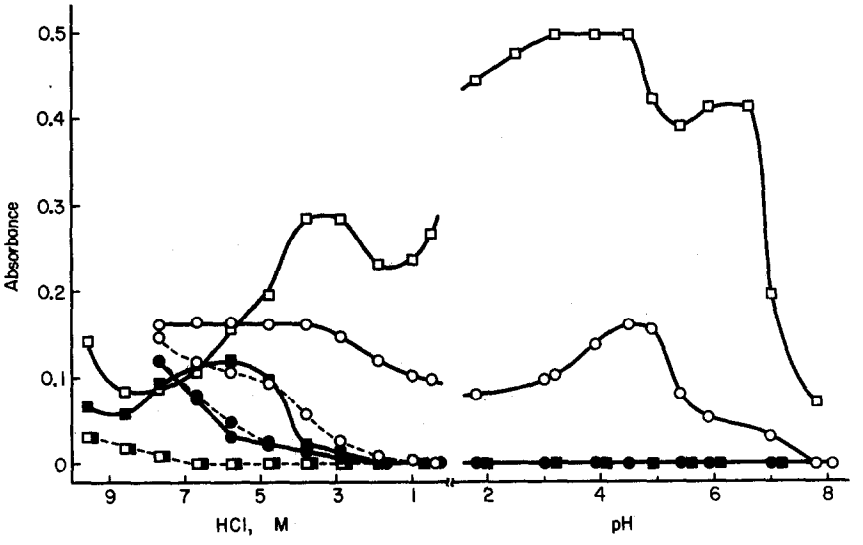


Fig. 1. Effect of acidity on the extraction of Se(IV) and Se(VI) with DDTC. ○, Se(IV)–MIBK; ●, Se(VI)–MIBK; □, Se(IV)–CCl_4; ■, Se(VI)–CCl_4; (– – –), reagent (DDTC) blank; aqueous phase, 25 ml; organic phase, 10 ml; Se(IV) or Se(VI), 2 μg.

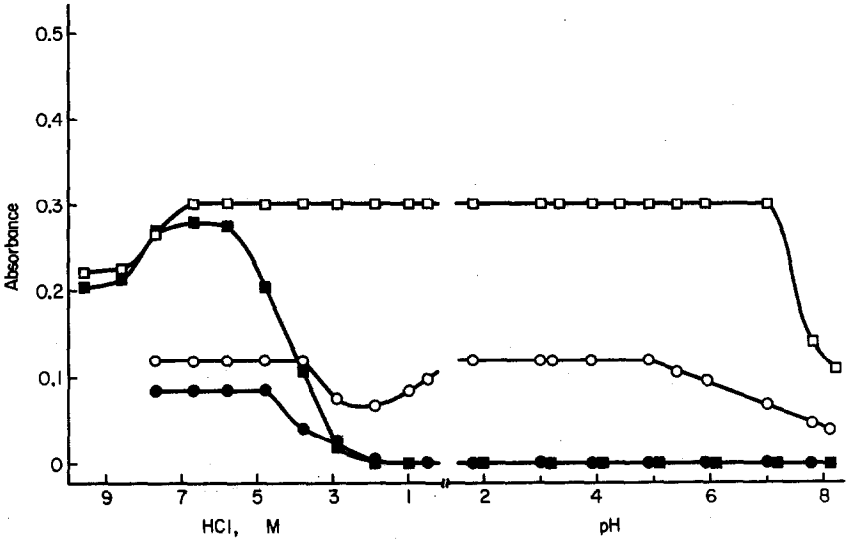


Fig. 2. Effect of acidity on the extraction of Se(IV) and Se(VI) with APDC. ○, Se(IV)–MIBK; ●, Se(VI)–MIBK; □, Se(IV)–CCl_4; ■, Se(VI)–CCl_4, aqueous phase, 25 ml; organic phase, 10 ml; Se(IV) or Se(VI), 2 μg.

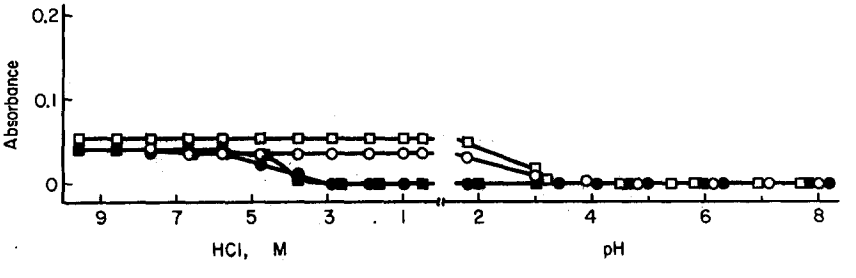


Fig. 3. Effect of acidity on the extraction of Se(IV) and Se(VI) with dithizone. ○, Se(IV)–MIBK; ●, Se(VI)–MIBK; □, Se(IV)–CCl_4; ■, Se(VI)–CCl_4; aqueous phase, 25 ml; organic phase, 10 ml; Se(IV) or Se(VI), 2 μg.

Table 1. Degree of extraction

Reagent	Solvent	pH	Extraction, %* Se(IV)
APDC	MIBK	1.4	95
APDC	MIBK	4.0	95
APDC	CCl_4	1.4	96
APDC	CCl_4	4.0	96
DDTC	MIBK	1.4	68
DDTC	MIBK	4.5	96
DDTC	CCl_4	1.4	73
DDTC	CCl_4	4.0	95
Dithizone	MIBK	1.4	69
Dithizone	MIBK	4.0	4
Dithizone	CCl_4	1.4	90
Dithizone	CCl_4	4.0	2
Blank	MIBK	1.4	1
Blank	MIBK	4.5	0
Blank	CCl_4	1.4	0
Blank	CCl_4	4.0	0

* Se(VI) was not extracted.

Table 1b. Degree of extraction in strongly acidic medium

Reagent	Solvent	[HCl], *M*	Extraction (%) Se(IV)	Se(VI)
APDC	MIBK	4.2	96	
APDC	MIBK	7.2	97	82
APDC	CCl_4	4.2	96	
APDC	CCl_4	7.2	97	86
DDTC	MIBK	4.8	95	
DDTC	MIBK	7.2	95	19
DDTC	CCl_4	3.6	44	
DDTC	CCl_4	7.2	20	15
Dithizone	MIBK	3.6	95	
Dithizone	MIBK	7.2	89	19
Dithizone	CCl_4	3.6	95	
Dithizone	CCl_4	7.2	90	6
Blank	MIBK	4.2	61	
Blank	MIBK	7.2	87	20
Blank	CCl_4	4.2	0	
Blank	CCl_4	7.2	0	0

absorption as for selenium(IV). The selenium(VI) is estimated from the difference between total selenium and selenium(IV).

RESULTS AND DISCUSSION

Optimization of the atomization system

The heating conditions were examined in the same way as for arsenic[1] and antimony[2] and followed the same pattern, the useful limits being 20–30 A for 30 sec (200–300°) for drying, 55–65 A for 120 sec (800–1000°) for ashing, and 220–260 A for 7 sec (2300–2700°) for atomization. The shielding-gas flow-rates should be the same as for arsenic or antimony:[1,2] 3 l./min.

Extraction

Extraction behaviour of Se(IV) and Se(VI). The extraction behaviour of selenium(IV) and (VI) with DDTC, APDC (ammonium pyrrolidinedithiocarbamate) and dithizone in methyl isobutyl ketone (MIBK) and carbon tetrachloride was investigated. The effect of acidity and the degree of extraction are shown in Figs. 1–3 and Table 1. Both sets of data are given because of the losses of selenium during the atomic-absorption heating cycle.

Table 2. Recovery tests on selenium(IV) and selenium(VI)

Added, *ng/ml*		Found, *ng/ml*		
Se(IV)	Se(VI)	Se(total)	Se(IV)	Se(VI)
0	80	78	0	78
20	60	80	21	59
40	40	81	41	40
60	20	79	60	19
80	0	80	80	0

In the DDTC system, selenium(IV) is extracted into either CCl_4 or MIBK in the pH range 1–8 whereas selenium(VI) is not. In fairly concentrated hydrochloric acidic medium selenium(VI) is extracted, and even then but poorly. In the atomic-absorption method, CCl_4 gives much higher sensitivity (3-fold) than MIBK. However, the extraction efficiency of the solvents, determined by the radio-tracer technique with ^{75m}Se, is the same for CCl_4 and MIBK (CCl_4 95% extraction at pH 4, MIBK 96% at pH 4.5). The low atomic-absorption sensitivity with the MIBK system may be due to loss of selenium by volatilization along with MIBK before the atomization stage. The species extracted from neutral medium was confirmed to be $Se(DDTC)_4$ by continuous variation plots.

With the APDC system, selenium(IV) is well extracted (~95%) into both solvents over a wide range of pH. The atomic-absorption sensitivity, however, is lower than that of the DDTC system. This may be because the APDC complex of selenium(IV) is more volatile than the DDTC complex in the carbon tube. Selenium(VI) is not appreciably extracted at pH 1–8, but in strongly acidic medium is considerably extracted.

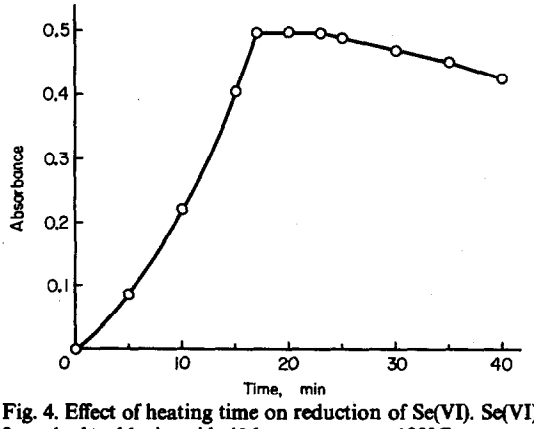


Fig. 4. Effect of heating time on reduction of Se(VI). Se(VI), 2 μg; hydrochloric acid, 4*M*; temperature, 100°C; aqueous phase 25 ml, organic phase 10 ml.

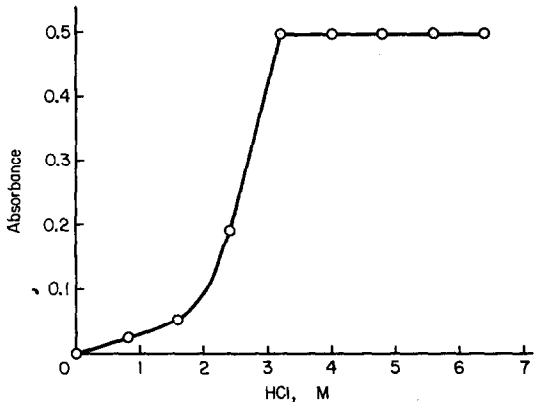


Fig. 5. Effect of hydrochloric acid concentration on reduction of Se(VI). Se(VI), 2 μg; temperature, 100°C; heating time, 20 min; aqueous phase 25 ml, organic phase 10 ml.

Table 3. Permissible amount of foreign ions in determination of 2 μg of Se/25 ml (to give < 10% error)

Ion	Added as	Limit [Ion]/[Se]
Fe^{3+}	Chloride	2 (23)
Co^{2+}	Chloride	6 (8)
Ni^{2+}	Chloride	94 (340)
Mn^{2+}	Chloride	16 (1000)
Cu^{2+}	Sulphate	13 (10)
Zn^{2+}	Chloride	25 (1000)
Al^{3+}	Potassium alum	10 (1000)
Pb^{2+}	Nitrate	60 (60)
Hg^{2+}	Chloride	39 (34)
Sn^{2+}	Sulphate	24 (25)
Cd^{2+}	Sulphate	14 (18)
Bi^{3+}	Chloride	14 (16)
Te^{4+}	Tellurous acid	7 (6)
As^{3+}	Arsenious acid	8 (8)
Sb^{3+}	Chloride	8 (10)
S^{2-}	Sodium salt	130

The following are tolerable in 1000-fold ratio to Se: Na^+, K^+, Ca^{2+}, Mg^{2+}, Cr^{3+}, Ag^+, As^{5+}, NH_4^+, F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, CH_3COO^-, PO_4^{3-}. Values in parentheses apply when 1% EDTA is present.

Dithizone does not extract selenium(IV) from neutral medium. From acidic medium selenium(IV) is well extracted, but the atomic-absorption sensitivity is the lowest among the three systems.

Differential determination of Se(IV) and Se(VI). From the results it is concluded that DDTC–CCl_4 extraction at pH 3.5–4.5 is best for the selective separation of selenium(IV) and (VI). Total selenium is separately determined by extraction after reduction of selenium(VI) to (IV). Recovery tests showed (Table 2) that the recommended procedure gave good results.

In the conventional method,[9] selenium(VI) is reduced to selenium(IV) in warm 4*M* hydrochloric acid. Temperature, time, and acid concentrations must be specified if quantitative reduction without loss of selenium is to be obtained. The optimum conditions for the reduction were therefore investigated, by tests with 2 μg of selenium(VI) in a boiling water-bath. Figure 4 shows that the heating time needed for the reduction in 4*M* hydrochloric acid medium is at least 17 min, but that there is an appreciable loss of selenium after 23 min. The optimum acidity is 3.2*M* hydrochloric acid or above (Fig. 5).

Effect of shaking time, and stability of the extracts. Extraction is quantitative in 15 sec and shaking for up to 20 min produces no further change in absorption. The absorption signal of the extract remains almost constant for at least 6 hr after the extraction.

Effect of phase-volume ratio on sensitivity. Ten ml of carbon tetrachloride were used for the extraction from various volumes of aqueous phase containing 2 μg of selenium(IV). A plot of relative absorption *vs.* phase-volume ratio slightly decreased with increasing V_w/V_0. If an appropriate V_w/V_0 ratio is chosen according to the selenium content, selenium may be determined over a wide concentration range from ng/ml to μg/ml levels.

Table 4. Analytical results on various samples

	Se(total), *ng/ml*		Se(IV), *ng/ml*		Se(VI), *ng/ml*	
Sample	added	found	added	found	added	found
River water	—	ND	—	ND	—	ND
River water	20	20	20	20	—	ND
River water	20	20	—	ND	20	20
River water	40	40	20	20	20	20
Waste water A	—	38	—	12	—	26
Waste water A	10	49	10	22	—	27
Waste water A	10	48	—	12	10	36
Waste water A	20	58	10	22	10	36
Waste water B	—	14	—	14	—	ND
Waste water B	10	23	10	24	—	ND
Waste water B	10	23	—	14	10	9
Waste water B	20	32	10	24	10	8
Sea-water	—	ND	—	ND	—	ND
Sea-water	20	20	20	21	—	ND
Sea-water	20	21	—	ND	20	21
Sea-water	40	39	20	21	20	18

ND: not detected.

Calibration curve and precision

Calibration curves prepared by use of selenium(IV) and reduced selenium(VI) solutions were similar. The linearity was good over the range 2–40 ng/ml with $V_w/V_0 = 5$. The sensitivity for 1% absorption was found to be 0.4 ng/ml. The relative standard deviation was *ca.* 3% for 80 ng/ml of selenium(IV) (10 determinations, 3 injections for each).

Interferences

The interference of large amounts of alkali and alkaline earth metals in the determination of selenium by direct injection[6] is avoided by the prior extraction of the selenium. However, large amounts of metal ions which react with DDTC lower the degree of extraction of selenium(IV). In many cases, such interferences can be reduced by masking with EDTA. Table 3 shows the effects of various ions; the data in parentheses were obtained with 1% of EDTA in the aqueous phase.

Application to water analysis

Results for differential determination of selenium (IV) and (VI) in various types of water are presented in Table 4 together with those of a recovery test run on the samples. All the samples were acidified with hydrochloric acid to *ca.* pH 1 immediately after sampling. According to the method proposed here, ng/ml levels of selenium(IV) and (VI) in waste water or seawater can be determined satisfactorily.

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REFERENCES

1. T. Kamada, *Talanta*, 1976, **23**, 835.
2. T. Kamada and Y. Yamamoto, *Talanta*, 1977, **24**, 330.
3. Y. Yamamoto, T. Kumamaru, Y. Hayashi and M. Kanke, *Anal. Letters*, 1972, **5**, 717.
4. Y. Yamamoto and T. Kumamaru, *Z. Anal. Chem.*, 1976, **281**, 353; **282**, 139.
5. R. B. Baird, S. Pourian and S. M. Gabrielian, *Anal. Chem.*, 1972, **44**, 1887.
6. T. Kamada, T. Kumamaru and Y. Yamamoto, *Bunseki Kagaku*, 1975, **24**, 89.
7. E. L. Henn, *Anal. Chem.*, 1975, **47**, 428.
8. D. R. Corbin and W. M. Barnard, *At. Absorption Newsletter*, 1976, **15**, 116.
9. APHA, AWWA and WPCF, *Standard Methods for the Examination of Water and Wastewater*, 13th Ed., p. 295, APHA, Washington, 1971.

Talanta, Vol. 25, pp. 21–40. Pergamon Press, 1978. Printed in Great Britain.

IDENT—A RADIOISOTOPE-IDENTIFICATION SUBROUTINE FOR USE WITH THE GAMMA-RAY SPECTRUM ANALYSIS PROGRAM SAMPO

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Summary—A radioisotope-identification and mass-determination subroutine has been added to the gamma-ray spectrum analysis program SAMPO. The subroutine IDENT contains a nuclear data library of 750 gamma-rays that are likely to be encountered in thermal-neutron activation analysis. Peaks found by SAMPO are compared with the library peaks and possible isotope identifications are made. To maximize the degree of confidence in the isotope identification, the subroutine carries out a half-life check and also confirms that the most prominent gamma-ray of the isotope concerned is present. Using the library data, together with information on the neutron flux, duration of the irradiation, subsequent decay time, and gamma-detection efficiency, the subroutine calculates the masses of elements identified in the sample, and can handle spectra acquired during either simple or cyclic irradiation. As well as the calculated masses the output contains information on identifications rejected by certain criteria. The nuclear data library used by the subroutine is presented in this paper in a simplified tabular form, and, as such, may be used for direct isotope identification and elemental mass determination.

The versatile gamma-ray spectrum analysis program SAMPO[1,2] is now used in many laboratories for the analysis of the complex spectra encountered in neutron-activation analysis. The SAMPO program includes routines for peak-finding, peak-fitting and peak intensity and energy determinations. The addition of the subroutine IDENT, described below, increases the usefulness of SAMPO by carrying out radioisotope identifications and elemental mass determinations after simple or cyclic thermal-neutron activation analysis.

THE NUCLEAR DATA LIBRARY

The nuclear data library, which forms part of the subroutine IDENT, contains the following information for each of about 750 gamma-rays that are likely to be encountered in thermal-neutron activation analysis:

(*i*) a reference number for each gamma-ray
(*ii*) the energy of the gamma-ray
(*iii*) the name of the isotope emitting the gamma-ray
(*iv*) the number of gamma-rays of this energy emitted per disintegration of the isotope
(*v*) the half-life of the isotope
(*vi*) the atomic weight of the target nucleus
(*vii*) the product of the thermal-neutron absorption cross-section and natural fractional abundance of the target nucleus
(*viii*) a reference to the parent nucleus if the isotope concerned is the daughter of another isotope produced by thermal-neutron capture.

The library also includes information on naturally occurring radioisotopes and also a few of the more common isotopes produced by fast-neutron reactions that may occur in the mixed-neutron field of a nuclear reactor.

The information is given in the following form.

Column 1: the reference number for the gamma-ray.

Column 2: the gamma-ray energy in keV to the nearest 0.1 keV.

Column 3: the name of the isotope.

Column 4: the absolute gamma-ray intensity, I_a (gammas/disintegration), quoted as precisely as it is known, up to a maximum of 3 significant figures; a blank indicates that the absolute intensity is unknown.

Column 5: the energy (in keV) of the gamma-ray of the highest intensity from the isotope concerned.

Column 6: the reference number of the most intense gamma-ray.

Column 7: the half-life of the isotope, $t_{1/2}$, to a maximum of 3 significant figures.

Column 8: the half-life in seconds, expressed in exponential form, *e.g.*, 5.97 EO5 = 5.97×10^5 sec.

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Column 9: the atomic weight of the target (3 significant figures); values given in brackets are not necessarily meaningful but inserted because demanded by the program.

Column 10: *either* the product of the thermal-neutron cross-section, σ (barns), and fractional natural abundance, f, of the target nucleus, *or* one of the following:

Background: a naturally occurring radioisotope ($t_{1/2}$ given as 10^{20} sec), and indicated by B in the program

Fast neutron: the product of a fast-neutron reaction (F in the program)

Daughter: the daughter of a nucleus produced by neutron capture (D in the program)

Unknown: the thermal-neutron cross-section is not available (Q in the program)

Column 11: the reference number of the radioactive parent, where appropriate.

Column 12: the name of the radioactive parent, where appropriate.

The data library and table have been compiled from information in Appendix VII of reference 3, together with data from *The Table of Isotopes*[4] and recent issues of *Nuclear Data Sheets*.[5]

The table provides sufficient information for the identification of radioisotopes contributing to a gamma-ray spectrum, and may also be used, independently of SAMPO and the subroutine IDENT, to determine the masses of the elements present in a sample which has undergone thermal-neutron activation, if the following additional information is available:

(i) the thermal-neutron flux (ϕ) ($cm^{-2}.sec^{-1}$)
(*ii*) the duration of irradiation (t_i) (sec)
(*iii*) the time between irradiation and gamma-counting (t_d) (sec)
(*iv*) the gamma-detector efficiency (ϵ)

The mass (in grams) is then given by the formula

$$\frac{AW\lambda \exp(\lambda t_d)}{0.6\epsilon I_a \phi \sigma f [1 - \exp(-\lambda t_i)][1 - \exp(-\lambda t_c)]} \quad (1)$$

where

A is the number of counts for the photopeak concerned,

W is the atomic weight of the target nucleus,

λ is the radioisotope decay constant = (ln 2)/$t_{\frac{1}{2}}$ (sec^{-1}),

t_c is the live counting time for the gamma spectrum (sec) and the other symbols are as already defined.

It should be noted that formula (1) is strictly true only when the fractional dead-time remains constant during the counting time, which should therefore be kept short compared to the decay rate of the sample being studied.

In the case of cyclic activation analysis where the sample is repeatedly transferred back and forth between the irradiation and counting position with a constant periodic time T, the mass (in grams) is given by the formula

$$\frac{B[1 - \exp(-\lambda T)]}{n - \exp(-\lambda T)\left|\dfrac{1 - \exp(-n\lambda T)}{1 - \exp(-\lambda T)}\right|} \quad (2)$$

where

B is formula (1),
n is the total number of cycles.

RADIOISOTOPE IDENTIFICATION BY THE IDENT SUBROUTINE

The sequence of operations carried out by IDENT is shown in the flow diagram (Fig. 1).

The subroutine takes the first peak (lowest energy peak) found by the main SAMPO program and compares its energy and energy-uncertainty with the energy of the first and subsequent peaks in the data library until a library peak is encountered which has an energy greater than the sum of the energy and energy-uncertainty of the SAMPO peak. Whenever a library peak is found which has an energy differing from that of the SAMPO peak by less than its energy-uncertainty, a flag is put on the library peak, indicating that it has been found in the spectrum, and the reference number of the library peak is recorded as a possible identification of the SAMPO peak. At this stage, depending on the magnitude of the energy-uncertainty, there may be several possible identifications of each SAMPO peak, and the subroutine allows for up to 15 before an error message is given. If no identification is made, a message to this effect is also given. Having dealt in this manner with the first SAMPO peak, the subroutine treats each subsequent SAMPO peak in the same way, except that it does not go back to the beginning of the data library each time but only goes back 20 library peaks from where it stopped with the previous SAMPO peak. This means that only a small part of the data library needs to be searched for each SAMPO peak.

For the sake of convenience in adding new peaks to the library, the library is made up of two sections: a fixed section for 713 gamma rays, and an updatable section to which additions can be made and which at present deals with 36 gamma-rays. Since the updatable section is relatively short, each SAMPO peak is compared to every library peak in the updatable section and therefore the peaks in this section do not need to be in any order.

When this stage of the subroutine is complete, several of the library peaks will have flags indicating that they have been linked with peaks found by SAMPO, and most of the SAMPO peaks will have been associated with one or more library peaks.

The next stage of the program carries out the following checks:

(*i*) is the gamma-ray of highest intensity of the isotope concerned present in the spectrum? (if the

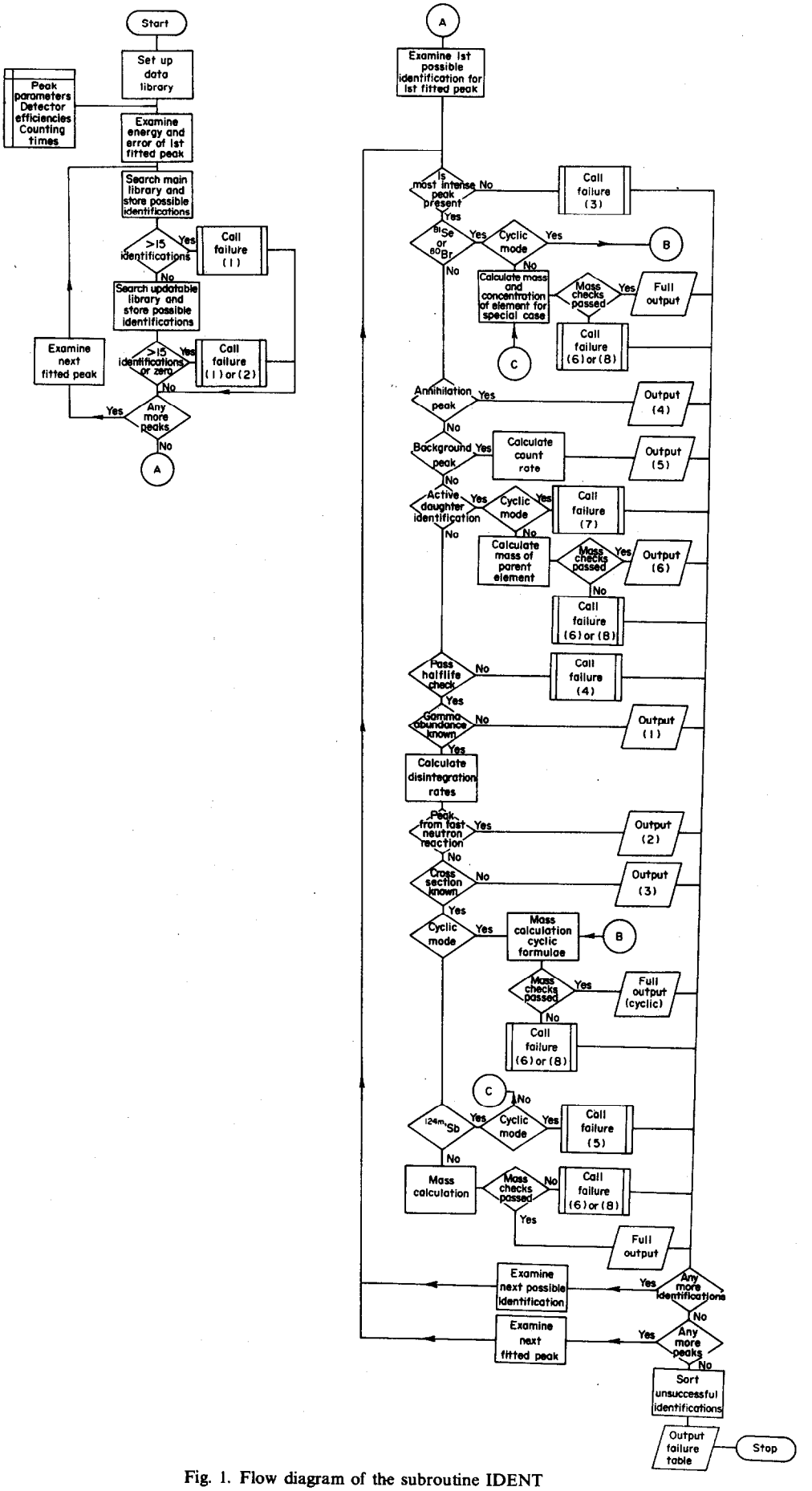


Fig. 1. Flow diagram of the subroutine IDENT

energy of the highest intensity gamma ray is outside the energy range of the spectrum this check is ignored)

(*ii*) if the isotope identified is ^{81}Se, ^{80}Br or $^{124m'}$Sb then a special calculation is carried out taking into account the fact that each isotope is produced by neutron irradiation together with its parent ^{81m}Se, ^{80m}Br, or $^{124m''}$Sb

(*iii*) if the energy of the SAMPO peak is 511 keV it is identified as annihilation radiation and no further calculations are carried out

(*iv*) if the isotope identified occurs in the natural background then only a simple calculation is carried out in which the total peak area is divided by the gamma-ray intensity (*i.e.*, gammas/disintegration) and the live counting time

(*v*) if the isotope identified is the daughter of a radioactive parent produced by neutron capture a calculation is carried out to determine the mass of the parent element

(*vi*) if the time between irradiation and counting of the sample is greater than 20 half-lives of the isotope identified, that identification is rejected

(*vii*) if the absolute intensity of the gamma-ray is unknown then no further calculations are carried out.

Having done these checks the program then calculates the disintegration rates of the identified isotopes both at the beginning of the counting time and at the end of the irradiation period, taking into account dead-time corrections and decay of the isotope during counting. This calculation uses the delay time between irradiation and counting, which is fed into the program on the IDENT control card.

If the isotope concerned is not produced by fast-neutron reaction, and if its thermal-neutron cross-section is known, then the program uses data on the sample-irradiation time and thermal-neutron flux (also on the IDENT control card) to determine the mass of the element concerned in the activated sample. If the resulting mass is negative or is greater than the total mass of the sample the identification is rejected.

The subroutine deals with spectra accumulated in cyclic activation analysis, as well as the straightforward activation-analysis process where a gamma-ray spectrum is accumulated after a single irradiation.

Because cyclic activation is used for isotopes having half-lives of the order of seconds an additional criterion is included for acceptance of possible identifications. The formation of active daughter products is most unlikely to have had time to occur and so peaks assigned to such nuclides are rejected. Furthermore those isotopes which may be formed directly by (n, γ) reactions and by decay of an isomer (Se, Br, $^{124'}$Sb) are considered, for calculation purposes in the cyclic activation option, to have been formed only by the first of these processes.

For dead-time corrections two options are available.

(*a*) If the spectra are acquired cycle by cycle they may be corrected for an assumed constant fractional dead-time by a simple CLOCK-TIME/LIVE TIME multiplication, and then spectra for the same sample are added together. This is accomplished by relevant characters on the DATAIN and IDENTIFY control cards.

(*b*) If the analyser is left to acquire data for the *whole* of the experiment, so that only a single spectrum is acquired, then a simple dead-time correction can be made, on the assumption that the dead-time only arises during the count section of the period. This mode of analysis can be defined by a relevant character on the DATAIN card.

A complete listing of the subroutine follows the nuclear data library.

REFERENCES

1. J. T. Routti and S. G. Prussin, *Nucl. Instr. Meth.*, 1969, **72**, 125.
2. J. T. Routti, *SAMPO, A Fortran IV Program for Computer Analysis of Gamma Spectra from Ge(Li) Detectors*, University of California Lawrence Radiation Laboratory, UCRL-19452, 1969.
3. F. Adams and R. Dams, *Applied Gamma Ray Spectrometry*, 2nd Ed., Pergamon, Oxford, 1970.
4. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, New York, 1967.
5. *Nuclear Data Sheets*, Academic Press, New York.

THE NUCLEAR DATA LIBRARY AND PROGRAM IDENT

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
1	46.5	Pb210	0.41	46.5	1			1.00E20	(209)	Background	-	-
2	48.9	Tb161	0.148	57.2	4	6.9	d	5.97E05	(160)	Daughter	321	Gd161
3	51.4	Rh104m	0.482	51.4	3	4.34	m	2.64E02	103	1.10E+01	-	-
4	57.2	Tb161	0.16	57.2	4	6·9	d	5.97E05	(160)	Daughter	321	Gd161
5	57.4	Ce143	0.117	293.3	263	1.38	d	1.19E05	142	1.11E-01	-	-
6	57.5	Hf180m	0.48	332.2	299	5.50	h	1.98E04	179	2.75E-02	-	-
7	57.8	Ir192m	$5x10^{-5}$	316.5	283	1.50	m	9.00E01	191	9.63E+01	-	-
8	58.0	Dy159	0.02	58.0	8	145	d	1.25E07	158	9.02E-02	-	-
9	58.0	Gd159	0.02	363.6	327	18.6	h	6.68E04	158	8.47E-01	-	-
10	58.5	Co60m	0.021	58.5	10	10.5	m	6.30E02	59	1.80E+01	-	-
11	59.8	U237	0.36	208.0	189	6.75	d	5.83E05	(236)	Fast neutron	-	-
12	60.5	Eu155	0.0128	86.6	35	1.70	y	5.36E07	(154)	Daughter	65	Sm155
13	61.2	Sm145	0.127	61.2	13	340	d	2.94E07	144	2.21E-02	-	-
14	61.6	Sb122m	0.5	61.6	14	3.5	m	2.10E02	121	3.44E-02	-	-
15	63.1	Yb169	0.45	63.1	15	30.7	d	2.65E06	168	1.54E+01	-	-
16	63.6	Re188m	0.213	63.6	16	18.7	m	1.12E03	187	8.18E-01	-	-
17	65.5	Pm151	0.034	340.1	304	1.18	d	9.90E04	150	Daughter	81	Nd151
18	65.7	Ta182	0.028	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
19	66.0	Ge75	0.003	264.6	236	1.32	h	4.74E03	74	1.10E-01	-	-
20	67.7	Ta182	0.412	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
21	69.7	Gd153	0.0236	97.4	56	242	d	2.09E07	152	Unknown	-	-
22	69.7	Sm153	0.0525	103.2	63	1.94	d	1.68EC5	152	5.59E+01	-	-
23	72.3	W187	0.11	685.7	500	1.0	d	8.64E04	186	1.14E+01	-	-
24	74.6	Tb161	0.098	57.2	4	6.91	d	5.97E05	(160)	Daughter	321	Gd161
25	74.7	U239	0.51	74.7	25	23.5	m	1.41E03	238	2.71E+00	-	-
26	76.3	Sb122m	0.17	61.6	14	3.5	m	2.10E02	121	3.44E-02	-	-
27	77.6	Rh104m	0.025	51.4	3	4.4	m	2.64E02	103	1.10E+01	-	-
28	77.6	Hg197	0.18	77.6	28	2.71	d	2.34E05	196	1.32E+00	-	-
29	77.6	Pt197	0.2	77.6	29	20	h	7.20E04	196	2.39E-01	-	-
30	80.2	I131	0.026	364.5	328	8.08	d	6.98E05	(130)	Daughter	121	Te131
31	80.6	Ho166	0.062	80.6	31	1.12	d	9.65E04	165	6.40E+01	-	-
32	80.6	Ho166m	0.126	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
33	81.0	Ba133	0.343	356.0	318	10.5	y	3.31E08	132	6.79E-03	-	-
34	84.4	Tm170	0.034	84.4	34	128	d	1.11E07	169	1.25E+02	-	-
35	86.6	Eu155	0.32	86.6	35	1.70	y	5.36E07	(154)	Daughter	65	Sm155
36	86.6	Th233	0.27	86.6	36	22.3	m	1.34E03	232	7.40E+00	-	-
37	86.8	Tb160	0.134	879.4	569	72.3	d	6.25E06	159	4.60E+01	-	-
38	87.7	As77	0.001	238.8	216	1.61	d	1.39E05	76	Daughter	234	Ge77
39	87.9	Tb161	0.0017	57.2	4	6.91	d	5.97E05	160	Daughter	321	Gd161
40	88.0	Pd109	0.046	88.0	40	13.5	h	4.86E04	108	3.26E+00	-	-
41	88.0	Cd109	0.046	88.0	41	1.29	y	4.06E07	108	2.64E-02	-	-
42	88.3	Lu176m	0.1	88.3	42	3.72	h	1.34E04	175	1.75E+01	-	-
43	89.6	Hf175	0.034	343.4	307	70.0	d	6.05E06	174	6.52E-01	-	-
44	91.4	Nd147	0.28	91.4	44	11.1	d	9.59E05	146	3.44E-01	-	-
45	92.4	Re188m	0.0545	63.6	16	18.7	m	1.12E03	187	8.18E-01	-	-
46	93.1	Ta180m	0.04	93.1	46	8.14	h	2.93E04	(179)	Fast neutron	-	-
47	93.2	Cu67	0.23	184.2	166	2.57	d	2.22E05	(66)	Fast neutron	-	-
48	93.2	Cd107	0.05	93.2	48	6.5	h	2.34E04	106	1.22E-02	-	-
49	93.4	Hf180m	0.16	332.2	299	5.5	h	1.98E04	179	2.75E-02	-	-
50	93.6	Yb169	0.027	63.1	15	30.7	d	2.65E06	168	1.54E+01	-	-
51	94.7	Dy165	0.0358	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
52	95.9	Se79m	0.096	95.9	52	3.92	m	2.35E02	78	8.47E-02	-	-
53	96.7	Se75	0.033	264.6	235	122	d	1.05E07	74	2.61E-01	-	-
54	97.2	Rh104m	0.026	51.4	3	4.4	m	2.64E02	103	1.10E+01	-	-
55	97.4	Sm153	0.0073	103.2	63	1.94	d	1.68E05	152	5.59E+01	-	-
56	97.4	Gd153	0.303	97.4	56	242	d	2.09E07	152	Unknown	-	-
57	99.0	Pt195m	0.11	99.0	57	4.10	d	3.54E05	194	2.96E-02	-	-
58	99.2	Tm168	0.04	198.3	183	93.1	d	8.04E06	(167)	Fast neutron	-	-
59	100.1	Ta182	0.14	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
60	102.5	Gd161	0.14	361.0	321	3.7	m	2.22E02	160	8.47E-01	-	-
61	103.0	Se81m	0.08	103.0	61	56.8	m	3.41E03	80	4.98E-02	-	-
62	103.2	Gd153	0.22	97.4	56	242	d	2.09E07	152	Unknown	-	-
63	103.2	Sm153	0.283	103.2	63	1.94	d	1.68E05	152	5.59E+01	-	-
64	103.4	Ta180m	0.006	93.1	46	8.14	h	2.93E04	(179)	Fast neutron	-	-
65	104.2	Sm155	0.73	104.2	65	21.8	m	1.31E03	154	1.13E+00	-	-
66	105.3	Eu155	0.2	86.6	35	1.70	y	5.36E07	(154)	Daughter	65	Sm155
67	105.4	Lu177m	0.13	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
68	105.9	Re188m	0.115	63.6	16	18.7	m	1.12E03	187	8.18E-01	-	-
69	106.1	Np239	0.23	106.1	69	2.35	d	2.03E05	238	Daughter	25	U 239
70	108.2	Ba131m	0.4	108.2	70	14.6	m	8.76E02	(130)	Unknown	-	-
71	108.2	Dy165m	0.03	108.2	71	1.26	m	7.55E01	164	5.64E+02	-	-
72	109.3	Te125m	0.003	109.3	72	58	d	5.01E06	124	2.31E-01	-	-
73	109.8	Yb169	0.18	63.1	15	30.7	d	2.65E06	168	1.54E+01	-	-
74	111.2	Re184	0.15	902.8	576	38	d	3.28E06	(183)	Fast neutron	-	-
75	111.6	Er171	0.205	308.3	275	7.53	h	2.71E04	170	1.34E+00	-	-
76	113.0	Lu177	0.028	208.4	192	6.75	d	5.83E05	176	5.46E+01	-	-
77	113.0	Lu177m	0.23	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
78	113.7	Ta182	0.019	1121.3	343	115	d	3.64E05	174	1.75E+01	-	-
79	113.8	Yb175	0.018	396.3	614	4.19	d	9.94E06	181	2.11E+01	-	-
80	114.6	Nd149	0.18	211.4	194	1.8	h	6.48E03	148	2.29E-01	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life	$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
81	116.7	Nd151	0.468	116.7	81	12.4 m	7.20E02	150	8.40E-02	-	-
82	116.7	Er171	0.023	308.3	275	7.53 h	2.71E04	170	1.34E+00	-	-
83	118.2	Yb169	0.0193	63.1	15	30.7 d	2.65E06	168	1.54E+01	-	-
84	121.1	Se75	0.17	264.6	235	122 d	1.05E07	74	2.61E-01	-	-
85	121.5	Zn71	0.03	511.6	407	2.4 m	1.44E02	70	6.20E-04	-	-
86	121.6	Lu177m	0.067	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
87	121.6	Yb177	0.03	150.3	122	1.9 h	6.84E03	176	8.91E-01	-	-
88	121.8	Eu152m	0.08	841.6	559	9.36 h	3.37E04	151	1.34E+03	-	-
89	121.8	Eu152	0.37	344.2	308	12.2 y	3.85E08	151	2.82E+03	-	-
90	121.9	Co57	0.87	121.9	90	270 d	2.33E07	(56)	Fast neutron	-	-
91	123.1	Eu154	0.38	123.1	91	16.0 y	5.05E08	153	1.67E+02	-	-
92	124.0	Er171	0.091	308.3	275	7.53 h	2.71E04	170	1.34E+00	-	-
93	124.2	Ba131	0.28	124.2	93	11.5 d	9.94E05	130	8.89E-03	-	-
94	125.4	W185	2.32×10^{-4}	125.4	94	75.1 d	6.49E06	184	6.45E-01	-	-
95	127.1	Tc101	0.022	306.8	273	14.2 m	8.52E02	(100)	Daughter	447	Mo101
96	127.4	Cs134m	0.14	127.4	96	3.14 h	1.13E04	133	2.60E+00	-	-
97	127.4	Ni57	0.14	1378.4	661	1.50 d	1.30E05	(56)	Fast neutron	-	-
98	128.6	Lu177m	0.17	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
99	129.4	Os191	0.25	129.4	99	15.4 d	1.33E06	190	3.30E+00	-	-
100	129.7	Ru105	0.05	724.5	520	4.44 h	1.60E04	104	9.06E-02	-	-
101	130.5	Yb169	0.115	63.1	15	30.7 d	2.65E06	168	1.54E+01	-	-
102	133.1	Hf181	0.4	482.2	388	44.6 d	3.85E06	180	3.52E+00	-	-
103	133.7	Ba131	0.1	124.2	93	11.5 d	9.94E05	130	8.89E-03	-	-
104	133.9	Hg197m	0.42	133.9	104	1.0 d	8.64E04	196	3.65E-02	-	-
105	134.3	W187	0.09	685.7	500	1.0 d	8.64E04	186	1.14E+01	-	
106	136.0	Se75	0.57	264.6	235	122 d	1.05E07	74	2.61E-01	-	-
107	136.0	W181	8.8×10^{-4}	151.7	125	145 d	1.25E07	180	Unknown	-	-
108	136.3	Co57	0.11	121.9	90	270 d	2.33E07	(56)	Fast neutron	-	-
109	137.2	Re186	0.092	137.2	109	3.77 d	3.26E05	185	4.08E+01	-	-
110	137.4	Yb175	0.0013	396.3	343	4.21 d	3.64E05	174	1.75E+01	-	-
111	138.3	Yb177	0.02	150.3	122	1.9 h	6.84E03	176	8.91E-01	-	-
112	138.4	In116m	0.03	1293.4	644	54 m	3.24E03	115	1.47E+02	-	-
113	138.8	Nd151	0.078	116.7	81	12.4 m	7.20E02	150	8.40E-02	-	-
114	139.0	Os193	0.031	460.4	377	1.31 d	1.13E05	192	6.56E-01	-	-
115	139.8	Ge75m	0.34	139.8	115	49 s	4.90E01	74	7.35E-02	-	-
116	140.5	Mo99	0.813	140.5	116	2.75 d	2.38E05	98	1.21E-01	-	-
117	141.2	Sm155	0.0135	104.2	65	21.8 m	1.31E03	154	1.13E00	-	-
118	144.7	Yb175	0.00354	396.3	343	4.21 d	3.64E05	176	1.75E+01	-	-
119	145.4	Ce141	0.48	145.4	119	32.5 d	2.81E06	140	5.31E-01	-	-
120	146.8	Ta182m	0.158	171.6	154	15.8 m	9.50E02	181	7.00E-02	-	-
121	149.7	Te131	0.689	149.7	121	25.0 m	1.49E03	130	6.90E-02	-	-
122	150.3	Yb177	0.16	150.3	122	1.9 h	6.84E03	176	8.91E-01	-	-
123	150.8	Cd111m	0.3	245.4	222	48 m	2.88E03	110	1.24E-02	-	-
124	151.1	Sr85m	0.14	231.5	212	1.17 h	4.20E03	84	3.64E-03	-	-
125	151.7	W181	0.0016	151.7	125	145 d	1.25E07	180	Unknown	-	-
126	152.4	Ta182	0.0715	1121.3	614	115 d	9.94E06	181	2.11E+01	-	-
127	153.1	Lu177m	0.17	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
128	153.8	Dy165m	0.0024	108.2	71	1.26 m	7.55E01	164	5.64E+02	-	-
129	155.0	Re188	0.149	155.0	129	17.0 h	6.11E04	187	4.49E+01	-	-
130	156.0	Nd149	0.04	211.4	194	1.8 h	6.48E03	148	2.29E-01	-	-
131	156.4	Ta182	0.0272	1121.3	614	115 d	9.94E06	181	2.11E+01	-	-
132	158.3	Hg199m	0.53	158.3	132	42 m	2.52E03	198	2.00E-03	-	-
133	158.3	Au199	0.37	158.3	133	3.15 d	2.72E05	198	Daughter	421	Pt199
134	158.4	Sn117m	0.87	158.4	134	14 d	1.21E06	116	8.54E-04	-	-
135	158.4	In117m	0.14	315.2	281	1.9 h	6.84E03	116	Daughter	242	Cd117
136	158.4	In117	0.87	552.9	425	1.1 h	3.96E03	116	Daughter	242	Cd117
137	158.8	Te123m	0.84	158.8	137	104 d	8.99E06	122	2.46E-02	-	-
138	159.8	Ge77m	0.12	215.5	198	54 s	5.40E01	76	7.67E-03	-	-
139	159.8	Sc47	0.73	159.8	139	3.43 d	2.96E05	46	Daughter	646	Ca47
140	160.2	Sn123m	0.84	160.2	140	39.3 m	2.36E03	122	9.42E-03	-	-
141	160.6	Hf179m	0.094	214.3	196	19 s	1.90E01	178	1.36E+01	-	-
142	161.9	Se77m	0.5	161.9	142	17.5 s	1.75E01	76	1.98E+00	-	-
143	161.9	As77	0.0025	238.8	216	1.61 d	1.39E05	76	Daughter	234	Ge77
144	162.3	Th233		86.6	36	22.3 m	1.34E03	232	7.40E+00	-	-
145	162.9	Os185	0.0067	646.1	482	94 d	8.12E06	184	Unknown	-	-
146	164.6	U237	0.02	208.0	189	6.75 d	5.83E05	(236)	Fast neutron	-	-
147	165.4	Gd161	0.017	361.0	321	3.7 m	2.22E02	160	8.47E-01	-	-
148	165.8	Ce139	0.806	165.8	148	138 d	1.19E07	138	2.60E-03	-	-
149	165.8	Ba139	0.214	165.8	149	1.41 h	5.09E03	138	2.87E-01	-	-
150	167.7	Pm151	0.078	340.1	304	28.4 h	9.90E04	150	Daughter	81	Nd151
151	169.3	Th233	0.007	86.6	36	22.3 m	1.34E03	232	7.40E+00	-	-
152	170.0	Mg27	0.007	844.0	560	9.45 m	5.67E02	26	3.05E-03	-	-
153	171.4	In111	0.89	245.4	223	2.81 d	2.43E05	(110)	Fast neutron	-	-
154	171.6	Ta182m	0.452	171.6	154	15.8 m	9.50E02	181	7.00E-02	-	-
155	172.1	Pd111m	0.75	172.1	155	5.5 h	1.98E04	110	4.72E-03	-	-
156	172.2	Pt191	0.035	538.9	419	2.80 d	2.42E05	190	1.91E-02	-	-
157	172.9	Sm153	7×10^{-4}	103.2	63	1.94 d	1.68E05	152	5.59E+01	-	-
158	174.4	Lu177m	0.13	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
159	175.3	Ga70	0.0016	1039.4	599	21.2 m	1.27E03	69	1.14E+00	-	-
160	176.2	Sb125	0.06	427.8	360	2.00 y	6.31E07	124	Daughter	298	Sn125m
161	177.2	Pm151	0.036	340.1	304	28.4 h	9.90E04	150	Daughter	81	Nd151
162	177.2	Yb169	0.22	63.1	15	30.7 d	2.65E06	168	1.54E+01	-	-
163	179.0	Pt191	0.0101	538.9	419	2.80 d	2.42E05	190	1.91E-02	-	-
164	179.4	Ta182	0.0314	1121.3	614	115 d	9.94E06	181	2.11E+01	-	-
165	181.1	Mo99	0.068	140.5	116	2.75 d	2.38E05	98	1.21E-01	-	-
166	184.2	Cu67	0.4	184.2	166	2.57 d	2.22E05	(66)	Fast neutron	-	-
167	184.3	Tm168	0.164	198.3	167	93.1 d	3.78E10	165	1.00E+00	-	-
168	184.4	Ho166m	0.739	184.4	183	1200 y	8.04E06	(167)	Fast neutron	-	-
169	185.0	Ta182m	0.226	171.6	154	15.8 m	9.50E02	181	7.00E-02	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
170	185.9	Pt199	0.09	542.8	421	30	m	1.80E03	198	2.90E-01	-	-
171	186.2	Ra226	0.04	186.2	171			1.00E20	(225)	Background	-	-
172	186.7	Os190m	0.7	616.4	463	10	m	6.00E02	189	1.29E-03	-	-
173	188.9	Pd109m	0.58	188.9	173	4.75	m	2.85E02	108	5.34E-02	-	-
174	190.2	In114m	0.17	190.2	174	50	d	4.32E06	113	3.38E-01	-	-
175	191.4	Hg197	0.02	77.6	28	2.71	d	2.34E05	196	1.32E+00	-	-
176	191.4	Pt197	0.06	77.6	29	20	h	7.20E04	196	2.39E-01	-	-
177	191.9	Mo101	0.182	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
178	192.5	Fe59	0.028	1099.2	609	45.1	d	3.90E06	58	3.41E-03	-	-
179	194.5	Ge77		264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
180	197.0	Tb160	0.0524	879.4	569	72.3	d	6.25E06	159	4.60E+01	-	-
181	197.4	019	0.97	197.4	181	29	s	2.90E01	18	4.28E-07	-	-
182	197.8	Yb169	0.36	63.1	15	30.7	d	2.65E06	168	1.54E+01	-	-
183	198.3	Tm168	0.499	198.3	183	93.1	d	8.04E06	(167)	Fast neutron	-	-
184	198.3	Ta182	0.0154	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
185	198.6	Ge75	0.014	264.6	236	1.32	h	4.74E03	74	1.10E-01	-	-
186	202.4	Y90m	0.97	202.4	186	3.14	h	1.13E04	89	1.00E-03	-	-
187	203.8	Hg205		203.8	187	5.6	m	3.36E02	204	2.74E-02	-	-
188	204.3	Lu177m	0.136	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
189	208.0	U237	0.23	208.0	189	6.75	d	5.83E05	(236)	Fast neutron	-	-
190	208.2	Au199	0.08	158.3	133	3.15	d	2.72E05	198	Daughter	421	Pt199
191	208.4	Lu177m	0.62	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
192	208.4	Lu177	0.061	208.4	192	6.75	d	5.83E05	176	5.46E+01	-	-
193	211.4	Ge77	0.32	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
194	211.4	Nd149	0.27	211.4	194	1.8	h	6.48E03	148	2.29E-01	-	-
195	212.2	Te121m	0.826	212.2	195	154	d	1.33E07	120	1.78E-03	-	-
196	214.3	Hf179m	0.94	214.3	196	19	s	1.90E01	178	1.36E+01	-	-
197	215.3	Hf180m	0.82	332.2	299	5.5	h	1.98E04	179	2.75E-02	-	-
198	215.5	Ge77m	0.21	215.5	198	54	s	5.40E01	76	7.67E-03	-	-
199	215.5	Ge77	0.29	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
200	215.6	Tb160	0.0402	879.4	569	72.3	d	6.25E06	169	4.60E+01	-	-
201	215.7	Ru97	0.853	215.7	201	2.91	d	2.51E05	98	1.09E-02	-	-
202	215.9	Ho166m	0.026	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
203	216.1	Ba131	0.19	216.1	203	11.5	d	9.94E05	130	8.89E-03	-	-
204	219.7	Pt191	0.0082	538.9	419	2.80	d	2.42E05	190	1.91E-02	-	-
205	222.1	Ta182	0.075	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
206	224.9	Se83	0.44	356.6	319	25	m	1.50E03	82	3.68E-04	-	-
207	226.0	Gd159	0.0019	363.6	327	18.6	h	6.68E04	158	8.47E-01	-	-
208	228.2	Np239	0.12	106.1	69	2.35	d	2.03E05	238	Daughter	25	U239
209	228.5	Lu177m	0.37	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
210	229.3	Ta182	0.0363	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
211	229.5	Hf175	0.0085	343.4	307	70	d	6.05E06	174	6.52E-01	-	-
212	231.5	Sr85m	0.85	231.5	212	1.17	h	4.20E03	84	3.64E-03	-	-
213	231.6	Ce143	0.023	293.3	263	1.38	d	1.19E05	142	1.11E-01	-	-
214	235.7	Nb95m		235.7	214	3.75	d	3.24E05	94	Daughter	519	Zr95
215	238.6	Pb212	0.47	238.6	215			1.00E20	(211)	Background	-	-
216	238.8	As77	0.025	238.8	216	1.61	d	1.39E05	76	Daughter	234	Ge77
217	240.0	Nd149	0.045	211.4	194	1.8	h	6.48E03	148	2.29E-01	-	-
218	240.1	Pm151	0.036	340.1	304	28.4	h	9.90E04	150	Daughter	81	Nd151
219	242.0	Pb214	0.04	352.0	315			1.00E20	(213)	Background	-	-
220	244.6	Eu152	0.08	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
221	245.4	Ag111	0.01	341.9	306	7.40	d	6.39E05	110	Daughter	442	Pd111
222	245.4	Cd111m	0.94	245.4	227	48	m	2.88E03	110	1.24E-02	-	-
223	245.4	In111	0.94	245.4	223	2.81	d	2.43E05	(110)	Fast neutron	-	-
224	245.6	Sm155	0.04	104.2	65	21.8	m	1.31E03	154	1.13E+00	-	-
225	246.5	Pt199	0.04	542.8	421	30	m	1.80E03	198	2.90E-01	-	-
226	249.7	As77	0.00375	238.8	216	1.61	d	1.39E05	76	Daughter	234	Ge77
227	250.1	Lu177	0.00118	208.4	192	6.75	d	5.83E05	176	5.46E+01	-	-
228	254.3	Zr97	0.0128	743.4	525	17	h	6.12E04	96	1.40E-04	-	-
229	255.2	Sn113	0.018	255.2	229	115	d	9.94E06	112	8.55E-03	-	-
230	255.6	Nd151	0.168	116.7	81	12.4	m	7.20E02	150	8.40E-02	-	-
231	261.0	Yb169	0.0178	63.1	15	30.7	d	2.65E06	168	1.54E+01	-	-
232	262.9	Ru105	0.072	724.5	520	4.44	h	1.60E04	104	9.06E-02	-	-
233	264.1	Ta182	0.0363	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
234	264.5	Ge77	0.45	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
235	264.6	Se75	0.6	264.6	235	122	d	1.05E07	74	2.61E-01	-	-
236	264.6	Ge75	0.11	264.6	236	1.32	h	4.74E03	74	1.10E-01	-	-
237	267.6	U237	0.0076	208.0	189	6.75	d	5.83E05	(236)	Fast neutron	-	-
238	268.2	Ba135m	0.156	268.2	238	1.19	d	1.03E05	134	3.87E-03	-	-
239	268.3	Pt191	0.024	538.9	419	2.80	d	2.42E05	190	1.91E-02	-	-
240	269.6	Nd149	0.0177	211.4	194	1.80	h	6.48E03	148	2.29E-01	-	-
241	271.0	Eu152m	8×10^{-4}	841.6	559	9.36	h	3.37E04	151	1.34E+03	-	-
242	273.3	Cd117	0.267	273.3	242	2.73	h	9.84E03	116	1.59E-01	-	-
243	275.1	Nd147	0.0196	91.4	44	11.1	d	9.59E05	146	3.44E-01	-	-
244	275.2	Pm151	0.066	340.1	304	28.4	h	9.90E04	150	Daughter	81	Nd151
245	275.8	Se81	0.0056	275.8	245	18.0	m	1.08E03	80	2.49E-01	61	Se81m
246	276.1	Ba133m	0.175	276.1	246	1.62	d	1.40E05	132	Unknown	-	-
247	276.4	Ba133	0.073	356.0	318	10.5	y	3.31E08	132	6.79E-03	-	-
248	277.5	Np239	0.14	106.1	69	2.35	d	2.03E05	238	Daughter	25	U239
249	278.5	Te129	0.0165	459.5	376	1.20	h	4.32E03	128	4.45E-02	-	-
250	279.1	Hg203	0.77	279.1	250	46.9	d	4.05E06	202	1.19E00	-	-
251	279.1	Pb203	0.81	279.1	251	2.18	d	1.88E05	(202)	Fast neutron	-	-
252	279.6	Se75	0.25	264.6	235	122	d	1.05E07	74	2.61E-01	-	-
253	279.8	Dy165	0.00498	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
254	280.3	Os193	0.0137	460.4	377	1.31	d	1.13E05	192	6.56E-01	-	-
255	280.5	Ho166m	0.301	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
256	281.8	Lu177m	0.14	208.4	191	155	d	1.34E07	176	2.60E-02	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life	$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
257	281.8	As77	0.0012	238.8	216	1.61 d	1.39E05	76	Daughter	234	Ge77
258	282.5	Yb175	0.029	396.3	343	4.19 d	3.64E05	174	1.75E+01	-	-
259	283.5	Gd161	0.051	361.0	321	3.7 m	2.22E02	160	8.47E-01	-	-
260	284.3	I131	0.054	364.5	328	8.08 d	6.98E05	130	Daughter	121	Te131
261	286.1	Pm149	0.02	286.1	261	2.21 d	1.91E05	148	Daughter	194	Nd149
262	290.0	Se81	0.0034	275.8	245	18 m	1.08E03	80	2.49E-01	61	Se81m
263	293.3	Ce143	0.514	293.3	263	1.38 d	1.19E05	142	1.11E-01	-	-
264	293.6	Ir194	0.02	328.0	296	19.7 h	7.09E04	193	6.76E+01	-	-
265	295.4	Pb214	0.19	352.0	315		1.00E20	(213)	Background	-	-
266	295.8	Ir192	0.29	316.5	283	74.4 d	6.43E06	191	3.85E+02	-	-
267	295.9	Er171	0.289	308.3	275	7.53 h	2.71E04	170	1.34E+00	-	-
268	298.6	Tb160	0.274	879.4	569	72.3 d	6.25E06	169	4.60E+01	-	-
269	299.9	Pa233	0.063	311.8	278	27.0 d	2.33E06	232	Daughter	36	Th233
270	302.9	Ba133	0.186	356.0	318	10.5 y	3.31E08	132	6.79E-03	-	-
271	305.5	Gd159	5.6×10^{-4}	363.6	327	18.6 h	6.68E04	158	8.47E-01	-	-
272	306.2	Rh105	0.051	319.1	287	1.47 d	1.27E05	104	Daughter	520	Ru105
273	306.8	Tc101	0.889	306.8	273	14.2 m	8.54E02	100	Daughter	447	Mo101
274	307.7	Yb169	0.111	63.1	15	30.7 d	2.65E06	168	1.54E+01	-	-
275	308.3	Er171	0.644	308.3	275	7.53 h	2.71E04	170	1.34E+00	-	-
276	308.4	Ir192	0.3	316.5	283	74.4 d	6.43E06	191	3.85E+02	-	-
277	311.5	Pd109	0.005	88.0	40	13.5 h	4.86E04	108	3.26E+00	-	-
278	311.8	Pa233	0.34	311.8	278	27.0 d	2.33E06	232	Daughter	36	Th233
279	312.9	K42	0.002	1524.7	676	12.5 h	4.51E04	41	8.12E-02	-	-
280	315.0	Gd161	0.186	361.0	321	3.7 m	2.22E02	160	8.47E-01	-	-
281	315.2	In117m	0.31	315.2	281	1.9 h	6.84E03	116	Daughter	242	Cd117
282	315.7	Np239	0.015	106.1	69	2.35 d	2.03E05	238	Daughter	25	U239
283	316.5	Ir192	0.81	316.5	283	74.4 d	6.43E06	191	3.85E+02	-	-
284	316.5	Ru105	0.117	724.5	520	4.44 h	1.60E04	104	9.06E-02	-	-
285	316.9	Pt199	0.08	542.8	421	30 m	1.80E03	198	2.90E-01	-	-
286	318.4	Ta182m	0.063	171.6	154	15.8 m	9.50E02	181	7.00E-02	-	-
287	319.1	Rh105	0.192	319.1	287	1.47 d	1.27E05	104	Daughter	520	Ru105
288	319.2	Lu177m	0.1	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
289	319.4	Nd147	0.03	91.4	44	11.1 d	9.59E05	146	3.44E-01	-	-
290	320.0	Cr51	0.09	320.0	290	27.8 d	2.40E06	50	7.33E-01	-	-
291	320.0	Ti51	0.51	320.0	291	5.78 m	3.47E02	50	7.35E-03	-	-
292	321.5	Os193	0.014	460.4	377	1.31 d	1.13E05	192	6.56E-01	-	-
293	324.5	Ru97	0.101	215.7	201	2.91 d	2.51E05	96	1.09E-02	-	-
294	326.3	Nd149	0.05	211.4	194	1.8 h	6.48E03	148	2.29E-01	-	-
295	327.7	Lu177m	0.18	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
296	328.0	Ir194	0.1	328.0	296	19.7 h	7.09E04	193	6.76E+01	-	-
297	328.8	La140	0.205	1596.5	683	1.68 d	1.45E05	139	8.89E+00	-	-
298	332.0	Sn125m	0.97	332.0	298	9.5 m	5.70E02	124	5.98E-03	-	-
299	332.2	Hf180m	0.93	332.2	299	5.5 h	1.98E04	179	2.75E-02	-	-
300	332.4	U237	0.013	208.0	189	6.75 d	5.83E05	(236)	Fast neutron	-	-
301	333.0	Au196	0.25	355.7	317	6.20 d	5.36E05	(195)	Fast neutron	-	-
302	334.1	Np239	0.02	106.1	69	2.35 d	2.03E05	238	Daughter	25	U239
303	336.6	In115m	0.5	336.6	303	4.5 h	1.62E04	114	Daughter	414	Cd115
304	340.1	Pm151	0.224	340.1	304	28.4 h	9.90E04	150	Daughter	81	Nd151
305	340.3	Pa233	0.039	311.8	278	27.0 d	2.33E06	232	Daughter	36	Th233
306	341.9	Ag111	0.06	341.9	306	7.40 d	6.39E05	110	Daughter	442	Pd111
307	343.4	Hf175	0.866	343.4	307	70 d	6.05E06	174	6.52E-01	-	-
308	344.2	Eu152	0.27	344.2	308	12.2 y	3.85E08	151	2.82E+03	-	-
309	344.2	Eu152m	0.025	841.6	559	9.36 h	3.37E04	151	1.34E+03	-	-
310	345.0	Cd117	0.133	273.3	242	2.73 h	9.84E03	116	1.59E-01	-	-
311	345.7	Hf181	0.13	482.2	388	44.6 d	3.85E06	180	3.52E+00	-	-
312	346.3	Pt197m	0.13	346.5	312	1.47 h	5.28E03	196	1.26E-02	-	-
313	348.2	Gd159	0.0021	363..	327	18.6 h	6.68E04	158	8.47E-01	-	-
314	351.2	Pt191	0.033	538.9	419	2.8 d	2.42E05	190	1.91E-02	-	-
315	352.0	Pb214	0.36	352.0	315		1.00E20	(213)	Background	-	-
316	355.5	Zr97	0.0218	743.4	525	17 h	6.12E04	96	1.40E-04	-	-
317	355.7	Au196	0.94	355.7	317	6.2 d	5.36E05	(195)	Fast neutron	-	-
318	356.0	Ba133	0.623	356.0	318	10.5 y	3.31E08	132	6.79E-03	-	-
319	356.6	Se83	0.69	356.6	319	25 m	1.50E03	82	3.68E-04	-	-
320	359.9	Pt191	0.0597	538.9	419	2.8 d	2.42E05	190	1.91E-02	-	-
321	361.0	Gd161	0.56	361.0	321	3.7 m	2.22E02	160	8.47E-01	-	-
322	361.0	Te127m	0.001	417.4	355	105 d	9.07E06	126	1.87E-02	-	-
323	361.0	Te127	0.001	417.4	356	9.39 h	3.38E04	126	1.68E-01	-	-
324	361.2	Os190m	0.94	616.4	463	5.0 m	6.00E02	189	1.29E-03	-	-
325	361.7	Dy165	0.0084	94.7	51	2.33 h	8.40E03	164	7.75E+02	-	-
326	361.7	Dy165m	0.0043	108.2	71	1.26 m	7.55E01	164	5.64E+02	-	-
327	363.6	Gd159	0.103	363.6	327	18.6 h	6.68E04	158	8.47E-01	-	-
328	364.5	I131	0.82	364.5	328	8.08 d	6.98E05	130	Daughter	121	Te131
329	366.4	Mo99	0.015	140.5	116	2.75 d	2.38E05	98	1.21E-01	-	-
330	366.5	Ni65	0.045	1481.7	672	2.56 h	9.22E03	64	1.74E-02	-	-
331	367.3	Ge77	0.15	264.5	234	11.3 h	4.07E04	76	9.63E-03	-	-
332	373.1	Ba131	0.13	216.1	203	11.3 d	9.76E05	130	8.89E-03	-	-
333	373.6	Hg199m	0.15	158.3	132	42 m	2.52E03	198	2.00E-03	-	-
334	375.2	Pa233	0.0056	311.8	278	27 d	2.33E06	232	Daughter	36	Th233
335	376.5	Pd111		580.0	442	22 m	1.32E03	110	2.71E-02	155	Pd111m
336	378.8	Lu177m	0.29	208.4	191	155 d	1.34E07	176	2.60E-02	-	-
337	383.9	Ba133	0.088	356.0	318	10.5 y	3.31E08	132	6.79E-03	-	-
338	387.5	Os193	0.0137	460.4	377	1.31 d	1.13E05	192	6.56E-01	-	-
339	388.2	I126	0.34	388.2	339	13.1 d	1.13E06	(125)	Fast neutron	-	-
340	388.5	Sr87m	0.8	388.5	340	2.83 h	1.02E04	86	1.28E-01	-	-
341	390.0	Zn71	0.038	511.6	407	2.4 m	1.44E02	70	6.20E-04	-	-
342	391.4	In113m	0.64	391.4	342	1.73 h	6.24E03	112	Daughter	229	Sn113
343	396.3	Yb175	0.062	396.3	343	4.19 d	3.64E05	176	1.75E+01	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
344	398.2	Pa233	0.011	311.8	278	27	d	2.33E06	232	Daughter	36	Th233
345	400.7	Se75	0.12	264.6	235	122	d	1.05E07	74	2.61E-01	-	-
346	401.4	Pb203	0.05	279.1	251	2.18	d	1.88E05	(202)	Fast neutron	-	-
347	409.4	Pt191	0.0796	538.9	419	2.80	d	2.42E05	190	1.91E-02	-	-
348	410.9	Ho166m	0.117	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
349	411.0	Eu152	0.0189	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
350	411.8	Au198	0.95	411.8	350	2.70	d	2.37E05	197	9.88E+01	-	-
351	414.1	Lu177m	0.17	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
352	415.6	Pa233	0.015	311.8	278	27	d	2.33E06	232	Daughter	36	Th233
353	416.4	Ge77	0.25	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
354	417.0	In116m	0.36	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
355	417.4	Te127m	0.008	417.4	355	105	d	9.07E06	126	1.87E-02	-	-
356	417.4	Te127	0.008	417.4	356	9.39	h	3.38E04	126	1.68E-01	-	-
357	418.8	Lu177m	0.21	208.4	191	155	d	1.34E07	176	2.60E-02	-	-
358	423.5	Nd149	0.09	211.4	194	1.8	h	6.48E03	148	2.29E-01	-	-
359	425.9	Au196	0.06	355.7	317	6.20	d	5.36E05	(195)	Fast neutron	-	-
360	427.8	Sb125	0.31	427.8	360	2.0	y	6.31E07	124	Daughter	298	Sn125m
361	432.8	Hf175	0.014	343.4	307	70	d	6.05E06	174	6.52E-01	-	-
362	433.9	Ag108	0.0045	632.9	473	2.4	m	1.44E02	107	1.80E+01	-	-
363	434.0	Cd117	0.1	273.3	242	2.73	h	9.84E03	116	1.59E-01	-	-
364	438.7	Zn69m	0.95	438.7	364	13.8	h	4.97E04	68	1.86E-02	-	-
365	440.1	Nd147	0.02	91.4	44	11.1	d	9.59E05	166	3.44E-01	-	-
366	440.2	T1202	0.95	440.2	366	12.0	d	1.04E06	(201)	Fast neutron	-	-
367	442.7	I128	0.14	442.7	367	25.3	m	1.52E03	127	6.40E+00	-	-
368	443.1	Hf180m	0.80	332.2	299	5.5	h	1.98E04	179	2.75E-02	-	-
369	443.9	Eu152	0.0486	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
370	445.7	Pm151	0.04	340.1	304	28.4	h	9.90E04	150	Daughter	81	Nd151
371	447.5	Tm168	0.223	198.3	183	9.31	d	8.04E05	(167)	Fast neutron	-	-
372	452.3	Te131	0.182	149.7	121	25.0	m	1.49E03	130	6.90E-02	-	-
373	456.5	Pt191	0.033	538.9	419	2.80	d	2.42E05	190	1.91E-02	-	-
374	459.2	Th233	0.01	86.6	36	22.3	m	1.34E03	232	7.40E+00	-	-
375	459.5	Te129m		695.8	503	33.4	d	2.89E06	128	5.40E-03	-	-
376	459.5	Te129	0.15	459.5	376	1.14	h	4.12E03	128	4.45E-02	-	-
377	460.4	Os193	0.039	460.4	377	1.31	d	1.13E05	192	6.56E-01	-	-
378	463.1	Sb125	0.1	427.8	360	2.0	y	6.31E07	124	Daughter	298	Sn125m
379	464.6	Cs132	0.02	667.7	493	6.2	d	5.36E05	(131)	Fast neutron	-	-
380	468.1	Ir192	0.49	316.5	283	74.4	d	6.43E06	191	3.85E+02	-	-
381	469.4	Ru105	0.175	724.5	520	4.44	h	1.60E04	104	9.06E-02	-	-
382	475.1	Rh102	0.57	475.1	382	209	d	1.81E07	(101)	Fast neutron	-	-
383	475.1	Rh102m	0.95	475.1	383	2.50	y	7.88E07	(101)	Fast neutron	-	-
384	478.1	Re188	0.011	155.0	129	17	h	6.11E04	187	4.49E+01	-	-
385	479.3	W187	0.23	685.7	500	1.0	d	8.64E04	186	1.14E+01	-	-
386	479.3	Y90m	0.91	202.4	186	3.14	h	1.13E04	89	1.00E-03	-	-
387	480.1	Gd161	0.017	361.0	321	3.7	m	2.22E02	160	8.47E-01	-	-
388	482.2	Hf181	0.81	482.2	388	44.6	d	3.85E06	180	3.52E+00	-	-
389	484.9	Cd115m	0.031	934.1	582	44.0	d	3.80E06	114	4.04E-02	-	-
390	487.1	La140	0.46	1596.5	683	1.68	d	1.45E05	139	8.89E+00	-	-
391	489.5	Ca47	0.05	1296.9	646	4.7	d	4.06E05	46	9.90E-06	-	-
392	490.4	Ce143	0.022	293.3	263	1.38	d	1.19E05	142	1.11E-01	-	-
393	491.1	Th233		86.6	36	22.3	m	1.34E03	232	7.40E+00	-	-
394	491.2	I126	0.05	388.2	339	13.1	d	1.13E06	(125)	Fast neutron	-	-
395	492.5	Cd115	0.1	527.7	414	2.21	d	1.91E05	114	3.17E-01	-	-
396	492.7	Te131	0.05	149.7	121	24.8	m	1.49E03	130	6.90E-02	-	-
397	493.5	Pt199		542.8	421	30	m	1.80E03	198	2.90E-01	-	-
398	496.3	Ba131	0.053	216.1	203	11.5	d	9.94E05	130	8.89E-03	-	-
399	497.1	Ru103	0.863	497.1	399	39.4	d	3.40E06	102	4.42E-01	-	-
400	499.4	Th233		86.6	36	22.3	m	1.34E03	232	7.40E+00	-	-
401	505.9	Mo101	0.114	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
402	507.6	Te121	0.175	573.1	441	17.0	d	1.47E06	120	2.67E-04	-	-
403	507.8	Zr97	0.0524	743.4	525	17.0	h	6.12E04	96	1.40E-04	-	-
404	509.8	T1202	0.0285	440.2	366	12.0	d	1.04E06	(201)	Fast neutron	-	-
405	510.0	Se83	0.414	356.6	319	25.0	m	1.50E03	82	3.68E-04	-	-
406	511.0	Annihilation			406			1.00E20	(1)	Annihilation	-	
407	511.6	Zn71	0.32	511.6	407	2.4	m	1.44E02	70	6.20E-04	-	-
408	514.0	Sr85	1.0	514.0	408	64	d	5.53E06	84	7.61E-03	-	-
409	515.5	Dy165m	0.0153	108.2	71	1.26	m	7.55E01	164	5.64E+02	-	-
410	520.8	As77	0.008	238.8	216	1.61	d	1.39E05	76	Daughter	234	Ge77
411	520.9	Br83	6.3×10^{-4}	529.3	415	2.33	h	8.39E03	82	Daughter	319	Se83
412	521.5	T1202	0.001	440.2	366	12.0	d	1.04E06	(201)	Fast neutron	-	-
413	526.3	I128	0.014	442.7	367	25.3	m	1.52E03	127	6.40E+00	-	-
414	527.7	Cd115	0.26	527.7	414	2.30	d	1.99E05	114	3.17E-01	-	-
415	529.3	Br83	0.014	529.3	415	2.33	h	8.39E03	82	Daughter	319	Se83
416	529.5	Gd161	0.011	361.0	321	3.7	m	2.22E02	160	8.47E-01	-	-
417	529.8	Ho166m	0.103	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
418	531.0	Nd147	0.13	91.4	44	11.1	d	9.56E05	146	3.44E-01	-	-
419	538.9	Pt191	0.136	538.9	419	2.80	d	2.42E05	190	1.91E-02	-	-
420	540.4	Nd149	0.1	211.4	194	1.80	h	6.48E03	148	2.29E-01	-	-
421	542.8	Pt199	0.24	542.8	421	30	m	1.80E03	198	2.90E-01	-	-
422	544.8	Tc101	0.056	306.8	273	14.2	m	8.52E02	100	Daughter	447	Mo101
423	545.8	Dy165	0.00162	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
424	551.4	W187	0.05	685.7	500	24.0	h	8.64E04	186	1.14E+01	-	-
425	552.9	In117	1.0	552.9	425	1.10	h	3.96E03	116	Daughter	242	Cd117
426	552.9	In117m	0.47	552.9	426	1.93	h	6.95E03	116	Daughter	242	Cd117
427	554.3	Br82	0.66	776.6	537	1.49	d	1.29E05	81	1.48E+00	-	-
428	555.8	Rb86m		555.8	428	1.04	m	6.21E01	85	7.22E-02	-	-
429	555.8	Rh104	0.02	555.8	429	42.3	s	4.40E01	103	1.44E+02	-	-
430	555.8	Rh104m	0.02	51.4	3	4.34	m	2.64E02	103	1.10E+01	-	-
431	557.7	Os193	0.021	460.4	377	1.31	d	1.13E05	192	6.56E-01	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
432	558.1	Ge77	0.18	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
433	558.2	In114m	0.035	190.2	174	50.0	d	4.32E06	113	3.38E-01	-	-
434	559.2	As76	0.43	559.2	434	1.10	d	9.47E04	75	4.50E+00	-	-
435	563.2	Cs134	0.08	604.7	456	2.07	y	6.53E07	133	3.06E+01	-	-
436	564.0	Sb122	0.66	564.0	436	2.75	d	2.38E05	121	3.47E+00	-	-
437	565.7	Dy165	0.00132	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
438	565.8	Se81	0.009	275.8	245	18.0	m	1.08E03	80	2.49E-01	61	Se81m
439	569.3	Cs134	0.14	604.7	456	2.07	y	6.53E07	133	3.06E+01	-	-
440	571.0	Ho166m	0.052	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
441	573.1	Te121	0.795	573.1	441	17.0	d	1.47E06	120	2.67E-04	-	-
442	580.0	Pd111		580.0	442	22.0	m	1.32E03	110	2.71E-02	155	Pd111m
443	583.1	Tl208	0.86	2614.3	708			1.00E20	(207)	Background	-	-
444	585.0	Ba131	0.0038	216.1	203	11.5	d	9.94E05	130	8.89E-03	-	-
445	588.3	Ir192	0.04	316.5	283	74.4	d	6.43E06	191	3.85E+02	-	-
446	588.6	Zr89m	0.87	588.6	446	4.40	m	2.64E02	(88)	Fast neutron	-	-
447	590.8	Mo101	0.194	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
448	590.9	Pm149	0.001	286.1	261	2.21	d	1.91E05	148	Daughter	194	Nd149
449	591.5	Eu154	0.06	123.1	91	16.0	y	5.05E08	153	1.67E+02	-	-
450	595.8	As74	0.61	595.8	450	17.5	d	1.51E06	(73)	Fast neutron	-	-
451	600.4	Sb125	0.164	427.8	360	2.00	y	6.31E07	124	Daughter	298	Sn125m
452	600.9	Ga72	0.055	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
453	602.1	Te131	0.04	149.7	121	24.8	m	1.49E03	130	6.90E-02	-	-
454	602.7	Sb124	0.979	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
455	604.2	Ir192	0.09	316.5	283	74.4	d	6.43E06	191	3.85E+02	-	-
456	604.7	Cs134	0.98	604.7	456	2.07	y	6.53E07	133	3.06E+01	-	-
457	606.6	Sb125	0.0558	427.8	360	2.00	y	6.31E07	124	Daughter	298	Sn125m
458	608.4	Ti51	0.015	320.0	291	5.78	m	3.47E02	50	7.35E-03	-	-
459	608.5	As74	0.0061	595.8	450	17.5	d	1.51E06	(73)	Fast neutron	-	-
460	609.3	Bi214	0.47	609.3	460			1.00E20	(213)	Background	-	-
461	610.3	Ru103	0.055	497.1	399	39.4	d	3.40E06	102	4.42E-01	-	-
462	612.3	Ir192	0.06	316.5	283	74.4	d	6.43E06	191	3.85E+02	-	-
463	616.4	Os190m	0.99	616.4	463	10.0	m	6.00E02	189	1.29E-03	-	-
464	617.0	Br80	0.07	617.0	464	17.7	m	1.06E03	79	4.29E+00	714	Br80m
465	618.1	W187	0.06	685.7	500	24.0	h	8.64E04	186	1.14E+01	-	-
466	619.0	Br82	0.41	776.6	537	1.49	d	1.29E05	81	1.48E+00	-	-
467	620.0	Ba131	0.0038	216.1	203	11.5	d	9.94E05	130	8.89E-03	-	-
468	620.6	Dy165	9.7×10^{-4}	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
469	626.9	Tc101	0.0044	306.8	273	14.2	m	8.52E02	100	Daughter	447	Mo101
470	629.9	Ga72	0.248	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
471	630.3	Re186	2.54×10^{-4}	137.2	109	3.77	d	3.26E05	185	4.08E+01	-	-
472	631.7	Tm168	0.081	198.3	183	93.1	d	8.04E06	(167)	Fast neutron	-	-
473	632.9	Ag108	0.017	632.9	473	2.42	m	1.45E02	107	1.80E+01	-	-
474	633.1	Re188	0.0143	155.0	129	17.0	h	6.11E04	187	4.49E+01	-	-
475	633.4	Dy165	0.0057	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
476	634.6	As74	0.14	595.8	450	17.5	d	1.51E06	(73)	Fast neutron	-	-
477	635.8	Sb125	0.11	427.8	360	2.00	y	6.31E07	124	Daughter	298	Sn125m
478	636.4	I131	0.068	364.5	328	8.08	d	6.98E05	130	Daughter	121	Te131
479	640.4	Br80	0.0021	617.0	464	17.7	m	1.06E03	79	4.29E+00	714	Br80m
480	644.6	Ir194	0.025	328.0	296	19.7	h	7.09E04	193	6.76E+01	-	-
481	645.8	Sb124	0.072	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
482	646.1	Os185	0.81	646.1	482	94.0	d	8.12E06	184	Unknown	-	-
483	649.3	Se81	0.003	275.8	245	18.0	m	1.08E03	80	2.49E-01	61	Se81m
484	654.4	Te131	0.0136	149.7	121	24.8	m	1.49E03	130	6.90E-02	-	-
485	654.8	Nd149	0.09	211.4	194	1.80	h	6.48E03	148	2.29E-01	-	-
486	657.0	As76	0.06	559.2	434	1.10	d	9.47E04	75	4.50E+00	-	-
487	657.8	Ag110m	0.96	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
488	657.9	Nb97	0.985	657.9	488	1.20	h	4.33E03	96	Daughter	525	Zr97
489	661.6	Ba137m	0.89	661.6	489	2.6	m	1.56E02	136	7.81E-04	-	-
490	664.5	Ce143	0.068	293.3	263	1.38	d	1.19E05	142	1.11E-01	-	-
491	665.7	Br80	0.01	617.0	464	17.7	m	1.06E03	79	4.29E+00	714	Br80m
492	666.3	I126	0.33	388.2	339	13.1	d	1.13E06	(125)	Fast neutron	-	-
493	667.7	Cs132	0.93	667.7	493	6.2	d	5.36E05	(131)	Fast neutron	-	-
494	670.0	Th233	0.0025	86.6	36	22.3	m	1.34E03	232	7.40E+00	-	-
495	670.5	Ho166m	0.0516	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
496	672.5	Re188	0.0011	155.0	129	17	h	6.11E04	187	4.49E+01	-	-
497	675.9	Au198	0.01	411.8	350	2.70	d	2.33E05	197	9.88E+01	-	-
498	676.4	Ru105	0.167	724.5	520	4.44	h	1.60E04	104	9.06E-02	-	-
499	677.9	Ag110m	0.096	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
500	685.7	W187	0.27	685.7	500	24	h	8.64E04	186	1.14E+01	-	-
501	692.5	Sb122	0.034	564.0	436	2.75	d	2.38E05	121	3.47E+00	-	-
502	695.5	Mo101	0.066	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
503	695.8	Te129m	0.06	695.8	503	33.4	d	2.89E06	128	5.40E-03	-	-
504	697.5	Rh102m	0.41	475.1	383	2.5	y	7.88E07	(101)	Fast neutron	-	-
505	698.3	Br82	0.27	776.6	537	35.8	h	1.29E02	81	1.48E+00	-	-
506	702.6	Nb94	0.98	871.1	566	20,000	y	6.40E11	93	1.10E+00	-	-
507	704.3	Br80	0.0021	617.0	464	17.7	m	1.06E03	79	4.29E+00	714	Br80m
508	706.4	Ag110m	0.19	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
509	711.7	Ho166m	0.525	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
510	714.3	Pt199	0.03	542.8	421	30	m	1.80E03	198	2.90E-01	-	-
511	715.3	Dy165	0.0053	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
512	717.4	Os185	0.042	646.1	482	94	d	8.12E06	184	Unknown	-	-
513	717.8	Se83	0.25	356.6	319	25	m	1.50E03	82	3.68E-04	-	-
514	717.6	Pm151	0.04	340.1	304	28.4	h	9.90E04	150	Daughter	81	Nd151
515	721.9	Ce143	0.064	293.3	263	1.38	d	1.19E05	142	1.11E-01	-	-
516	722.1	I131	0.016	364.5	328	8.08	d	6.98E05	130	Daughter	121	Te131
517	722.8	Sb124	0.111	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
518	723.1	Eu154	0.21	1274.3	638	16	y	5.05E08	153	1.67E+02	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
519	724.0	Zr95	0.49	756.6	530	65	d	5.62E06	94	1.39E-02	-	-
520	724.5	Ru105	0.49	724.5	520	4.4	h	1.60E04	104	9.06E-02	-	-
521	725.1	In114m	0.035	190.2	174	50	d	4.32E06	113	3.38E-01	-	-
522	727.3	Bi212	0.07	727.3	522			1.00E20	(211)	Background	-	-
523	739.6	Mo99	0.14	140.5	116	2.75	d	2.38E05	98	1.21E-01	-	-
524	741.3	Tm168	0.116	198.3	183	93.1	d	8.04E06	(167)	Fast neutron	-	-
525	743.4	Zr97	0.928	743.4	525	17	h	6.12E04	96	1.40E-04	-	-
526	743.5	I128	0.002	442.7	367	25.3	m	1.52E03	127	6.40E+00	-	-
527	752.3	Ho166m	0.118	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
528	753.3	I126	0.033	388.2	339	13.1	d	1.13E06	(125)	Fast neutron	-	-
529	754.0	Ce139m	0.93	754.0	529	55	s	5.50E01	138	1.00E-04	-	-
530	756.6	Zr95	0.49	724.0	519	65	d	5.62E06	94	1.39E-02	-	-
531	763.9	Ag110m	0.23	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
532	765.8	Nb95	1.0	765.8	532	35	d	3.02E06	94	Daughter	519	Zr95
533	766.8	Rh102m	0.3	475.1	383	2.5	y	7.88E07	(101)	Fast neutron	-	-
534	767.5	As76	0.0086	559.2	434	26.3	h	9.47E04	75	4.50E00	-	-
535	768.1	Bi214	0.05	609.3	460			1.00E20	213	Background	-	-
536	772.9	W187	0.04	685.7	500	24	h	8.64E04	186	1.14E+01	-	-
537	776.6	Br82	0.83	776.6	537	35.8	h	1.29E05	81	1.48E+00	-	-
538	778.0	Mo99	0.049	140.5	116	2.75	d	2.38E05	98	1.21E-01	-	-
539	778.6	Eu152	0.14	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
540	786.5	Ga72	0.0321	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
541	792.0	Re184	0.41	902.8	576	38	d	3.28E06	(183)	Fast neutron	-	-
542	795.8	Cs134	0.88	604.7	456	2.1	y	6.53E07	133	3.06E+01	-	-
543	796.6	Er171	0.0064	308.3	275	7.5	h	2.71E04	170	1.34E+00	-	-
544	798.7	Se83	0.157	356.6	319	25	m	1.50E03	82	3.68E-04	-	-
545	802.0	Cs134	0.0882	604.7	456	2.1	y	6.53E07	133	3.06E+01	-	-
546	810.2	Ga72	0.02	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
547	810.3	Co58	0.99	810.3	547	71.3	d	6.16E06	(57)	Fast neutron	-	-
548	810.3	Ho166m	0.56	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
549	815.7	La140	0.223	1596.5	683	40.2	h	1.45E05	139	8.89E+00	-	-
550	816.0	Tm168	0.468	198.3	183	93	d	8.04E06	(167)	Fast neutron	-	-
551	818.0	Ag110m	0.08	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
552	818.8	In116m	0.17	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
553	827.8	Br82	0.25	776.6	537	35.8	h	1.29E05	81	1.48E+00	-	-
554	828.0	Se81	0.002	275.8	245	18	m	1.08E03	80	2.49E-01	61	Se81m
555	829.0	Re188	0.0045	155.0	129	17	h	6.11E04	187	4.49E+01	-	-
556	830.6	Ho166m	0.0948	184.4	167	1200	y	3.78E10	165	1.00E+00	-	-
557	834.0	Ga72	0.956	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
558	834.8	Mn54	1.0	834.8	558	291	d	2.51E07	(53)	Fast neutron	-	-
559	841.6	Eu152m	0.13	841.6	559	9.3	h	3.37E04	151	1.34E+03	-	-
560	844.0	Mg27	0.7	844.0	560	9.45	m	5.67E02	26	3.05E-03	-	-
561	846.9	Mn56	0.99	846.9	561	2.58	h	9.29E03	55	1.33E+01	-	-
562	860.5	Tl208	0.12	2614.3	708			1.00E20	(207)	Background	-	-
563	863.5	Co58	0.014	810.3	547	71.3	d	6.16E06	(57)	Fast neutron	-	-
564	867.5	As76	8.6×10^{-4}	559.2	434	26.3	h	9.47E04	75	4.50E+00	-	-
565	871.1	Nb94m	0.0048	871.1	565	6.3	m	3.76E02	93	1.00E+00	-	-
566	871.1	Nb94	1.0	871.1	506	20,000	y	6.40E11	93	1.10E+00	-	-
567	874.8	Os185	0.067	646.1	482	94	d	8.12E06	184	Unknown	-	-
568	875.8	Ru105	0.034	724.5	520	4.4	h	1.60E04	104	9.06E-02	-	-
569	879.4	Tb160	0.3	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
570	880.3	Os185	0.054	646.1	482	94	d	8.12E06	184	Unknown	-	-
571	884.5	Ag110m	0.71	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
572	889.4	Sc46	1.0	889.4	572	84	d	7.25E06	45	2.30E+01	-	-
573	894.3	Re184	0.178	902.8	576	38	d	3.28E06	(183)	Fast neutron	-	-
574	898.0	Rb88	0.145	1836.0	691	17.8	m	1.07E03	87	3.34E-02	-	-
575	898.0	Y88	0.91	1836.0	692	104	d	8.99E06	(87)	Fast neutron	-	-
576	902.8	Re184	0.4	792.0	541	38	d	3.28E06	(183)	Fast neutron	-	-
577	909.2	Zr89	0.99	909.2	577	3.25	d	2.81E05	(88)	Fast neutron	-	-
578	910.3	Zn71	0.078	511.6	407	2.4	m	1.44E02	70	6.20E-04	-	-
579	911.0	Ac228	0.25	911.0	579			1.00E20	(227)	Background	-	-
580	928.5	Ti51	0.05	320.0	291	5.8	m	3.47E02	50	7.35E-03	-	-
581	931.1	Re188	0.006	155.0	129	17	h	6.11E04	187	4.49E+01	-	-
582	934.1	Cd115m	0.019	934.1	582	44	d	3.80E06	114	4.04E-02	-	-
583	934.6	Nb92m	0.99	934.6	583	10	d	8.73E05	(91)	Fast neutron	-	-
584	937.2	Ag110m	0.32	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
585	938.4	Ir194	0.004	328.0	296	19.7	h	7.09E04	193	6.76E+01	-	-
586	963.5	Eu152m	0.12	841.6	559	9.3	h	3.37E04	151	1.34E+03	-	-
587	964.1	Eu152	0.15	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
588	966.2	Tb160	0.255	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
589	968.8	Ac228	0.123	911.0	579			1.00E20	(227)	Background	-	-
590	969.4	Ru105	0.0234	724.5	520	4.4	h	1.60E04	104	9.06E-02	-	-
591	983.5	Sc48	1.0	1037.4	597	43.9	h	1.58E05	(47)	Fast neutron	-	-
592	995.1	Dy165	5.5×10^{-4}	94.7	51	2.33	h	8.40E03	164	7.75E+02	-	-
593	997.2	Te131	0.033	149.7	121	25	m	1.49E03	130	6.90E-02	-	-
594	1005.5	Eu154	0.185	1274.3	638	16	y	5.05E08	153	1.67E+02	-	-
595	1012.4	Mo101	0.114	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
596	1014.1	Mg27	0.3	844.0	560	9.45	m	5.67E02	26	3.05E-03	-	-
597	1037.4	Sc48	1.0	983.5	591	43.9	h	1.58E05	(47)	Fast neutron	-	-
598	1039.0	Cu66	0.09	1039.0	598	5.1	m	3.06E02	65	7.11E-01	-	-
599	1039.4	Ga70	0.005	1039.4	599	21.2	m	1.27E03	69	1.14E+00	-	-
600	1043.9	Br82	0.29	776.6	537	35.8	h	1.29E05	81	1.48E+00	-	-
601	1047.0	Rh102m	0.41	475.1	383	2.5	y	7.88E07	(101)	Fast neutron	-	-
602	1050.5	Ga70	0.005	1039.4	599	21.2	m	1.27E03	69	1.14E+00	-	-
603	1050.7	Ga72	0.069	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
604	1076.6	Rb86	0.088	1076.6	604	18.6	d	1.61E06	85	7.22E-01	-	-
605	1079.8	Yb177	0.05	150.3	122	1.9	h	6.84E03	176	8.91E-01	-	-
606	1085.8	Ge77	0.06	264.6	234	11.3	h	4.07E04	76	9.63E-03	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		t½, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
607	1086.0	Eu152	0.12	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
608	1097.1	In116m	0.53	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
609	1099.2	Fe59	0.565	1099.2	609	45.1	d	3.90E06	58	3.41E-03	-	-
610	1115.4	Zn65	0.49	1115.4	610	245	d	2.12E07	64	2.25E-01	-	-
611	1115.4	Ni65	0.16	1481.7	672	2.56	h	9.22E03	64	1.74E-02	-	-
612	1120.0	Bi214	0.17	609.3	460			1.00E20	(213)	Background	-	-
613	1120.3	Sc46	1.0	1120.3	613	83.9	d	7.25E06	45	2.30E+01	-	-
614	1121.3	Ta182	0.349	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
615	1136.0	Cs132	0.005	667.7	493	6.2	d	5.36E05	(131)	Fast neutron	-	-
616	1140.5	Sb122	0.007	564.0	436	2.75	d	2.38E05	121	3.47E+00	-	-
617	1147.0	Te131	0.05	149.7	121	25	m	1.49E03	130	6.90E-02	-	-
618	1148.1	Zr97	0.0264	743.4	525	17	h	6.12E04	96	1.40E-04	-	-
619	1157.5	Ta182	0.0099	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
620	1173.1	Co60	1.0	1332.4	655	5.26	y	1.65E08	59	3.70E+01	-	-
621	1177.9	Tb160	0.155	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
622	1180.6	Nd151	0.153	116.7	81	12.4	m	7.20E02	150	8.40E-02	-	-
623	1189.0	Ta182	0.164	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
624	1199.9	Tb160	0.0236	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
625	1203.5	As74	0.00244	595.8	450	17.5	d	1.51E06	(73)	Fast neutron	-	-
626	1215.8	As76	0.043	559.2	434	26.3	h	9.47E04	75	4.50E+00	-	-
627	1221.4	Ta182	0.273	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
628	1228.8	As76	0.011	559.2	434	26.3	h	9.47E04	75	4.50E+00	-	-
629	1231.0	Ta182	0.116	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
630	1240.9	Yb177	0.03	150.3	122	1.9	h	6.84E03	176	8.91E-01	-	-
631	1256.6	Sb122	0.007	564.0	436	2.75	d	2.38E05	121	3.47E+00	-	-
632	1256.7	Br80	0.0007	617.0	464	17.7	m	1.06E03	79	4.29E+00	714	Br80m
633	1257.5	Ta182	0.0151	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
634	1260.1	Ga72	0.011	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
635	1266.2	Si31	0.0007	1266.2	635	2.6	h	9.43E03	30	3.43E-03	-	-
636	1271.9	Tb160	0.076	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
637	1273.3	Al29	0.94	1273.3	637	6.6	m	3.94E02	(28)	Fast neutron	-	-
638	1274.3	Eu154	0.37	1274.3	638	16	y	5.05E08	153	1.67E+02	-	-
639	1274.5	Na22	1.0	1274.5	639	2.58	y	8.13E07	(21)	Fast neutron	-	-
640	1276.8	Ga72	0.0157	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
641	1277.4	Tm168	0.016	198.3	183	93	d	8.04E06	(167)	Fast neutron	-	-
642	1289.9	Cd115m	0.009	934.1	582	44	d	3.80E06	114	4.04E-02	-	-
643	1291.6	Fe59	0.432	1099.2	609	45.1	d	3.90E06	58	3.41E-03	-	-
644	1293.4	In116m	0.8	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
645	1293.6	Al41	0.99	1293.6	645	1.83	h	6.60E03	40	6.08E-01	-	-
646	1296.9	Ca47	0.74	1296.9	646	4.7	d	4.06E05	46	9.90E-06	-	-
647	1300.0	In114m	0.00164	1300.0	647	50	d	4.32E06	113	3.38E-01	-	-
648	1303.0	Cd117	0.19	273.3	242	2.4	h	8.64E03	116	1.06E-01	-	-
649	1311.6	Sc48	1.0	1311.6	649	1.83	d	1.58E05	(47)	Fast neutron	-	-
650	1312.1	Tb160	0.0297	879.4	569	72	d	6.25E06	159	4.60E+01	-	-
651	1315.0	Eu152m	0.012	841.6	559	9.3	h	3.37E04	151	1.34E+03	-	-
652	1317.2	Br82	0.26	776.6	537	35.8	h	1.29E05	81	1.48E+00	-	-
653	1325.5	Sb124	0.0147	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
654	1332.4	Co60m	0.0025	58.5	10	10.5	m	6.30E02	59	1.80E+01	-	-
655	1332.4	Co60	1.0	1173.1	620	5.26	y	1.65E08	59	3.70E+01	-	-
656	1345.9	Cu64	0.006	1345.9	656	12.7	h	4.58E04	63	3.11E+00	-	-
657	1362.3	Zr97		743.4	525	17	h	6.12E04	96	1.40E-04	-	-
658	1364.8	Cs134	0.034	604.7	456	2.1	y	6.53E07	133	3.06E+01	-	-
659	1367.5	Ge77	0.0135	264.5	234	11.3	h	4.07E04	76	9.63E-03	-	-
660	1368.4	Na24	1.0	2753.6	710	15	h	5.40E04	23	5.30E-01	-	-
661	1378.4	Ni57	0.86	1378.4	661	36	h	1.30E05	(56)	Fast neutron	-	-
662	1379.4	Ho166	0.0093	80.6	31	26.8	h	9.65E04	165	6.40E+01	-	-
663	1384.0	Ag110m	0.21	657.8	487	253	d	2.19E07	109	1.46E+00	-	-
664	1388.1	Pd111		580.0	442	22	m	1.32E03	110	2.71E-02	155	Pd111m
665	1388.9	Eu152m	0.011	841.6	559	9.3	h	3.37E04	151	1.34E+03	-	-
666	1407.5	Eu152	0.22	344.2	308	12.2	y	3.85E08	151	2.82E+03	-	-
667	1434.4	V52	1.0	1434.4	667	3.75	m	2.26E02	51	4.89E+00	-	-
668	1436.6	Sb124	0.0109	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
669	1458.9	Pd111		580.0	442	22	m	1.32E03	110	2.71E-02	155	Pd111m
670	1460.7	K40	0.11	1460.7	670			1.00E20	(39)	Background	-	-
671	1474.7	Br82	0.17	776.6	537	35.8	h	1.29E05	81	1.48E+00	-	-
672	1481.7	Ni65	0.25	1481.7	672	2.56	h	9.22E03	64	1.74E-02	-	-
673	1488.9	Pd111		580.0	442	22	m	1.32E03	110	2.71E-02	-	Pd111m
674	1507.7	In116m	0.11	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
675	1508.6	Zr89m	0.06	588.6	446	4.4	m	2.64E02	(88)	Fast neutron	-	-
676	1524.7	K42	0.18	1524.7	676	12.5	h	4.51E04	41	8.12E-02	-	-
677	1532.3	Mo101	0.054	590.8	447	14.6	m	8.77E02	100	1.92E-02	-	-
678	1575.6	Pr142	0.037	1575.6	678	19.1	h	6.89E04	141	1.20E+01	-	-
679	1576.1	Cd117	0.17	273.3	242	2.4	h	8.64E03	116	1.06E-01	-	-
680	1581.8	Ho166	0.00181	80.6	31	26.8	h	9.65E04	165	6.40E+01	-	-
681	1588.3	Ac228		911.0	579			1.00E20	(227)	Background	-	-
682	1595.3	Eu154	0.037	1274.3	638	16	y	5.05E08	153	1.67E+02	-	-
683	1596.5	La140	0.954	1596.5	683	40.2	h	1.45E05	139	8.89E+00	-	-
684	1596.7	Ga72	0.0427	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
685	1633.1	F20	1.0	1633.1	685	11	s	1.10E01	19	1.00E-02	-	-
686	1642.0	C138	0.38	2166.8	701	37.5	m	2.24E03	37	9.91E-02	-	-
687	1691.0	Sb124	0.488	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
688	1731.6	Na24DE		1368.4	660	15	h	5.40E04	23	5.30E-01	-	-
689	1778.9	Al28	1.0	1778.9	689	2.3	m	1.39E02	27	2.35E-01	-	-
690	1810.7	Mn56	0.29	846.9	561	2.58	h	9.29E03	55	1.33E+01	-	-
691	1836.0	Rb88	0.221	1836.0	691	17.8	m	1.07E03	87	3.34E-02	-	-
692	1836.0	Y88	1.0	1836.0	692	104	d	8.99E06	(87)	Fast neutron	-	-
693	1861.1	Ga72	0.0524	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-

No.	Photopeak energy, keV	Isotope	Absolute γ-ray intensity	Most intense γ-ray, keV	No. of largest peak	Half-life		$t_{\frac{1}{2}}$, sec	At. wt. of target	Cross-sect. x nat. abund.	No. of parent	Parent
(1)	(2)	(3)	(4)	(5)	(6)	(7)		(8)	(9)	(10)	(11)	(12)
694	1997.4	Cd117m	0.15	273.3	242	3.4	h	1.22E04	116	5.31E-02	-	-
695	2061.0	Ca49DE		3083.0	711	8.8	m	5.28E02	48	2.04E-03	-	-
696	2080.4	S37DE		3102.4	712	5.1	m	3.03E02	36	1.96E-05	-	-
697	2091.0	Sb124	0.06	602.7	454	60.2	d	5.20E06	123	1.43E+00	-	-
698	2112.0	In116m	0.2	1293.4	644	54	m	3.24E03	115	1.47E+02	-	-
699	2112.8	Mn56	0.15	846.9	561	2.58	h	9.29E03	55	1.33E+01	-	-
700	2118.6	Rb88	0.0095	1836.0	691	17.8	m	1.07E03	87	3.34E-02	-	-
701	2166.8	C138	0.47	2166.8	686	37.5	m	2.24E03	37	9.91E-02	-	-
702	2201.6	Ga72	0.259	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
703	2242.6	Na24SE		1368.4	660	15	h	5.40E04	23	5.30E-01	-	-
704	2425.8	Al29	0.06	1273.3	637	6.6	m	3.94E02	(27)	Fast neutron	-	-
705	2507.8	Ga72	0.128	834.0	557	14.1	h	5.08E04	71	1.99E+00	-	-
706	2572.0	Ca49SE		3083.0	711	8.8	m	5.28E02	48	2.04E-03	-	-
707	2591.4	S37SE		3102.4	712	5.1	m	3.03E02	36	1.96E-05	-	-
708	2614.3	Tl208	1.0	2614.3	708			1.0CE20	(207)	Background	-	-
709	2677.6	Rb88	0.023	1836.0	691	17.8	m	1.07E03	87	3.34E-02	-	-
710	2753.6	Na24	1.0	1368.4	660	15	h	5.40E04	23	5.30E-01	-	-
711	3083.0	Ca49	0.917	3083.0	711	8.8	m	5.28E02	48	2.04E-03	-	-
712	3102.4	S37	0.9	3102.4	712	5.1	m	3.03E02	36	1.96E-05	-	-
713	4071.0	Ca49	0.073	3083.0	711	8.8	m	5.28E02	48	2.04E-03	-	-
714		Br80m				4.4	h	1.58E04	79	1.47E+00	-	-
					SECTION FOR UPDATING							
715	88.6	Hf178m	0.54	426.6	729	4.5	s	4.50E00	177	2.60E-1	-	-
716	99.6	W183m	0.09	108.0	718	5.28	s	5.28E00	182	1.30E-1	-	-
717	104.3	Yb177m	0.65	104.3	717	6.31	s	6.31E00	176		-	-
718	108.0	W183m	0.19	108.0	718	5.28	s	5.28E00	182	1.30E-1	-	-
719	142.8	Sc46m	0.455	142.8	719	18	s	1.80E01	45	1.00E+1	-	-
720	160.5	W183m	0.06	108.0	718	5.28	s	5.28E00	182	1.30E-1	-	-
721	162.7	In116m2	0.385	162.7	721	2.15	s	2.15E00	115	3.83	-	-
722	197.8	O19	0.97	197.8	722	27.2	s	2.72E01	(19)	Fast neutron	-	-
723	207.9	Er167m	0.43	207.9	723	2.23	s	2.23E00	166	3.34	-	-
724	213.7	Hf178m	0.75	426.6	729	4.5	s	4.50E00	177	2.60E-1	-	-
725	214.0	Pd107m	0.69	214.0	725	20.9	s	2.09E01	106		-	-
726	227.4	Yb177m	0.228	104.3	717	6.31	s	6.31E00	176		-	-
727	325.4	Hf178m	0.94	426.6	729	4.5	s	4.50E00	177	2.60E-1	-	-
728	346.4	Na24DE	* 2.0	346.4	728	15	h	5.40E04	23	5.30E-1	-	-
729	426.6	Hf178m	0.97	426.6	729	4.5	s	4.50E00	177	2.60E-1	-	-
730	569.7	Pb207m	0.98	569.7	730	0.795	s	7.95E-1	206	7.56E-3	-	-
731	657.8	Ag110	0.045	657.8	731	23.3	s	2.33E01	109	4.32E+1	-	-
732	671.4	C138m	1.00	671.4	732	0.700	s	7.00E-1	37	1.23E-3	-	-
733	857.4	Na24SE	* 2.0	857.4	733	15	h	5.40E04	23	5.30E-1	-	-
734	1063.6	Pb207m	0.83	569.7	730	0.795	s	7.95E-1	206	7.56E-3	-	-
735	1293.2	In116	0.012	1293.2	735	14.3	s	1.43E01	115	4.31E+1	-	-
736	1356.9	O19	0.59	197.8	722	27.2	s	2.72E01	(19)	Fast neutron	-	-
737	2754.0	N16	0.01	2754.0	737	7.08	s	7.08E00	(16)	Fast neutron	-	-
738	208.0	Br79m	0.70	208.0	738	5.48	s	5.48E00	(78)	Fast neutron	-	-
739	505.0	Sb124m	0.20	505.0	739	1.55	m	9.30E01	123	1.26E-2	742	Sb124m2
740	602.7	Sb124m	0.20	602.7	740	1.55	m	9.30E01	123	1.26E-2	742	Sb124m2
741	645.8	Sb124m	0.20	645.8	741	1.55	m	9.30E01	123	1.26E-2	742	Sb124m2
742		Sb124m2						1.23E03	123	5.30E-3		-
743	1144.8	C138DE	* 2.0	2166.8	701	37.5	m	2.24E03	37	9.91E-2	-	-
744	1655.8	C138SE	* 2.0	2166.8	701	37.5	m	2.24E03	37	9.91E-2	-	-
745	1090.8	Mn56DE	* 2.0	2112.8	699	2.58	h	9.29E03	55	1.33E+1	-	-
746	1601.8	Mn56SE	* 2.0	2112.8	699	2.58	h	9.29E03	55	1.33E+1	-	-
747	2658.0	Mn56	0.0066	846.9	561	2.58	h	9.29E03	55	1.33E+1	-	-
748	3370.6	Mn56	0.002	846.9	561	2.58	h	9.29E03	55	1.33E+1	-	-
749	788.7	Mn56DE	* 2.0	1810.7	690	2.58	h	9.29E03	55	1.33E+1	-	-
750	1299.7	Mn56SE	* 2.0	1810.7	690	2.58	h	9.29E03	55	1.33E+1	-	-
					CORRECTIONS TO MAIN LIBRARY (added in proof)							
78	113.7	Ta182	0.019	1121.3	614	115	d	9.94E06	181	2.11E+01	-	-
79	113.8	Yb175	0.018	396.3	343	4.19	d	3.64E05	174	1.75E+01	-	-
167	184.3	Tm168	0.164	198.3	183	93.1	d	8.04E06	(167)	Fast neutron	-	-
168	184.4	Ho166m	0.739	184.4	168	1200	y	3.78E10	165	1.00E+00	-	-
200	215.6	Tb160	0.0402	879.4	569	72.3	d	6.25E06	159	4.60E+01	-	-
201	215.7	Ru97	0.853	215.7	201	2.91	d	2.51E05	96	1.09E-02	-	-
313	348.2	Gd159	0.0021	363.6	327	18.6	h	6.68E04	158	8.47E-01	-	-
343	396.3	Yb175	0.062	396.3	343	4.19	d	3.64E05	174	1.75E+01	-	-
429	555.8	Rh104	0.02	555.8	429	42.3	s	4.23E01	103	1.44E+02	-	-
673	1488.9	Pd111		580.0	442	22	m	1.32E03	110	2.71E-02	155	Pd111m

* Indicates not known
SE indicates single escape peak
DE indicates double escape peak

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      PROGRAM IDENT                                                          ULRC     2
C                                                                            ULRC     3
C A SUBROUTINE OF SAMPO. THIS SUBROUTINE MATCHES THE PEAKS FOUND WITH        ULRC     4
C THE NUCLEAR DATA LIBRARY,CALCULATES ABSOLUTE DISINTEGRATION RATES AND      ULRC     5
C MASSES OF ELEMENTS                                                         ULRC     6
C                                                                            ULRC     7
      COMMON/ONE/LCNTT,CLKT                                                  ULRC     8
      COMMON/DESMON/CTIME,TIRR,TDEC,FLUX,CYCN,TWDASH,CMODE,MASS              ULRC     9
      COMMON/FAILS/FNO,FENG,FERR,FISO,FRES                                   ULRC    10
      COMMON/TWO/CONS                                                        ULRC    11
      COMMON/IOTAPE/INTAPE,IOUTAP,KOUT                                       ULRC    12
      COMMON/NUMBER/NUMF,NUMP,NUMLIM                                         ULRC    13
      COMMON/   3   /NPEAK(100),FITCH(100),ENERG(100),ENER(100),             ULRC    14
     1    CHER(100),PEAK(100),EFFSUM(100),EFER(100),PKER(100)                ULRC    15
      REAL LAMDA,LAMDAP,LCNTT,MASS                                           ULRC    16
      INTEGER FAIL,FNO(50),FISO(50), COMMENT(6,3),X                          ULRC    17
      DIMENSION EKEV(750),JBIG(750),ABUN(750),ATWT(750),ISOT(750),           ULRC    18
     1HALFT(750),SIG(750),NPRT(750),ND(750)                                  ULRC    19
      DIMENSION IDEN(100,15)                                                 ULRC    20
      DIMENSION FENG(50),FERR(50),FRES(50,4),Z(50,4)                         ULRC    21
      DATA(COMMENT(1,J),J=1,3)/10HGAMMA RAY ,10HABUNDANCE ,10HNOT KNOWN      ULRC    22
     1/                                                                      ULRC    23
      DATA(COMMENT(2,J),J=1,3)/10HFAST NEUTR,10HON REACTIO,1HN/              ULRC    24
      DATA(COMMENT(3,J),J=1,3)/10HNEUTRON X-,10HSECTION NO,7HT KNOWN/        ULRC    25
      DATA (COMMENT(4,J),J=1,3)/10HANNIHILATI,10HON PEAK   ,1H /             ULRC    26
      DATA (COMMENT(5,J),J=1,3)/10HBACKGROUND,5H PEAK,1H /                   ULRC    27
      DATA(COMMENT(6,J),J=1,3)/10H= MASS OF ,6HPARENT,1H /                   ULRC    28
C                                                                            ULRC    29
C *** SUBROUTINES CALLED FROM IDENT....WORK ,FAILURE                         ULRC    30
C                                                                            ULRC    31
C *** FUNCTIONS USED BY IDENT ARE:                                           ULRC    32
C      D(LAMDA,T) = (1-EXP(-LAMDA*T))                                        ULRC    33
C     XXP(X) = EXP(X)  IF X> -675.84      ELSE XXP(X)=0                      ULRC    34
C     N.B. ON THE CDC 6600 AT U.L.C.C. AN ARGUMENT SMALLER THAN              ULRC    35
C     THAT QUOTED ABOVE CAUSES AN EXECUTION ERROR.                           ULRC    36
C                                                                            ULRC    37
C ***  RELEVANT VARIABLES PASSED TO IDENT IN COMMON BLOCKS FROM SAMPO         ULRC    39
C                                                                            ULRC    40
C     LCNTT       - LIVE TIME                                                ULRC    41
C     CLKT        - CLOCK TIME                                               ULRC    42
C     CTIME       - COUNTING TIME IF NOT READ IN AS PART OF SPECTRUM         ULRC    43
C     TIRR        - IRRADIATION TIME                                         ULRC    44
C     TDEC        - DELAY TIME                                               ULRC    45
C     FLUX        - THERMAL NEUTRON FLUX                                     ULRC    46
C     CYCN        - NUMBER OF CYCLES IF IN CYCLIC MODE                       ULRC    47
C     TWDASH      - TIME BETWEEN END OF COUNT AND IRRADIATION                ULRC    48
C     CMODE       - SIGNIFIES DEAD TIME CORRECTION IN CYCLIC MODE            ULRC    49
C     MASS        - ACTUAL MASS OF SAMPLE                                    ULRC    50
C     INTAPE      - INPUT CHANNEL NUMBER                                     ULRC    51
C     IOUTAP      - OUTPUT CHANNEL NUMBER                                    ULRC    52
C     NUMP        - NUMBER OF PEAKS IN SPECTRUM                              ULRC    53
C     ENERG(I)    - ENERGY OF PEAK(I)                                        ULRC    54
C     ENER(I)     - ERROR ON ENERGY OF PEAK(I)                               ULRC    55
C     PEAK(I)     - AREA OF PEAK(I)                                          ULRC    56
C     PKER(I)     - ERROR OF PEAK AREA(I)                                    ULRC    57
C     EFFSUM(I)   - PEAK AREA(I)/EFFICIENCY AT THAT ENERGY                   ULRC    58
C                                                                            ULRC    59
C *** LIMITATIONS                                                            ULRC    60
C     THE SUBROUTINE IS DIMENSIONED TO ALLOW FOR A MAXIMUM OF 15 PEAKS       ULRC    61
C     IN ANY ONE INTERVAL AND 50 UNSUCCESSFUL IDENTIFICATIONS                ULRC    62
C     IN EACH SPECTRUM                                                       ULRC    63
C     THESE LIMITS MAY BE INCREASED IF NECESSARY                             ULRC    64
C                                                                            ULRC    65
C                                                                            ULRC    66
C ***  NUCLEAR  DATA  LIBRARY                                                ULRC    67
C                                                                            ULRC    68
C                                                                            ULRC    69
C  EKEV  IS GAMMA RAY ENERGY IN KEV                                          ULRC    70
C  JBIG IS THE GAMMA RAY OF ISOT WHICH HAS THE LARGEST ABUNDANCE             ULRC    71
C  ABUN IS THE ABSOLUTE GAMMA RAY ABUNDANCE                                  ULRC    72
C  ISOT IS THE RADIOACTIVE NUCLIDE                                           ULRC    73
C  HALFT IF THE HALF-LIFE IN SECONDS                                         ULRC    74
C  ATWT IS THE ATOMIC WEIGHT OF THE TARGET NUCLEUS                           ULRC    75
C     SIG IS THE PRODUCT OF TARGET NUCLEUS NATURAL ABUNDANCE AND ITS         ULRC    76
C        THERMAL NEUTRON CROSS SECTION IN BARNS                              ULRC    77
C  NPRT  INDICATES RADIOACTIVE PARENT                                        ULRC    78
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      DATA (EKEV(I),I=1,713) /46.5, 48.9, ETC FROM LIBRARY COLUMN 2 /          ULRC    80
      DATA (JBIG(I),I=1,713) /  1,   4, ETC FROM LIBRARY COLUMN 6 /
      DATA (ABUN(I),I=1,713)/ .41,.148, ETC FROM LIBRARY COLUMN 4 /
      DATA (ISOT(I),I=1,713) /6HPB210 , 6HTB161 , ETC FROM LIBRARY COLUMN 3/
      DATA (HALFT(I),I=1,713) /1.00E20, 5.97E05, ETC FROM LIBRARY COLUMN 8 /
      DATA (ATWT(I),I=1,713) / 209.,160.,103., ETC FROM LIBRARY COLUMN 9 /
      DATA (SIG(I),I=1,713) /1HB ,  1HD  , 1.10E+1, ETC FROM LIBRARY COLUMN 10 /

       DATA   NPRT(2), NPRT(4), NPRT(12), NPRT(17), NPRT(24), NPRT(30),        ULRC   716
     1 NPRT(35), NPRT(38), NPRT(39), NPRT(66), NPRT(69), NPRT(95),            ULRC   717
     2 NPRT(133), NPRT(135), NPRT(136), NPRT(143), NPRT(150), NPRT(160),      ULRC   718
     3 NPRT(161), NPRT(190), NPRT(208), NPRT(214), NPRT(216), NPRT(218),      ULRC   719
     4 NPRT(221), NPRT(226), NPRT(244), NPRT(245), NPRT(248), NPRT(257),      ULRC   720
     5 NPRT(260), NPRT(261), NPRT(262), NPRT(269), NPRT(272), NPRT(273),      ULRC   721
     6 NPRT(278), NPRT(281), NPRT(282), NPRT(287), NPRT(302), NPRT(303),      ULRC   722
     7 NPRT(304), NPRT(305), NPRT(306), NPRT(328), NPRT(334), NPRT(335),      ULRC   723
     8 NPRT(342), NPRT(344), NPRT(352), NPRT(360), NPRT(370), NPRT(378),      ULRC   724
     9 NPRT(410), NPRT(411), NPRT(415), NPRT(422), NPRT(425), NPRT(426),      ULRC   725
     A NPRT(438), NPRT(442), NPRT(448), NPRT(451), NPRT(457), NPRT(464),      ULRC   726
     A NPRT(469), NPRT(477), NPRT(478), NPRT(479), NPRT(483), NPRT(488),      ULRC   727
     B NPRT(491), NPRT(507), NPRT(514), NPRT(516), NPRT(532), NPRT(554),      ULRC   728
     C NPRT(632)                        /  321,  321,  65,  81,  321,  121,   ULRC   729
     D  65,  234,  321,  65,  25,  447,  421,  242,  242,  234,  81,  298,  81,  ULRC   730
     E 421,  25,  519,  234,  81,  442,  234,  81,  61,  25,  234,  121,  194,  ULRC   731
     F  61,  36,  520,  447,  36,  242,  25,  520,  25,  414,  81,  36,  442,  ULRC   732
     G 121,  36,  155,  229,  36,  36,  298,  81,  298,  234,  319,  319,  447,  ULRC   733
     H 242,  242,  61,  155,  194,  298,  298,  714,  447,  298,  121,          ULRC   734
     I 714,  61,  525,  714,  714,  81,  121,  519,  61,  714/                  ULRC   735
      DATA NPRT(664),NPRT(669) / 155, 155 /                                    ULRC   736
      DATA NPRT(139)/646/                                                      ULRC   737
      DATA HALFT(714), SIG(714) / 1.58E04, 1.47 /                              ULRC   738
C                                                                              ULRC   739
C     THE FOLLOWING IS THE UPDATABLE SECTION OF THE DATA LIBRARY. THIS         ULRC   740
C     IS SMALL IN COMPARISON WITH THE MAIN LIBRARY AND HENCE A COMPLETE        ULRC   741
C     SCAN IS MADE FOR EACH PEAK. ARBITRARY ADDITIONS CAN BE MADE.             ULRC   742
C                                                                              ULRC   743
      DATA(EKEV(I),I=715,750)/ INSERT AS BEFORE /
      DATA(JBIG(I),I=715,750)/ INSERT AS BEFORE /
      DATA(ABUN(I),I=715,750)/ INSERT AS BEFORE /
      DATA(ISOT(I),I=715,750)/ INSERT AS BEFORE /
      DATA(HALFT(I),I=715,750)/ INSERT AS BEFORE /
      DATA(ATWT(I),I=715,750)/ INSERT AS BEFORE /
      DATA(SIG (I),I=715,750)/ INSERT AS BEFORE /
      DATA NPRT(739),NPRT(740),NPRT(741)/742,742,742/                          ULRC   784
                                                                               ULRC   785
C   ABUN = 2.0 INDICATES ABUNDANCE NOT KNOWN                                   ULRC   787
C   HALFT = 1.00E20 INDICATES BACKGROUND PEAK OR ANNIHILATION PEAK             ULRC   788
C   SIG = 2HB INDICATES BACKGROUND PEAK                                        ULRC   789
C   SIG = 1HF INDICATES PEAK ARISING FROM A FAST NEUTRON REACTION              ULRC   790
C   SIG = 1HD INDICATES PEAK ARISING FROM RADIOACTIVE DAUGHTER                 ULRC   791
C   SIG = 1HA INDICATES ANNIHILATION RADIATION - 511 KEV                       ULRC   792
C   SIG = 1HQ INDICATES NEUTRON CROSS SECTION NOT KNOWN                        ULRC   793
C                                                                              ULRC   794
C *** SET INITIAL VALUES                                                       ULRC   796
C                                                                              ULRC   797
      IF(CLKT.EQ.0.0) CLKT=CTIME                                               ULRC   798
      IF(LCNTT.EQ.0.0) LCNTT=CTIME                                             ULRC   799
      IF(TIRR.EQ.0.) TIRR = 1000.                                              ULRC   800
      IF(TDEC.EQ.0.) TDEC = 1000.                                              ULRC   801
      IF(FLUX.EQ.0.) FLUX = 1.2                                                ULRC   802
      NLIB=750                                                                 ULRC   803
      CONS=ALOG(2.0)                                                           ULRC   804
      FAIL=0                                                                   ULRC   805
      DO 740 I=1,NLIB                                                          ULRC   806
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  740 ND(I)=0                                                                    ULRC  807
      FLUX=FLUX * 1.E13                                                          ULRC  808
      IF(MASS.NE.0) WRITE(IOUTAP,4001) MASS                                      ULRC  809
      IF(MASS.EQ.0.0) WRITE(IOUTAP,4000)                                         ULRC  810
      WRITE(IOUTAP,999) CLKT,LCNTT                                               ULRC  811
      IF(CYCN) 25,25,26                                                          ULRC  812
   25 WRITE(IOUTAP,1000)                                                         ULRC  813
      GO TO 27                                                                   ULRC  814
   26 IF(CMODE.EQ.0.0) TCNT=CLKT/CYCN                                            ULRC  815
      IF(CMODE.NE.0.0) TCNT=CLKT/CYCN-TDEC-TIRR-TWDASH                           ULRC  816
      TPER=TIRR+TDEC+TCNT+TWDASH                                                 ULRC  817
      WRITE(IOUTAP,2003) CYCN,TIRR,TDEC,TCNT,TWDASH,TPER,FLUX                    ULRC  818
      WRITE(IOUTAP,2000)                                                         ULRC  819
   27 CONTINUE                                                                   ULRC  820
      J=1                                                                        ULRC  821
      DO 100 L = 1,NUMP                                                          ULRC  822
      DO 4 K = 1,15                                                              ULRC  823
    4 IDEN(L,K) = 0                                                              ULRC  824
      K=0                                                                        ULRC  825
C                                                                                ULRC  826
C     SEARCH MAIN LIBRARY                                                        ULRC  827
C                                                                                ULRC  828
      DO 20 I=J,713                                                              ULRC  829
      IF(ABS(ENERG(L)-EKEV(I)).LE.ENER(L)) GO TO 10                              ULRC  830
      IF(EKEV(I).GT.(ENERG(L)+ENER(L))) GO TO 30                                 ULRC  831
      GO TO 20                                                                   ULRC  832
   10 K = K+1                                                                    ULRC  833
      IF(K.EQ.16) GO TO 40                                                       ULRC  834
      IDEN(L,K) = I                                                              ULRC  835
      ND(I)=1                                                                    ULRC  836
   20 CONTINUE                                                                   ULRC  837
   30 IF(I.GT.20) J=I-20                                                         ULRC  838
C                                                                                ULRC  839
C     PERFORM COMPLETE SCAN OF UPDATABLE SECTION FOR EACH PEAK                   ULRC  840
C                                                                                ULRC  841
      DO 21 I=715,NLIB                                                           ULRC  842
      IF(ABS(ENERG(L)-EKEV(I)).LE.ENER(L)) GO TO 22                              ULRC  843
      GO TO 21                                                                   ULRC  844
   22 K=K+1                                                                      ULRC  845
      IF(K.EQ.16) GO TO 40                                                       ULRC  846
      IDEN(L,K)=I                                                                ULRC  847
      ND(I)=1                                                                    ULRC  848
   21 CONTINUE                                                                   ULRC  849
      IF(K.EQ.0) CALL FAILURE(2,FAIL,L,ENERG(L),ENER(L),DUM,DUM)                 ULRC  850
      GO TO 100                                                                  ULRC  851
   40 CALL FAILURE(1,FAIL,L,ENERG(L),ENER(L),DUM,DUM)                            ULRC  852
  100 CONTINUE                                                                   ULRC  853
      DO 200 L = 1,NUMP                                                          ULRC  854
      DO 140 K = 1,15                                                            ULRC  855
      CONC=0.0                                                                   ULRC  856
      IF(IDEN (L,K)) 200,200,102                                                 ULRC  857
  102 M = IDEN(L,K)                                                              ULRC  858
      J = JBIG(M)                                                                ULRC  859
      IF(ND(J).EQ.0.AND.EKEV(J).GE.ENERG(1).AND.EKEV(J).LE.ENERG(NUMP))          ULRC  860
     X GO TO 135                                                                 ULRC  861
C  SE81  AND BR80  REQUIRE SPECIAL TREATMENT SINCE BOTH THEY AND THEIR           ULRC  862
C PARENTS SE81M, BR80M ARE PRODUCED BY NEUTRON CAPTURE                           ULRC  863
      IF(J.EQ.245.OR.J.EQ.464) GO TO 1125                                        ULRC  864
      GO TO 1127                                                                 ULRC  865
 1125 IF(CYCN) 126,126,127                                                       ULRC  866
 1127 CONTINUE                                                                   ULRC  867
      IF(SIG(M).EQ.1HA) GO TO 108                                                ULRC  868
      IF(SIG(M).EQ.1HB) GO TO 110                                                ULRC  869
      IF(SIG(M).EQ.1HD) GO TO 112                                                ULRC  870
      T=20.*HALFT(M)                                                             ULRC  871
      IF(TDEC.GT.T) GO TO 130                                                    ULRC  872
      IF(ABUN(M).EQ.2.) GO TO 104                                                ULRC  873
C                                                                                ULRC  874
C *** CALCULATES DISINTEGRATION RATES CORRECTED FOR (CONSTANT)                   ULRC  875
C *** DEAD TIME                                                                  ULRC  876
C                                                                                ULRC  877
      LAMDA=CONS/HALFT(M)                                                        ULRC  878
      DRC=EFFSUM(L)*LAMDA*CLKT/(ABUN(M)*D(LAMDA,CLKT)*LCNTT)                     ULRC  879
      DRI=DRC*XXP(LAMDA*TDEC)                                                    ULRC  880
      IF(SIG(M).EQ.1HF) GO TO 105                                                ULRC  881
      IF(SIG(M).EQ.1HQ) GO TO 107                                                ULRC  882
      IF(CYCN.EQ.0.0) GO TO 101                                                  ULRC  883
      IF(CMODE.NE.0) EFFSUM(L)=EFFSUM(L)*CLKT/LCNTT                              ULRC  884
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C ***  MASS CALCULATION FOR CYCLIC MODE                                  ULRC  886
C                                                                        ULRC  887
  127 LAMDA=CONS/HALFT(M)                                                ULRC  888
      TMASS=EFFSUM(L)*ATWT(M)*LAMDA                                      ULRC  889
      TMASS=1.0E06*TMASS/(0.6*SIG(M)*FLUX*ABUN(M))                       ULRC  890
      DRES=D(LAMDA,TIRR)*D(LAMDA,TCNT)*(XXP(-LAMDA*TDEC))                ULRC  891
      DRES=DRES/D(LAMDA,TPER)                                            ULRC  892
      DRES=DRES*(CYCN-(XXP(-LAMDA*TPER))*(1.0-XXP(-CYCN*LAMDA*TPER))/    ULRC  893
     1D(LAMDA,TPER))                                                     ULRC  894
      TMASS=TMASS/DRES                                                   ULRC  895
      IF(TMASS.LT.0.0) GO TO 6002                                        ULRC  896
      IF(MASS.EQ.0.0) GO TO 7001                                         ULRC  897
      CONC=(TMASS/MASS)*1.0E06                                           ULRC  898
      IF(TMASS.GT.MASS) GO TO 6001                                       ULRC  899
 7001 CONTINUE                                                           ULRC  900
      IF(CONC.EQ.0.0) WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),     ULRC  901
     XISOT(M),ABUN(M),TMASS,PKER(L)                                      ULRC  902
      IF(CONC.NE.0.0) WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),     ULRC  903
     XISOT(M),ABUN(M),TMASS,PKER(L),CONC                                 ULRC  904
      GO TO 140                                                          ULRC  905
C                                                                        ULRC  906
C *** SB 124M(1) REQUIRES SPECIAL TREATMENT SINCE IT AND SB 124M(2) ARE  ULRC  907
C *** BOTH PRODUCED BY NEUTRON CAPTURE.                                  ULRC  908
C                                                                        ULRC  909
  101 IF(J.EQ.739.OR.J.EQ.740.OR.J.EQ.741) GO TO 125                     ULRC  910
      GO TO 1126                                                         ULRC  911
  125 IF(CYCN) 126,126,129                                               ULRC  912
  129 CALL FAILURE(5,FAIL,L,ENERG(L),ENER(L),ISOT(M),DUM)                ULRC  913
      GO TO 140                                                          ULRC  914
 1126 CONTINUE                                                           ULRC  915
C                                                                        ULRC  916
C     MASS CALCULATION FOR SIMPLE DECAY                                  ULRC  917
C                                                                        ULRC  918
      EMASS=DRI*ATWT(M)*1.E6/(.6*FLUX*SIG(M)*D(LAMDA,TIRR))              ULRC  919
      IF(EMASS.LT.0.0) GO TO 6002                                        ULRC  920
      IF(MASS.EQ.0.0) GO TO 7002                                         ULRC  921
      CONC=(EMASS/MASS)*1.0E06                                           ULRC  922
      IF(EMASS.GT.MASS) GO TO 6001                                       ULRC  923
 7002 CONTINUE                                                           ULRC  924
  103 IF(CONC.EQ.0.0) WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),     ULRC  925
     XISOT(M),ABUN(M),DRC,DRI,EMASS                                      ULRC  926
      IF(CONC.NE.0.0) WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),     ULRC  927
     XISOT(M),ABUN(M),DRC,DRI,EMASS,CONC                                 ULRC  928
      GO TO 140                                                          ULRC  929
  104 WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),ISOT(M)              ULRC  930
      WRITE(IOUTAP,1001) (COMMENT(1,J),J=1,3)                            ULRC  931
      GO TO 140                                                          ULRC  932
  105 IF(CYCN) 120,120,121                                               ULRC  933
  120 WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),ISOT(M),ABUN(M),     ULRC  934
     1DRC,DRI                                                            ULRC  935
      WRITE(IOUTAP,1001) (COMMENT(2,J),J=1,3)                            ULRC  936
      GO TO 140                                                          ULRC  937
  121 WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),ISOT(M),ABUN(M)      ULRC  938
      WRITE(IOUTAP,1001) (COMMENT(2,J),J=1,3)                            ULRC  939
      GO TO 140                                                          ULRC  940
  107 WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),ISOT(M),ABUN(M)      ULRC  941
     X, DRC, DRI                                                         ULRC  942
      WRITE(IOUTAP,1001) (COMMENT(3,J),J=1,3)                            ULRC  943
      GO TO 140                                                          ULRC  944
  108 WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M)                      ULRC  945
      WRITE(IOUTAP,1001) (COMMENT(4,J),J=1,3)                            ULRC  946
      GO TO 140                                                          ULRC  947
  110 DRC=PEAK(L)/(ABUN(M)*LCNTT)                                        ULRC  948
      WRITE(IOUTAP,2005) L,ENERG(L),ENER(L),EKEV(M),ISOT(M),ABUN(M)      ULRC  949
     X, DRC                                                              ULRC  950
      WRITE(IOUTAP,1001) (COMMENT(5,J),J=1,3)                            ULRC  951
      GO TO 140                                                          ULRC  952
  112 IF(CYCN) 113,113,114                                               ULRC  953
  114 CALL FAILURE(7,FAIL,L,ENERG(L),ENER(L),ISOT(M),DUM)                ULRC  954
      GO TO 140                                                          ULRC  955
  113 N=NPRT(M)                                                          ULRC  956
      T=20.*(HALFT(M)+HALFT(N))                                          ULRC  957
      IF(TDEC.GT.T) GO TO 130                                            ULRC  958
```

```
C *** CALCULATES MASS OF PARENT ELEMENT FROM ACTIVE DAUGHTER                    ULRC  960
C                                                                              ULRC  961
      CALL WORK (1,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  962
      DRC = EFFSUM (L) * (LAMDA-LAMDAP) / (ABUN (M) * (AP-AD) )                ULRC  963
      DRC=DRC*CLKT/LCNTT                                                       ULRC  964
      CALL WORK (2,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  965
      DRI = EFFSUM (L) * (LAMDA-LAMDAP) / (ABUN (M) * (AP-AD) )                ULRC  966
      DRI=DRI*CLKT/LCNTT                                                       ULRC  967
      CALL WORK (3,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  968
      EMASS = EFFSUM (L) * (LAMDA-LAMDAP) *ATWT (N) *1.E6/ (ABUN (M) * (AP-AD) *.6*  ULRC  969
     XFLUX*SIG (N) )                                                           ULRC  970
      IF (EMASS.LT.0.0) GO TO 6002                                             ULRC  971
      IF (MASS.EQ.0.0) GO TO 7003                                              ULRC  972
      CONC= (EMASS/MASS) *1.0E06                                               ULRC  973
      IF (EMASS.GT.MASS) GO TO 6001                                            ULRC  974
 7003 CONTINUE                                                                 ULRC  975
      IF (CONC.EQ.0.0) WRITE (IOUTAP,2005) L,ENERG (L) ,ENER (L) ,EKEV (M) ,   ULRC  976
     XISOT (M) ,ABUN (M) ,DRC,DRI,EMASS                                        ULRC  977
      IF (CONC.NE.0.0) WRITE (IOUTAP,2005) L,ENERG (L) ,ENER (L) ,EKEV (M) ,   ULRC  978
     XISOT (M) ,ABUN (M) ,DRC,DRI,EMASS,CONC                                   ULRC  979
      COMMENT (6,3) =ISOT (N)                                                  ULRC  980
      WRITE (IOUTAP,1001) (COMMENT (6,J) ,J=1,3)                               ULRC  981
      GO TO 140                                                                ULRC  982
  126 N=NPRT (J)                                                               ULRC  983
      T = 20.* (HALFT (M) +HALFT (N) )                                         ULRC  984
      IF (IDEC.GT.T) GO TO 130                                                 ULRC  985
C                                                                              ULRC  986
C     SPECIAL CASES FOR SE81M AND BR80M                                        ULRC  987
C                                                                              ULRC  988
      CALL WORK (1,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  989
      CALL WORK (4,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  990
      DRC = EFFSUM (L) / (ABUN (M) *B)                                         ULRC  991
      DRC=DRC*CLKT/LCNTT                                                       ULRC  992
      CALL WORK (2,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  993
      CALL WORK (4,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  994
      DRI = EFFSUM (L) / (ABUN (M) *B)                                         ULRC  995
      DRI=DRI*CLKT/LCNTT                                                       ULRC  996
      CALL WORK (3,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  997
      CALL WORK (4,HALFT (M) ,HALFT (N) ,AP,AD,SIG (N) ,SIG (M) ,B,LAMDA,LAMDAP)  ULRC  998
      EMASS = EFFSUM (L) *ATWT (M) *1.E6/ (ABUN (M) *B*FLUX* (SIG (M) +SIG (N) ) *.6)  ULRC  999
      IF (EMASS.LT.0.0) GO TO 6002                                             ULRC 1000
      IF (MASS.EQ.0.0) GO TO 7004                                              ULRC 1001
      CONC= (EMASS/MASS) *1.0E06                                               ULRC 1002
      IF (EMASS.GT.MASS) GO TO 6001                                            ULRC 1003
 7004 CONTINUE                                                                 ULRC 1004
      GO TO 103                                                                ULRC 1005
  130 CALL FAILURE (4,FAIL,L,ENERG (L) ,ENER (L) ,ISOT (M) ,DUM)               ULRC 1006
      GO TO 140                                                                ULRC 1007
  135 CALL FAILURE (3,FAIL,L,ENERG (L) ,ENER (L) ,ISOT (M) ,EKEV (J) )         ULRC 1008
      GO TO 140                                                                ULRC 1009
 6001 CALL FAILURE (6,FAIL,L,ENERG (L) ,ENER (L) ,ISOT (M) ,DUM)               ULRC 1010
      GO TO 140                                                                ULRC 1011
 6002 CALL FAILURE (8,FAIL,L,ENERG (L) ,ENER (L) ,ISOT (M) ,DUM)               ULRC 1012
  140 CONTINUE                                                                 ULRC 1013
  200 CONTINUE                                                                 ULRC 1014
      IF (FAIL.EQ.0.0) GO TO 2006                                              ULRC 1015
C                                                                              ULRC 1016
C *** SORT AND OUTPUT UNSUCCESSFUL PEAK IDENTIFICATIONS                        ULRC 1017
C                                                                              ULRC 1018
      WRITE (IOUTAP,2)                                                         ULRC 1019
      IF (FAIL.LE.50) GO TO 7005                                               ULRC 1020
      WRITE (IOUTAP,7006)                                                      ULRC 1021
      FAIL=50                                                                  ULRC 1022
 7005 WRITE (IOUTAP,3)                                                         ULRC 1023
      DO 3001 I=1,FAIL                                                         ULRC 1024
      M=0                                                                      ULRC 1025
      DO 3002 J=2,FAIL                                                         ULRC 1026
      IF (FNO (J) .GT.FNO (J-1) ) GO TO 3002                                   ULRC 1027
      M=M+1                                                                    ULRC 1028
      Y=FNO (J)                                                                ULRC 1029
      V=FENG (J)                                                               ULRC 1030
      W=FERR (J)                                                               ULRC 1031
      X=FISO (J)                                                               ULRC 1032
      DO 4005 K=1,4                                                            ULRC 1033
 4005 Z (J,K) =FRES (J,K)                                                      ULRC 1034
      FNO (J) =FNO (J-1)                                                       ULRC 1035
      FENG (J) =FENG (J-1)                                                     ULRC 1036
      FERR (J) =FERR (J-1)                                                     ULRC 1037
      FISO (J) =FISO (J-1)                                                     ULRC 1038
      DO 4002 K=1,4                                                            ULRC 1039
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```
4002 FRES(J,K)=FRES(J-1,K)                                              ULRC 1040
     FENG(J-1)=V                                                        ULRC 1041
     FNO(J-1)=Y                                                         ULRC 1042
     FERR(J-1)=W                                                        ULRC 1043
     FISO(J-1)=X                                                        ULRC 1044
     DO 4003 K=1,4                                                      ULRC 1045
4003 FRES(J-1,K)=Z(J,K)                                                 ULRC 1046
3002 CONTINUE                                                           ULRC 1047
     IF(M.EQ.0) GO TO 3003                                              ULRC 1048
3001 CONTINUE                                                           ULRC 1049
3003 CONTINUE                                                           ULRC 1050
     DO 5 J=1,FAIL                                                      ULRC 1051
   5 WRITE(IOUTAP,6) FNO(J),FENG(J),FERR(J),FISO(J),(FRES(J,I),I=1,4)   ULRC 1052
2006 CONTINUE                                                           ULRC 1053
   2 FORMAT(1H1,//*   THE FOLLOWING PEAKS WERE REJECTED*//)             ULRC 1054
   3 FORMAT(* NUMBER  ENERGY  ENERGY   ISOTOPE  REASON FOR REJECTION*.  ULRC 1055
    1/,17X,*ERROR*,//)                                                  ULRC 1056
   6 FORMAT(1X,I5,F10.1,F7.1,      *   *,A7,2X,4A10)                    ULRC 1057
 999 FORMAT(//5X,*CLOCK TIME *,2X,F10.3,* SECS.  LIVE TIME  *,F10.3,*   ULRC 1058
    1SECS.*//)                                                          ULRC 1059
1000 FORMAT(/,* PEAK IDENTIFICATION*//,                                 ULRC 1060
    X97H****** FOUND  PEAK ******  ******* LIBRARY PEAK *******  DISINT ULRC 1061
    XEGRATION RATES   MASS OF   CONC IN,/                               ULRC 1062
    X97H NUMBER   ENERGY   ENERGY  ENERGY   ISOTOPE   ABUNDANCE   START ULRC 1063
    X       END OF    ELEMENT    P.P.M.,/                               ULRC 1064
    X97H                  ERROR                                  OF     ULRC 1065
    X       IRRAD-   (MICROG.)          ,/                              ULRC 1066
    X97H                                                       COUNT    ULRC 1067
    X       IATION                      )                               ULRC 1068
1001 FORMAT(1H+,100X,3A10)                                              ULRC 1069
2000 FORMAT(/,* PEAK IDENTIFICATION*//,                                 ULRC 1070
    ^97H****** FOUND  PEAK ******  ******* LIBRARY PEAK *******  MASS O ULRC 1071
    XF        MASS    CONC IN           ,/                            ULRC 1072
    X97H NUMBER   ENERGY   ENERGY  ENERGY   ISOTOPE   ABUNDANCE  ELEMEN ULRC 1073
    XT       ERROR      P.P.M          ,/                             ULRC 1074
    X97H                  ERROR                                (MICROG ULRC 1075
    X.)                               )                               ULRC 1076
2003 FORMAT(5X,*CYCLIC IRRADIATION DATA*,//,                            ULRC 1077
    15X,*NO. OF CYCLES                *,F8.2,/,                         ULRC 1078
    15X,*IRRADIATION TIME              *,F8.2,* SECS*/,                 ULRC 1079
    15X,*DELAY TIME BEFORE COUNTING    *,F8.2,* SECS*/,                 ULRC 1080
    15X,*COUNT TIME PER CYCLE          *,F8.2,* SECS*/,                 ULRC 1081
    15X,*DELAY TIME BEFORE NEXT IRRADN. *,F8.2,* SECS*/,                ULRC 1082
    15X,*PERIOD                        *,F8.2,* SECS*//,                ULRC 1083
    15X,*FLUX      *,1PE10.2,* N/CM2/SEC *)                             ULRC 1084
2005 FORMAT(I6,F10.1,F7.1,F10.1,3X,A7,1PE12.2,1PE10.2,2X,1P3E10.2)      ULRC 1085
4000 FORMAT(/5X,*NO SAMPLE MASS GIVEN ON RESULTS CARD HENCE NO CHECK DO ULRC 1086
    1NE*)                                                               ULRC 1087
4001 FORMAT(/5X,*MASS OF SAMPLE*E12.6,*  MICROGRAMS*)                   ULRC 1088
7006 FORMAT(/5X,*MORE THAN 50 REJECTIONS(FIRST 50 ONLY LISTED) - CHECK  ULRC 1089
    1CALIBRATION AND ENERGY ERROR*//)                                   ULRC 1090
     END                                                                ULRC 1091
     SUBROUTINE FAILURE(MN,FAIL,L,A,B,C,D)                              ULRC 1092
     COMMON/FAILS/FNO,FENG,FERR,FISO,FRES                               ULRC 1093
     INTEGER FNO,FISO,FAIL,C                                            ULRC 1094
     DIMENSION FMESS(8,4),FNO(50),FENG(50),FERR(50),FISO(50),FRES(50,4) ULRC 1095
     DATA BLANK/1H /                                                    ULRC 1096
     DATA (FMESS(1,J),J=1,4)/10HINTERVAL C,10HONTAINS >1,10H5 LIBRARY ,  ULRC 1097
    110HPEAKS     /                                                     ULRC 1098
     DATA (FMESS(2,J),J=1,4)/10HNO LIBRARY,10H PEAK IN T,10HHIS ENERGY, ULRC 1099
    19H INTERVAL/                                                       ULRC 1100
     DATA (FMESS(3,J),J=1,4)/10HMOST INTEN,10HSE PEAK AT,1H ,10HKEV ABS ULRC 1101
    1ENT/                                                               ULRC 1102
     DATA (FMESS(4,J),J=1,4)/10HDECAY TIME,10H > 20 HALF,6H LIVES,1H /  ULRC 1103
     DATA (FMESS(5,J),J=1,4)/10HUNLIKELY.I,10HDENTIFY ON,10H SINGLE IR, ULRC 1104
    110HRADNS ONLY/                                                     ULRC 1105
     DATA(FMESS(6,J),J=1,4)/10HCALCULATED,10H MASS > SA,9HMPLE MASS,    ULRC 1106
    11H /                                                               ULRC 1107
     DATA(FMESS(7,J),J=1,4)/10HACTIVE DAU,10HGHTER UNID,10HENTIFIED/C,  ULRC 1108
    110HYCLIC MODE/                                                     ULRC 1109
     DATA(FMESS(8,J),J=1,4)/10HNEGATIVE M,10HASS. CHECK,8H EFFITDO,1H /  ULRC 1110
     FAIL=FAIL+1                                                        ULRC 1111
     IF(FAIL.GT.50) RETURN                                              ULRC 1112
     FNO(FAIL)=L                                                        ULRC 1113
     FENG(FAIL)=A                                                       ULRC 1114
     FERR(FAIL)=B                                                       ULRC 1115
     DO 10 J=1,4                                                        ULRC 1116
```

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   10 FRES(FAIL,J)=FMESS(MN,J)                                          ULRC 1117
      GO TO (20,20,30,30,30,30,30,30) MN                                ULRC 1118
   20 FISO(FAIL)=BLANK                                                  ULRC 1119
      RETURN                                                            ULRC 1120
   30 FISO(FAIL)=C                                                      ULRC 1121
      IF(MN.NE.3) RETURN                                                ULRC 1122
      ENCODE(8,1,FRES(FAIL,3)) D                                        ULRC 1123
    1 FORMAT(F8.2)                                                      ULRC 1124
      RETURN                                                            ULRC 1125
      END                                                               ULRC 1126
      SUBROUTINE WORK(MODE,TM,TN,AP,AD,SN,SM,B,LAMDA,LAMDAP)            ULRC 1127
C                                                                       ULRC 1128
C *** ROUTINE TO ECONOMISE ON REPEATED EXPRESSIONS IN MASS CALCULATIONS  ULRC 1129
C                                                                       ULRC 1130
      COMMON/ONE/LCNTT,CLKT                                             ULRC 1131
      COMMON/TWO/CONS                                                   ULRC 1132
      COMMON/DESMON/CTIME,TIRR,TDEC                                     ULRC 1133
      REAL LAMDA,LAMDAP,LCNTT                                           ULRC 1134
      GO TO (1,2,3,4) MODE                                              ULRC 1135
    1 LAMDA=CONS/TM                                                     ULRC 1136
      LAMDAP=CONS/TN                                                    ULRC 1137
      AP=LAMDA*D(LAMDAP,CLKT)/LAMDAP                                    ULRC 1138
      AD=LAMDAP*D(LAMDA,CLKT)/LAMDA                                     ULRC 1139
      RETURN                                                            ULRC 1140
    2 AP=AP*XXP(-LAMDAP*TDEC)                                           ULRC 1141
      AD=AD*XXP(-LAMDA*TDEC)                                            ULRC 1142
      RETURN                                                            ULRC 1143
    3 AP=AP*D(LAMDAP,TIRR)                                              ULRC 1144
      AD=AD*D(LAMDA,TIRR)                                               ULRC 1145
      RETURN                                                            ULRC 1146
    4 B=(AP-AD)*SN/((LAMDA-LAMDAP)*(SN+SM))+AD*SM/(LAMDAP*(SN+SM))      ULRC 1147
      RETURN                                                            ULRC 1148
      END                                                               ULRC 1149
      FUNCTION D(LAMDA,T)                                               ULRC 1150
C                                                                       ULRC 1151
C *** FUNCTION TO EVALUATE THE EXPRESSION (1.0-EXP(-LAMDA*T))           ULRC 1152
C                                                                       ULRC 1153
C                                                                       ULRC 1154
C *** XXP IS USED FOR EXP IN CASE OF VERY SMALL ARGUMENTS               ULRC 1155
C                                                                       ULRC 1156
      REAL LAMDA                                                        ULRC 1157
      D=1.0-XXP(-LAMDA*T)                                               ULRC 1158
      RETURN                                                            ULRC 1159
      END                                                               ULRC 1160
      FUNCTION XXP(X)                                                   ULRC 1161
      IF(X.LT.-675.84) GO TO 100                                        ULRC 1162
      XXP=EXP(X)                                                        ULRC 1163
      RETURN                                                            ULRC 1164
  100 XXP=0.0                                                           ULRC 1165
      RETURN                                                            ULRC 1166
      END                                                               ULRC 1167
```

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SHORT COMMUNICATIONS

EMISSIONSSPEKTROGRAPHISCHE BESTIMMUNG VON STICKSTOFFSPUREN ÜBER DIE CYANBANDENEMISSION IN $A^{III}B^{V}$-HALBLEITERN

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Zusammenfassung—Mit einer emissionsspektrographischen Methode wurden Stickstoffspuren in GaAs und GaP bestimmt. Der Stickstoff, der in den pulverförmigen Proben als Nitrid gebunden ist, reagiert mit dem Kohlenstoff der Pulvermischungen bei den Temperaturen des Wechselstrombogens zum CN-Radikal. Die CN-Bande bei 388,4 nm (Bandenkopf) und die Sc I Atomlinie bei 390,7 nm (Standard) wurden für die Analyse verwendet. Die Methode wurde optimiert. Die Nachweisgrenze (3*s*-Kriterium) ist 100 ppm Stickstoff (500 ng) bezogen auf 5 mg der $A^{III}B^{V}$-Halbleiterproben.

Da Stickstoff mit Gallium ein stabiles Nitrid (GaN) bildet, ist es möglich, daß er als isoelektronisches Dotierungselement in andere $A^{III}B^{V}$-Halbleiter, wie Galliumphosphid und Galliumarsenid, eingebaut wird.

Über die analytische Bestimmung des Stickstoffs in solchen Verbindungen sind bisher keine Veröffentlichungen erschienen. Die Bestimmung des Stickstoffs über Lösungen ist schwierig, weil eine hydrolytische Auflösung im alkalischen Medium wegen Verunreinigungsgefahr und Stickstoffverlusten problematisch ist und weil eine oxydative Auflösung im sauren Medium wegen der extremen Stabilität des Galliumnitrid in diesem Medium nicht möglich ist.

Wir untersuchten aus diesem Grund die Möglichkeit, Stickstoff mit Hilfe einer spektroskopischen Methode direkt in den $A^{III}B^{V}$-Festkörpern zu bestimmen. Atomspektroskopische Methoden im üblichen Sinne sind für die Bestimmung des Stickstoffs nicht anwendbar, da die anregbaren empfindlichen Stickstofflinien im Schumann-UV liegen. Für die intensive Anregung von Ionenlinien des Stickstoffs, die in einem günstigeren Spektralbereich liegen, reicht die Energie der für Spurenbestimmungen vorteilhaften Bogenanregung nicht aus.

Es ist jedoch bekannt, daß der elementare Stickstoff bei den Temperaturen des Gleichstrombogenplasmas mit Kohlenstoff zum Cyanradikal reagiert. Wir nahmen an, daß auch der im Galliumnitrid gebundene Stickstoff im Kontakt mit Kohlenstoff bei hohen Temperaturen nach

$$GaN + C \rightarrow Ga + CN$$

reagieren müßte.

Da das Cyanradikal in Bogenplasmen entsprechender Zusammensetzung vorhanden ist und auch eine intensive Bandenemission im Spektralgebiet zwischen 370 und 450 nm aufweist, versuchten wir, auf dieser Basis eine Bestimmungsmethode auszuarbeiten.

Es ist bekannt, daß die Intensität von Bandenemissionen ebenfalls der Teilchenkonzentration im Plasma proportional ist.[1] Hinweise für die analytische Nutzung der Cyanemission geben Timofeev und Korolev.[2] Die physikalisch-chemischen und spektroskopischen Eigenschaften des Cyanradikals sind ebenfalls für eine emissionsspektrographische Bestimmung günstig. Das Cyanradikal besitzt infolge seiner hohen Dissoziationsenergie von 7,8 bis 8 eV[3] eine hohe thermische Stabilität. Die Normtemperature für die Anregung des neutralen Teilchens liegt mit 7350 K relativ hoch,[4] so daß keine Störungen durch negative Intensitäts–Temperatur-Korrelationen zu erwarten sind. Darüberhinaus sind Molekülbanden im allgemeinen genügend selbstabsorptionsfrei. Die violetten Cyanbanden des Kohlebogens zeigen merkliche Selbstabsorption erst bei Verwendung von reinem Stickstoff unter einem Druck von mehr als 1 atm.[5]

EXPERIMENTELLE BEDINGUNGEN UND IHRE OPTIMIERUNG

Es wurde festgestellt, daß die Cyanbande bei 388,4 nm (Bandenkopf) die intensivste Emission aufwies. Da das Ziel unserer Untersuchungen die Ausarbeitung einer Spurenbestimmungsmethode war, wurde kein Wert auf eine spektrale Auflösung der Bande wegen der damit verbundenen Intensitätsverluste gelegt und ein Spektrograph mittlerer Dispersion gewählt. Dieser erlaubte eine genügende allgemeine Auflösung und eine Auswertung der Bandenkopfintensität. Die Anregung erfolgte im Wechselstromdauerbogen, der im Stromstärkebereich zwischen 7 und 15 A überprüft wurde.

Apparatives

Spektrograph. Quarzprismenspektrograph Q 24 (VEB C. Zeiss, Jena, DDR) Reziproke Lineardispersion bei 390 nm: 3 nm/mm Spaltbreite: 0,015 mm.

Anregung. Abreißbogenerzeuger ABR-3, (VEB C. Zeiss, Jena, DDR) Wechselstromdauerbogen: 12 A.

Cyanbande. 388,4 nm (Bandenkopf) Grundzustand: $\chi^2\,\Sigma^+$ O angeregter Zustand: $B^2\,\Sigma^+$ O Anregungspotential E_a: 3,2 eV.

Elektroden. vgl. Abb. 1 Elektrodenabstand: 3 mm, kontinuierlich nachgeregelt.

Probemenge. 5 mg GaP bzw. GaAs, für die Eichung mit GaN dotiert.

Registrierung. Spektralplatte ORWO WO-3, gelb, extrahart (VEB Fotochemisches Kombinat, Filmfabrik Wolfen, DDR).

Die Untersuchungen zur Optimierung des Signal–Untergrund-Verhältnisses erstreckten sich auf die Erzielung einer möglichst vollständigen Bildung des Cyanradikals, der möglichst vollständigen Entfernung des Luftstickstoffs bei Gewährleistung einer genügend einfachen Arbeitsweisen

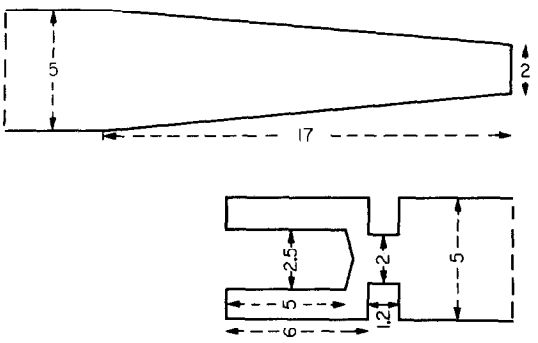


Abb. 1. Verwendete Elektrodenkombination (Maße in mm)

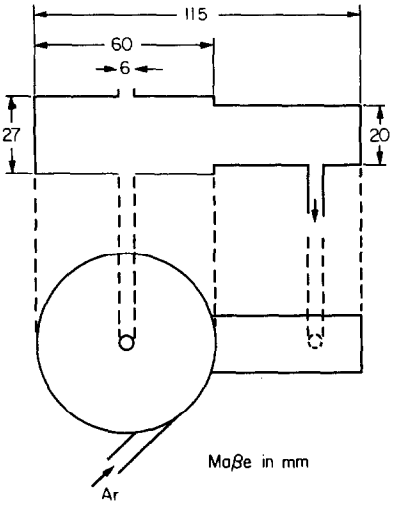


Abb. 2. Schutzgasküvette aus Quarz (Maße in mm).

und der Auffindung eines zuverlässig arbeitenden inneren Standards.

Es wurden verschiedene Mischungen der Probe mit Kohlenstoffpulver getestet: GaX:C wie 1:3 bis 1:16 (X = P, As). Dabei wurde festgestellt, daß ein Verhältnis vom 1:6 am günstigsten ist. Die sich damit ergebende Gesamtprobemenge von 35 mg konnte gut in die Elektrode eingeführt werden. Die ausreichende Erwärmung der Elektrode als Voraussetzung für die Vollständigkeit der gewünschten thermochemischen Reaktion war gewährleistet. Die wichtigste Voraussetzung für die erfolgreiche Anwendung der Methode war die Ausschaltung des Luftstickstoffs. In der Abb. 2 ist eine einfache Quarzküvette dargestellt, die diesem Ziel am nächsten kam und eine einfache Arbeitsweise ermöglichte. Die Elektroden werden durch die eingezeichneten Öffnungen (5,5 mm) eingeführt. Damit ergibt sich eine lichte Weite der Öffnung von 0,25 mm. Die verwendete Elektrodenkombination (vgl. Abb. 1) zeigte ein ruhiges Abbrandverhalten. Zur Ausschaltung des Luftstickstoffs wurden verschiedene Gaskombinationen bei unterschiedlichen Strömungs geschwindigkeiten getestet. Das Ergebnis ist in der Tabelle 1 dargestellt.

Mit zunehmender Strömungsgeschwindigkeit der Gase wurde die Untergrundschwärzung kleiner, d.h. das Eindiffundieren von Stickstoff in die Küvette wurde vermindert. Reines Argon erwies sich, offensichtlich wegen seiner hohen Reinheit, als bestes Reaktionsmedium. Mit zunehmendem O_2-Gehalt erfolgte der Elektrodenabbau und damit die Probeverdampfung schneller. Das führte jedoch nicht zu einer Verbesserung des Signal–Untergrund-Verhältnisses, so daß auch aus diesem Grund Argon als Reaktionsmedium günstig war. Aus wirtschaftlichen Gründen wurden eine Strömungsgeschwindigkeit von 500 l./hr gewählt, weil eine weitere Erhöhung der Strömungsgeschwindigkeit nur geringfügige Verbesserungen der Untergrundschwärzung ergab. Die Untergrundschwärzung wird dann bestimmt durch die Restkonzentration des Stickstoffs im Argon und durch den adsorptiv an der Elektrode gebundenen Stickstoff (Porösität der an Luft gelagerten Elektroden, Stopfen der Probe an Luft) bestimmt. Zur Entfernung dieser Stickstoffrestgehalte wurde eine Minute vor Zündung des Bogens Argon durch die Küvette geblasen. Außerdem wurde die Vorbrenn-und Belichtungszeit optimiert. Wir gingen davon aus, daß der adsorptiv gebundene Stickstoff nach Zündung des Bogens schnell aus der Elektrode und der Küvette vertrieben werden kann. Es zeigte sich, daß eine Vorbrennzeit von 5 s am günstigsten war. Größere Vorbrennzeiten konnten wegen der ebenfalls schnellen Reaktion des Galliumnitrid mit Kohlenstoff nicht angewandt werden.

Aus der Abb. 3, in der die Fahrspektren des Cyanradikals und des verwendeten inneren Standards dargestellt sind, geht hervor, daß eine vollständige Reaktion des Galliumnitrid mit dem Kohlenstoff innerhalb von 60 s verlief. Die Belichtungszeit wurde deshalb mit 60 s festgelegt.

Scandiumoxid erwies sich als innerer Standard am günstigsten. Die Verdampfung dieser Substanz erfolgte parallel zur Cyanbildungsreaktion (vgl. Abb. 3), wobei natürlich eine vollständige spektrochemische Übereinstimmung dieser beiden Reaktionen nicht vorausgesetzt werden kann. Die Sc I Linie bei 390,7 nm war bereits genügend frei von einer Beeinflussung durch die Cyanbande. Ihr Anregungspotential ist dem der Cyanbande sehr ähnlich. Ein Gehalt von 0,5% Sc_2O_3 im Kohlepulver war ausreichend.

Optimierte Bedingungen

Atmosphäre: Ar, 500 l./hr, Küvette vgl. Abb. 2
Probemischung: 5 mg GaX + 30 mg Kohlepulver, 0,5% ig an Sc_2O_3 (X = As, P)

Tabelle 1. CN-Bandenkopfintensitäten (*S*-Werte) in Abhängigkeit von der Inertgaszusammensetzung und Strömungsgeschwindigkeit in Gegenwart von Galliumarsenid

Strömungsgeschwindigkeit, *l./hr*	Untergrundschwärzungswerte in Gegenwart verschiedener Gase							
	Ar	Ar:O_2 80:20	Ar:O_2 70:30	Ar:O_2 60:40	He	He:O_2 80:20	He:O_2 70:30	He:O_2 60:40*
100	1,37	1,40	1,41	1,43	1,66	1,67	1,70	1,71
200	0,53	0,55	0,56	0,58	0,79	0,82	0,84	0,84
300	0,29	0,31	0,33	0,35	0,53	0,55	0,56	0,57
400	0,16	0,17	0,19	0,21	0,31	0,33	0,33	0,35
500	0,09	0,10	0,10	0.12	0,24	0,24	0,25	0,26
800	0,07	0,07	0,08	0,08	0,21	0,21	0,22	0,24

* Volumenanteile

Tabelle 2. Ergebnisse der Stickstoffbestimmung im GaAs und GaP (5 mg) durch Emissionsspektrographie

Matrix	Nachweisgrenzen (3s-Krit.) absolut, *ng*	relativ *ppm*	relativ *Atom/cm³*	Konzentrationsbereich, *ppm*	Restkonzentration, *µg*
GaAs	500	100	$2{,}3 \times 10^{19}$	10^2–10^4	9
GaP	500	100	$1{,}8 \times 10^{19}$	10^2–10^4	11

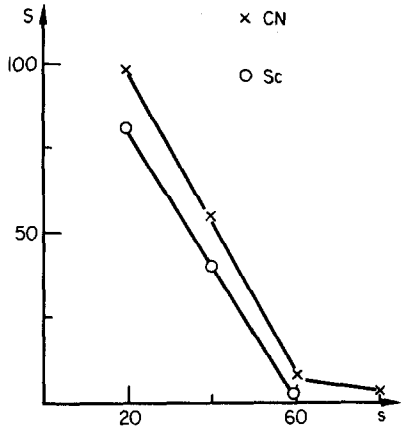


Abb. 3. Fahrspektren für die Cyanbandenemission bei 388,4 nm und die Sc I Linienemission bei 390,7 nm (*S*: Schwärzung, *s*: Zeit in Sekunden)

Vorbrennzeit: 5 s
Belichtungszeit: 60 s
Innerer Standard: Sc I, 390,7 nm, E_a: 3,17 eV

ERGEBNISSE UND DISKUSSION

Die Ergebnisse der Stickstoffspurenbestimmung im Galliumphosphid und Galliumarsenid sind in der Tabelle 2 zusammengefaßt worden. Zur Aufstellung der Eichgeraden wurden aus den *W*-transformierten Schwärzungswerten die *Y*-und *I*-Werte ermittelt (I = relative Lichtintensität, $Y = \lg I$; $S = \lg 1/T$; $W = \lg (1/T - 1)$; T = Transmission). Die Gesamtintensitätswerte wurden durch die Intensitätswerte der Restgehalte korrigiert. Begrenzend für die Bestimmung ist nach wie vor die gemessene Restkonzentration. Es wurde festgestellt, daß dieser Restgehalt nicht auf den adsorptiv gebundenen Stickstoff zurückzuführen ist. Eine Entscheidung, ob der Restgehalt aus dem verwendeten Argon stammt oder trotz der hohen Strömungsgeschwindigkeit durch Diffusion in die Elektrode gelangt konnte nicht getroffen werden. Es ist jedoch wahrscheinlicher, daß der Restgehalt des Argons an Stickstoff die Blindwerte verusacht. Die gemessenen Blindwerte würden dann bedeuten, daß in dem verwendeten Argon etwa 1 ppm Stickstoff enthalten ist. Auf eine nur mit hohem Aufwand auf einem anderen Wege durchführbare Restkonzentrationsbestimmung des Stickstoffs im Argon wurde verzichtet. Versuche zur zusätzlichen Reinigung des Argons durch hocherhitztes Magnesium oder Calcium brachten keine Verbesserung. Dies ist auf die hohen Strömungsgeschwindigkeiten des Argons zurückzuführen.

Die Ergebnisse zeigen jedoch, daß es mit der erarbeiteten Methode gelingt, Stickstoffspuren in relativ geringen Probemengen zu bestimmen.

LITERATUR

1. G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand, Amsterdam, 1945.
2. F. E. Timofeev und V. V. Korolev, *Zavodsk. Lab.*, 1973, **39**, 969.
3. W. Neumann, *Spektroskopische Methoden der Plasmadiagnostik*, in *Ergebnisse der Plasmaphysik und Gaselektronik*, herausgg. von R. Rompe und M. Steenbeck, Band 1, Akademieverlag, Berlin, 1967.
4. H. Maecker, *Z. Phys.*, 1953, **136**, 119.
5. P. J. Somers und J. A. Smit, *Appl. Sci. Res.* B, 1956, **6**, 1.

Summary—Traces of nitrogen in GaP and GaAs are determined by an emission spectrographic method. The nitrogen, which is bound in the powder samples as nitride, reacts with the carbon of the powder mixture at the temperatures of the a.c. arc to form the CN-radical. The CN-band at 388.4 nm (head of the band) and the Sc I atomic line at 390.7 nm (standard) are used for the analysis. The detection limit (3*s*-criterion) is 100 ppm nitrogen (500 ng) in 5 mg of $A^{III}B^{V}$-semiconductor sample.

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ANALYTICAL APPLICATION OF PHENYLBENZENE SULPHAZIDE IN SEPARATION AND DETERMINATION OF SELENIUM

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Summary—In this paper the utility of phenylbenzene sulphazide is illustrated by its application to the determination of selenium and the separation of this element from tellurium, lead, copper, bismuth, nickel and iron. Selenious acid is reduced to black selenium in acid media at 100°. To minimize interference by other elements but yet give rapid recoveries of selenium an acidity of 40% (v/v) formic/acetic acid is recommended. The co-precipitation of tellurium is prevented by adding tartaric acid. Oxalate, tartrate, citrate, EDTA and phosphate do not interfere.

For the determination of selenium, hydroxylamine,[1] sulphur dioxide,[2] thiourea,[3] 1-amidino-2-thiourea,[4] and copper(I) chloride[5] have been employed. Practically all these methods are based on the reduction of selenium(IV) and (VI) to the element. The principal problem has been the elimination of interference by tellurium. The hydroxylamine method is more suitable for selenium but the reaction is slow and long digestion is needed, usually 4 hr, and significant amounts of selenium may be lost by volatilization of the monochloride if incorrect conditions are used. Elements forming insoluble chlorides interfere. Both hydrazine hydrochloride and sulphate tend to cause precipitation of tellurium with the selenium. Such drawbacks do not apply to selenium and tellurium recoveries in the method proposed here. Hovorka[6] used hydrazine hydrate in hydrochloric, perchloric and tartaric acids and reported that the determination of selenium in perchloric acid was unsatisfactory. Ooba and Uneo[7] studied this reaction in perchloric acid for determining selenium in chalcogenide materials containing arsenic, sulphur, selenium and tellurium. They considered a minimum of 4-hr digestion at 100° to be necessary. Other reagents have not found wide acceptance on account of similar disadvantages. In all these methods except the hydroxylamine procedure, red selenium is precipitated, and the drying conditions are critical, because the red selenium is transformed into the black form on heating, and any water present is trapped by occlusion during the change. These limitations narrow the applicability of these methods for the determination of selenium in presence of tellurium. The purpose of this paper is to describe an accurate and relatively rapid gravimetric method for selenium. It is based on reduction of selenious acid to black elementary selenium with phenylbenzene sulphazide in formic/acetic acid media. The reagent was first prepared by Grandmougin[8] by the action of benzenesulphonyl chloride on phenylhydrazine in ether medium, but it has not previously been used for analytical purposes. The procedure affords a clean separation of selenium from tellurium, copper, lead and several other elements which are usually present in selenium-containing materials.

EXPERIMENTAL

Reagents

Standard solutions of selenium(IV) and tellurium(VI). Prepared by dissolving 8.6 g of selenious acid or 11.5 g of telluric acid in doubly distilled water and diluting to one litre. The concentrations were Se 5.16 mg/ml (by the hydroxylamine hydrochloride method[9]) and Te 6.06 mg/ml (by the thiourea method[3]).

Solutions of other elements. Prepared by dissolving suitable salts in water or dilute hydrochloric acid to give concentrations of 10 mg/ml.

Preparation and properties of reagent. Phenylbenzene sulphazide was obtained from phenylhydrazine and benzenesulphonyl chloride.[8] Phenylhydrazine (5 ml) in 25 ml of ether was slowly added to a well-cooled solution of 8.5 ml of benzenesulphonyl chloride in 25 ml of ether, with stirring. The white crystalline derivative was filtered off, washed with small amounts of ether and dried in air. The reagent is freely soluble in alcohol, yield 7.5 g, m.p. 148–150° (decomp.). A 2% solution of the reagent in rectified spirit was used (1 ml ≡ 3 mg of Se).

Procedure

Selenium solution (containing 10–200 mg of the element) was transferred with a calibrated pipette to a 400-ml beaker. To this an appropriate amount of reagent solution was added and formic acid was added until its concentration was 40% v/v. The solution was then diluted to 100 ml with water and heated for 30 min on a boiling water-bath to complete the reaction. The black elementary selenium was immediately filtered off on a porosity-4 sintered-glass filter, washed first with hot water, then with alcohol, and dried at 110° to constant weight. The maximum error ranged from 0.4% for the lowest sample weight to 0.1% for the highest. Alternatively a 40% v/v acetic acid medium can be used, but 60 min heating is then required.

Separation of selenium from tellurium

Tellurium is co-precipitated with selenium in this procedure but addition of 2 g of tartaric acid suppresses the interference. The selenium is precipitated in about 30 min from formic acid solution and in 60 min from acetic acid solution.

The tellurium can be recovered from the filtrate by adjusting the pH to 4–5 with ammonia and heating on a boiling water-bath with 0.5 g of reagent for 60 min. The precipitate is collected on a porosity-4 crucible, washed with hot water and alcohol, and dried. The relative standard deviation is 0.1% for 50–100 mg each of selenium and tellurium.

Separation of selenium from copper

The problem of this separation arises in the analysis of some natural raw materials such as copper selenide.

Table 1. Influence of formic/acetic acid and time allowed for precipitation (reagent added 0.3 g; 61.9 mg of Se taken)

Formic acid (acetic acid) % *v/v*	Time allowed for pptn., *min*	Selenium found, *mg*
10	120	61.8
(10)	180	61.8
20	60	61.9
(20)	120	61.9
40	30	61.9
(40)	60	61.8
60	30	61.9
(50)	60	62.0
80	30	61.9
(60)	60	61.9

As a test of the present method, two synthetic mixtures containing differing amounts of these metals were analysed for selenium. A portion of sample solution was treated with 40 ml of formic acid and 20 ml of hydrochloric acid. An appropriate amount of reagent solution was added and the volume adjusted to 100 ml. The hydrochloric acid was to keep the copper in solution. The method gave acceptable recovery of the selenium.

Separation of selenium from tellurium, copper, bismuth, iron, lead and nickel

The interference of copper is prevented as just described, by addition of 20 ml of hydrochloric acid, and that of tellurium and bismuth with 2 g of tartaric acid. The other elements do not interfere. The average recovery of 72 and 103 mg of selenium was 99.8–99.9%.

RESULTS AND DISCUSSION

The optimum reaction conditions have been established. The reduction to elemental selenium is accomplished in both formic acid and acetic acid media at boiling water-bath temperature. The reaction times needed for complete precipitation at different acid concentrations are shown in Table 1. The reduction time needed is much longer for acetic acid medium than for formic acid.

Effect of diverse ions

The effect of various ions in formic acid media was investigated. Co-precipitation of tellurium was completely suppressed by adding 2 g of tartaric acid. Interference from tellurium could also be eliminated with oxalic acid but recoveries of tellurium from the filtrate were then not quantitative. Copper is also co-precipitated, but this can be prevented by addition of hydrochloric acid. EDTA was tried unsuccessfully for suppressing the precipitation of copper; some copper was still always co-precipitated.

Table 2. Effect of diverse ions

Ion added, *mg*	Selenium, *mg* Taken	Found
Cu(II) 120	103.2	103.1
Mn(II) 60		103.3
Al(III) 12		103.3
Fe(III) 130		103.1
Ni(II) 100		103.2
Ci(II) 75		103.1
Zn(II) 70		103.1
Ca(II) 100		103.2
As(III) 95	82.6	82.5
Sb(III) 100		82.4
Bi(III) 100		82.5
Cd(II) 70		82.6
Sr(II) 70		82.5
Phosphate 125		82.7
Nitrate 1000		82.5
Oxalate 500		82.7
Sulphate 1000		82.7
Tartrate 3000		82.5
EDTA 1000		82.7

Table 2 gives the results (for a final acidity of 40% formic acid and 0.6 g of reagent). The complexing agents oxalate, tartrate, citrate, EDTA and phosphate do not interfere with the determination. Selenium may be completely separated from large amounts of tellurium, lead, copper, bismuth, iron, nickel, cobalt and zinc. Nitrate, sulphate and chloride do not interfere.

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REFERENCES

1. V. Lenher and C. H. Kao, *J. Am. Chem. Soc.*, 1925, **47**, 2454.
2. *Idem, ibid.*, 1925, **47**, 769.
3. S. S. R. Murty, *Indian J. Chem.*, 1965, **3**, 298.
4. R. A. Nadkarni and B. C. Haldar, *J. Indian Chem. Soc.*, 1964, **41**, 813.
5. G. J. Mishra and J. P. Tandon, *Indian J. Chem.*, 1967, **5**, 560.
6. V. Hovorka, *Collection Czech. Chem. Commun.*, 1932, **4**, 300.
7. S. Ooba and S. Uneo, *Talanta*, 1975, **22**, 51.
8. E. Grandmougin, *Ber.*, 1907, **40**, 422.
9. A. I. Vogel, *A Test Book of Quantitative Inorganic Analysis*, p. 509. Longmans, London, 1962.

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THE LUMINESCENCE PROPERTIES OF SOME ANTI-INFLAMMATORY AND ANTIPYRETIC DRUGS

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Summary—Twenty anti-inflammatory and antipyretic drugs have been examined for their fluorescence and phosphorescence characteristics, and conditions established for detection of fourteen of them at trace levels.

The antipyretic and anti-inflammatory drugs are several families of chemical compounds which can lower body temperature in feverish patients or reduce or prevent the inflammatory changes seen in a number of diseases. The anti-inflammatory drugs have been determined by a variety of analytical techniques, the most commonly used being colorimetry (*e.g.* ref. 1), ultraviolet spectrometry[2] and gas chromatography.[3] Other methods include thin-layer chromatography (TLC),[4] NMR[5] and polarography.[6]

There have been several studies of the luminescence properties of anti-inflammatory drugs. Weissbach *et al.*[7] have described a fluorimetric assay for salicylic acid and Moye and Winefordner[8] a phosphorimetric assay for aspirin in plasma: as the phosphorescence intensity of salicylic acid is only 1/500 of that of aspirin, the former does not interfere in the determination of the latter.

Mehta and Schulman[9] found that analytically useful native fluorescence could be obtained for mefenamic and flufenamic acids in either dioxan or chloroform as the solvent. Very recently Strojny and de Silva[10] published a paper on the luminescence determination of anti-inflammatory agents in plasma following separation by TLC. They studied the salicylates, carbazole and tetrahydrocarbazole derivatives, in addition to three compounds investigated in the present work (indomethacin, phenylbutazone and mefenamic acid). The present paper describes the fluorescence and phosphorescence properties of a number of other anti-inflammatory drugs and their analogues.

EXPERIMENTAL

The antipyretic and anti-inflammatory compounds and analogues studied are shown in Table 1. Compounds 1 and 2 were kindly donated by Parke, Davis and Co., compound 3 by Merck, Sharp and Dohme Ltd., compound 4 by Sinclair Pharmaceuticals Ltd., compound 5 by Fisons Ltd. Pharmaceutical Division, compounds 6, 7 and 8 by Geigy Pharmaceuticals and compounds 9–20 by The Boots Co. Ltd.

The melting points of compounds 1–9 were found to be within 2° of the literature values. The melting points of compounds 10–20 were not determined, as only very small quantities were available: they were therefore used as obtained. The solvents used were ethanol (analytical-reagent grade), water (triply distilled from an all-glass apparatus), and ethanol containing 1*M* concentrations of either hydrochloric acid or sodium hydroxide. Fluorescence spectra at room temperature were obtained with a "Fluoricord" spectrofluorimeter (Baird-Atomic Ltd., Braintree, Essex) with a spectral bandwidth of 5 nm. Luminescence spectra and phosphorescence lifetimes at 77 K were obtained by using a "Fluorispec" SF100E spectrofluorimeter (Baird-Atomic Ltd.), fitted with a Dewar flask and rotating-cylinder phosphoroscope as previously described, and employing a spectral bandwidth of 6 nm.[11] All luminescence spectra were uncorrected for instrumental characteristics.

RESULTS AND DISCUSSION

The room-temperature fluorescence characteristics of the compounds under study, in acidic, neutral and alkaline ethanol solution are summarized in Table 2. Compounds showing $\leq 5\%$ of full-scale deflection on the fluorimeter under the conditions described above were classified as "non-fluorescent". By this criterion compounds 1, 2, 4–7, 9, 10 and 15–18 were non-fluorescent in all conditions, although Strojny and de Silva[10] recently found mefenamic acid (compound 2) and phenylbutazone (compound 7) to be weakly fluorescent at room temperature. The fluorescence of compounds 8 and 12–14, 19 and 20 was generally too feeble to be of analytical value. Sulphinpyrazone was non-fluorescent in alkaline ethanol and 4-animophenylacetic acid was non-fluorescent in acid conditions, when it is presumably in a cationic form. Indomethacin (compound 3) was found to be significantly fluorescent only in alkaline ethanol, probably because of its hydrolysis to *p*-chlorobenzoic acid and fluorescent 2-methyl-3-carboxymethyl-5-methoxyindole: this conclusion is supported by the results obtained at 77 K (see below). This fluorescence was sufficiently intense to permit the determination of indomethacin at submicrogram levels, and microgram quantities of the biphenyl derivatives (compounds 11, 19 and 20) could also be detected. The excitation and emission wavelengths of these compounds were similar to those of biphenyl itself.[12]

Table 3 summarizes the luminescence properties of the compounds in neutral ethanol at 77 K. Several compounds that showed no significant fluorescence at room temperature were strongly fluorescent at 77 K, presumably because of the virtual abolition of bimolecular quenching in the

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Table 1. Compounds studied

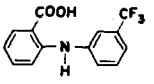
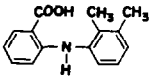
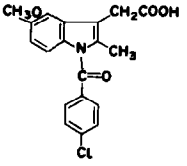
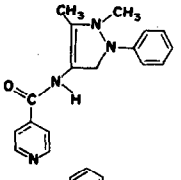
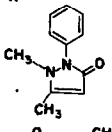
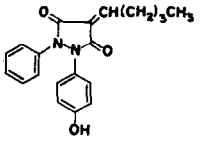
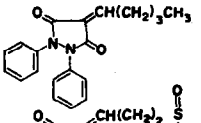
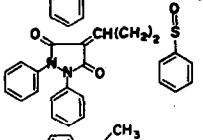
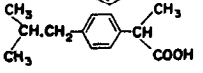
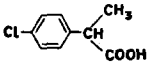
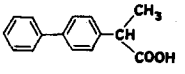
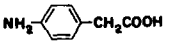
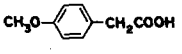
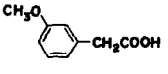
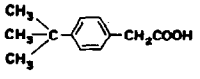
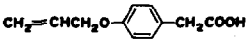
No.	Compound	Formula
1	Flufenamic acid	
2	Mefanamic acid	
3	Indomethacin	
4	Nifenazone	
5	Phenazone	
6	Oxyphenbutazone	
7	Phenylbutazone	
8	Sulphinpyrazone	
9	Ibuprofen	
10	2-(4-Chlorophenyl)propionic acid	
11	2-(4-Biphenyl)propionic acid	
12	4-Aminophenylacetic acid	
13	4-Methoxyphenylacetic acid	
14	3-Methoxyphenylacetic acid	
15	4-t-Butylphenylacetic acid	
16	4-Allyloxyphenylacetic acid	

Table 1. *Continued*

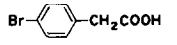
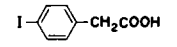
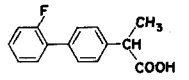
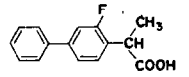
No.	Compound	Formula
17	4-Bromophenylacetic acid	
18	4-Iodophenylacetic acid	
19	2-(2-Fluro-4-biphenyl)propionic acid	
20	2-(2-Fluoro-4-biphenyl)propionic acid	

Table 2. Room temperature fluorescence characteristics

Compound No.	1*M* acid		neutral		1*M* alkali	
	λ_e	λ_f	λ_e	λ_f	λ_e	λ_f
3	N.F.		N.F.		310	355
8	290	470	290	470	N.F.	
11	282	320	282	320	282	320
12	N.F.		300	345	300	345
13	335	375	335	375	335	375
14	280	300	280	300	280	300
19	280	310	280	310	280	310
20	280	310	280	310	280	310

λ_e = wavelength of excitation maximum, *nm*.
λ_f = wavelength of fluorescence maximum, *nm*.

latter conditions. Thus, submicrogram quantities of flufenamic acid (1), mefanamic acid (2), nifenazone (4), oxyphenbutazone (6), phenylbutazone (7), and sulphinpyrazone (8) could be readily detected: as might be expected in view of their similar structures, the fluorescence spectra of the three last-named compounds were almost identical. These results are in agreement with those of Strojny and de Silva,[10] who obtained detection limits of 0.1 and 0.5 μg/ml for mefenamic acid and phenylbutazone respectively.

Several of the other compounds showed analytically useful phosphorescence at 77 K. In neutral or acidic ethanol, indomethacin (Fig. 1a) showed a featureless phosphorescence band with maximum emission at 485 nm, maximum excitation at 330 nm and a phosphorescence lifetime of 1.0–1.1 sec. These results are in good agreement with those of Strojny and de Silva.[10] The latter authors were also able to detect a feeble phosphorescence from phenylbutazone and mefenamic acid, but in the present work such signals could not be distinguished from the background phosphorescence of the solvent. In alkaline ethanol, the indomethacin spectra are entirely different, having an excitation maximum at 310 nm, a strongly featured phosphorescence emission centred at 430 nm, and a phosphores-

Table 3. Low temperature luminescence characteristics in ethanol

Compound No.	λ_e, *nm*	λ_f, *nm*	λ_p, *nm*	τ_p, *sec*
1	335	(420),510		
2	(285),350,360	405		
3*	330		485	1.0
4	300	460		
5	285	370	405,420	0.6
6	280	430		
7	285	435		
8	280	440		
10	(250),(270),275		435	0.035
11	280	(300),320,(332)	(425),465,(495)	4.4
12*	(255),29[illegible]	350	405	4.0
13	285		395	3.5
14	290		400	3.5
19	290	310	(430),460,(480)	3.1
20	280	310	(430),455,(475)	3.3

* In neutral ethanol—see text.
Figures in brackets represent subsidiary maxima.
τ_p = phosphorescence lifetime.

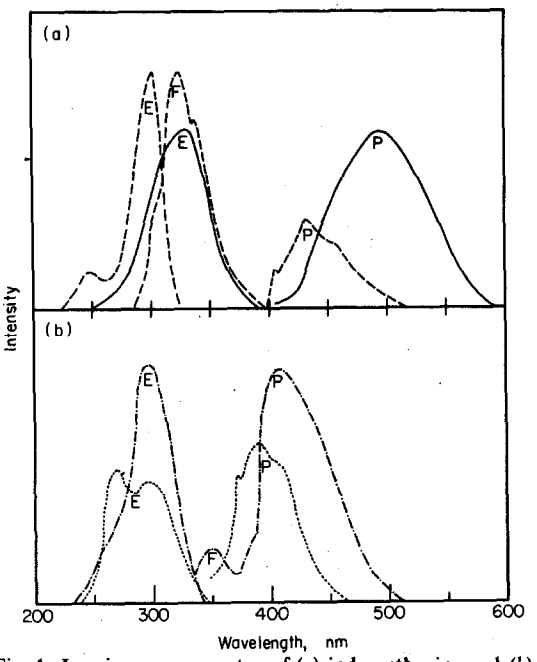


Fig. 1. Luminescence spectra of (*a*) indomethacin, and (*b*) *p*-aminophenylacetic acid at 77 K. —— indomethacin in neutral ethanol; ------ indomethacin in alkaline ethanol; -·-·-·- *p*-aminophenylacetic acid in neutral ethanol; ····· *p*-aminophenylacetic acid in acidic ethanol: the intensity scales are not the same for each spectrum. E = excitation; F = fluorescence; P = phosphorescence.

cence lifetime of 5.7 sec: these properties are strongly reminiscent of those of tryptophan and other compounds containing the indole nucleus,[13] and almost certainly arise from the presence of 2-methyl-3-carboxymethyl-5-methoxyindole (see above). In all circumstances, the phosphorescence of indomethacin was of sufficient intensity to allow the detection of submicrogram concentrations. *p*-Aminophenylacetic acid (Fig. 1b) also showed phosphorescence phenomena strongly dependent on the acidity of the solution. In neutral or alkaline ethanol it showed an intense phosphorescence which permitted its detection at ng/ml levels, but in acid media this phosphorescence was much weaker, the practical detection limit being only approximately 10 μg/ml. The three biphenyl derivatives (compounds 11, 19 and 20) were also strongly phosphorescent, their properties again being similar to those of biphenyl itself.[12] Phenazone exhibited a very feeble fluorescence at 370 nm and a strong phosphorescence with twin maxima at 405 and 420 nm. Both 3- and 4-methoxyphenylacetic acid (compounds 13, 14) were strongly phosphorescent, but 2-(4-chlorophenyl)propionic acid (compound 10) showed a feeble phosphorescence with a very short lifetime.

These results indicate that, of the 20 compounds studied, all but six could be determined at trace levels by luminescence spectrometry, and the optimum conditions have been established. In most cases the lowest detection limit would be obtained at the temperature of liquid nitrogen.

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REFERENCES

1. V. E. Starostenko and N. T. Bubon, *Farmatsia*, 1971, **20**, 41.
2. J. E. Wallace, *J. Pharm. Sci.*, 1968, **57**, 2053.
3. A. Windorfer, Jr., and H. J. Röttger, *Arzneim. Forsch.*, 1974, **24**, 893.
4. B. Demetrion and B. G. Osborne, *J. Chromatog.*, 1974, **90**, 405.
5. K. Rehse, *Arch. Pharm. (Weinheim)*, 1970, **303**, 617.
6. H. Oelschläger and D. Hamel, *ibid.*, 1969, **302**, 847.
7. H. Weissbach, T. Walker and S. Udenfriend, *J. Biol. Chem.*, 1958, **230**, 865.
8. H. A. Moye and J. D. Winefordner, *J. Agr. Food Chem.* 1965, **13**, 516.
9. A. C. Mehta and S. G. Shulman, *Talanta*, 1973, **20**, 702.
10. N. Strojny and J. A. F. de Silva, *J. Chromat. Sci.*, 1975, **13**, 583.
11. L. A. Gifford, J. N. Miller, D. L. Phillipps, D. T. Burns and J. W. Bridges, *Anal. Chem.*, 1975, **47**, 1699.
12. W. J. McCarthy and J. D. Winefordner, *J. Assoc. Off. Agr. Chemists*, 1965, **48**, 915.
13. J. W. Longworth, *Biopolymers*, 1966, **4**, 1131.

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DETERMINATION OF IODIDE WITH POTASSIUM DICHROMATE AND SODIUM VANADATE IN THE PRESENCE OF ACETONE

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Summary—The determination of iodide with potassium dichromate and sodium vanadate in 6–8*M* phosphoric acid medium by potentiometric or visual titration is described. Ferroin and barium diphenylamine sulphonate (BDAS) are used as the indicators in the visual titration with potassium dichromate and sodium vanadate respectively. Acetone is used to stabilize the iodonium ions liberated, in the visual titration. Iodide can also be determined with sodium vanadate in 2–4*M* sulphuric acid medium with BDAS as indicator in the presence of oxalic acid as catalyst and acetone to stabilize the liberated iodine cations. The visual procedures are applied for the determination of iodide in tincture of iodine. The formal potentials of the iodine/iodide couple in various phosphoric acid media are reported.

The standardization of thiosulphate solution by titration of the iodine liberated by potassium dichromate from excess of potassium iodide is well known. The difficulties encountered in liberation of the iodine have been much discussed.[1] Hendrixon[2] determined dichromate by adding excess of iodide and titrating the surplus with permanganate. Singh *et al.* followed the Hendrixon method but used potassium chlorate[3] or chloramine-T[4] to determine the excess of iodide and sodium sulphite[5] to titrate the liberated iodine. Hendrixon[2] also titrated iodide directly with dichromate but pointed out that the concentration of sulphuric acid should be at least 2*N* and reported that a long time is needed to reach the end-point. Kolthoff[6] also studied this reaction in hydrochloric and sulphuric acid media. Gyani and Prasad[7] studied the reduction of dichromate with iodide and proposed that a temperature of 30° should be maintained. Singh and Singh[8] and Sierra and Mora[9] determined iodide by Andrews titration with sodium vanadate in hydrochloric acid medium. Gopala Rao *et al.*[10,11] have observed that the formal potential of the chromium(VI)/chromium(III) and vanadium(V)/vanadium(IV) couples is enhanced in phosphoric acid medium. We have now studied the effect of phosphoric acid on the formal potential of the iodine/iodide couple and titrated iodide with potassium dichromate and sodium vanadate in phosphoric acid medium, with visual and potentiometric end-point determination. In the visual titrations acetone is used to remove the iodine cation which is produced during the titration. Ferroin is used in the dichromate titration and barium diphenylamine sulphonate (BDAS) in the vanadate titration. Iodide can also be titrated in sulphuric acid medium with sodium vanadate, with oxalic acid as catalyst in the presence of acetone (BDAS as indicator).

EXPERIMENTAL

Apparatus

The potentiometric assembly used was that described earlier.[12]

Reagents

Potassium iodide solution, 0.1*M*. Standardized by silver nitrate titration[13] and checked by ceric sulphate titration.[1]

Tri-iodide solution. An approximately 0.005*M* iodine solution in 0.01*M* potassium iodide (with a little excess of iodine present) standardized by titration with standard arsenic(III) solution.[1] The iodide concentration is determined by titration with potassium iodate.[13]

Potassium dichromate solution, 0.1*N*.

Sodium vanadate solution, 0.1*N*. Prepared from ammonium metavanadate after conversion into sodium vanadate in the usual manner, and standardized by iron(II) titration.

Syrupy phosphoric acid. Concentration determined by titration.[11]

Procedures

Determination of formal redox potential of iodine/iodide couple. The procedure was similar to that used by Furman and Miller.[14] The volume of the syrupy phosphoric acid required to give the desired concentration in a total volume of 40.0 ml was taken and diluted. Carbon dioxide was passed through it for about 10 min, then 5.0 ml of tri-iodide solution were added to the cell followed by a volume of 0.01*M* potassium iodide solution such that the total concentration of iodide relative to that of iodine was 1:1. The potential was recorded when it had become stable.

Determination of iodide in phosphoric acid medium. About 45–60 ml of orthophosphoric acid were taken in the titration vessel to give a 6–8*M* concentration in a total volume of 100 ml at the equivalence point. After any necessary dilution of the phosphoric acid with distilled water, carbon dioxide was passed through it for about 10 min. A suitable volume of sample was added and titrated potentiometrically or with an indicator. The potentials could be read immediately. For visual titrations 20 ml of acetone were added to the phosphoric acid before dilution and 0.05 ml of ferroin (potassium dichromate as titrant) or 0.2 ml of BDAS (sodium vanadate as titrant) was used as indicator.

Determination of idodide with sodium vanadate in sulphuric acid medium. Enough 50% v/v sulphuric acid was taken in the titration vessel to give a 2–4*M* concentration at the equivalence point. Then 2–10 ml of 1*M* oxalic acid and 20 ml of acetone were added and the titration mixture was diluted with distilled water so that the total volume at the equivalence point would be about 100 ml. Carbon dioxide was passed through the solution for about 10 min and then a suitable volume of iodide solution, followed by 0.2 ml of BDAS indicator, was added. The mixture was titrated with 0.1*M* sodium vanadate to a sharp colour change from light blue to deep violet.

Table 1. Formal redox potentials (NHE) of iodine/iodide couple in various phosphoric acid media (temperature 28°C)

[Phosphoric acid], *M*	Formal potential, *mV*
0	671
1	666
2	656
4	642
6	626
8	606
9	584
10	561
11	539*

* A little turbidity of iodine is observed.

RESULTS AND DISCUSSION

The formal redox potentials of the iodine/iodide couple measured at various phosphoric acid concentrations and uncorrected for liquid–liquid junction potentials are given in Table 1. They decrease with increasing acid concentration.

The effect of phosphoric acid concentration on the potentiometric and visual titrations was studied over the range 2–10*M*. Since at high acid concentrations iodide is oxidized by oxygen in the solutions and the atmosphere, an inert atmosphere (CO_2) is used. Quantitative results are obtained potentiometrically in 6–8*M* phosphoric acid media. There is a sharp potential break of about 250–275 mV for 1 drop of 0.1*N* dichromate at the equivalence point. The sodium vanadate titrations are similar in character. The maximum error in potentiometric titration of 15–250 mg of iodide was 0.2% with dichromate and 0.4% with vanadate.

In visual titrations ferroin does not function satisfactorily as indicator with vanadate, nor does BDAS with dichromate. If free iodine appears at the beginning of the titration it disappears on vigorous shaking as the titration is continued. In sulphuric acid medium, when less than 2.0 ml of 1*M* oxalic acid is present the reaction between iodide and vanadate is slow. The addition of up to 25 ml of 1*M* oxalic acid per 100 ml of titration solution has no effect on the titration. The indicator correction is negligible for titration of 25–200 mg of iodide. The maximum errors were 0.2% for dichromate and 0.4% for vanadate in phosphoric or sulphuric acid medium.

In the visual titrations in the presence of acetone the normality of the iodide solution is found to be exactly twice the molarity determined potentiometrically with ceric sulphate,[15] potassium permanganate[16] or potassium iodate,[16] showing that the iodide is oxidized to the iodonium ion, which is stabilized by formation of iodoacetone.

Analysis of tincture of iodine

The visual procedure has been applied to the determination of iodide in tincture of iodine. Free iodine is first titrated with thiosulphate and then the total tri-iodide (iodide + iodine) is determined by the visual procedure described. For the purpose of calculation it is considered that the iodine undergoes a 1-electron oxidation by the dichromate or vanadate. From the two titrations the amount of iodide present can be calculated. The results obtained are given in Table 2.

Interferences

Chloride, acetate, borate, oxalate, citrate, tartrate, zinc and cobalt(II) do not interfere. Bromide interferes in the visual procedures but not in the potentiometric titration. Nitrite, iron(II), arsenic(III) and ascorbic acid interfere at all concentrations.

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REFERENCES

1. I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuana, *Volumetric Analysis* III, pp. 231, 234 and 634. Interscience, New York, 1957.
2. W. S. Hendrixon, *J. Am. Chem. Soc.*, 1921, **43**, 14, 1309.
3. B. Singh and I. I. Malik, *J. Indian Chem. Soc.*, 1937, **14**, 435.
4. B. Singh and S. Singh, *ibid.*, 1939, **16**, 95.
5. B. Singh and A. Rehmann, *ibid.*, 1940, **17**, 173.
6. I. M. Kolthoff, *Rec. Trav. Chim.*, 1920, **39**, 208.
7. B. P. Gyani and S. N. Prasad, *J. Indian Chem. Soc.*, 1955, **32**, 313.

Table 2. Determination of iodide in tincture of iodine (*g*/100 *ml*)

Method	Iodide found by B.P. method*	Std. devn.	Iodide found by proposed method*	Std. devn.
$K_2Cr_2O_7$				
Sample 1	2.705	0.002	2.706	0.002
Sample 2	2.657	0.002	2.656	0.002
$NaVO_3$ in phosphoric acid				
Sample 1	2.698	0.003	2.701	0.003
Sample 2	2.658	0.001	2.656	0.002
$NaVO_3$ in sulphuric acid				
Sample 1	2.702	0.002	2.702	0.002
Sample 2	2.656	0.003	2.656	0.001

* Mean of five determination.

8. B. Singh and R. Singh, *Anal. Chim. Acta*, 1954, **10**, 408.
9. F. Sierra and G. A. Mora, *An. Real. Soc. Espan. Fis. Quim.*, 1958, **52B**, 13.
10. G. G. Rao and P. K. Rao, *Talanta*, 1963, **10**, 1251.
11. G. G. Rao and L. S. A. Dikshitulu, *ibid.*, 1963, **10**, 1023.
12. N. K. Murty and K. R. Rao, *Analyst*, 1976, **101**, 310.
13. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd Ed., pp. 262, 308 and 318. Longmans, London, 1961.
14. N. H. Furmann and C. O. Miller, *J. Am. Chem. Soc.*, 1937, **59**, 152.
15. P. Lewis, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 199.
16. R. Berg, *Z. Anal. Chem.*, 1926, **69**, 369.
17. *The British Pharmacopoeia*, p. 518. Pharmaceutical Press, London, 1968.

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DETERMINATION OF SOME ORGANIC THIO-COMPOUNDS BY PRECIPITATION OF MERCURIC SULPHIDE FROM MERCURY(II) AMMINE COMPLEXES—II DETERMINATION OF THIOUREA AND SOME OF ITS DERIVATIVES

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Summary—A gravimetric method based on precipitation of mercuric sulphide has been developed for determination of thiourea and some of its derivatives (acetylthiourea and *sym*-diphenylthiourea). Concentrated nitric acid is added to 0.1*M* mercuric nitrate, the solution is made alkaline with concentrated ammonia solution and thiourea (dissolved in concentrated ammonia solution), acetylthiourea (dissolved in methanol) or diphenylthiourea (dissolved in acetone) is added and the mixture is boiled. The precipitate is filtered off, washed, and dried at 110°. The determination takes about 40 min. The method gives satisfactory results for thiourea and very good ones for diphenylthiourea and acetylthiourea.

Thiourea is often used in analytical chemistry. It forms complexes with several metals in acid medium, and this is the basis of colorimetric determinations of bismuth,[1] antimony,[2] tin,[3] osmium,[4] palladium,[5] rhenium,[6] ruthenium[7] and tellurium.[8] It is also used as a masking agent because it can form soluble complexes (*e.g.*, with copper). In alkaline medium the thiourea complexes of heavy metals become desulphurized and sulphides of these metals are precipitated. This reaction is the basis for determination of bismuth, mercury, lead and silver[9] and for the application of thiourea in systematic qualitative analysis.[10] Precipitation of complex salts, containing thiourea, has been used for cadmium, copper, lead, thallium and mercury determinations.[11,12]

Some thiourea derivatives are also used in analytical chemistry (*e.g.*, *sym*-diphenylthiourea for determination of tellurium,[13] acetylthiourea for determinations of heavy metals[14]) and have been of importance in industrial applications (*e.g.* diphenylthiourea is used as a vulcanization accelerator).

The wide use of thiourea and its derivatives in analytical and co-ordination chemistry and in industry calls for development of methods of determination. Oxidization and desulphurization have been the main types of reaction used in conventional methods. They were reviewed by Gupta in 1963.[15] Since then ceric salts,[16] bromide–bromate,[17] chlorate–bromide,[18] bromine cyanide,[19] *N*-bromosuccinimide,[20] *N*-chlorobenzamide[21] and *N*-chloroacetamide[22] have been used. Kurzawa and Zientkiewicz based a catalytic method on the reaction of sodium azide and iodine.[23]

Desulphurization methods[15] use silver,[24] cadmium,[25] zinc[26] and mercury.[27,28]

Mercurometric titration[29–31] and titration in non-aqueous solution[15,32–34] have also been used.

Gravimetric methods are very seldom used in determination of thiourea and its derivatives. Gupta[35] developed a gravimetric method, based on precipitating lead sulphide, which was then converted into lead sulphate. Mercury salts have been used only in titrations.

The object of the present work was to develop a quick, relatively accurate gravimetric method.

EXPERIMENTAL

Reagents

Thiourea and acetylthiourea were recrystallized from water, and *sym*-diphenylthiourea was recrystallized from ethanol.

Procedures

Determination of thiourea. Concentrated nitric acid (15 ml) is added to *V* ml of 0.1*M* mercuric nitrate ($V = 0.2 \times$ number of mg of thiourea taken or 10 ml, whichever is the larger), then 80 ml of concentrated ammonia solution are progressively added with stirring. The solution is heated to about 60° and the weighed sample of thiourea, dissolved in 20 ml of concentrated ammonia solution, is added to it. The solution is heated to boiling point, kept boiling for 10 min and set aside.

8. B. Singh and R. Singh, *Anal. Chim. Acta*, 1954, **10**, 408.
9. F. Sierra and G. A. Mora, *An. Real. Soc. Espan. Fis. Quim.*, 1958, **52B**, 13.
10. G. G. Rao and P. K. Rao, *Talanta*, 1963, **10**, 1251.
11. G. G. Rao and L. S. A. Dikshitulu, *ibid.*, 1963, **10**, 1023.
12. N. K. Murty and K. R. Rao, *Analyst*, 1976, **101**, 310.
13. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd Ed., pp. 262, 308 and 318. Longmans, London, 1961.
14. N. H. Furmann and C. O. Miller, *J. Am. Chem. Soc.*, 1937, **59**, 152.
15. P. Lewis, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 199.
16. R. Berg, *Z. Anal. Chem.*, 1926, **69**, 369.
17. *The British Pharmacopoeia*, p. 518. Pharmaceutical Press, London, 1968.

Talanta, Vol. 25, pp. 52–53. Pergamon Press, 1978. Printed in Great Britain.

DETERMINATION OF SOME ORGANIC THIO-COMPOUNDS BY PRECIPITATION OF MERCURIC SULPHIDE FROM MERCURY(II) AMMINE COMPLEXES—II DETERMINATION OF THIOUREA AND SOME OF ITS DERIVATIVES

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Summary—A gravimetric method based on precipitation of mercuric sulphide has been developed for determination of thiourea and some of its derivatives (acetylthiourea and *sym*-diphenylthiourea). Concentrated nitric acid is added to 0.1*M* mercuric nitrate, the solution is made alkaline with concentrated ammonia solution and thiourea (dissolved in concentrated ammonia solution), acetylthiourea (dissolved in methanol) or diphenylthiourea (dissolved in acetone) is added and the mixture is boiled. The precipitate is filtered off, washed, and dried at 110°. The determination takes about 40 min. The method gives satisfactory results for thiourea and very good ones for diphenylthiourea and acetylthiourea.

Thiourea is often used in analytical chemistry. It forms complexes with several metals in acid medium, and this is the basis of colorimetric determinations of bismuth,[1] antimony,[2] tin,[3] osmium,[4] palladium,[5] rhenium,[6] ruthenium[7] and tellurium.[8] It is also used as a masking agent because it can form soluble complexes (*e.g.*, with copper). In alkaline medium the thiourea complexes of heavy metals become desulphurized and sulphides of these metals are precipitated. This reaction is the basis for determination of bismuth, mercury, lead and silver[9] and for the application of thiourea in systematic qualitative analysis.[10] Precipitation of complex salts, containing thiourea, has been used for cadmium, copper, lead, thallium and mercury determinations.[11,12]

Some thiourea derivatives are also used in analytical chemistry (*e.g.*, *sym*-diphenylthiourea for determination of tellurium,[13] acetylthiourea for determinations of heavy metals[14]) and have been of importance in industrial applications (*e.g.* diphenylthiourea is used as a vulcanization accelerator).

The wide use of thiourea and its derivatives in analytical and co-ordination chemistry and in industry calls for development of methods of determination. Oxidization and desulphurization have been the main types of reaction used in conventional methods. They were reviewed by Gupta in 1963.[15] Since then ceric salts,[16] bromide–bromate,[17] chlorate–bromide,[18] bromine cyanide,[19] *N*-bromosuccinimide,[20] *N*-chlorobenzamide[21] and *N*-chloroacetamide[22] have been used. Kurzawa and Zientkiewicz based a catalytic method on the reaction of sodium azide and iodine.[23]

Desulphurization methods[15] use silver,[24] cadmium,[25] zinc[26] and mercury.[27,28]

Mercurometric titration[29–31] and titration in non-aqueous solution[15,32–34] have also been used.

Gravimetric methods are very seldom used in determination of thiourea and its derivatives. Gupta[35] developed a gravimetric method, based on precipitating lead sulphide, which was then converted into lead sulphate. Mercury salts have been used only in titrations.

The object of the present work was to develop a quick, relatively accurate gravimetric method.

EXPERIMENTAL

Reagents

Thiourea and acetylthiourea were recrystallized from water, and *sym*-diphenylthiourea was recrystallized from ethanol.

Procedures

Determination of thiourea. Concentrated nitric acid (15 ml) is added to *V* ml of 0.1*M* mercuric nitrate ($V = 0.2 \times$ number of mg of thiourea taken or 10 ml, whichever is the larger), then 80 ml of concentrated ammonia solution are progressively added with stirring. The solution is heated to about 60° and the weighed sample of thiourea, dissolved in 20 ml of concentrated ammonia solution, is added to it. The solution is heated to boiling point, kept boiling for 10 min and set aside.

Table. 1

Compound	Taken, *mg*	Found, *mg*	Error, %
Thiourea	25.7	25.6	−0.4
	50.3	50.4	+0.2
	102.5	103.1	+0.6
	151.2	152.0	+0.5
	202.9	204.1	+0.6
sym-Diphenylthiourea	25.7	25.6	−0.4
	47.5	47.6	+0.2
	101.5	101.3	−0.2
	150.6	150.6	0
	203.8	203.6	−0.2
Acetylthiourea	25.1	25.0	−0.4
	52.2	52.2	0
	101.3	101.6	+0.3
	150.7	151.3	+0.4
	200.9	201.1	+0.1

Just after the precipitate has settled it is collected on a porosity 4 or 5 sintered-glass crucible, washed with water and then several times with methanol and dried for 15 min at 110°. The conversion factor is 0.3272.

Determination of diphenylthiourea. Concentrated nitric acid (15 ml) is added to V ml of 0.1M mercuric nitrate (V = 0.1 × number of mg of diphenylthiourea or 5 ml, whichever is the larger), then 100 ml of water and finally at least 30 ml of concentrated ammonia solution are added with stirring. The solution is heated to about 60° and the weighed sample of diphenylthiourea dissolved in 10 ml of acetone is added to it. The solution is heated to boiling point, kept boiling for 5–10 min and set aside. After the resulting precipitate has settled (a few minutes) it is collected on a porosity 4 or 5 sintered-glass crucible, washed with water and then 4 or 5 times with acetone (about 10 ml each time) and several times with methanol. The first portions of the filtrate are not clear after washing with acetone. The precipitate is dried for 15 min at 110°. The conversion factor is 0.9812.

Determination of acetylthiourea. A weighed sample of acetylthiourea is dissolved in methanol (or hot water or acetone) and analysed as for diphenylthiourea, but with V = number of mg of acethylthiourea or 10 ml, whichever is the larger. The precipitate is washed with water and then several times with methanol. The conversion factor is 0.5078.

RESULTS

Results are presented in Table 1; they are satisfactory for thiourea, and very good for diphenylthiourea and acetylthiourea. The diphenylthiourea should be dissolved in acetone; precision is lower if ethanol or methanol is used.

It is more difficult to desulphurize thiourea than its derivatives, so thiourea should be determined in a solution containing a higher ammonia concentration. If there is too little ammonia the desulphurization is not complete and the results are too high because the precipitate contains complexes of mercury with thiourea.

A determination takes about 40 min. The method should be applicable to other derivatives of thiourea.

REFERENCES

1. W. Nielsch and G. Böltz, *Z. Anal. Chem.*, 1954, **142**, 321; 1954, **143**, 13, 168.
2. *Idem, Microchim. Acta*, 1954, 314.
3. *Idem, Z. Anal. Chem.*, 1954, **143**, 161.
4. K. I. Jensen, *Anal. Chem.*, 1965, **37**, 1430.
5. W. Nielsch, *Mikrochim. Acta*, 1954, 532.
6. D. I. Riabczikov and A. I. Lazarev, *Zh. Analit. Khim.*, 1961, **16**, 366.
7. A. Musil and R. Pietsch, *Z. Anal. Chem.*, 1953, **137**, 259.
8. W. Nielsch and L. Giefer, *ibid.*, 1955, **144**, 191, 1955, **145**, 347.
9. R. Sołoniewicz, *Chem. Anal.* (*Warsaw*), 1962, 7, 625, 965; 1964, **9**, 393, 509.
10. J. Masłowska and R. Sołoniewicz, *ibid.*, 1969, **14**, *1305*.
11. C. Mahr, *Angew. Chem.*, 1940, **53**, 257.
12. M. Czakis-Sulikowska and R. Sołoniewicz, *Chem. Anal.* (*Warsaw*), 1964, **9**, 59.
13. H. Yoshida and S. Hikime, *Talanta*, 1964, **11**, 1349.
14. W. Hermanowicz, to be published.
15. P. C. Gupta, *Z. Anal. Chem.*, 1963, **196**, 412.
16. B. C. Verma and S. Kumur, *Talanta*, 1973, **20**, 916.
17. P. C. Gupta, *Analyst*, 1963, **88**, 896.
18. E. S. V. V. Dutt and C. Radhakrishnamuty, *Analasis*, 1973, **2**, 268.
19. R. C. Paul, R. K. Chauman and R. Parkash, *Talanta*, 1974, **21**, 663.
20. R. L. Tiwari and U. C. Ponde, *Analyst*, 1969, **94**, 813.
21. B. Singh, B. C. Verma and R. L. Sapra, *Z. Anal. Chem.*, 1963, **196**, 323.
22. B. Singh, S. C. Mistandra, B. C. Verma and Z. Fresenius, *ibid.*, 1971, **257**, 348.
23. Z. Kurzawa and M. Zietkiewicz, *Chem. Anal.* (*Warsaw*), 1974, **19**, 119.
24. A. M. Bhatti, M. K. Ralhan and Z. Fresenius, *Z. Anal. Chem.*, 1972, **260**, 370.
25. B. Buděšínský, E. Vaníčková and J. Körbl, *Collection Czech. Chem. Commun.*, 1960, **25**, 456.
26. K. Lesz, H. Wieczorkiewicz and T. Lipiec, *Chem. Anal.* (*Warsaw*), 1961, **6**, 1033.
27. F. K. Gulierez, *An. Real. Soc. Esp. Fis. Quim.*, 1955, **51**, 639.
28. R. Setton, *Bull. Soc. Chim. France*, 1958, 861.
29. M. Wroński, *Chem. Anal.* (*Warsaw*), 1960, **5**, 101; 1961, **6**, 859,
30. K. B. Yatsimirskii and A. A. Astaszeva, *Zh. Analit. Khim.*, 1956, **11**, 442.
31. M. Wroński, *Z. Anal. Chem.*, 1960, **3**, 174.
32. J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, 1951, **23**, 589.
33. J. S. Fritz, *ibid.*, 1952, **24**, 674.
34. I. Berger, *Acta Chem. Scand.*, 1954, **8**, 427.
35. R. D. Gupta, *Proc. Raj. Acad. Sci.*, 1951, **2**, 16.

Talanta, Vol. 25, pp. 54–55. Pergamon Press, 1978. Printed in Great Britain.

A RAPID TITRIMETRIC DETERMINATION OF IRON IN COPPER CONCENTRATES AND COPPER-BEARING LEACH SOLUTIONS

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Summary—A titrimetric method for the determination of iron(III) in the presence of copper is presented. This method involves the reduction of iron(III) with titanous sulphate followed by titration with dichromate. It has been successfully used for the determination of iron in both leach solutions and copper concentrates with a relative error of 1%.

The standard analytical method[1] for the determination of total iron in leach liquors involves the reduction of iron(III) to iron(II) with stannous chloride, the excess of which is oxidized by mercuric chloride, followed by titration of ferrous ion with standard dichromate solutions, with diphenylamine as indicator. This method, when applied to solutions containing copper, presents a problem in that copper (II) is reduced to copper (I) which is not oxidized by mercuric chloride, but is titrated with dichromate, so the total iron determined will be high. One method of elimination of the interference due to copper is to use either metallic copper or test lead as the reducing agent.[2]

Titanous sulphate completely reduces iron(III) to iron(II) and can be used for the determination of total iron, provided that all the iron is first oxidized to iron(III). However, copper(II) is reduced to copper metal along with the reduction of iron(III) by titanous sulphate in sulphate medium and prevents visual determination of the end-point when potassium thiocyanate is used as indicator. On the other hand, the reduction to metallic copper can be used as an indication that the ion(III) has all been reduced. The metallic copper can then be dissolved by the addition of mercuric perchlorate solution, followed by the titration of the iron(II) with dichromate solution. A detailed study was therefore undertaken for the determination of iron in the presence of copper, with titanous sulphate as the reducing agent.

EXPERIMENTAL

Reagents

Ferric sulphate solution. Dissolve 1.2500 g of high-purity iron in dilute sulphuric acid with hydrogen peroxide as the oxidizing agent and make up to 250 ml in a standard flask.

Mercuric perchlorate solution, 8%. Treat 40 g of mercuric nitrate with 25 ml of conc. nitric acid and 10 ml of conc. perchloric acid and evaporate the solution on a hot-plate to perchloric acid fumes. Repeat with another 10 ml of perchloric acid. Dissolve the resulting salt in water and make up to 500 ml.

Sulphuric–phosphoric acid mixture. Mix 260 ml of conc. sulphuric acid and 740 ml of syrupy orthophosphoric acid.

Titanous sulphate solution. Dissolve 5 g of titanium metal in 500 ml of dilute sulphuric acid (1 + 3). Separate the undissolved metal and dilute the solution with enough distilled water to dissolve all the titanous sulphate. Store the solution in a brown bottle in a dark place.

Stannous chloride solution. Dissolve 15 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of conc. hydrochloric acid.

Titration procedure

Pipette an aliquot of the sample solution (5–40 ml, depending on the iron content of the sample, 3–0.25 g/l.) into a 500-ml conical flask and add 5 or 2 ml of 20% copper sulphate solution (depending upon the amount of copper present in the sample) followed by 5–10 drops of 10% sulphosalicylic acid solution. Then add titanous sulphate solution dropwise from a burette, with shaking, until the disappearance of the violet colour. On appearance of the grey-blue colour, add titanous sulphate solution in 75–100% excess (or until the appearance of a turbidity due to the precipitated copper). Next add 10 ml of mercuric perchlorate solution, with shaking, followed by 20 ml of sulphuric acid (1 + 1), 5 ml of sulphuric–phosphoric acid mixture, 150 ml of distilled water and some oxidized sodium diphenylamine sulphonate indicator. Titrate with potassium dichromate solution to the appearance of a permanent blue-violet.

Dissolution procedure for copper concentrate

Treat a 1-g sample of the copper concentrate with 25 ml of conc. nitric acid and heat on a hot-plate. When all the sample has dissolved (about 1 hr) evaporate the solution nearly to dryness. Add 2 ml of sulphuric acid (1 + 1) and 40 ml of distilled water and heat for about 30 min. Filter the solution into a 100-ml standard flask and wash the residue several times with hot water transferring the washings to the filter funnel. Make up the solution to 100 ml.

RESULTS AND DISCUSSION

In the well-established method for the redox titration of iron with dichromate, stannous chloride is used for initial reduction of the iron(III), but when copper(II) is present this method give results high by as much as 60% because of the copper(I) produced in the reduction process. This prompted the search for other reducing agents. Titanous sulphate was found to give satisfactory results, but a detailed study of the conditions was necessary.

During the reduction of iron(III) in the presence of copper, the excess of titanous sulphate reduces the cupric ion

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Table 1. Effect of HCl concentration on the determination of 26.98 mg of iron

[HCl], *M*	Fe found, *mg*	Error, %
0.05	28.03	+3.8
0.50	29.81	+10.5
1.00	29.00	+7.5
2.00	27.84	+3.2
3.00	41.35	+53.3
4.50	43.87	+62.6

to metallic copper, and this can be taken as an indication that the iron has been completely reduced. It was found advantageous, however, to use sulphosalicylic acid as indicator for this purpose, the accuracy being better.

Ferric iron is reduced with reagents such as amalgamated zinc, hydrogen sulphide or sulphurous acid in 1–2*N* sulphuric acid, and the effect of the acid concentration on the reduction with titanium(III) was therefore studied. At higher acidities the iron–sulphosalicylic acid complex is unstable and it is found difficult to decide when the reduction is complete. For this reason further work was done with 0.12*N* sulphuric acid medium.

There seems to be no difference in the effect of excess of titanous sulphate in the range 20–100% and a 75% excess was chosen for further work. The concentration of cupric ion was varied to determine the effect of the copper. The results (see Table 4) show that a Cu:Fe ratio of at least 5 was optimal. Solutions containing low concentrations of copper should have more added copper.

Nickel, copper and lead in 1:1 w/w ratio to iron were found to have no effect on the results.

The applicability of the method in chloride medium was also investigated. It was found that completion of the reduction step was difficult to judge visually and the results are seriously in error because of precipitation and subsequent titration of cuprous chloride (Table 1).

PRACTICAL APPLICATIONS

The method has been applied to the determination of iron in bacterial leach solutions containing copper and various amounts of iron (0.28–3.4 g/l.) in sulphate medium. The results presented in Table 2 show that the values of iron determined by the proposed method compare favourably with the values obtained by atomic-absorption spectrophotometry.

Table 2. Analysis of bacterial leach solutions

Fe:Cu	Analysis by atomic absorption, *g/l.* Cu	Fe	Proposed method, Fe, *g/l.*	
1:1.4	4.73	3.41	3.27 3.45 3.46 3.39	3.39
1:4	5.40	1.28	1.29 1.28 1.25 1.30	1.28
1:4	5.34	1.43	1.38 1.35 1.32 1.32	1.34
1:12	5.37	0.43	0.45 0.44 0.45	0.45
1:19	5.20	0.28	0.28 0.28 0.28 0.28	0.28

A copper concentrate (McIntyre Mines Ltd., Schumachor, Ontario) was also analysed by the proposed method (24.4, 23.0, 23.3, 23.6, 23.5%) and by dichromate titration after separation of iron from copper by double precipitation with ammonia (23.6%). The results are in good agreement, showing the method to be capable of general application in sulphate medium with a relative error of about 2%.

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REFERENCES

1. A. I. Vogel, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Wiley, New York, 1961.
2. R. J. C. MacDonald, *Dept. Energy, Mines and Resources, Mines Branch, Ottawa, Canada, Internal Rept.* EMI 73-12. October, 1973.

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IDENTIFICATION ET DETERMINATION COLORIMETRIQUE DU TITANE AVEC L'ACIDE 2-MERCAPTO-3(2-FURYL)PROPENOIQUE

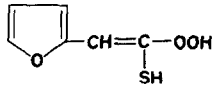
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Résumé—On décrit une méthode pour l'identification et le dosage du titane(IV), en employant comme réactif l'acide 2-mercapto-3(2-furyl)propénoïque. Le complexe, de couleur rouge, se developpe entre pH 3 et 5, avec un maximum d'absorbance à 490 nm. Le complexe peut être extrait quantitativement dans l'alcool amylique et d'autres solvants organiques. La sensibilité est $D = 10^{-7}$. La loi de Lambert–Beer est satisfaite entre 0,05 et 2,7 ppm, l'intervalle le meilleur se trouvant entre 0,23 et 1,4 ppm. L'absorptivité molaire est $3{,}5 \cdot 10^4$ $l.mole^{-1}.cm^{-1}$.

Ce travail fait partie de l'étude des acides β-aryl α-mercapto propénoïques comme réactifs analytiques. Dans des travaux précédents, on a rendu compte de la capacité de l'acide 2-mercapto-3(2-furyl)propénoïque à former des complexes colorés avec des ions inorganiques[1] et de son application à l'identification et à la détermination du molybdène.[2] Dans ce travail, il est mis en evidence que le titane(IV) forme un complexe rouge avec le réactif à pH 3–5, qui peut être extrait quantitativement par l'alcool amylique et d'autres solvants organiques avec une sensibilité, $D = 10^{-7}$, supérieure à celle fourmie par le peroxyde d'hydrogène, l'acide chromotropique, le cupferron, le thymol, le tiron, etc.[3]

La réaction sans extraction préalable est très peu sélective, mais par extraction elle atteint une selectivité semblable à celle des autres réactifs proposés pour cet ion. La coloration est stable pendant une heure à température ambiante, et l'absorptivité molaire est $3{,}5 \cdot 10^4$ $l.mole^{-1}.cm^{-1}$. Le réactif a été appliqué avec de bons résultats à la détermination du titane(IV) dans un ciment.



PARTIE EXPERIMENTALE

Réactifs

Acide 2-mercapto-3(2 furyl)propénoïque à 1% dans l'éthanol. La solution doit être employée dans les huit heures suivant sa préparation.

Solution de Ti(IV). Préparée à partir de tétrachlorure de titane, standardisée gravimétriquement avec la 8-hydroxyquinoléine.[4] Les solutions de travail ont été preparées par dilution convenable de cette solution.

Alcool amylique. Liberé des impuretés acides par lavage avec une solution de carbonate de sodium et de l'eau distillée.

Méthodes

Identification. Ajouter un léger excès de réactif (0,5 à 1 ml) à 2 ml de solution à essayer dans un tube pour semi-microanalyse et en régler le pH entre 3 et 5; en présence de Ti(IV) il apparait une coloration rouge. Ajouter 0,5 ml d'oxyde d'éthyle, agiter, la couche de solvant organique prend une coloration rouge. Sensibilité $D = 10^{-7}$.

Le Co(II) et le Se(IV) interfèrent en donnant une coloration jaune qui peut être extraite. Leurs sensibilités sont notablement moindres ($D = 10^{-5}$ et $10^{-4,7}$).

Détermination sans extraction préalable. Introduire dans une fiole jaugée de 25 ml un volume de solution contenant de 1,25 à 67,5 μg de Ti(IV). Ajouter 1 ml de la solution du réactif, ajuster le pH entre 3 et 5, et amener jusqu'au volume avec de l'eau distillée. Agiter et mesurer l'absorbance à 490 nm. On construit une courbe d'étalonnage de la même manière.

Procédé par extraction. A la solution de titane, ajouter 10 ml d'une solution de nitrate de sodium à 1%, 1 ml de solution du réactif, ajuster le pH entre 3 et 5, ajouter 10 ml d'alcool amylique, agiter la mélange pendant 1 mn dans une ampoule à décanter, reprendre la couche organique, et extraire la couche aqueuse de nouveau avec 5 ml d'alcool amylique. Les extraits combinés sont séchés sur du sulfate de sodium anhydre, transférés quantitativement dans une fiole jaugée de 25 ml et dilués jusqu'au volume avec de l'alcool amylique. Mesurer l'absorbance à 490 nm. Construire la courbe d'étalonnage de même manière.

Procédé pour la détermination dans un ciment. La mèthode a été appliquée à la détermination de Ti(IV) dans un ciment dont la composition était: SiO_2 21,8%, CaO 63,1%, Al_2O_3 4,6%, Fe_2O_3 2,6%, MgO 1,5%, SO_3 2,6%, K_2O 1,0%, Na_2O 0,11% et TiO_2 0,24%, fourni par le Département de Chimie Inorganique.

Eliminer la silice (1 g de l'échantillon) avec $FH\text{-}H_2SO_4$, solubiliser le résidu par fusion avec $KHSO_4$ et traiter par l'acide sulfurique dilué.

Le titane est précipité de la solution avec NaOH en présence de triéthanolamine, qui empêche la précipitation du fer et de l'aluminium. Dissoudre le précipité dans de l'acide chlorhydrique et amener à 100 ml. Prélever 20 ml de cette solution, ajouter 1 ml de réactif et déterminer la teneur en Ti(IV) suivant le procédé par extraction indiqué plus haut.

Résultats: % TiO_2 trouvé = 0,244, 0,244, 0.243, 0,244.

Tableau 1. Tolérance des ions étrangers dans le dosage de Ti(IV) = 1 ppm dans le volume final

Ion ajouté	Tolérance, *ppm*
Ag(I)	15
Pb(II)	15
Hg(II)	10
Cu(II)	3
Bi(III)	10
Mo(VI)	8
Fe(II) et (III)	10
V(V)	20
Co(II)	5
Se(IV)	5

RESULTATS ET DISCUSSION

Caracteristiques du complexe

Le spectre d'absorption du complexe de titane dans l'eau et dans l'extrait en alcool amylique à pH 3–5 est reproductible pour diverses concentrations du métal et présente un maximum d'absorbant à 490 nm. Le réactif n'absorbe pas à cette longeur d'onde. La quantité de réactif nécessaire est de 0,5 ml de solution à 1% pour 1 ppm, et le volume conseillé est 1 ml. La coloration atteint le maximum d'intensité dans 5 mn qui suivent l'addition du réactif et est stable pendant au moins 1 h à température ambiante. La loi de Beer est suivie entre 0,05 et 2,7 ppm. Le graphique de Ringbom[5] montre que l'intervalle le meilleur se trouve entre 0,23 et 1,40 ppm. L'absorptivité molaire est $3{,}5 \cdot 10^4$ l. $mole^{-1}.cm^{-1}$. L'erreur relative de la moyen est $\pm 0{,}2\%$ pour un degré de confiance de 95% (21 déterminations).

Effet d'autres ions

Les ions qui gênent sont Ag, Pb, Cu(II), Bi, Cd, Hg(II), Pd(II), Mo(VI), Fe(II) et (III), V(V), Tl(III), Ni et Co(II), qui réagissent avec le réactif dans les mêmes conditions; toutefois, leurs sensibilités sont inférieures.

Al, Cr(III), Mn(II), Be, Zn, Ce(IV), La et W(VI), ne donnent pas de réaction appréciable, mais donnent lieu à une exaltation de l'absorbance du titane.

Les ions gênant dans la technique avec extraction par l'alcool amylique et les tolérances correspondantes pour une déviation inférieure à 1% sont donnés dans le tableau 1.

Composition du complexe

On a trouvé que la composition du complexe était 1:1 par la méthode des variations continues, la méthode des rapports molaires et la méthode des pentes.

La constante d'instabilité approximative du complexe en solution aqueuse, déterminée par la méthode de Turner et Anderson[6] est $2{,}22 \cdot 10^{-6}$.

BIBLIOGRAPHIE

1. A. Izquierdo, et J. Calmet, *Quím. Anal.*, 1974, **28**, 148.
2. *Idem*, *Analusis*, 1976, **4**, 202.
3. F. Feigl, et V. Anger, *Spot Tests in Inorganic Analysis*, *6th* Ed., Elsevier, Amsterdam, 1972.
4. A. I. Vogel, *Quantitative Inorganic Analysis*, *3rd* Ed., Longmans, London, 1968.
5. A. Ringbom, *Z. Anal. Chem.*, 1938, **115**, 332.
6. S. E. Turner et R. C. Anderson, *J. Am. Chem. Soc.*, 1949, **71**, 912.

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ANNOTATION

STABILITY CONSTANTS OF COMPLEXES FORMED BY SOME METAL IONS WITH 2-(PHENYLIMINOMETHYL)PYRIDINE AND 2-(*o*-HYDROXYPHENYLIMINOMETHYL)PYRIDINE

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Summary—The stability constants of some metal complexes of these two reagents have been determined.

Geary *et al.*[1,2] have reported the stability constants of the 2-(*o*-hydroxyphenyliminomethyl)pyridine complexes of Cu(II), Ni, Co(II), Zn and UO_2(II) determined in dioxan–water mixtures. They stated that this azomethine and others, and their metal complexes, are insoluble in water, but we have established that its solubility in water is about 2 g/l. and consequently we have been able to determine the stability constants of the complexes of this ligand (I) with Ni, Co(II), Cd, Cu(II), Mn(II), Pb, Zn and Fe(II) in aqueous solution. In addition, we have established the constants of the 2-(phenyliminomethyl)pyridine (II) complexes of Ni, Co(II) and Cu(II).

EXPERIMENTAL

Reagents

The two organic reagents were prepared and identified by following the procedure previously described[3,4] and used as $10^{-3}M$ solutions.*

The metal ion solutions ($10^{-2}M$) were prepared from $CoCl_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $Cd(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2 \cdot H_2O$ and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and standardized by conventional methods.

The sodium hydroxide titrant was prepared from the metal.

Procedure

The azomethines (freshly prepared in order to avoid hydrolysis) were titrated in a double-walled titration vessel, at 20 ± 1°. The ionic strength was adjusted to 0.1 with potassium nitrate. The hydrogen-ion concentrations were calculated from pH measurements and the apparent hydrogen-ion activity-coefficient values.

RESULTS AND DISCUSSION

The dissociation constants of (I)[3] have been found to be $pK_1 = 3.54$, $pK_2 = 4.9$, and of (II) $pK_1 = 3.9$, $pK_2 = 5.3$, $pK_3 = 9.6$, the latter set being in good agreement with those reported by Otomo and Kodama.[5] From these constants and application of the Bjerrum method[6] to the data obtained in the titrations of Ni, Co(II), Cd, Cu(II), Mn(II), Pb, Zn, and Fe(II) in the presence of (II), and the modified method of Irving and Rossotti[7] to the data of the titrations of Ni, Co(II) and Cu(II) in the presence of (I), the stability constants of the complexes have been calculated (Table 1).

Table 1. Values of the stability constants for the complexes with some bivalent cations

		Ni	Co	Cd	Cu	Mn	Pb	Zn	Fe
(I)	$\log K_1$	6.78	6.24	—	5.89	—	—	—	—
(II)	$\log K_1$	8.04	7.81	6.36	8.32	4.39	7.38	7.29	7.39
	$\log K_2$	5.43	—	*	5.61	—	4.58	4.21	6.88

* Precipitates at pH ⩾ 7.1

As seen from Table 1, the Irving and Williams order is followed for (II), whereas in the case of (I) the constant for the Cu(II) complex is lower than that for Ni(II) or Co(II).

The results are also in agreement with the work of Bayer[9] on the complexes formed by glyoxal-bis(*o*-hydroxyanil) with Ni, Co(II), Cd, Cu(II), Mn(II), and Zn, with the exception of its Mn(II) complex which is more stable than the Zn and Cd complexes.

* We previously used the names 2-pyridyleneaniline and 2-pyridylene-*o*-hydroxyaniline.

REFERENCES

1. W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta*, 1962, **26**, 575.
2. *Idem*, *ibid.*, 1962, **27**, 71.
3. F. Capitan, F. Salinas and L. F. Capitán-Vallvey, *An. Quim.*, in the press.
4. *Idem*, *Bol. Soc. Quim. Peru*, in the press.
5. M. Otomo and K. Kodama, *Bull. Chem. Soc. Japan*, 1973, **46**, 24.
6. J. Bjerrum, *Metal Ammines in Aqueous Solution*, Haase, Copenhagen, 1941.
7. H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2910.
8. H. M. Irving and R. J. P. Williams, *Nature*, 1948, **162**, 746.
9. E. Bayer, *Ber.*, 1957, **90**, 2325.

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TALANTA MINI-REVIEW*

ANALYTICAL METHODS FOR THE DETERMINATION OF TUNGSTEN

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Summary—Methods developed and employed in the recent literature (1969–1975) for the detection and determination of tungsten in a wide variety of matrices are reviewed. This paper is a supplement to the books, monographs and review papers which deal with the earlier literature.

The chemical determination of tungsten is more difficult than that of many of the other transition metals, particularly in the ppm–ppM (parts per milliard) range. Dissolution procedures are frequently a problem, as W(VI) is soluble only in relatively strongly acidic media, and an auxiliary complexing agent, such as fluoride, is frequently required. Many common analytical techniques for trace analysis, such as atomic-absorption spectroscopy, are not well suited to the determination of tungsten because of lack of sensitivity. As a result, the trace analysis is frequently performed by use of techniques which do not require that the sample is in solution. The precision and accuracy of these techniques is often poor, and there are numerous interferences. A number of publications have dealt with the analytical chemistry of tungsten. Reviews of the literature have been published by Chernikov and Goryushina,[1] Bagshawe,[2] Busev *et al.*[3] and Chalmers.[4] *Analytical Chemistry* publishes biennial reviews of analytical methods for the determination of non-ferrous metals, including tungsten. Elwell and Wood have prepared two monographs, the first dealing with analysis of the "new" metals[5] and the second dealing exclusively with analytical methods for the determination of molybdenum and tungsten.[6] These give complete coverage of the published literature up to 1968.

The object of this review is to supplement these works by reference to material published between 1969 and 1975. An attempt has been made to include most of the pertinent information presented in this period so as to provide the practising analytical chemist with a variety of approaches, some better suited than others to the particular sample and problem in hand. The choice of method for a specific problem must be based on the level of precision and accuracy required, time, cost, availability of instrumentation and, most important, the nature and concentration of other elements in the matrix.

* For reprints of this Mini-Review, see Publisher's announcement near end of this issue TALMR 8.

SEPARATION TECHNIQUES

Solvent extraction

Owing to the many interfering ions normally present in materials being analysed for tungsten, several prior separation techniques are frequently employed. One of the easiest, fastest and operationally simplest methods used is solvent extraction.

The common solvent extraction techniques utilize either a complexing agent or binary or ternary systems comprised of a complexing agent and neutral donor ligand with or without a diluent.

Examples of the first type of system use extraction with ketones. Tungsten has been extracted into propylene carbonate (4-methyl-1,3-dioxolan-2-one)[7] but the extraction is not quantitative at the optimum pH (2.7–3.8) and tungsten can be separated from molybdenum only through repeated extractions. Isobutyl methyl ketone[8] has been used to extract tungsten from a 3:17 v/v mixture of 6 *M* hydrochloric acid and 2.4 *M* hydrofluoric acid, but again a single extraction is non-quantitative and the counter-current technique is utilized to separate tungsten from molybdenum.

Several binary systems using *N*-phenylbenzohydroxamic acid as complexing agent have been developed. Extraction of W(VI) and 24 other ions with this reagent in chloroform has been examined.[9] Various separations are given and extraction and back-extraction efficiencies with various aqueous phases are reported. Similar studies have been published more recently by Chwastowska *et al.*[10] The efficiency of separation of Mo(VI) from W(VI) with this reagent was studied and compared with that of a similar separation using cupferron;[11] the *N*-phenylbenzohydroxamic acid separation was found to be superior. The formation of a 1:2 extractable complex with benzohydroxamic acid has also been reported.[12] The complex absorbs ultraviolet light (λ_{max} at 290 nm) and this forms the basis for spectrophotometric determination of W(VI).

Traces of tungsten in steel have been determined after extraction with 4-methylpentan-2-ol (in benzene).[13] Ions which interfere are Hg(II), Pt(IV), UO_2^{2+}, VO_3^-, Mo(VI) and TeO_3^{2-}. Catechol is

another effective extractant for tungsten.[14,15] The anionic complex formed has a distribution coefficient ≃ 100 and absorbs ultraviolet light (λ_{max} = 360 nm). The formation and extraction of the 3,5-dinitrocatechol derivative has also been reported[16] and it may be preferred to catechol for certain matrices. The quantitative extraction of W(VI) over a wide pH range with 8-hydroxyquinoline and three of its derivatives has been investigated.[17] Again, the nature of the matrix would dictate the desirability of these methods.

The use of amines[18,19] (trioctylamine, dibutylamine) as extractants of anionic metal complexes (with SCN^- or F^-) has been reported. Specific examples of effective separations are given. Tungsten has been shown to be incompletely extracted by various alkyl derivatives of *N*-nitrosohydroxylamines.[20] Thompson and La Fleur[21] used α-benzoinoxime to separate and determine tungsten and molybdenum as a part of a group radiochemical separation for the activation analysis of steel.

Extractions of tungsten and other elements with ethyl acetate,[22] acetylacetone derivatives,[23] tributyl phosphate,[24] triethyl phosphorodithionate[25] and mesityl oxide[26] have been described. All have some analytical utility for tungsten, but, as in the other methods mentioned above, the analyst must choose his technique only after careful consideration of the interferences present in the matrix.

The analytical methods mentioned above concern themselves primarily with the isolation of tungsten (and other metals) from the bulk material. Various techniques have been reported for the isolation of elements from a tungsten matrix, *e.g.*, molybdenum,[27] rhenium,[28–30] scandium[31] and trace elements in general.[32,33] A review of industrial processes used in the recovery of various elements (including tungsten) has been prepared, which contains 51 references.[34] Foam fractionation,[35] although not specifically a solvent-extraction technique, has been used for similar purposes.

Chromatography

Paper chromatography, for many years a favoured technique for metal ion separation and qualitative identification, has largely been supplanted by the more versatile thin-layer chromatography. However, new developments, though fewer than in the past, continue to be presented. A reversed-phase technique using paper impregnated with a liquid anion-exchanger and 6 *M* hydrochloric acid as the mobile phase has been presented for W, Mo, Ge, Sn, Au, Pt, Sb, Ir and As.[36] Suitable developing reagents are given. Tungsten has been separated from V, Fe, Cr, U and Mo on anion-exchange paper (IRA-400, Cl^- form).[37] The developing solvents are generally mixtures of hydrochloric acid, lithium chloride, thenoyltrifluoroacetone or tributyl phosphate. Salicylic acid and its derivatives (in basic solution) have been found to be effective mobile phases for the separation of W(VI), Mo(VI), V(V) and Rh(VII).[38] W(VI), Mo(VI) and V(V) were separated by using various organic acids in a solution of their salts.[39] Various factors affecting the quality of the spearation were discussed. A similar mixture of ions was investigated, the solvent system acetone–hydrochloric acid–sulphuric acid being used.[40]

Brinkman *et al.*[41] have summarized the literature relating to the separation of metal ions by thin-layer chromatography up to 1972. References, experimental conditions and R_f values are presented in tabular form. This paper is particularly useful as a starting point in the selection of a TLC method for a specific application. Other general schemes for metal-ion separation are given by Husain and Kazmi,[42] who utilize a synthetic ion-exchanger as the stationary phase, and Volynets *et al.*,[43] who studied the behaviour of 59 elements on silica gel with acetone–water–hydrochloric acid as eluent. W(VI) has been separated from several other ions by use of a thin layer of hydrargillite and an eluent of toluene–heptane to resolve the 2-dithionaphthoates of the ions.[44] Catechol complexes of Mo, Nb and W have been separated by thin-layer chromatography.[45]

Rh, Mo, V and W have been separated by Gaibakyan and Babayan[46–49] and by Kuroda *et al.*,[50] with a wide variety of systems.

Electrophoresis studies have been carried out by a number of authors.[51–53] These studies involved only a limited number of ions and would be applicable only to relatively simple matrices. Electrophoresis has also been combined with the ring-oven technique.[54] Separation and semi-quantitative estimation (using a densitometer) were achieved for W, Mn, V and Mo in alloys. Again, such a method would not be suitable for complex materials.

Chromatography (both paper and thin-layer) of inorganic material requires some visualization technique for colourless and weakly coloured ions. Most of the papers cited above provide information on visualization. In addition Johri and Mehra[55] reported on the properties of quercetin as a spray reagent, Martinez and Castelo[56] reported the use of tin(II) chloride solution and Feigl and Caldas[57] presented the conditions and results (including the preparation of the reagent) for use of a solution of HgS_2^{2-}. .

The separation and determination of tungsten by gas chromatography has been very limited, owing to the difficulty of preparing stable, volatile tungsten-containing compounds. Investigations on tungsten halides[58,59] and tungsten carbonyls[60] have been published, but both are of limited analytical utility.

In contrast, liquid chromatography, involving adsorption, partition, or ion-exchange has been shown to be a useful and experimentally simple analytical technique for complex mixtures of ions. Alumina has been utilized to separate Re(VII) from W(VI)[61] as well as Nb(V), Mo(VI) and W(VI).[62] Tin oxide columns were shown to separate Mo(VI) and W(VI) from Te and Re.[63] The retention of various

Table 1. Summary of ion-exchange chromatographic separations involving tungsten

Ion-exchanger	Metals considered	Eluent	Reference
Aliquat 336/Kel-F	W, Cr, Mo	HCl	69
Aliquat 336/XAD-2	W, Mo, Sn, V	H_2O_2/H_2SO_4	70
Amberlite IRA-400	W, Mo	H_3PO_4	71
Anionite AV16	W, Mo, Nb, Ti, V	NaF/HCl/NaOH	72
Anionite AV17	W, Cr, Mo	$HF/HCl/H_2SO_4$	73
Anionite AV17	W, Mo, Nb	HF/HCl	74
Anionite AV17	Tl from W and others	pH = 2.5	75
Dowex 1	W, Mo, Nb, Ti, V, Zr	HF	76
Dowex 1	W, Nb, Ta, Ti	oxalic acid	77
Dowex 50WX8	W, Ti, V, Zr, and rare earths	sulphosalicylic acid	78
α-Hydroxyoximes/XAD-2	W from Mo	H_2SO_4/NH_3	79
Iminodiacetic acid resins	W, Mo	acid/base	80
Isobutyl methyl ketone/Teflon	W, Mo, Ta, Nb	HF	81
PTFE	W, Mo, Nb, Zr	HCl/tri-n-octylamine	82

ions, including tungsten, on metal sulphides[64] gave rise to several possible separations, but the use of this method to isolate tungsten appears impractical. Triethylaminoethylcellulose as an adsorbent with hydrochloric acid, hydrochloric acid–ammonium thiocyanate and acetic acid–nitric acid as eluents was the subject of a study by Kuroda and co-workers.[65–67] Over thirty metal ions were investigated and tungsten, which is strongly adsorbed, may be separated from ions with smaller distribution coefficients. Similar studies were made, using 8-hydroxyquinoline immobilized on controlled-pore glass.[68] Numerous ion-exchange systems have been investigated. For convenience, they are summarized in Table 1.

GRAVIMETRIC TECHNIQUES

Gravimetric methods of analysis for macro amounts of tungsten remain an important part of the analytical chemistry of this element, partly because the reactions and techniques are straightforward, although slow, and partly owing to the scarcity of reliable alternative methods.

The determination of tungsten as tungsten(VI) oxide is perhaps the most common of the gravimetric methods. Several modifications of the basic procedure have been made to enhance the precision and accuracy by minimizing the many co-precipitation problems and by enhancing the physical quality of the resulting precipitate. Among these are precipitation from a hot solution of hydrochloric acid–nitric acid to remove the iron interference by oxidation,[83] purification of the WO_3 by fusion with sodium carbonate,[84] precipitation from a tartaric acid solution,[85] introduction of various organic solvents (propanol, ethanediol, propionic acid or glycerol),[86] and precipitation from homogeneous solution with thioacetamide in basic solution to remove vanadium interference, followed by precipitation with perchloric acid, filtration and ignition.[87] The extent of precipitation of tungsten as tungsten(VI) oxide has been enhanced by the addition of iron, aluminium, or lead salts.[88]

Tungsten may also be determined by precipitation as silver tungstate.[89] Interfering species were found to be Na_2SO_4, SiO_3^{2-}, CH_3COO^-, $(NH_4)_2SO_4$, As(V), Cr(VI) and Cl^-. A relative error of $\simeq 1‰$ with interference from titanium, was found when tungsten was precipitated with 8-hydroxyquinoline from an aqueous acetone medium containing oxalate and EDTA.[90] Benzo-[*f*]-quinoline and tannin have been used to precipitate tungsten, but molybdenum precipitates simultaneously and the amount of tungsten must be found by difference after subsequent titrimetric determination of molybdenum.[91] Chitosan precipitates tungsten, from an acidic (acetic or formic acid) solution but there are several interferences.[92] Trace amounts of tungsten may be co-precipitated by a "gathering" technique involving hydrated oxides of iron or zirconium[93] and hydrated manganese dioxide.[94] Optimum conditions (pH, time, concentration) for these determinations have been found. A modification of the "H-tube" method[95] has been made which allows the determination of tungsten in its oxyhalides, (owing to its reactivity with nitric acid vapour at high temperature).[96]

New reagents proposed for the precipitation of tungsten include $K_2Pd(CN)_4$,[97] 4-benzhydryl-*N*,*N*-dimethylaniline,[98] 4,4′,4″-methylidynetris(*N*,*N*-dimethylaniline)[99] and 4,4′-(4-methylbenzylidene) bis(*N*,*N*-dimethylaniline),[100] Mo, V, P and Si interfere in the last three methods.

The electrogravimetric determination of tungsten has been reported to proceed more rapidly, and with an improved solid structure if a vibrating working electrode is used.[101]

Crossland and Fennell[102] compared three gravimetric techniques for tungsten: benzidine precipitation, precipitation from peroxotungstate solution, and precipitation of tributylamine tungstophosphate. The benzidine technique was preferred, but all three were found to be superior to titrimetric determination after reduction with lead.

TITRIMETRIC TECHNIQUES

The emphasis in the titrimetric determination of tungsten has shifted away from use of visual indicators, owing to their general unreliability. Most titrimetric methods recently developed have been poten-

tiometric, some involving ion-selective electrodes. However, some effort has been made to develop more reliable visual indicator systems. Notably, 3,6-bis-(4-nitro-2-sulphophenylazo)chromotropic acid (nitro-orthanilic S) has been used to titrate two- and three-component mixtures of WO_4^{2-}, CrO_4^{2-} and MoO_4^{2-} with standard Ba^{2+} solution.[103] The end-point colour change was followed photometrically (650 nm). 4-(2-Pyridylazo)resorcinol, 4-(2-thiazolylazo) resorcinol, 4-methoxy-2-(2-thiazolylazo)phenol and 4-hydroxy-3-(2-pyridylazo)naphthalene-1-sulphonic acid have been evaluated as indicators for the titration of WO_4^{2-}, MoO_4^{2-}, PO_4^{3-} and SO_4^{2-} with standard lead nitrate solution.[104] Results for tungsten were not reproducible. Octacyanotungstate(IV) ions have been titrated with *N*-bromosuccinimide, with Naphthol Blue Black as indicator.[105] A coefficient of variation of $\simeq 1\%$ was reported. The fluorescent indicators erythrosin[106] and acriflavine[107] have been utilized in the determination of both tungsten and molybdenum with results comparable to those of potentiometric or amperometric titration.

Tungsten has been determined amperometrically with a standard solution of diantipyrinylmethane.[108] The relative error was $< 4.5\%$; however, Mo(VI), V(V), PO_4^{3-} and As(V) were found to interfere. W(VI) may be converted into W(III) with tin and hydrochloric acid and the resulting solution titrated amperometrically with standard potassium ferricyanide or potentiometrically with standard potassium dichromate.[109]

A tungsten/calomel electrode pair has been utilized in the titration of tungsten (as WO_4^{2-}) with standard lead nitrate solution.[110] The first excess of Pb^{2+}, sensed by a lead membrane ion-selective electrode, serves as an end-point signal in similar systems.[111] The reaction of a standard solution of silver nitrate with WO_4^{2-} may be followed with a dithizone-impregnated membrane electrode.[112] A glass/calomel electrode system has been utilized to follow the pH of a solution of tungstate (as the mannitol complex) titrated with standard sulphuric acid.[113] A break occurs in the titration curve when one proton has been added per tungstate ion. A wax-impregnated carbon indicator electrode can be used to follow titration of W(VI) with standard chromous sulphate solution.[114] The relative error is less than 1% for mg amounts of tungsten.

Tungsten forms a stable complex anion with hydrogen peroxide. This has been used to advantage in a potentiometric titration with sodium sulphite.[115,116] Separate breaks are found for the free peroxide and the peroxide complex. Iron may be masked with fluoride. Other ions forming peroxide complexes interfere, and samples containing these ions require prior separation.

Vanadium(II) has been utilized as a reducing titrant[117] but the experimental conditions, especially the temperature, are somewhat stringent. The non-aqueous solvent system, isopropyl alcohol–ethanediol, has been investigated for titration of tungstate, as well as other ions, with perchloric or hydrochloric acid.[118]

New precipitate-forming and complex-forming titrations continue to be reported. For example, the micro determination of tungsten with pinacyanol chloride,[119] back-titration of excess of Pb^{2+} with EDTA, after precipitation of $PbWO_4$,[120,121] and back-titration of Fe(III) with EDTA[122] in a similar system. Goyal and Tandon[123] determined the equilibrium constants for complexes of W(VI) as well as Cr(VI) and Mo(VI) with various Azoxine S dyes with their potential analytical utility in mind.

Thermometric titration has been used in investigation of polytungstate formation[124] and the radiometric titration[125] of W(VI) has been reported.

FLUOROMETRIC AND SPECTROPHOTOMETRIC TECHNIQUES

Few compounds form fluorescent derivatives with tungsten species; consequently, the number of fluorometric methods for tungsten is quite small. 3-Hydroxyflavone is the principal fluorometric reagent for tungsten. The analytical chemistry of flavones in relation to the determination of metals (including tungsten) was reviewed in 1972 by Nevskaya and Nazarenko.[126] The review contains 150 references and is comprehensive. The reader is directed to this source for additional information on hydroxyflavones as fluorometric reagents. The only other fluorometric reagent reported during the time covered by this review is morin, which forms a 1:1 complex with W(VI) at pH 5.5.[127] The excitation wavelength is 410–415 nm and the fluorescence maximum occurs at 500–510 nm. Trace levels of tungsten (3 ng/ml) may be determined and the common interferents Nb(V), Ta(V) and Mo(VI) are inconsequential if present in concentrations equivalent to that of W(VI).

The majority of the spectrophotometric methods reported are modifications of previous methods, or older methods applied to specific analytical situations. Three of these methods (salicylfluorone, Catechol Violet and potassium thiocyanate) were compared by Pashchenko *et al.*[128] They found that the salicylfluorone method is the most sensitive, but molybdenum interferes. Existing procedures for the spectrophotometric determination of tungsten with thiocyanate have been exhaustively reviewed by Fogg *et al.*[129] (61 references). Comparisons of many of the existing methods are made. The same authors found the optimum conditions for the determination of tungsten in steel by the thiocyanate method.[130] The principal advantage of the method is the absence of V(V) interference coupled with the fact that moderate amounts of Mo(VI) may be tolerated. Golubstova and Lebedeva[131] suggest, however, that the Catechol Violet method would be preferable in the presence of molybdenum. Specific spectrophotometric methods, including modifications and specific applications are summarized in Table 2.

Table 2. Summary of spectrophotometric methods for the determination of tungsten

Colour-forming reagent	Material	λ_{opt} or λ_{max} nm	ϵ^* and/or concentration range; comments	Reference
Azo compounds	General	580	20–100 μg per sample	132
Azo compounds (Nezarson)	General	500	1.50×10^4	133
Azo compounds (chromotropic acid der.)	General	650	3.08×10^4; 0.08–0.4 μg/ml	134
Catechol (3,5-dinitro der.)	KOH	646	1.32×10^5; up to 6 μg/ml	135
Catechol (3,5-dinitro der.)	General	400	5–80 μg per sample	136
Catechol	Steel	440	0.2–2%	137
Catechol	Steel	580	0.02–0.25 μg per sample	138
Catechol	Steel	310	4.0×10^3; 2.5–10 μg/ml	139
Catechol	Mo–W	350 or 370	up to 1.4 mg per sample	140
Catechol	Mo–W	560	up to 2 mg per sample	141
Catechol	Mo–W	440	5–200 μmole per sample	142
Dithiol	Biological	630	5–100 nmole per sample	143
Dithiol	Biological, *etc.*	630	0.01–300 μg/ml	144
Dithiol	General	640	0.5 μg/ml and up	145
Dithiol	Rock	630 and 670	0.02 μg/ml and up	146
Dithiol	Rock and sediment	630	4 μg/ml and up	147
Dithiol	Sea-water	630	0.11 μg/ml and up	148
Dithiol	Ta and Nb	650	0.5 μg/ml and up	149
Dithiol der. (dimercaptomaleonitrile)	General	570	1–20 μg/ml	150
Dithiol der. (*o*-xylene-4,5-dithiol)	General	670	μg range	151
Fluorones (trihydroxy der.)	General	—	Characterization of properties of complexes	152
Fluorones (trihydroxy der.)	General	530	2.50×10^4	153
Fluorones (phenyl der.)	General	—	Characterization of properties of complexes	154
Gallein	General	590	up to 130 μg per sample	155
Hydrogen peroxide	General	262	50–160 μg/ml	156
Molybdate (heteropoly acid form)	General	765	up to 15 μg/ml	157
Molybdate (heteropoly acid form)	Mo–W	540/610	12 μg/ml and up	158
Molybdate (heteropoly acid form)	Mo–W	680/825	0.5–5 mg/50 ml	159
Pyrogallol	General	576	6.00×10^4; less than 45 μg	160
Pyrogallol	General	—	Stability constants reported	161
Quinalizarin	General	510	Stability constants reported	162
Quinalizarin (sulphonic acid der.)	General	—	Survey of metal-ion reactions	163
Quinoline der. (5,7-dibromo-8-hydroxyquinoline)	General	370/380	0.5 μg/ml and up	164
Quinoline der. (5,7-dichloro-8-hydroxy-2-methyl-quinoline)	General	—	Survey of metal-ion reactions 0.2 μg/ml and up	165
Quinoline der. (8-mercaptoquinoline)	General	530		166
Rhodamine B	General	—	Study of the effect of masking agents	167
Rhodamine 6 Zh	General	560	1 μg/ml and up	168
Solochrome Violet Rs	General	550	3.50×10^3; 4.4–88.2 μg/ml	169
Thiocyanate ion	Ind. dust			170
Thiocyanate ion	Ores			171
Thiocyanate ion	Rocks		[Data summarized in original method development]	172, 173
Thiocyanate ion	Steel			174, 175
Thiocyanate ion	Uranium			176

* $l.mole^{-1}.cm^{-1}$.

ELECTROLYTIC TECHNIQUES

Electrochemical methods based on use of an electrolytic cell (principally electrogravimetry, coulometry and polarography) have not been widely employed in the determination of tungsten in common matrices, mainly because of the interference caused by the many ions commonly associated with this element. No new electrogravimetric techniques have been reported during the time of this review. One coulometric method involves the generation of Pb^{2+} from a lead amalgam.[177] The Pb^{2+} reacts with WO_4^{2-} as in the familiar precipitate-forming titrations mentioned earlier. Prior separation of other similarly reactive species, such as PO_4^{3-}, MoO_4^{2-} and SO_4^{2-} is necessary.

Table 3. Applications of spectrographic techniques to the analytical determination of tungsten

Type of material	Comments	Reference
Alloy (gallium)	Concentration range: 0.001–0.1%; fluorination increases sensitivity	186
Alloy (slag)	Determination of optimum conditions for WO_3	187
Alloy (steel)	Determination of optimum spectral lines	188
Alloy (steel)	Involves preliminary transfer to Cu electrode	189
Alloy (steel)	Step-sector method without internal standard	190
Alloy (steel)	High-frequency plasma-torch excitation	191
Alloy (steel)	Concentration range: 10–100 ppm; prior separation used	192
Alloy (steel)	Far UV using high orders	193
Alloy (W–Mo)	Dilution technique for samples with high % W	194
Alloy (Zr)	Uses intermittent a.c. arc excitation	195
Ammonium perrhenate	Optimization of experimental conditions	196
Lanthanum and its oxide	Concentration range: 0.003–0.45 ppm	197
Limestone	Concentration range: 0.0001–0.2%; a.c. arc	198
Molybdenum	Enhancement of d.c. arc lines by addition of metal chlorides	199
Molybdenum	Gathering technique; concentration range: 6×10^{-4}–10%	200
Silica	Enhancement of d.c. arc lines by addition of metal chlorides	201
Ti, Hf, Nb, Ta, Zr	Sensitivity: 1–5 ppm; 8-A a.c. arc	202
Tungsten carbide	Optimum conditions for sample prep., excitation and exposure	203
Uranium and its compounds	Spark excitation of $CHCl_3$ extract	204
Uranium and its compounds	Extraction, evaporation, fusion; d.c. arc excitation	205
Uranium and its compounds	Preliminary separation using cupferron	206
Uranium and its compounds	Carrier-distillation method; study of variables	207
U_3O_8	Carrier-distillation method; avoids prior separation of uranium	208
Yttrium and its oxide	Discussion of sample preparation	209

Direct-current polarographic determination of tungsten in tungsten–vanadium alloys is possible after ion-exchange separation of the elements.[178] Shpak *et al.*[179] determined half-wave potentials for complexes of *N*-phenylcinnamohydroxamic acid in various extracting solvents. The tungstovanadophosphate complex was formed and d.c. polarography used to determine 2–10% tungsten in steel.[180] The reduction of W(VI) to W(III) has been investigated in oxalic acid media.[181] Alternating-current polarography has been successfully employed in the determination of tungsten in the presence of 100-fold amounts of Nb(V) and Ta(V).[182] Anodic-stripping voltammetry or square-wave polarography has been utilized to determine tungsten in U–Nb–Zr alloys.[183] A tartrate–hydrochloric acid supporting electrolyte was used. Kinetic polarography has demonstrated good sensitivity, accuracy and precision for tungsten, although Cr(VI), Fe(III), Mo(VI), Ti(IV) and V(V) are serious interferences.[184] Tributyl and tripropyl phosphates were found to preconcentrate UO_2^{2+} and WO_4^{2-} on the surface of a hanging mercury drop electrode through a complex-forming mechanism.[185]

SPECTROGRAPHIC METHODS

A wide variety of papers have been published relating to the determination of tungsten in alloys, rocks and ores, as well as other specific industrial products. These have been summarized in Table 3.

Important new developments involve the increase in sensitivity of spectrographic measurement brought about by improvement in instrumentation or techniques. Rippetoe *et al.*[210] studied the characteristics of a d.c. plasma arc for the determination of tungsten as well as other difficult metals. They found that reasonable calibration curves could be constructed for tungsten in the range 1–100 μg/ml. Sensitivity for tungsten in silica was enhanced by the addition of copper(I) chloride.[211] The lower limit of detection was 5 ppm. Other investigators had earlier found that the addition of lead chloride resulted in a sensitivity of 10 ppm.[199,201,212] Cross-over effects of elements of different volatilities were studied, and as expected, the presence of elements such as mercury and zirconium decreases tungsten line intensity.[213] This serves to highlight the multitude of matrix problems associated with the spectrographic determination of tungsten. Variables associated with a glow-discharge source have been studied and suggestions for optimum sensitivity made.[214] Two new gathering techniques have been published: one involves co-precipitation of tungsten with $Mg(OH)_2$–$Fe(OH)_3$–$Mg_3(PO_4)_2$–$FePO_4$ from basic media for the spectrographic determination of tungsten in water,[215] and in the other $Cd(OH)_2$ or $Zn(OH)_2$ gathers tungsten and numerous other elements from cadmium or zinc samples.[216] Chemical concentration of impurities, such as tungsten, is used in the analysis of various refractory bases.[217]

FLAME EMISSION AND ATOMIC-ABSORPTION SPECTROSCOPY

As mentioned earlier, the principal analytical problem associated with the determination of tungsten by flame emission or atomic absorption is sensitivity. Elements which form refractory oxides in a flame

present real difficulties for the analyst. Several excellent approaches have offered at least a partial solution to this problem.

Kirkbright *et al.*[218] used a silica separator in a nitrous oxide/acetylene burner to produce a high-temperature highly reducing zone in the flame. Detection limits for tungsten by flame emission were found to be 20 ppm. The same authors[219] later used argon- or nitrogen-shielded flames and achieved a flame emission detection limit of less than 1 ppm. Others report similar enhancement in sensitivity with shielded flames.[220]

Molecular emission by the fluorides of numerous elements has been studied and attempts made to characterize the emitting species.[221] Tungsten and other elements have been determined simultaneously by use of a vidicon detector.[222] Optimization of flame characteristics for each element was impossible; hence the detection limit for tungsten is not ideal.

Atomic absorption has generally been found to be less sensitive than flame emission analysis for tungsten. The effect of solution equilibria on the intensity of the atomic-absorption signal has been examined.[223] A d.c. arc excitation system yielded a sensitivity of 3.6 ppm for tungsten.[224] As expected, the authors found the apparatus more suited to emission measurements.

Specific kinds of samples analysed for tungsten by atomic-absorption processes include alloys,[225–228] metallurgical materials,[229] steel,[230] ores[231,232] and tantalum.[233]

X-RAY FLUORESCENCE METHODS

X-Ray fluorescence is a well established, sensitive and reliable method for the determination of many trace metals, including tungsten, in solids. It is often advantageous to analyse many tungsten-containing ores and alloys as solids to avoid problems associated with the dissolution of these samples. The absence of serious matrix interferences, along with a relatively uncluttered spectrum, makes X-ray fluorescence a desirable approach. Owing to the cost and complexity associated with this technique, however, it can be recommended only in those situations where many analyses must be performed. Progress has been made in the design of spectrometers which are smaller and less complex. Gallagher[234] reports the development of a portable X-ray spectrometer based upon γ-ray excitation by a radioactive source. Single analyses may be performed in $\simeq$ 1 min. Detection limits of 25 ppm for tungsten have been reported for similar instrumentation.[235] A general discussion of the theory and application of this technique has been presented.[236,237] Application of the technique to the rapid determination of tungsten in mineral ores[238] and geochemical[239] samples has been shown to be feasible. The second of these references states that 70–100 separate analyses were performed in one 8-hr period. Tin-119,[240] cobalt-57,[241,242] and promethium-147[241] were found to be satisfactory sources for the determination of tungsten.

Other advances in instrumentation include the evaluation of a 17-channel, automated, computer-linked system, which appears to have great potential for multielement analysis.[243] Sample preparation of powders in a graphite crucible yields tablets well-suited to X-ray fluorescence analysis.[244] WO_3 was determined with excellent precision. Pantony and Hurley[245] have discussed the theoretical and practical factors governing detection limits. Tungsten, as well as several other elements, was considered in detail. The technique of X-ray fluorescence has been applied to the determination of tungsten in iron, molybdenum and titanium,[246] high-alloy steels,[247] high-purity iron and low-alloy steels,[248] welding materials and steel,[249] complex alloys,[250] zirconium and zirconium alloys,[251] nickel alloys,[252] scheelite and wolframite ores,[253] and organometallic compounds.[254]

ACTIVATION ANALYSIS

Activation analysis, utilizing either neutrons or charged particles (principally protons) has long been recognized as one of the most sensitive techniques for trace analysis. In many instances samples containing small amounts of tungsten may be analysed directly without prior or post-destruction. This is especially true for alloys. In the case of biological materials. a prior ashing technique is used to improve the form and homogeneity of the material to be irradiated. Careful control of the energy and flux of the activating source, irradiation time, "cooling" time, as well as the energy "window" to be counted, provides a high degree of sensitivity and freedom from many interfering elements. If, however, the matrix is quite complex, it is often essential to reduce the complexity of the resulting energy spectrum by chemical separation of interfering substances before counting.

Dumesnil[255] has reviewed the analytical methods for determining tungsten and other elements by use of isotopic neutron sources or neutron generators; these were developed principally to free neutron-activation analysis from the need for a nuclear reactor. It has been found that 2.8-MeV neutrons produced by the reaction D(d, n)^{3}He minimize matrix interferences because they activate only a small number of elements.[256] Tables of sensitivities for the various elements, including tungsten, are given. Proton-activation analysis for tungsten has been discussed.[257]

Various aspects of instrument design and modification have been reported. These include a neutron generator,[258] an evacuated, low-temperature, germanium detector,[259] the development of equations for optimum sensitivity and discrimination,[260] and methods for estimating shielding coefficients and optimum sample weights.[261] Substoichiometric methods for the determination of tungsten have been presented by several authors.[262–264] Radiochemical separations of tungsten by solvent extraction[265] and ion-exchange[266] before counting have also been reported.

Table 4. Applications of activation analysis for the determination of tungsten

Type of material	Comments*	Reference
Air-pollution particulates	Collection on polystyrene filter followed by neutron irradiation	267
Air-pollution particulates	Collection on Millipore filter followed by neutron irradiation	268
Air-pollution particulates	Collection on cellulose filter followed by neutron irradiation	269
Alloy (general)	Neutron generator used; rel. error ± 4.2% for W	270
Alloy (steel)	Attempt to find internal isotopic tracers	271, 272
Alloy (steel)	Standard procedure applied	273, 274, 275
Enrichment products	γ-Excitation using ^{170}Tm	276
Graphite	Recommended for assessing graphite quality	277
Iron	Non-destructive; coefficient of variation is 1.3% for W	278
Iron	Non-destructive; 0.1% error	279
Iron	Destructive; irradiation, dissolution, separation, counting	280
Molybdenum	Non-destructive	281
Molybdenum	Destructive; irradiation, dissolution, separation, counting	282
Niobium	Neutron activation; ppm range; interferences studied	283
Niobium	Neutron activation; 0.001–1 ppm of W	284
Niobium	Proton activation; interferences studied	285
Niobium and tantalum	Detection limit of 1.7 ppm	286
Ore and rock	Beryllium and coal; results comparable to spectrophotometric methods	287
Ore and rock	Utilizes (γ, γ') reaction	288
Ore and rock	Sensitivity of 0.8 ppm of W	289
Ore and rock	Molybdenite ores; sensitivity of 15 ppm of W	290
Ore and rock	Ore concentrates; 2-min analysis; 0.01% sensitivity	291
Ore and rock	Rock samples; may be automated	292
Ore and rock	0.1% sensitivity for WO_3 in silica using ^{182}W(n, γ) ^{183}W	293
Organics (biological)	Epithermal neutrons used; more sensitive than thermal neutrons	294
Organics (fabrics)	Computer calculation of optimum irradiation and decay times	295
Organics (fish meal)	Precision of 10–15%; involves separation after irradiation	296
Organics (plants)	Ashing technique; irradiation, separation, counting	297
Ruby	ppm levels of W	298
Semiconductor	High sensitivity multielement analysis	299,300,301
Tantalum	Non-destructive determination; proton activation	302
Tin	Destructive determination involving separation	303
Titanium	Applied to behaviour of Ti during corrosion	304
Titanium and its oxide	Applied to single crystals	305
Titanium and its oxide	Simultaneous determination of 27 elements including W	306
Titanium and its oxide	Simultaneous determination of 16 elements including W	307
Water (natural)	No separation or concentration required	308
Water (mine)	Evaporation and chemical separation utilized	309

* Method involves neutron activation unless otherwise stated

Numerous applications of standard techniques to specific samples and sample types have been made. Modifications of a more general procedure must often be made to accommodate a certain matrix. These methods are summarized in Table 4.

KINETIC METHODS

Analytical methods for tungsten, based on the ability of W(VI) to catalyse certain reactions, have not been extensively investigated. This approach offers promise for several reasons. If chosen carefully, the reactions are often quite specific, offering freedom from many matrix effects and eliminating the need for prior separation. Owing to the nature of the catalytic effect, the methods are also quite sensitive. The instrumentation is usually quite inexpensive (usually potentiometric or spectrophotometric) and readily available. This is in marked contrast to methods such as X-ray fluorescence and activation analysis.

The catalysis (by W) of the reaction of hydrogen peroxide with iodide to form the tri-iodide ion forms the basis for the automated microdetermination of tungsten (0.5–3.0 μg) with 1–2% error.[310] The same reaction was followed with an iodide ion-selective electrode.[311] The reduction of Basic Blue K by Ti(III), catalysed by W(VI), has been followed spectrophotometrically,[312] and 10^{-8} *M* W(VI) determined. A similar reaction involving Malachite Green was investigated by reflectance spectroscopy, 0.06–0.6 μg being determined.[313] The high (± 29%) relative error could probably be reduced by a modification of the method.

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REFERENCES

1. Y. A. Chernikhov and V. G. Goryushina, *Zavodsk. Lab.*, 1946, **12**, 517.
2. B. Bagshawe, *Chemical Age*, 1954, **70**, 267, 309.
3. A. I. Busev, V. G. Tiptsova and A. D. Khlystova, *Zavodsk. Lab.*, 1962, **28**, 1414.

4. R. A. Chalmers, in *Comprehensive Analytical Chemistry*, Vol. Ic, C. L. Wilson and D. W. Wilson, eds., Elsevier, Amsterdam, 1962.
5. W. T. Elwell and D. F. Wood, *Analysis of the New Metals*, Pergamon, Oxford, 1971.
6. *Idem*, *Analytical Chemistry of Molybdenum and Tungsten*, Pergamon, Oxford, 1971.
7. C. Luca and A. Sapatino, *Rev. Chim.*, 1975, **26**, 251.
8. S. Kallmann, E. W. Hobart and H. K. Oberthin, *Anal. Chim. Acta*, 1968, **41**, 29.
9. H. Foerster, *J. Radioanal. Chem.*, 1970, **6**, 11.
10. J. Chwastowska, K. Lissowska and E. Sterlinska, *Chem. Anal. (Warsaw)*, 1974 **19**, 671.
11. I. V. Pyatnitskii and L. F. Kravtsova, *Ukr. Khim. Zh.*, 1969, **35**, 77.
12. E. N. Poluektova and V. A. Nazarenko, *Zh. Analit. Khim.*, 1967, **22**, 746.
13. S. P. Patil and V. M. Shinde, *Anal. Lett.*, 1973, **6**, 709.
14. M. Vrchlabský and L. Sommer, *Talanta*, 1968, **15**, 887.
15. T. D. Ali-Zade, G. A. Gamid-Zade and V. I. Kuliev, *Azerb. Khim. Zh.*, 1971, 130.
16. V. A. Nazarenko, E. N. Poluektova and G. C. Shitareva, *Zh. Analit. Khim.*, 1973, **28**, 101.
17. K. Awad, N. P. Rudenko, V. I. Kuznetsov and L. S. Gudym, *Talanta*, 1971, **18**, 279.
18. Yu. S. Tseryuta, V. V. Bagreev, N. A. Agrinskaya, N. V. Gushchin, A. S. Basov and Yu. A. Zolotov, *Zh. Analit. Khim.*, 1973, **28**, 946.
19. L. G. Anokhina and N. A. Agrinskaya, *Tr. Novocherk. Politekhn. Inst.*, 1974, (289), 14.
20. F. Buscarons and J. Canela, *Anal. Chim. Acta*, 1974, **70**, 113.
21. B. A. Thompson and P. D. LaFleur, *Anal. Chem.*, 1969, **41**, 852.
22. A. Fleury and F. Hubert, *Bull. Soc. Chim. France*, 1971, 3090.
23. W. M. Jackson and G. I. Gleason, *Anal. Chem.*, 1973, **45**, 2125.
24. E. Upor, L. Gorbicz and G. Nagy, *Magy. Kem. Folyoirat*, 1969, **75**, 549.
25. A. I. Busev, T. V. Rodionova and N. I. Verbitskaya, *Anal. Lett.*, 1972, **5**, 237.
26. V. M. Shinde and S. M. Khopkar, *Talanta*, 1969, **16**, 525.
27. V. Yatirajam and J. Ram, *Mikrochim. Acta*, 1973, 77.
28. V. Yatirajam and L. R. Kakkar, *Anal. Chim. Acta*, 1969, **44**, 468.
29. *Idem*, *Talanta*, 1970, **17**, 759.
30. A. T. Pilipenko and M. A. Mubayadzhyan, *Arm. Khim. Zh.*, 1970, **23**, 414.
31. L. L. Galkina and S. A. Strel'tsova, *Zh. Analit. Khim.*, 1970, **25**, 889.
32. T. E. Green, *Rept. Invest. U.S. Bur. Mines*, RI 7072, 1968.
33. A. K. De, *J. Indian Chem. Soc.*, 1974, **51**, 195.
34. D. S. Flett, *Rept. Warren Spring Lab.*, No. LR 90 (MST), 1968.
35. W. Charewicz and R. B. Grieves, *Anal. Lett.*, 1974, 7, 233.
36. A. Flieger and S. Przeslakowski, *Chem. Anal. Warsaw*, 1972, **17**, 333.
37. A. K. De and C. Bhattacharya, *ibid.*, 1972, **17**, 609.
38. D. S. Gaibakyan and Z. V. Sarkisyan, *Zh. Analit. Khim.*, 1974, **29**, 1991.
39. Z. Z. Termendzhyan and D. S. Gaibakyan, *Arm. Khim. Zh.*, 1974, **27**, 25.
40. K. G. Isaeva and M. E. Viktorova, *Zh. Analit. Khim.*, 1974, **29**, 382.
41. U. A. T. Brinkman, G. D. Vries and R. Kuroda, *J. Chromatog.*, 1973, **85**, 187.
42. S. W. Husain and S. K. Kazmi, *Experientia*, 1972, **28**, 988.
43. M. P. Volynets, A. N. Ermakov and T. V. Fomina, *Zh. Analit. Khim.*, 1970, **25**, 1864.
44. M. D. Gertner, R. K. Buman and A. A. Mironovich, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1974, 247.
45. J. Hlousková and M. Vrchlabský, *Scr. Fac. Sci. Natur. Univ. Purkynianae Brun.*, 1973, **3**, 39.
46. D. S. Gaibakyan, *Arm. Khim. Zh.*, 1969, **22**, 219.
47. D. S. Gaibakyan and K. S. Babayan, *Zavodsk. Lab.*, 1971, **37**, 9.
48. D. S. Gaibakyan, *Uch. Zap. Erevan. Univ. Estestv. Nauki*, 1971, **1**, 71.
49. *Idem*, *Arm. Khim. Zh.*, 1971, **24**, 861.
50. R. Kuroda, K. Kawabuchi and T. Ito, *Talanta*, 1968, **15**, 1486.
51. G. Marcu and M. Tomus, *Analusis*, 1972, **1**, 43.
52. D. S. Gaibakyan and S. I. Sagradyan, *Arm. Khim. Zh.*, 1971, **24**, 668.
53. D. S. Gaibakyan and Z. Z. Termendzhyan, *ibid.*, 1972, **25**, 14.
54. V. Armeanu and I. Niculescu, *Revue Roum. Chim.*, 1971, **16**, 1867.
55. K. N. Johri and H. C. Mehra, *Mikrochim. Acta*, 1971, 317.
56. F. B. Martinez and M. S. Castelo, *Microchem. J.*, 1971, **16**, 94.
57. F. Feigl and A. Caldas, *Anal. Chim. Acta*, 1970, **49**, 1.
58. R. M. Dagnall, B. Fleet, T. H. Risby and D. R. Deans, *Anal. Lett.*, 1971, **4**, 497.
59. V. P. Isakov, *Zh. Fiz. Khim.*, 1973, **47**, 702.
60. C. Pommier and G. Guiochon, *J. Chromatog. Sci.*, 1970, **8**, 486.
61. C. Klofutar, F. Krasovec and A. Kodre, *J. Radioanal. Chem.*, 1970, **5**, 3.
62. I. P. Kharlamov, N. P. Krivenkova and V. M. Byr'ko, *Zavodsk. Lab.*, 1970, **36**, 1428.
63. N. Renault and N. Deschamps, *Radiochem. Radioanal. Lett.*, 1973, **13**, 207.
64. B. Chayla, *Analusis*, 1973, **2**, 590.
65. R. Kuroda and K. Kawabuchi, *Z. Anal. Chem.*, 1972, **261**, 394.
66. R. Kuroda, T. Kondo and K. Oguma, *Talanta*, 1973, **20**, 533.
67. R. Kuroda, K. Oguma, M. Suzuki and Y. Fuchu, *Bunseki Kagaku*, 1975, **24**, 1.
68. K. F. Sugawara, H. H. Weetall and G. D. Schucker, *Anal. Chem.*, 1974, **46**, 489.
69. I. Stronski, *Radiochem. Radioanal. Lett.*, 1969, **1**, 191.
70. J. S. Fritz and J. J. Topping, *Talanta*, 1971, **18**, 865.
71. P. K. Padmanabhan and C. Venkateswarlu, *Compt. Rend. Acad. Bulgare Sci.*, 1973, **26**, 407.
72. T. N. Gudushauri and F. I. Brouchek, *Soobschch. Akad. Nauk. Gruz.*, 1973, **70**, 609.
73. V. S. Pakholkov, *Tr. Nauch-Issled. Inst. Khromatogr. Voronezh. Univ.*, 1968, 166.
74. V. I. Kurbatova, G. N. Emasheva and N. D. Fedorova, *Tr. Nauch-Issled. Inst. Stand. Obraztsov.* 1971, 7, 102.
75. V. D. Eristavi and M. G. Mgaloblishvili, *Zh. Analit. Khim.*, 1973, **28**, 375.
76. T. A. Ferraro, *Talanta*, 1969, **16**, 669.
77. A. Foldzinska, *Chem. Anal. Warsaw*, 1971, **16**, 821.
78. A. K. Das, J. C. Pal and S. Banerjee, *Anal. Chim. Acta*, 1969, **47**, 162.
79. J. S. Fritz and D. R. Beuerman, *Anal. Chem.*, 1972, **44**, 692.
80. S. Steinbach and R. Hering, *Z. Chem.*, 1971, **11**, 350.
81. J. S. Fritz and L. D. Dahmer, *Anal. Chem.*, 1968, **40**, 20.
82. I. M. Gibalo and N. A. Mymrik, *Zh. Analit. Khim.*, 1970, **25**, 1744.
83. D. Fantozzi, *Rev. Brasil. Quim.*, 1974, **78**, 79.
84. O. Y. Payuste, *Sb. Nauchn-Tekhn. Statei. Proektnotekhnol. Nauch-Issled. Inst. Tallin*, 1968, 177.

85. A. A. Roy, K. Syamalarao and B. N. Bhattacharyya, *Indian J. Technol.*, 1968, **6**, 185.
86. Z. G. Golubtsova, L. I. Lebedeva and T. P. Likhareva, *Vestn. Leningrad Univ., Fiz. Khim.*, 1968, **23**, 129.
87. M. J. Martinez Lope, A. Maceira Vidan and F. Burriel-Marti, *An. Quim.*, 1974, **70**, 223.
88. B. I. Polyakov and V. K. Rumyantsev, *Zh. Analit. Khim.*, 1972, **27**, 1412.
89. K. Varughese and K. Rao, *Anal. Chim. Acta*, 1971, **57**, 219.
90. A. V. Vinogradov and M. I. Dronova, *Zh. Analit. Khim.*, 1968, **23**, 696.
91. A. Y. Sheskol'skaya, *ibid.*, 1967, **22**, 812.
92. R. A. A. Muzzarelli, *Anal. Chim. Acta*, 1971, **54**, 133.
93. A. V. Vinogradov, M. I. Dronova and N. N. Lopatina, *Zavodsk. Lab.*, 1973, **39**, 150.
94. A. I. Novikov and N. V. Kopylova, *Dokl. Akad. Nauk Tadzh. SSR*, 1972, **15**, 38.
95. H. Schafer and K. D. Dohmann, *Z. Anorg. Allgem. Chem.*, 1959, **300**, 1.
96. J. Tillack, *Z. Anal. Chem.*, 1968, **239**, 81.
97. J. Hernandez Mendez, J. Medina Esteriche and J. V. Gimeno Adelantado, *Quim. Anal.*, 1975, **29**, 32.
98. E. Llorente Gomez, J. Zato del Corral and F. Burriel-Marti, *An. Quim.*, 1975, **71**, 164.
99. *Idem, ibid.*, 1975, **71**, 168.
100. *Idem, ibid.*, 1975, **71**, 173.
101. K. Kuchta, *GIT (Glas-Instrum.-Tech.) Fachz. Lab.*, 1973, **17**, 355.
102. B. Crossland and T. R. F. W. Fennell, *Analyst*, 1969, **94**, 989.
103. A. P. Kreshkov, V. V. Kuznetsov and P. G. Mezhlumvan, *Zh. Analit. Khim.*, 1974, **29**, 1349.
104. L. Sommer and L. Janoščová, *Collection Czech. Chem. Commun.*, 1974, **39**, 101.
105. S. S. Basson, L. D. C. Bok and S. R. Grobler, *Z. Anal. Chem.*, 1972, **260**, 117.
106. Z. T. Maksimycheva, G. S. Andrushko and Sh. T. Talipov, *Dokl. Akad. Nauk Uz. SSR*, 1971, **28**, 26.
107. G. S. Andrushko, Z. T. Maksimycheva and Sh. T. Talipov, *ibid.*, 1970, **27**, 26.
108. S. V. Lugovoi and L. D. Paklerova, *Zh. Analit. Khim.*, 1974, **29**, 1748.
109. I. Kulev, P. Gavanarov and D. Staney, *Rudodobiv Met. Sofia*, 1973, **28**, 28.
110 R. Geyer and M. Neumann, *Acta Chim. Acad. Sci. Hung.*, 1969, **60**, 349.
111. M. Mascini and A. Liberti, *Anal. Chim. Acta*, 1972, **60**, 405.
112. S. Lal, *Z. Anal. Chem.*, 1971, **255**, 210.
113. A. G. Sinclair, *Talanta*, 1969, **16**, 459.
114. D. P. Smith and M. T. Pope, *Anal. Chem.*, 1968, **40**, 1906.
115. I. V. Pyatnitskii and D. Chung, *Zh. Analit. Khim.*, 1969, **24**, 545.
116. *Idem, ibid.*, 1970, **25**, 91.
117. N. T. Akinchan and S. N. Prasad, *Indian J. Chem.*, 1973, **11**, 37.
118. A. P. Kreshkov and A. V. Kuznetsova, *Tr. Tambov. Inst. Khim. Mashinostr.*, 1970, 116.
119. P. P. Turov and D. S. Turova, *Zh. Analit. Khim.*, 1970, **25**, 934.
120. P. Bourret, J. Lecuire and C. Weis, *Chim. Anal. Paris*, 1970, **52**, 1114.
121. O. I. Popova and O. G. Seraya, *Zh. Analit. Khim.*, 1968, **23**, 791.
122. I. A. Crisan and D. C. Pricop, *Studia Univ. Babes-Bolyai, Ser. 1, Chem.*, 1968, **13**, 27.
123. S. S. Goyal and J. P. Tandon, *Talanta*, 1969, **16**, 106.
124. N. Kiba and T. Takeuchi, *ibid.*, 1973, **20**, 875.
125. C. Omboly, T. Szarvas and G. Vegh, *J. Radioanal. Chem.*, 1973, **13**, 59.
126. E. M. Nevskaya and V. A. Nazarenko, *Zh. Analit. Khim.*, 1972, **27**, 1699.
127. A. T. Pilipenko, A. I. Zhebentyaev and A. I. Voikova, *ibid.*, 1974, **29**, 1854.
128. E. N. Pashchenko, P. P. Dubinskaya, V. F. Mal'tsev and N. P. Volkova, *Zavodsk. Lab.*, 1974, **40**, 1430.
129. A. G. Fogg, D. R. Marriot and D. T. Burns, *Analyst*, 1970, **95**, 848.
130. *Idem, ibid.*, 1970, **95**, 854.
131. Z. G. Golubtsova and L. I. Lebedeva, *Vestn. Leningrad. Univ., Fiz. Khim.*, 1974, 152.
132. S. B. Savvin, E. G. Namvrina and R. S. Tramm, *Zh. Analit. Khim.*, 1972, **27**, 108.
133. A. M. Lukin, N. A. Kaslina, V. I. Fadeeva and G. S. Petrova, *Vestn. Mosk. Univ., Ser. II Khim.*, 1972, 247.
134. S. B. Savvin, E. G. Namvrina and L. A. Okhanova, *Zh. Analit. Khim.*, 1973, **28**, 1119.
135. V. A. Nazarenko, E. N. Poluektova and G. C. Shitareva, *ibid.*, 1973, **28**, 1966.
136. E. N. Poluektova and G. G. Shitareva, *ibid.*, 1972, **27**, 1301.
137. M. M. Tananaiko, O. N. Godovana and N. I. Verblyudova, *Visn. Kiivs'k. Univ., Ser. Kiz. Khim.*, 1969, 7.
138. E. N. Pashchenko and V. F. Mal'tsev, *Zavodsk. Lab.*, 1968, **34**, 12.
139. I. P. Shesterova, S. T. Talipov and V. K. Ismailova, *Uzbeksk. Khim. Zh.*, 1973, 12.
140. A. I. Busev and T. A. Sokolova, *Zh. Analit. Khim.*, 1968, **23**, 1348.
141. L. I. Lebedeva, Z. G. Golubtsova and N. G. Yanklovich, *J. Anal. Chem. USSR*, 1971, **26**, 1754.
142. S. Y. Shnaiderman and A. S. Gumen, *Zh. Analit. Khim.*, 1972, **27**, 2060.
143. J. Cardenas and L. E. Mortenson, *Anal. Biochem.*, 1974, **60**, 372.
144. B. F. Quin and R. R. Brooks, *Anal. Chim. Acta*, 1972, **58**, 301.
145. S. Kallmann, E. W. Hobart and H. K. Oberthin, *Talanta*, 1968, **15**, 982.
146. K. Kawabuchi and R. Kuroda, *ibid.*, 1970, **17**, 67.
147. R. E. Stanton, *Proc. Australasian. Inst. Mining. Met.*, 1970, (236), 59.
148. K. Kawabuchi and R. Kuroda, *Anal. Chim. Acta*, 1969, **46**, 23.
149. B. M. Dobkina and G. B. Sazikova, *Zavodsk. Lab.*, 1968, **34**, 32.
150. A. K. Chakrabarti and S. P. Bag, *Anal. Chim. Acta*, 1972, **59**, 225.
151. E. Hoyer, H. Mueller and H. Wagler, *Wiss. Z. Karl-Marx-Univ. Leipzig*, 1972, **21**, 47.
152. V. P. Antonovich, T. P. Yakovleva, E. M. Nevskaya and V. A. Nazarenko, *Zh. Analit. Khim.*, 1974, **29**, 2341.
153. O. A. Tataev, K. N. Bagdasarov, S. A. Akhmedov, K. A. Mirzaeva, K. G. Buganov and E. A. Yarysheva, *Izv. Sev.-Kavk. Nauchn. Tsentra Vyssh. Shk., Ser. Estestv. Nauk*, 1973, 30.
154. J. Vrbský and J. Fogl, *Collection Czech. Chem. Commun.*, 1970, **35**, 2497.
155. I. Mori, *Bunseki Kagaku*, 1974, **23**, 291.
156. G. A. Parker and D. F. Boltz, *Anal. Lett.*, 1968, **1**, 679.
157. J. C. Guyon and J. Y. Marks, *Anal. Chem.*, 1968, **40**, 837.
158. B. E. Reznik, G. M. Ganzburg and G. V. Mal'tseva, *Zh. Analit. Khim.*, 1968, **23**, 1848.
159. G. V. Mal'tseva and B. E. Reznik, *ibid.*, 1973, **28**, 1751.
160. Y. Shijo and T. Takeuchi, *Bunseki Kagaku*, 1973, **22**, 1341.
161. M. Bartušek, *Collection Czech. Chem. Commun.*, 1973, **38**, 2255.
162. S. Rani and S. K. Banerji, *Indian J. Chem.*, 1971, **9**, 495.

163. F. Capitan-Garcia and A. Guiaraum, *Rev. Univ. Ind. Santander*, 1970, 27.
164. F. G. Zharovskii and D. O. Gorina, *J. Anal. Chem. USSR*, 1971, **26**, 666.
165. A. Izquierdo and G. Lacort, *Inform. Quim. Anal.*, 1970, **24**, 208.
166. V. A. Nazarenko and E. N. Poluektova, *Zh. Analit. Khim.*, 1971, **26**, 1331.
167. A. I. Busev, V. M. Byr'ko, N. P. Kovtun and L. G. Karalashvili, *ibid.*, 1970, **25**, 237.
168. L. A. Nenasheva, *Nauch. Tr. Vses. Nauch-Issled. Proekt. Inst. Tugoplavk. Metal. Tverd. Splavov*, 1973, 121.
169. M. Pleniceanu and O. Rusu, *Revue Roum. Chim.*, 1975, **20**, 267.
170. T. M. Urusova, *Gigiena i Sanit.*, 1969, 72.
171. S. A. Strel'tsova and M. M. Radzhabova, *Zavodsk. Lab.*, 1968, **34**, 277.
172. J. L. Girardin and M. Puyo, *Bull. Cent. Rech. Pau*, 1970, **4**, 247.
173. E. G. Lillie and L. P. Greenland, *J. Res. U.S. Geol. Surv.*, 1973, **1**, 555.
174. D. R. Marriott, A. G. Fogg and D. T. Burns, *Proc. Soc. Anal. Chem.*, 1970, **7**, 145.
175. A. G. Fogg, T. J. Jarvis, D. R. Marriot and D. T. Burns, *Analyst*, 1971, **96**, 475.
176. C. Toussaint and G. Cattin, *Analusis*, 1972, **1**, 347.
177. V. N. Basov, P. K. Agasyan and T. N. Testoedova, *Zavodsk Lab.*, 1974, **40**, 924.
178. D. I. Eristavi, V. D. Eristavi and A. G. Daneliya, *Zh. Analit. Khim.*, 1971, **26**, 183.
179. E. A. Shpak, A. I. Samchuk and A. T. Pilipenko, *ibid.*, 1974, **29**, 938.
180. N. A. Polotebnova and L. M. Danilina, *Zavodsk. Lab.*, 1970, **36**, 261.
181. I. I. Kulev and E. F. Speranskaya, *Zh. Analit. Khim.*, 1967, **22**, 1371.
182. D. I. Kurbatov and S. B. Il'kova, *ibid.*, 1974, **29**, 1430.
183. Y. Arragon, *Report* 1973, CEA-R-4475.
184. T. A. O'Shea and G. A. Parker, *Anal. Chem.*, 1972, **44**, 184.
185. H. Berge and H. Ringstorff, *Anal. Chim. Acta*, 1971, **55**, 193.
186. V. G. Miskar'yants and L. A. Nikitina, *Zavodsk. Lab.*, 1972, **38**, 1467.
187. A. Svehla, *Chem. Listy*, 1974, **68**, 1075.
188. M. Novotny and K. Oulehla, *Hutnicke Listy*, 1968, **23**, 892.
189. A. I. Sherstyuk, V. N. Vovk and L. I. Vlasova, *Zavodsk. Lab.*, 1974, **40**, 1471.
190. F. Burriel-Marti and A. Herrero, *Quim. Anal.*, 1974, **28**, 15.
191. S. Mitsuyasu, *Bunseki Kagaku*, 1970, **19**, 207.
192. S. M. Ku, *Hua Hsueh*, 1971, 85.
193. F. Malamand, *Analusis*, 1972, **1**, 420.
194. A. D. Khlystova and E. T. Kabesheva, *Vestn. Mosk. Univ., Ser. II. Khim.*, 1971, **12**, 98.
195. T. Matsumura and T. Mizuno, *Bunseki Kagaku*, 1969, **18**, 1439.
196. N. I. Tarasevich, A. D. Khlystova and E. I. Shuvalova, *Zh. Analit. Khim.*, 1973, **28**, 1419.
197. B. Y. Kaplan, Z. P. Kirillova, Y. I. Merisov, M. G. Nazarova, E. I. Petrova and G. S. Skripkin, *Zavodsk. Lab.*, 1974, **40**, 256.
198. M. Matherny and N. Pliesovska, *Chem. Zvesti*, 1973, **27**, 327.
199. N. I. Tarasevich, A. D. Khlystova and E. I. Shuvalova, *Vestn. Mosk. Univ., Ser. II. Khim.*, 1973, **14**, 204.
200. A. D. Khlystova and N. I. Tarasevich, *Zavodsk. Lab.*, 1968, **34**, 1327.
201. E. I. Shuvalova, A. D. Khlystova, N. I. Tarasevich and N. G. Gongalyuk, *Vestn. Mosk. Univ., Ser. II. Khim.*, 1973, (4), 490.
202. O. P. Turulina and N. F. Zakhariya, *Zh. Analit. Khim.*, 1973, **28**, 1754.
203. A. C. Knott, K. Kinson and C. B. Belcher, *Anal. Chim. Acta*, 1972, **59**, 119.
204. R. J. Muzik and O. A. Vita, *ibid.*, **57**, 331.
205. E. P. Moseeva, G. P. Pinchuk, A. B. Sokolov, A. G. Karabash and S. I. Peizulaev, *Zh. Analit. Khim.*, 1974, **29**, 1589.
206. A. Heres, *Report* 1973, CEA-R-4433.
207. F. Alvarez-Aldaun and C. Capdevila Perez, *An. Quim.*, 1974, **70**, 601.
208. C. E. Pepper and G. R. Blank, *U.S. At. Energy Comm. Rept.*, NLCO-1105, 1973.
209. R. L. Slyusareva, L. I. Kondrat'eva and S. I. Peizulaev, *Zavodsk. Lab.*, 1973, **39**, 1465.
210. W. E. Rippetoe, E. R. Johnson and T. J. Vickers, *Anal. Chem.*, 1975, **47**, 436.
211. E. I. Shuvalova, A. D. Khlystova, N. I. Tarasevich and N. G. Gongalyuk, *Zh. Analit. Khim.*, 1974, **29**, 384.
212. N. I. Tarasevich, A. D. Khlystova and E. I. Shuvalova, *ibid.*, 1971, **26**, 1958.
213. C. Alvarez-Herrero, F. Burriel-Marti and M. A. Palacios Corvillo, *Inform. Quim. Anal.*, 1972, **26**, 126.
214. P. W. Boumans, *Anal. Chem.*, 1972, **44**, 1219.
215. M. P. Lebedinskaya and V. T. Chuiko, *Zh. Analit. Khim.*, 1973, **28**, 2413.
216. V. G. Tiptsova-Yakovleva and A. G. Dvortsan, *Zavodsk. Lab.*, 1971, **37**, 676.
217. T. M. Moroshkina, *Trudy Komis. po Analit. Khim.*, 1968, **16**, 62.
218. G. F. Kirkbright, A. Semb and T. S. West, *Talanta*, 1968, **15**, 441.
219. G. F. Kirkbright, M. Sargent and T. S. West, *ibid.*, 1969, **16**, 245.
220. M. D. Amos, P. A. Bennett and K. G. Brodie, *Resonance Lines*, 1970, **2**, 3.
221. R. M. Dagnall, B. Fleet, T. H. Risby and D. R. Deans, *Talanta*, 1971, **18**, 155.
222. K. W. Busch, N. G. Howell and G. H. Morrison, *Anal. Chem.*, 1974, **46**, 575.
223. P. E. Thomas and W. F. Pickering, *Talanta*, 1971, **18**, 127.
224. M. Marinkovic and T. J. Vickers, *Appl. Spectry.*, 1971, **25**, 319.
225. R. C. Rooney and C. G. Pratt, *Analyst*, 1972, **97**, 400.
226. A. M. Saltykova, N. K. Davidovich and S. G. Melamed, *Zh. Analit. Khim.*, 1972, **27**, 1216.
227. G. G. Welcher and O. H. Kriege, *At. Absorption Newsletter*, 1970, **9**, 61.
228. I. G. Yudelevich and V. P. Shaburova, *Chem. Anal. Warsaw*, 1974, **19**, 941.
229. J. L. Jimenez Seco and A. G. Coedo, *Rev. Met. Madrid*, 1970, **6**, 64.
230. D. M. Knight and M. K. Pyzyna, *At. Absorption Newsletter*, 1969, **8**, 129.
231. B. F. Quinn and R. R. Brooks, *Anal. Chim. Acta*, 1973, **65**, 206.
232. E. Keller and M. L. Parsons, *At. Absorption Newsletter*, 1970, **9**, 92.
233. R. W. Morrow, *U.S. At. Energy Comm. Rept.*, Y-1812, 1972.
234. M. J. Gallagher, *Proc. 9th Commonw. Min. Metall. Congr. (1969)*, 1970, **2**, 691.
235. P. G. Burkhalter and H. E. Marr, *Intern. J. Appl. Radiation Isotopes*, 1970, **21**, 395.
236. F. L. Chan and W. B. Jones, *Advan. X-Ray Anal.*, 1972, **15**, 209.
237. J. Kuusi, M. Virtanen and P. Jauho, *Nucl. Technol.*, 1972, **13**, 216.
238. G. J. Wenk and L. R. Wilkinson, *AMDEL (Aust. Miner. Develop. Lab.) Bull.*, 1974, **17**, 1.
239. E. I. Zaitsev, E. M. Margolin, O. P. Polytsya, V. V.

Pan'kin and K. I. Shchekin, *Zh. Analit. Khim.*, 1974, **29**, 668.
240. A. P. Ochkur, E. P. Leman, V. V. Kotel'nikov, V. M. Ivanov and Y. P. Yanshevskii, *At. Energ.*, 1973, **35**, 204.
241. V. I. Bochenin, *Zavodsk. Lab.*, 1973, **39**, 1351.
242. Z. S. Karamanova and N. S. Bochvarov, *Isotopenpraxis*, 1974, **10**, 100.
243. H. Hughes and P. H. Scholes, *Br. Steel Corp. Open Rept*, GS/TECH/V/6/72/C.
244. H. M. Lueschow and H. P. Schaefer, *Z. Anal. Chem.*, 1970, **250**, 317.
245. D. A. Pantony and P. W. Hurley, *Analyst*, 1972, **97**, 497.
246. F. Maeda and T. Hayasaka, *Bunseki Kagaku*, 1970, **19**, 1036.
247. K. Ohls, J. Brauner and P. Friedhoff, *Z. Anal. Chem.*, 1973, **265**, 342.
248. J. M. Griffiths and H. R. Whitehead, *NPL Rept. Chem.*, 1972, (16).
249. B. Zitnansky, *Radioisotopy*, 1972, **13**, 1135.
250. H. Schneider, *Erzmetall.*, 1969, **22**, 338.
251. T. Nakajima, Y. Ouchi and K. Kato, *Bunseki Kagaku*, 1971, **20**, 330.
252. B. Brachfeld, *Appl. Spectry.*, 1974, **28**, 449.
253. K. G. Carr-Brion and K. W. Payne, *Analyst*, 1968, **93**, 441.
254. J. M. McCall, D. E. Leyden and C. W. Blount, *Anal. Chem.*, 1971, **43**, 1324.
255. P. Dumesnil, *Report* 1972, CEA-N-1593.
256. G. Weber and M. Guillaume, *J. Radioanal. Chem.*, 1970, **5**, 425.
257. N. N. Krasmov, Y. G. Sevastyanov, I. O. Konstantinov, V. G. Vinogradova, and V. V. Malukhin, *ibid.*, 1973, **16**, 395.
258. S. Gangadharan, S. Yegnasubramanian, S. C. Misra and U. C. Gupta, *ibid.*, 1975, **24**, 57.
259. G. I. Borisov, A. M. Demidov and E. A. Zakharov, *At. Energ.*, 1969, **26**, 14.
260. K. Heydorn, *J. Radionanal. Chem.*, 1972, **10**, 245.
261. T. A. Yankovskaya, E. M. Lobanov and M. M. Usmanova, *Zh. Analit. Khim.*, 1973, **28**, 2311.
262. R. A. Nadkarni and B. C. Haldar, *J. Radioanal. Chem.*, 1971, **8**, 45.
263. N. K. Baishya and R. B. Heslop, *Anal. Chim. Acta*, 1971, **53**, 87.
264. L. T. McClendon and J. R. DeVoe, *Anal. Chem.*, 1969, **41**, 1454.
265. A. R. Byrne, *Yugosl. At. Energy Comm. Rept.*, IJS-R-596, 1971.
266. A. Z. Miklishanskii, Y. A. Leikin, Y. V. Yakovlev and B. V. Savel'ev, *Zh. Analit. Khim.*, 1974, **29**, 1284.
267. R. Dams, J. A. Robbins, K. A. Rahn and J. W. Winchester, *Anal. Chem.*, 1970, **42**, 861.
268. M. Miyamaru and F. W. Lima, *Relat. Inst. Energ. Atom. S. Paulo, IEA*-326, 1974.
269. H. Vogg and R. Haertel, *Z. Anal. Chem.*, 1973, **267**, 257.
270. A. Barwinski, A. Buczek, L. Gorski, J. Janczyszyn, S. Kwiecinski, L. Loska and M. Geisler, *Isotopenpraxis*, 1968, **4**, 15.
271. H. Jaskolska, L. Rowinska and M. Radwan, *J. Radioanal. Chem.*, 1971, **8**, 235.
272. *Idem, ibid.*, 1971, **7**, 29.
273. H. Zwittlinger, *ibid.*, 1973, **14**, 147.
274. H. Jaskolska, L. Rowinska, L. Walis and M. Radwan, *ibid.*, 1973, **13**, 41.
275. C. S. P. Iyer and R. Parthasarathy, *Radiochem. Radioanal. Lett.*, 1972, **12**, 201.
276. I. N. Plaksin, E. I. Andrievskii, G. A. Ivashchenko, G. I. Mikhailov and L. P. Starchik, *Nauch. Soobshch. Inst. Gorn. Dela. Moscow*, 1969, **47**, 18.
277. D. Reed and D. A. Hilton, *Radiochem. Radioanal. Lett.*, 1970, **5**, 293.
278. C. De Wispelaere, J. P. Op de Beeck and J. Hoste, *Anal. Chim. Acta*, 1973, **64**, 321.
279. E. Havranek, A. Bumbalová and M. Herchl, *Chem. Listy*, 1973, **67**, 290.
280. C. De Wispelaere, J. P. Op de Beeck and J. Hoste, *Anal. Chim. Acta*, 1974, **70**, 1.
281. N. Lavi, *ibid.*, 1975, **74**, 269.
282. M. Fedoroff, *Bull. Soc. Chim. France*, 1970, 1233.
283. G. I. Shmanenkova, V. I. Firsov, V. P. Shchelkova and M. N. Shchulepnikov, *Zh. Analit. Khim.*, 1973, **28**, 323.
284. G. V. Sukhov and V. I. Firsov, *Zavodsk. Lab.*, 1972, **38**, 297.
285. V. Krivan, *Anal. Chem.*, 1975, **47**, 469.
286. J. N. Barrandon, P. Benaben, J. L. Debrun and M. Valladon, *Anal. Chim. Acta*, 1974, **73**, 39.
287. N. Tamura, *Radiochem. Radioanal. Lett.*, 1974, **18**, 135.
288. S. Kodiri, I. Abrams, L. Pelekis and L. P. Starchik, *Zavodsk. Lab.*, 1973, **39**, 39.
289. O. Abbosov, I. Abrams, L. Pelekis and L. P. Starchik, *Latr. PSR Zinat. Akad. Vestis, Fiz. Tekh. Zinet. Ser*, 1972, 18.
290. Z. Randa, J. Benada, J. Kuncir and M. Vobecky, *Radiochem. Radioanal. Lett.*, 1970, **3**, 227.
291. O. Abbosov, I. Abrams, A. Babaev, L. Pelekis and L. P. Starchik, *Dokl. Akad. Nauk Tadzh. SSR*, 1972, **15**, 18.
292. O. Johansen and E. Steinnes, *Talanta*, 1970, **17**, 407.
293. H. Zinner, R. Henkelmann and H. Staerk, *Radiochem. Radioanal. Lett.*, 1972, **10**, 191.
294. N. V. Bagdavadze and L. M. Mosulishvili, *J. Radionanal. Chem.*, 1975, **24**, 65.
295. V. G. Lambrev, G. G. Akalaev and V. V. Nekrasov, *Radiochem. Radioanal. Lett.*, 1971, **6**, 133.
296. G. Lunde, *J. Sci. Food Agr.*, 1968, **19**, 432.
297. M. Neuburger and A. Fourcy, *J. Radioanal. Chem.*, 1968, **1**, 289.
298. B. A. Thompson and E. C. Miller, *J. Res. Natl. Bur. Std., A*, 1971, **75**, 429.
299. E. N. Gil'bert and V. A. Pronin, *Izv. Sibirsk. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1969, 168.
300. D. Lafeuille and D. Roche, *Analusis*, 1973, **2**, 207.
301. F. De Corte, A. Speecke and J. Hoste, *J. Radioanal. Chem.*, 1971, **9**, 9.
302. V. Krivan, D. L. Swindle and E. A. Schweikert, *Anal. Chem.*, 1974, **46**, 1626.
303. W. Maenhaut, F. Adams and J. Hoste, *J. Radioanal. Chem.*, 1973, **14**, 295.
304. A. A. Uzbekov, G. G. Akalaev, I. V. Riskin and V. A. Likhobabin, *Zavodsk. Lab.*, 1972, **38**, 816.
305. R. Neirinckx, F. Adams and J. Hoste, *Anal. Chim. Acta*, 1969, **48**, 1.
306. *Idem, ibid.*, 1969, **46**, 165.
307. *Idem, ibid.*, 1968, **43**, 369.
308. G. F. Clemente and G. C. Mastinu, *J. Radioanal. Chem.*, 1974, **20**, 707.
309. A. A. Abdullaev, A. S. Zakhidov and P. K. Nishanov, *Izv. Akad. Nauk Uz. SSR, Ser. Fiz.-Mat. Nauk*, 1968, 60.
310. T. P. Hadjiioannou and C. G. Valkana, *Chim. Chronika, Athens, Greece*, 1967, **32**, 89.
311. A. Altinata and B. Pekin, *Anal. Lett.*, 1973, **6**, 667.
312. E. S. Omarova, E. F. Speranskaya and M. T. Kozlovskii, *Zh. Analit. Khim.*, 1968, **23**, 1826.
313. V. K. Pavlova and R. N. Voevutskaya, *ibid.*, 1974, **29**, 731.

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SENSITIVITY CALIBRATION FOR THE SPARK-SOURCE MASS-SPECTROMETRIC ANALYSIS OF ALUMINIUM AND ITS ALLOYS

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Summary—The analysis of aluminium and its alloys has been studied with use of five standards from Johnson Matthey and ten aluminium alloys from Aluminium Pechiney. The relative sensitivity coefficients for Mg, Al, Si, Ti, Cr, Mn, Ni, Cu, Zn, Sn and Pb were determined *vs.* iron as an internal standard. They were obtained, by using electrical detection, with a mean precision of 10% relative standard deviation. The sensitivity coefficients measured appear to be independent of the elemental concentration, but for some elements, especially the more volatile ones, remarkable changes were noticed when sparking conditions were altered and when the electrode temperature was changed by cooling with liquid nitrogen.

Spark-source mass-spectrometric analysis requires sensitivity calibration with standard reference materials. The relative sensitivity coefficient (S_R) for an element x in the aluminium matrix is defined here as the ratio of the concentration of this element x and an internal standard y as determined by mass spectrometry, divided by the ratio of the certified concentrations of x and y in the reference materials used. Iron, which is present in all the samples analysed, was chosen as the internal standard. This allowed an easy comparison of the results with previous studies of other matrices.[1,2]

Several authors[3–15] have studied the analysis of aluminium samples by spark-source mass-spectrometry; nearly all of them used photoplate detection. In this paper, photoplate detection was used for qualitative analysis as its higher resolution makes it easier to detect interferences; the quantitative analysis, however, was performed by using electrical detection in the more precise magnetic peak-switching mode.

EXPERIMENTAL

Apparatus

The instrument used is a double-focusing mass spectrometer with Mattauch-Herzog geometry with a spherical electric field and equipped with a radiofrequency spark source (JMS-01-BM-2, JEOL, Tokyo). The electrical detection system (MS-ED-01, JEOL) has two modes of operation: magnetic scanning and magnetic peak-switching. The apparatus has been described in detail elsewhere.[1]

Samples

Five Johnson Matthey aluminium standards (AA 1–AA 5) were analysed. They are prepared for use as standards in the spectrochemical analysis of unalloyed aluminium and are in the form of extruded rods 140 mm long and 6 mm in diameter. Table 1 lists the certified concentrations. The precision of the values quoted was not indicated in the analysis report. It was assumed that the values listed do not deviate from the "true" concentration by more than ±1 in the last significant figure reported and that the standard deviation is half this uncertainty.

From the various standard samples manufactured by Aluminium Pechiney for industrial spectrographic analysis, ten samples were chosen which represent three types of alloy: Al–Si–Cu, Al–Cu and Al–Mn. They were available as discs of 55 mm diameter and 4 mm thickness. The composition of these alloys is indicated in Table 2. The intervals indicated are the 95% confidence limits.

Sample preparation

The samples were processed into electrodes shaped as thin plates (10 × 2 × 1 mm). The Aluminium Pechiney samples were cast in moulds and it was feared that concentration gradients might occur, especially near the surfaces. A minimum of 1 mm was therefore discarded from the edges. The ends of the electrodes to be sparked edge to edge were ground flat with corundum paper. The electrodes were then degreased with trichloroethylene (*p.a.*) and washed with acetone (*p.a.*) and distilled water. They were sparked for at least 15 min before starting the measurements.

In preliminary trials the electrodes were also etched in hydrofluoric acid but selective etching was noticed; better results were obtained when no acid etching was performed.

Mass-spectrometric procedure

It was found that the following conditions ensured stable sparking between aluminium electrodes: spark-source voltage 30 kV, pulse length 20 μsec, repetition frequency 1 kHz. With the conditions optimized for steel samples (65 kV, 20 μsec, 3 kHz) very violent sparking occurred and the electrodes soon fused together. Furthermore, the ion source, and especially the accelerating and the object slits, became contaminated. Nevertheless, in order to examine the in-

Table 1. Composition of the Johnson Matthey aluminium standards (% *w/w*)

Element	AA1	AA2	AA3	AA4	AA5
Si	0.06	0.10	0.18	0.32	0.59
Ti	0.002	0.005	0.011	0.02	0.06
Mn	0.002	0.007	0.018	0.07	0.15
Fe	0.055	0.10	0.19	0.76	0.39
Ni	0.0025	0.004	0.010	0.02	0.05
Cu	0.0015	0.006	0.020	0.065	0.15
Zn	0.002	0.005	0.010	0.025	0.06

Table 2. Composition of the aluminium alloy standards from Aluminium Pechiney (% w/w)

	Al–Si–Cu							Al–Mn		
	A-S10U4	A-S12U			Al–Cu			A-M4		
Element	6604/88	8306/293	8308/175	8317/231	5042/114	5044/88	5054/129	7533/184	7535/146	7538/93
Mg	0.0150 ±0.0020	0.580 ±0.020	0.290 ±0.015	0.160 ±0.010	0.15 ±0.02	0.30 ±0.02		0.1600 ±0.0150	0.1250 ±0.0100	0.0620 ±0.0050
Si	10.85 ±0.40	8.35 ±0.20	11.15 ±0.35	13.95 ±0.40	0.30 ±0.05	0.60 ±0.07	0.07 ±0.01	0.89 ±0.05	0.69 ±0.05	0.39 ±0.03
Ti	0.100 ±0.005	0.100 ±0.007	0.180 ±0.010	0.052 ±0.003	0.0030 ±0.0005	0.104 ±0.006	0.200 ±0.010	0.3200 ±0.0300	0.2100 ±0.0150	0.1000 ±0.0070
Cr	0.0105 ±0.0006							0.1080 ±0.0050	0.0570 ±0.0060	0.0220 ±0.0020
Mn	0.1040 ±0.0050	0.185 ±0.010	0.335 ±0.015	0.630 ±0.025	0.31 ±0.02	0.110 ±0.005	0.0075 ±0.0010	2.00 ±0.10	3.90 ±0.15	5.70 ±0.25
Fe	0.360 ±0.018	1.25 ±0.05	0.78 ±0.04	0.32 ±0.02	0.35 ±0.02	0.58 ±0.03	0.21 ±0.01	0.320 ±0.025	0.615 ±0.040	0.970 ±0.040
Co										0.0010 ±0.0002
Ni	0.105 ±0.005	0.140 ±0.005	0.049 ±0.002	0.330 ±0.010	0.43 ±0.03	0.25 ±0.02		0.0015 ±0.0003	0.0530 ±0.0030	0.0980 ±0.0080
Cu	3.02 ±0.15	1.26 ±0.05	0.78 ±0.03	0.30 ±0.01	7.10 ±0.20	8.90 ±0.30	11.00 ±0.30	0.0370 ±0.0020	0.1600 ±0.0100	0.2500 ±0.0150
Zn	0.0125 ±0.0008	0.780 ±0.030	0.460 ±0.020	0.160 ±0.007	2.95 ±0.15	1.00 ±0.05	0.10 ±0.01	0.1450 ±0.0050	0.1000 ±0.0050	0.0540 ±0.0040
Sn	0.0115 ±0.0015	0.270 ±0.015	0.100 ±0.007	0.029 ±0.003			0.096 ±0.006	0.1020 ±0.0070	0.0620 ±0.0040	0.0190 ±0.0020
Pb	0.060 ±0.004	0.345 ±0.020	0.158 ±0.012	0.063 ±0.003	0.35 ±0.03	0.15 ±0.01	0.010 ±0.002	0.1100 ±0.0100	0.0860 ±0.0100	0.0380 ±0.0060

fluence of sparking conditions on the results obtained, eight samples were also sparked under these conditions. The ion-accelerating voltage was always kept at 29 kV.

For peak-switching, an integrated monitor charge of 0.9 nC was collected per measurement in about 15 sec. The object slit was adjusted to a width of 100 μm and the α- and β-slits (in front of and behind the electrostatic analyser) to 2.0 mm. The collector slit was wider than in previous studies,[1,2] namely 1.2 mm. This allowed the measurement of the complete isotopic ion beam and the reduction of the influence of magnetic field instabilities. No extra interferences were caused as the spectra were not too complicated.

When photoplate detection was used, the slits were adjusted as follows: main slit 20 μm, α-slit 0.3 mm and β-slit 0.4 mm.

RESULTS AND DISCUSSION

Spectral interferences

To detect spectral interferences, the spectra were first recorded under conditions of high mass-resolution (about 10000), on ion-sensitive plates. The interferences that were observed are listed in Table 3. The

Table 3. Spectral interferences in the aluminium spectra studied

Element	Isotope	Interference	Samples for which interference occurred	Samples for which interference was corrected by using the species in brackets	
Mg	24/25	$^{48}Ti^{2}/^{50}Ti^{2}$	6604	7533, 7535, 7538	($^{47,49}Ti^{2}$)
	26	$^{52}Cr^{2}$	6604, 7533, 7535, 7538		
Si	28	$^{56}Fe^{2}$	AA1-5, 5045	5042, 5044, 7535, 7538	($^{57}Fe^{2}$)
	29	$^{58}Ni^{2}$	5042, 5044, 7538	AA1-5, 5045, 7535	($^{61}Ni^{2}$)
	30	$^{60}Ni^{2}$	5042, 5044	AA1-5, 5045, 7535, 7538	($^{61}Ni^{2}$)
Ti	50	^{50}Cr	7535, 7538		
Cr	50	^{50}Ti	6604, 7533, 7535, 7538		
Fe	54	$^{27}Al_2$	all samples		
	58	^{58}Ni	all samples		
Co	59	$^{118}Sn^{2}$	7538		
Ni	58	^{58}Fe, $^{116}Sn^{2}$	AA1-5, 7533	6604, 8306, 8308, 7535, 7538	($^{56,57}Fe$, $^{117,119}Sn^{2}$)
	60	$^{120}Sn^{2}$	7533	6604, 8306, 8308, 7535, 7538	($^{117,119}Sn^{2}$)
	61	$^{122}Sn^{2}$	8306, 8308, 7535, 7535	6604	($^{117,119}Sn^{2}$)
	62	$^{124}Sn^{2}$	8306, 8308, 7533, 7535, 7538	6604, 7538	($^{117,119}Sn^{2}$)
	64	^{64}Zn	all samples		
Zn	64	^{64}Ni	6604, 8317, 7538		
	70	Al_2O	all samples		

Table 4. Experimentally determined S_R values for the Johnson Matthey aluminium standards

Element	AA1	AA2	AA3	AA4	AA5
Al	1.04 ± 0.05	0.95 ± 0.06	0.97 ± 0.05	0.96 ± 0.04	1.18 ± 0.07
Si	1.0 ± 0.1	0.88 ± 0.08	0.93 ± 0.09	0.96 ± 0.08	0.85 ± 0.06
Ti	2.0 ± 0.2	1.08 ± 0.09	1.5 ± 0.1	1.24 ± 0.07	1.24 ± 0.09
Mn	2.0 ± 0.1	1.34 ± 0.07	1.51 ± 0.08	1.46 ± 0.09	1.34 ± 0.09
Fe	1	1	1	1	1
Ni	0.75 ± 0.05	0.85 ± 0.06	0.81 ± 0.05	0.81 ± 0.04	0.78 ± 0.04
Cu	1.09 ± 0.08	0.59 ± 0.04	0.72 ± 0.06	0.80 ± 0.05	0.75 ± 0.05
Zn	2.4 ± 0.3	1.5 ± 0.1	1.6 ± 0.1	1.6 ± 0.1	1.7 ± 0.3

plus signs of the charge superscripts are omitted since all species mentioned are positive ions.

Nearly all elements had one or more interference-free isotopes. For the others, interferences below 20% were corrected for by using other spectral information for the interfering ion. Only magnesium in sample 6604, cobalt in 7538 and nickel in 7533, could not be determined by using magnetic peak-switching under the conditions selected.

Quantitative analysis

The five aluminium standards from Johnson Matthey and ten aluminium alloys from Aluminium Pechiney were analysed and the relative sensitivity coefficients were calculated for the certified elements. At least 80 integrations were carried out for each interference-free isotope at two or more times. The results were averaged and the corresponding standard deviations calculated. They are listed in Tables 4 and 5. The average precision of the measurements was 7.5% relative standard deviation for the Johnson Matthey samples. For the Aluminium Pechiney standards it was somewhat worse, namely 9%; when the results for the more volatile elements Mg, Sn and Pb were discarded, the average relative standard deviation was 8%.

There is fair agreement between the S_R values from the different standards except for lead in sample 5045. This sample was independently analysed by energy-dispersive X-ray fluorescence[16] and the concentration found was also considerably lower than the quoted value, namely 0.003 ± 0.001% instead of 0.010 ± 0.002%. Therefore, the result for lead in sample 5045 was excluded.

Average sensitivity coefficients for the analysis of aluminium and its alloys

The estimated relative errors of the certified values (Tables 1 and 2) differ widely. Several of them were quoted to only one significant figure. Therefore, the

Table 5. Experimentally determined S_R values for the aluminium alloy standards from Aluminium Pechiney (Fe: S_R = 1)

	Al–Si–Cu				Al–Cu			Al–Mn		
Element	6604	8306	8308	8317	5042	5044	5045	7533	7535	7538
Mg	*	3.5 ±0.6	3.8 ±0.5	3.6 ±0.5	2.4 ±0.3	3.0 ±0.3	†	2.5 ±0.2	3.1 ±0.3	3.5 ±0.5
Al	0.97 ±0.04	1.10 ±0.04	1.23 ±0.06	1.07 ±0.06	1.22 ±0.07	1.21 ±0.07	1.27 ±0.05	1.15 ±0.06	1.11 ±0.06	1.25 ±0.08
Si	0.75 ±0.06	0.77 ±0.05	0.85 ±0.04	0.76 ±0.06	1.0 ±0.1	0.87 ±0.09	1.1 ±0.1	0.85 ±0.05	0.77 ±0.05	0.9 ±0.1
Ti	1.4 ±0.1	1.66 ±0.08	1.7 ±0.1	1.7 ±0.1	2.4 ±0.2	1.7 ±0.1	1.7 ±0.1	1.64 ±0.08	1.7 ±0.1	1.6 ±0.1
Cr	1.5 ±0.1	†	†	†	†	†	†	1.51 ±0.09	1.6 ±0.1	1.7 ±0.1
Mn	1.7 ±0.2	1.6 ±0.1	1.8 ±0.1	1.6 ±0.1	1.3 ±0.1	1.43 ±0.09	1.2 ±0.1	1.39 ±0.08	1.46 ±0.09	1.6 ±0.1
Ni	0.67 ±0.05	0.80 ±0.08	0.80 ±0.08	0.75 ±0.05	0.69 ±0.07	0.68 ±0.07	†	*	0.65 ±0.07	0.74 ±0.07
Cu	0.65 ±0.05	0.72 ±0.05	0.71 ±0.05	0.59 ±0.05	0.59 ±0.04	0.60 ±0.06	0.58 ±0.04	0.62 ±0.04	0.58 ±0.04	0.69 ±0.05
Zn	2.2 ±0.2	1.9 ±0.3	2.2 ±0.3	1.8 ±0.2	1.8 ±0.2	2.2 ±0.2	1.5 ±0.2	2.0 ±0.2	2.2 ±0.2	2.0 ±0.2
Sn	2.8 ±0.3	2.7 ±0.3	3.5 ±0.4	1.7 ±0.2	†	†	1.6 ±0.2	2.2 ±0.3	2.0 ±0.2	2.4 ±0.3
Pb	3.2 ±0.5	3.9 ±0.7	4.9 ±0.8	2.7 ±0.4	2.7 ±0.3	2.2 ±0.3	(0.42)** ±0.06	3.5 ±0.4	2.6 ±0.3	4.1 ±0.7

* Interference (see Table 3).
† Not certified (see Table 2).
** Discarded (see text).

Table 6. Weighted average relative sensitivity coefficients for the analysis of aluminium and its alloys (Fe: $S_R = 1$)

Element	Relative sensitivity coefficient	Number of reference materials used
Mg	3.0 ± 0.4	8
Al	1.08 ± 0.06	15
Si	0.84 ± 0.08	15
Ti	1.6 ± 0.2	15
Cr	1.6 ± 0.1	4
Mn	1.5 ± 0.1	15
Ni	0.74 ± 0.07	13
Cu	0.67 ± 0.05	15
Zn	1.8 ± 0.2	15
Sn	2.2 ± 0.3	8
Pb	2.8 ± 0.4	9
Overall mean relative standard deviation 10%		

standard deviation of the S_R-values was calculated from

$$s = \frac{ab'}{b}\sqrt{\left(\frac{s_a}{a}\right)^2 + \left(\frac{s_b}{b}\right)^2 + \left(\frac{s_{b'}}{b'}\right)^2}$$

where a refers to the value measured by mass spectrometry, b and b' to the quoted values for the element determined and the reference element.

The weighted average of the measured sensitivity coefficients and the corresponding standard deviation were then calculated from

$$\bar{S}_R = \frac{\Sigma(S_{R_i}/s_i^2)}{\Sigma(1/s_i^2)} \quad \text{and} \quad s = \frac{\sqrt{N}}{\sqrt{\Sigma(1/s_i^2)}}.$$

The results are listed in Table 6. The overall mean relative standard deviation was 10%. This corresponds to the precision previously found for iron and steel samples[1] and is better than that found for copper samples.[2] It is an indication of the satisfactory homogeneity of the samples used in this work. A systematic survey showed no evidence that the relative sensitivity coefficients vary with the elemental concentration. For all elements, the slope of the most probable straight line fitted through the data points did not differ significantly from zero. By way of example, Fig. 1 shows the dependence of S_R on concentration for manganese and copper, the two elements with the largest concentration range in the samples studied. The exceptionally large uncertainty in the S_R value corresponding to the lowest manganese concentration is almost completely due to the uncertainty in the certified value, for which one significant figure (0.02% w/w) was given.

All the elements determined in this work, except magnesium and titanium, were previously determined in copper samples.[2] There is a fair agreement between the S_R values found, except for zinc, for which the sensitivity was significantly higher in aluminium than in copper. It was noticed, however, that the sensitivity coefficient of zinc in aluminium samples depended on the sparking conditions.

Influence of the sparking conditions

Eight of the samples were analysed as described above but with other sparking conditions, namely: spark-source voltage 65 kV (instead of 30 kV), repetition frequency 3 kHz (instead of 1 kHz), pulse length unchanged at 20 μsec. The results are listed in Table 7.

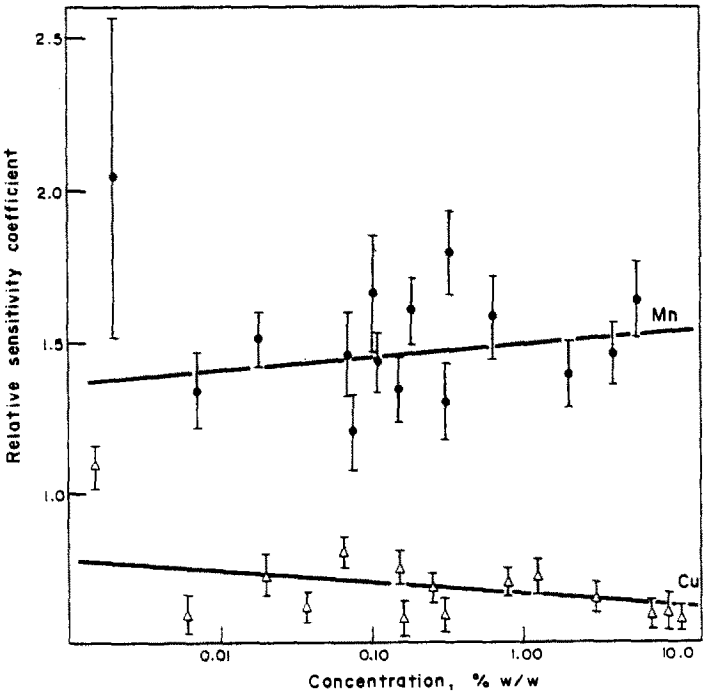


Fig. 1. Relative sensitivity coefficients of manganese and copper as a function of their concentration in the aluminium samples.

Table 7. Relative sensitivity coefficients for spark-source voltage 65 kV, repetition frequency 3 kHz and pulse length 20 μsec. (Fe: $S_R = 1$)

Element	AA-3	AA-4	AA-5	8306	8317	5042	7535	7538	Weighted average
Mg				6 ± 1	8 ± 1	7 ± 1	7.7 ± 0.7	9 ± 1	7 ± 1
Al	1.30 ± 0.05	1.23 ± 0.06	1.29 ± 0.08	1.40 ± 0.06	1.3 ± 0.1	1.4 ± 0.1	1.34 ± 0.08	1.46 ± 0.09	1.32 ± 0.08
Si	0.91 ± 0.08	1.00 ± 0.08	0.81 ± 0.06	0.83 ± 0.06	0.87 ± 0.07	1.2 ± 0.1	0.79 ± 0.06	1.0 ± 0.1	0.87 ± 0.08
Ti	1.5 ± 0.1	1.3 ± 0.1	1.3 ± 0.1	1.5 ± 0.1	1.5 ± 0.1	2.6 ± 0.3	1.4 ± 0.1	1.4 ± 0.1	1.5 ± 0.2
Cr							1.7 ± 0.1	1.8 ± 0.1	1.7 ± 0.2
Mn	2.0 ± 0.1	1.9 ± 0.1	1.6 ± 0.1	2.1 ± 0.1	2.0 ± 0.2	1.6 ± 0.2	1.9 ± 0.1	2.0 ± 0.2	1.9 ± 0.2
Ni	0.77 ± 0.05	0.75 ± 0.05	0.74 ± 0.04	0.69 ± 0.08	0.63 ± 0.04	0.67 ± 0.06	0.68 ± 0.07	0.71 ± 0.07	0.69 ± 0.07
Cu	0.72 ± 0.06	0.75 ± 0.05	0.74 ± 0.05	0.73 ± 0.06	0.62 ± 0.06	0.59 ± 0.05	0.65 ± 0.05	0.71 ± 0.06	0.69 ± 0.06
Zn	4.1 ± 0.5	3.6 ± 0.4	2.0 ± 0.4	3.8 ± 0.7	3.5 ± 0.5	2.5 ± 0.5	5.6 ± 0.7	4.2 ± 0.6	3.4 ± 0.5
Sn				3.7 ± 0.6	2.2 ± 0.3		4.4 ± 0.6	3.1 ± 0.6	2.9 ± 0.4
Pb				5.2 ± 0.9	3.4 ± 0.4	3.4 ± 0.9	5.9 ± 0.9	7 ± 2	4.1 ± 0.8

Table 8. Average ratio of the relative sensitivity coefficients for two different sparking conditions

Element	Δ b.p., °C	Δ m.p., °C	$S_R^{(2)}/S_R^{(1)}$*
Zn	−1843	−1115	2.0 ± 0.5
Mg	−1660	−886	2.4 ± 0.4
Pb	−1010	−1207	1.6 ± 0.4
Mn	−788	−291	1.27 ± 0.06
Sn	−480	−1303	1.5 ± 0.4
Si	−395	−125	1.06 ± 0.07
Al	−283	−875	1.21 ± 0.09
Cu	−183	−452	1.02 ± 0.05
Cr	−78	+322	1.03†
Ni	−18	−82	0.94 ± 0.07
Fe	0	0	1
Ti	537	125	1.0 ± 0.1

* $S_R^{(1)}$ = spark-source voltage 30 kV, repetition frequency 1 kHz, $S_R^{(2)}$ = spark-source voltage 65 kV, repetition frequency 3 kHz.

† Present in only two of the samples.

Δ b.p. = b.p. (element)—b.p.(Fe); Δ m.p. = m.p. (element —m.p.(Fe).

The precision decreased to 12% r.s.d. for the new sparking conditions, from 10% because violent sparking occurred and the electrodes often fused together. The physical appearance of the electrodes under both sparking conditions was different: after a normal sparking cycle individual craters were apparent, whereas after the changed sparking conditions no craters were visible, suggesting that the electrode surface had been partially melted.

Remarkable changes in the sensitivity coefficients were observed, especially for the more volatile elements magnesium and zinc. To exclude the influence of the uncertainty in the quoted values (Tables 1 and 2), the ratio of the measured S_R values for the two different sparking conditions was calculated. The average of the ratios for the eight samples and the corresponding standard deviation are summarized in Table 8, together with the differences between the boiling and melting points of the element determined and the reference element iron. It can be seen that for the elements with boiling and melting points considerably lower than those of iron, the sensitivity coefficients are significantly higher under the more drastic sparking conditions (Table 7) than under normal conditions (Table 6).

This effect was only slightly reduced when the electrodes were cooled with liquid nitrogen, as shown in Table 9 where the S_R values for sample 7535 under the two sparking conditions are tabulated. It is clear that the S_R values of the more volatile elements can

Table 9. Influence of sparking conditions and electrode cooling on the measured relative sensitivity coefficient (sample Aluminium Pechiney 7535)

	Cooling			Without cooling		
Element	$S_R^{(1)}$	$S_R^{(2)}$	$S_R^{(2)}/S_R^{(1)}$*	$S_R^{(1)}$	$S_R^{(2)}$	$S_R^{(2)}/S_R^{(1)}$
Zn	1.6 ± 0.2	3.6 ± 0.4	2.3 ± 0.3	2.2 ± 0.2	5.6 ± 0.7	2.5 ± 0.4
Mg	1.8 ± 0.2	4.3 ± 0.4	2.4 ± 0.3	3.1 ± 0.3	7.7 ± 0.7	2.5 ± 0.3
Pb	2.0 ± 0.2	4.0 ± 0.5	2.0 ± 0.3	2.6 ± 0.3	5.9 ± 0.9	2.3 ± 0.4
Mn	1.35 ± 0.08	1.8 ± 0.1	1.3 ± 0.1	1.46 ± 0.09	1.9 ± 0.1	1.3 ± 0.1
Sn	1.5 ± 0.2	2.6 ± 0.3	1.7 ± 0.3	2.0 ± 0.2	4.4 ± 0.6	2.2 ± 0.4
Si	0.69 ± 0.05	2.74 ± 0.05	1.07 ± 0.09	0.77 ± 0.05	0.79 ± 0.06	1.03 ± 0.09
Al	0.87 ± 0.04	1.15 ± 0.06	1.32 ± 0.08	1.11 ± 0.06	1.34 ± 0.08	1.21 ± 0.09
Cu	0.60 ± 0.05	0.63 ± 0.05	1.1 ± 0.1	0.58 ± 0.04	0.65 ± 0.05	1.1 ± 0.1
Cr	1.5 ± 0.1	1.6 ± 0.1	1.1 ± 0.1	1.6 ± 0.1	1.7 ± 0.1	1.0 ± 0.1
Ni	0.64 ± 0.06	0.64 ± 0.07	1.0 ± 0.1	0.65 ± 0.07	0.68 ± 0.07	1.0 ± 0.1
Fe	1	1	1	1	1	
Ti	1.7 ± 0.1	1.6 ± 0.1	0.94 ± 0.09	1.7 ± 0.1	1.4 ± 0.1	0.88 ± 0.08

* $S_R^{(1)}$ = spark-source voltage 30 kV, repetition frequency 1 kHz, $S_R^{(2)}$ = spark-source voltage 65 kV, repetition frequency 3 kHz.

Table 10. Temperature of the electrodes after different sparking conditions

Time after end of sparking, *sec*	Temperature of electrodes, °C		
	Without cooling		With cooling
	65 kV, 3 kHz	30 kV, 1 kHz	65 kV, 3 kHz
75	71	35	—
210	58	32	−55

be decreased not only by choosing less violent spark conditions (*i.e.*, by choosing lower electrode temperatures), but also by cooling the electrodes. For instance, the $S_R^{(1)}$ values without cooling always lie between the $S_R^{(1)}$ and $S_R^{(2)}$ values with cooling. The temperature of the electrodes was measured after sparking, with a Comark 1605-1 electronic thermometer and an NiCr/NiAl thermocouple. The electrodes were pressed from both sides against the thermocouple. The results of a few measurements of the temperature are shown in Table 10.

CONCLUSIONS

The sensitivity calibration for aluminium and its alloys with magnetic peak-switching showed that for the elements certified in the aluminium standards from Johnson Matthey and in the aluminium alloys from Aluminium Pechiney, the relative sensitivity coefficients varied from 0.67 for copper to 3.0 for magnesium. No significant changes of the sensitivity coefficients with the elemental concentration were noticed.

The precision was 10% relative standard deviation which is the same as that found for iron and steel samples[1] and better than that for copper and brass samples.[2] This is an indication of the good homogeneity of the samples studied here.

When the relative sensitivity coefficients found are compared with those previously determined in other matrices, there is a fair agreement except for zinc. It was found, however, that the sensitivity coefficients of zinc and other elements with boiling and melting points considerably lower than those of the internal standard iron, showed remarkable changes when the sparking conditions were varied.

REFERENCES

1. E. van Hoye, F. Adams and R. Gijbels, *Talanta*, 1976, **23**, 789.
2. *Idem, ibid.* 1977, **24**, 625.
3. M. S. Chupakhin and G. G. Glavin, *Zh. Analit. Khim.*, 1963, **18**, 618.
4. J. Kai and M. Miki, *Mass Spectry. (Tokyo)*, 1964, **12**, 81.
5. R. D. Craig and A. Riddoch, *Paper 56, 12th Annual Conference on Mass Spectrometry and Allied Topics*, Montreal, 1964.
6. J. S. Halliday, P. Swift and W. A. Wolstenholme, *Advan, Mass Spectry.*, 1966 **3**, 143.
7. M. Ménétrier, *Meth. Phys. Analyse (GAMS)*, 1968, **4**, 155.
8. G. Vidal, P. Galmard and P. Lanusse, *ONERA, Note Technique*, No. 125, 1968.
9. F. Degrève, C. Le Bars, R. Dablainville and R. Figaret, *Rev. Phys. Appliquée*, 1970, **5**, 627.
10. N. Yamaguchi and R. Suzuki, *Mass Spectry. (Tokyo)*, 1970, **18**, 1260.
11. O. H. Herbjornsen, *Phys. Norvegica*, 1968, **3**, 70.
12. D. Nicholas, *Proc. Soc. Anal. Chem.*, 1971, **8**, 110.
13. F. Konishi, *Mass Spectry. (Tokyo)*, 1971, **19**, 284.
14. R. A. Bingham and R. M. Elliott, *Anal. Chem.*, 1971, **43**, 43.
15. F. Degrève and R. Figaret, *31ième Congrès du G.A.M.S., Paris*, 1972.
16. P. Verbeke, H. Nullens and F. Adams, *Anal. Chim. Acta.*, in press.

Talanta, Vol. 25, pp. 79–84. Pergamon Press, 1978. Printed in Great Britain.

DETERMINATION OF POLYTHIONATES AND THIOSULPHATE IN MINING EFFLUENTS AND MILL CIRCUIT SOLUTIONS*

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Summary—A method is described for the determination of total polythionates plus thiosulphate by acidimetric titration. The titration can be carried out either at the Methyl Orange (pH = 4.30) or at the phenolphthalein (pH = 8.20) end-point, with standard sodium hydroxide solution, to determine the amount of acid produced on oxidation of the thiosulphate and polythionates. The precision and accuracy are good and samples containing as little as 0.1 mg of the thio salt can be analysed very easily. Results obtained by this method are compared with those obtained by a colorimetric method and are in good agreement.

The Canada Centre for Mineral and Energy Technology (CANMET) is involved in an investigation of the problem of the occurrence of polythionates and thiosulphate in the flotation and leaching of sulphide ores. These compounds add seriously to the pollution of natural water-ways because they eventually decompose to form sulphuric acid. Much of the decomposition takes place in the mining mill treatment circuits or tailings ponds and the acid so formed is neutralized with lime before discharge to the rivers. Unfortunately the decomposition is not fully complete during the retention period in the ponds and acid continues to be formed downstream with subsequent effect on fish and other aquatic life.

In order to assess the magnitude of the problem as well as the technological efficiency and/or economic feasibility of methods proposed to overcome it, analytical methods are necessary to determine the thio salts. Recent reviews[1,2] have outlined the analytical methods proposed for the determination of the various forms of sulphur acids, including individual polythionates. Because of the very complex nature of the thio salt formation and their reactions[3] there are still many difficulties to overcome in the analysis of mixtures of polythionates containing other forms of sulphur such as thiosulphate, sulphite, sulphide, dithionate, *etc.* in either acid or alkaline solutions. A colorimetric method developed by Mizoguchi *et al.*[4] has been investigated in our laboratories for the determination of the individual thiosulphate, trithionate and tetrathionate concentrations in mining effluents and mill circuit samples.[5] This method has been found to be very satisfactory but for many purposes a simpler and relatively rapid method for the determination of the total polythionate and thiosulphate concentration would be helpful, *e.g.*, for the monitoring and control of processes for the removal of the thio salts either in the mill circuits or in the tailings ponds when a knowledge of the individual salts is not as important.

In this paper, we discuss an acidimetric method that has been developed by the Noranda Research Centre[6] for the determination of total polythionates plus thiosulphate. This method involves titration of the acid liberated on addition of mercuric chloride (*i.e.*, oxidation of thiosulphate and polythionates to produce sulphuric acid) after adjustment of the initial pH to either 4.30 or 8.20 with dilute sodium hydroxide or sulphuric acid. This method was originally proposed by Feld[7] and later modified by Kurtenacker *et al.*[8] and Jay.[9] The results of our studies on pure potassium tri- and tetrathionate, sodium thiosulphate, various synthetic mixtures, as well as several mill circuit and mining samples are discussed and compared with results obtained by a colorimetric method used to determine the individual concentrations of thiosulphate, trithionate and tetrathionate.

Principle of the method

A suitable portion of the solution containing a polythionate having 3, 4 or 5 sulphur atoms is acidified to either pH 4.30 or pH 8.20 with 0.005*N* sulphuric acid and sodium hydroxide, and mercuric chloride is added to release acid quantitatively. The stoichiometric equation is:

$$2S_xO_6^{2-} + 3HgCl_2 + 4H_2O \rightarrow HgCl_2.2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} + (2x\text{-}6)S.$$

A similar equation applies for the thiosulphate:

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HgCl_2.2Hgs + 4H^+ + 4Cl^- + 2SO_4^{2-}.$$

In both cases the acid generated is titrated with standard sodium hydroxide solution to determine the sum of the concentration of the four sulphur anions: $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$.

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EXPERIMENTAL

Reagents

All chemicals were of analytical grade except the potassium tri- and tetrathionate which were prepared in this laboratory[10] on the basis of the methods described by Stamm *et al.*[1]

Formaldehyde solution (37–38%).

Mercuric chloride, 2% solution. Prepared freshly every week.

Potassium biphthalate, 0.0100N solution (primary standard). Anhydrous potassium biphthalate (2.042 g) dissolved in 1000 ml of CO_2-free water.

Potassium iodide, 20% solution.

Sodium hydroxide solution, 0.005N. Prepared freshly every week with CO_2-free water and standardized at least twice a week with the potassium biphthalate solution, with phenolphthalein as indicator.

Sulphuric acid, 0.005N. Standardized with the standard sodium hydroxide solution.

Procedures

A. In the absence of sulphite. Pipette a suitable volume of sample containing 0.10–25 mg of $S_2O_3^{2-}$ (or polythionate equivalent) and dilute it to approximately 30 ml with distilled water in a 100-ml beaker. Insert a magnetic stirrer bar and pH electrodes and stir constantly at a moderate speed. Titrate the solution with 0.005*N* sulphuric acid or sodium hydroxide to an initial pH of 4.30 (if the solution is very basic or acidic use 0.1*N* acid or alkali to avoid excessive dilution). Add 5 ml of 2% mercuric chloride solution and dilute the solution to approximately 60 ± 5 ml after removing the electrodes. Let the solution stand for 5 min at room temperature to complete the oxidation reactions, then heat just to boiling. Cool to room temperature. With constant stirring add 20% potassium iodide solution slowly dropwise until the resulting orange precipitate that develops disappears. Insert the pH electrodes again and titrate the liberated acid with 0.005*N* sodium hydroxide to the pH 4.30 end-point. Use the same procedure for a blank determination, *i.e.*, with distilled water instead of a sample; in this case, after addition of the 20% potassium iodide solution, titrate with 0.005*N* sulphuric acid to the pH 4.30 end-point. From the volume of standard acid used in the blank titration calculate the volume of standard 0.005*N* sodium hydroxide equivalent to it. Determine the blank several times and calculate the average value, which need only be checked infrequently thereafter. The concentration of the polythionates and thiosulphate is expressed as thiosulphate, *i.e.*

$$S_2O_3^{2-} = 56000(V + V_b)M/A$$

where V and V_b are the volumes (ml) of sodium hydroxide solution (molarity M) used for the sample and blank titrations respectively, and A is the volume (ml) of sample.

If buffer species such as acetate are present, titrate to pH 8.20 instead of 4.30.

B. In the presence of sulphite. High results are obtained for the determination of total polythionates in the presence of sulphite by the procedure above because the sulphite also produces acid. The following modified procedure is used for samples containing sulphite.

Pipette a suitable volume of sample and add 1 ml of 37–38% formaldehyde solution for every mg of sulphite present and titrate to an end-point of pH 8.20 with 0.005*N* sodium hydroxide. Then follow procedure A for the completion of the determination, starting at the point where the mercuric chloride solution is added.

RESULTS AND DISCUSSION

The titrimetric results obtained in tests with pure potassium tri- and tetrathionate and sodium thiosulphate, synthetic mixtures in the absence and in the presence of sulphite, as well as several mill circuit and mining samples are shown in Tables 1–8.

Table 1. Determination of thio salts by the mercuric chloride–acidimetric titration method at pH 4.30

Thio salt taken, *as mg* $S_2O_3^{2-}$		Thio salt found, *mg*	Difference, *mg*
$S_2O_3^{2-}$	2.76	2.67	−0.09
	2.76	2.70	−0.06
	5.51	5.31	−0.20
	5.51	5.60	+0.09
	11.02	10.57	−0.45
$S_3O_6^{2-}$	0.96	1.02	+0.06
	0.96	1.00	+0.04
	0.96	1.02	+0.06
	1.92	2.05	+0.13
	1.92	2.09	+0.17
	9.61	10.13	+0.52
$S_4O_6^{2-}$	0.45	0.45	+0.00
	0.56	0.56	−0.00
	0.90	0.89	−0.01
	1.12	1.12	−0.00
	2.24	2.23	−0.01
	4.48	4.40	−0.08
	11.20	11.10	−0.10
	22.40	21.84	−0.56

As shown in Tables 1 and 2 the recoveries are consistently slightly high for trithionate and consistently low for tetrathionate at the pH 4.30 end-point. On the other hand the recoveries are slightly high for both compounds at the pH 8.20 end-point. This effect is most probably due to a slight decomposition of the salts. Good recoveries are obtained for synthetic mixtures when titrations are performed to either end-point, as shown in Tables 3 and 4. The maximum error in the titration of the thiosulphate solutions was found to be +4% and +1.5% at the pH 4.30 and 8.20 end-points respectively. For the potassium trithionate solutions the maximum errors were +5% and +6% and for potassium tetrathionate +2.5% and +6% at pH 4.30 and pH 8.20 respectively. These were maximum errors, however, and generally the error was within +1% with pure salt solutions and synthetic mixtures. The values obtained for mill circuit

Table 2. Determination of thio salts by the mercuric chloride–acidimetric titration method at pH 8.20

Thio salt taken, *as mg* S_2O_3		Thio salt found, *mg*	Difference, *mg*
$S_2O_3^{2-}$	1.10	1.11	+0.01
	2.75	2.79	+0.04
	5.51	5.55	+0.04
	11.02	11.07	+0.05
$S_3O_6^{2-}$	0.48	0.51	+0.03
	0.96	0.98	+0.02
	1.93	2.05	+0.12
$S_4O_6^{2-}$	0.56	0.55	−0.01
	1.12	1.19	+0.07
	2.24	2.27	+0.03
	4.48	4.52	+0.04
	11.02	11.20	+0.08

Table 3. Determination of polythionates in synthetic mixed solutions by the mercuric chloride-acidimetric titration method at pH 4.30

$S_2O_3^{2-} + S_3O_6^{2-} + S_4O_6^{2-}$, *as mg* $S_2O_3^{2-}$	Thio salts taken, *as mg* S_2O_3	Thio salts found, *as mg* S_2O_3	Difference, *mg*
1.10 + 0.38 + 0.90	2.38	2.36	−0.02
1.10 + 1.92 + 1.97	4.99	4.89	−0.10
2.77 + 1.92 + 0.50	5.19	4.99	−0.20
5.55 + 1.92 + 0.50	7.97	7.86	−0.11
2.20 + 3.84 + 4.48	10.52	10.52	+0.00
2.77 + 9.61 + 0.22	12.60	13.09	+0.49
5.55 + 9.61 + 0.90	16.06	16.50	+0.44

Table 4. Determination of polythionates in synthetic mixed solutions by the mercuric chloride-acidimetric titration method at pH 8.20

Thio salt taken, *as mg* $S_2O_3^{2-}$	Thio salt taken, *as mg* $S_2O_3^{2-}$	Thio salt found, *as mg* $S_2O_3^{2-}$	Difference, *mg*
$S_2O_3^{2-} + S_4O_6^{2-}$			
0.13 + 0.45	0.58	0.60	+0.02
0.64 + 0.56	1.20	1.19	+0.01
0.32 + 1.12	1.44	1.47	+0.03
1.28 + 0.22	1.50	1.53	+0.02
1.10 + 2.24	3.34	3.35	+0.01
2.75 + 1.12	3.87	3.89	+0.02
5.51 + 2.24	7.75	7.81	+0.06
22.04 + 4.48	26.52	26.10	−0.42
$S_2O_3^{2-} + S_3O_6^{2-}$			
1.10 + 0.48	1.58	1.61	+0.03
2.75 + 0.96	3.71	3.87	+0.16
5.51 + 1.93	7.44	7.50	+0.06
11.02 + 3.86	14.88	14.98	+0.10
$S_2O_3^{2-} + S_3O_6^{2-} + S_4O_6^{2-}$			
1.10 + 0.48 + 0.56	2.14	2.15	+0.01
2.75 + 0.96 + 1.12	4.80	4.84	−0.04
2.75 + 1.45 + 1.68	5.88	5.93	+0.05
5.51 + 1.93 + 2.24	9.68	9.80	+0.12
11.02 + 1.93 + 2.24	15.19	15.12	−0.07

samples and mining samples are in good agreement with values obtained colorimetrically, as shown in Tables 5 and 6. The precision and accuracy of the acidimetric method are good and samples containing as little as 0.1 mg of the thio salt can be analysed without any difficulty. In fact, the method is sufficiently sensitive for the absence of a turbidity on adding the mercuric chloride solution to indicate that less than 10 ppm of thio salts are present in a 10-ml sample. The lower limit of detection, however, may be considerably influenced by the presence of interferences such as Fe^{2+} and SO_3^{2-} and the procedures used to eliminate them. In such cases a lower detection limit of 0.5 mg may be acceptable.

Interferences

Samples containing sulphite give higher results because mercuric chloride oxidizes sulphite to sulphate with the formation of hydrogen ions. Sulphite will exist in mill circuit samples if sulphur dioxide

Table 5. Determination of polythionates in mill samples by the mercuric chloride-acidimetric titration method at pH 4.30 (sulphite absent)

Sample	Colorimetric, $S_2O_3^{2-}$ *mg/l.*†	Titrimetric, $S_2O_3^{2-}$ *mg/l.**	Difference, *mg*
1	457.5	451.2	−6.2
2	374.5	369.5	−5.0
3	70.6	71.9	+1.3
4	57.2	58.0	+0.8
5	None	None	—
6	17	16	−1.0
7	<1	<1	—
8	91	83	−8
9	568	572	+4
10	529	534	+5
11	<1	None	—
12	<1	None	—
13	<1	<1	—
14	<1	<1	—

† The results shown are the summation of polythionates expressed as $S_2O_3^{2-}$.

* Average of two individual titrations.

Table 6. Determination of polythionates in mining effluent samples by the mercuric chloride acidimetric titration method

Sample	pH 4.30 without formaldehyde	pH 4.30 with formaldehyde	ph 8.20 without formaldehyde	pH 8.20 with formaldehyde	Colorimetric
	mg $S_2O_3^{2-}$/l.*		mg $S_2O_3^{2-}$/l.*		mg $S_2O_3^{2-}$/l.**†
1	1615	1625	1609	1171	1178
2	1518	1620	1555	1231	1211
3	359	201	357	250	220
4	788	609	—	—	596
5	367	146	293	170	170
6	1243	879	1193***	796***	974

† Colorimetric and acidimetric analysis performed on the same day.
* Average of two individual titrations.
** The results shown are the summation of the polythionates expressed as $S_2O_3^{2-}$.
*** This sample gave a light yellow precipitate at this pH which may be due to Fe^{2+}, Al^{3+}, *etc.*

is used in certain operations in the mill. The results of tests in which various amounts of sulphite solution were added to the thiosulphate solutions are shown in Tables 7 and 8. Different results were obtained, depending on which end-point pH was used.

The species HSO_3^-, which is predominant in sulphite solutions at pH 4.30, will release one more hydrogen ion upon reacting with mercuric chloride than will SO_3^{2-}, which predominates at pH 8.20. This accounts for the increased acidity generated at the lower pH value. It is well known that formaldehyde will preferentially react with sulphite in solution and it is used to remove its interference in the iodometric titration of thiosulphate.[12] We have investigated this effect by adding various amounts of formaldehyde to solutions containing thiosulphate and sulphite, and then titrating to both end-points. The results are shown in Tables 7 and 8. In both cases formaldehyde masks the sulphite but it is much more effective at pH 8.20. With a low concentration of thio salt, the relative error may be very large, especially at pH 4.30. Hence, to minimize the error the samples should be titrated to a pH 8.20 end-point for the determination of total polythionates when formaldehyde is used to mask the sulphite. The formaldehyde used contained significant amounts of acid (most probably formic acid) but the effect of this was overcome by pretitrating to the appropriate end-point before adding the mercuric chloride.

It has been suggested that sulphite ions can also be removed by pretitrating the solution with standard iodine solution and adjusting the pH to 4.30.[6] We

Table 7. Effect of sulphite on the determination of thiosulphate by the mercuric chloride–acidimetric method at pH 4.30

Sulphite present, mg SO_3^{2-}	Formaldehyde present, ml	Thiosulphate taken, mg	Thiosulphate found, mg	Difference, mg
2	Nil	Nil	1.99	+1.99
8	Nil	Nil	7.11	+7.11
8	1	Nil	2.37	+2.37
Nil	Nil	1.10	1.03	−0.07
Nil	1	1.10	1.13	+0.03
1.6	Nil	1.10	2.53	+1.43
1.6	1	1.10	1.40	+0.30
1.6	2	1.10	1.45	+0.35
1.6	3	1.10	1.53	+0.43
1.6	5	1.10	1.72	+0.62
1.6	10	1.10	1.70	+0.60
Nil	Nil	2.20	2.04	−0.16
1.6	1	2.20	2.99	+0.79
1.6	2.5	2.20	2.14	−0.06
1.6	5	2.20	3.10	+0.90
Nil	Nil	5.51	5.35	−0.16
4	Nil	5.51	12.41	+6.90
8	Nil	11.03	23.66	+12.63
8	1	11.03	15.24	+11.85
32	Nil	44.12	67.70	+23.58
32	4	44.12	56.07	+11.85
8	1	22.06	28.62	+6.16
8	2	22.06	30.18	+8.18
8	5	22.06	31.86	+8.82
8	10	22.06	32.42	+10.36

Table 8. Effect of sulphite on the determination of thiosulphate by the mercuric chloride-acidimetric method at pH 8.20

Sulphite present, *mg* SO_3^{2-}	Formaldehyde present, *ml*	Thiosulphate taken, *mg*	Thiosulphate found, *mg*	Difference, *mg*
2	Nil	Nil	0.57	+0.57
8	Nil	Nil	3.55	+3.55
8	1	Nil	1.61	+1.61
8	2	Nil	0.46	+0.46
Nil	Nil	1.10	1.09	−0.01
Nil	1	1.10	1.13	+0.03
1.6	Nil	1.10	2.09	+0.99
1.6	1	1.10	1.15	+0.05
1.6	2	1.10	1.20	+0.10
1.6	5	1.10	1.45	+0.35
1.6	10	1.10	1.44	+0.34
1.6	2.5	2.20	2.27	+0.07
1.6	5	2.20	2.42	+0.22
1.6	10	2.20	2.32	+0.12
Nil	Nil	11.03	11.05	+0.02
8	1	22.06	22.42	+0.32
8	5	22.06	21.89	−0.17
8	10	22.06	21.25	−0.81

do not recommend this method, however, because we found that this procedure introduced an error of approximately +8% with pure thiosulphate solutions and the results were highly irregular and inconsistent with solutions also containing sulphide.

Several mill samples from a Canadian mining mill processor were analysed by titrating to both pH end-points by both methods, namely, iodometric titration and formaldehyde addition for sulphite removal. Our results, as shown in Table 6, confirm the errors that are encountered by titrating to a pH 4.30 end-point when sulphite is present and addition of formaldehyde is used to mask sulphite. The results for samples 3–6 obtained at pH 4.30 in the presence of formaldehyde are in reasonably good agreement with the colorimetric results, whereas the results for samples 1 and 2 are not. This difference in behaviour is believed to be due to the presence of an excessive amount of sulphite in samples 1 and 2, which is not sufficiently masked by the formaldehyde at the lower pH. On the other hand, at the pH 8.20 end-point and in the presence of formaldehyde the results agree within experimental error with those obtained by the colorimetric method. Therefore we conclude that for mining samples containing sulphite ions, the titration to end-point pH 8.20 is very satisfactory provided formaldehyde is added. Concern has been expressed that toxic chlorinated ethers may be generated when formaldehyde is used to mask sulphite.[6] The potential hazard is small but the analysis should nevertheless be performed in a fume-hood or a well-ventilated area.

Mercuric chloride reacts with sulphides in solution to produce sulphuric acid, therefore high results are obtained. This interference is overcome by adding zinc carbonate slurry[12] or by removing sulphide as H_2S at pH 4 and under vacuum.[6]

High results are obtained in the presence of ferrous ions. This interference can be removed by adding some sodium carbonate, filtering off the precipitate and titrating the filtrate to the pH 4.30 end-point. For example, a mining sample solution that contained ferrous ions gave values for total polythionates (expressed as $S_2O_3^{2-}$) of 6.39 and 5.47 m*M* before and after addition of sodium carbonate respectively.

It has been shown by the Noranda group[6] that addition of an excess of mercuric chloride yields higher results because it produces acidity due to hydrolysis at pH levels near the end-point pH. This may be overcome by addition of potassium iodide solution. We have found that 5 ml of a 2% solution is sufficient for sample aliquots containing up to at least 20 mg of $S_2O_3^{2-}$.

An excessive addition of 20% potassium iodide solution should be avoided because low results will be obtained.

CONCLUSIONS

The results obtained by the mercuric chloride acidimetric titration method compare favourably with those obtained by a colorimetric procedure in which the individual thio salts are determined. The acidimetric titration method determines only the sum of the polythionates, expressed as $S_2O_3^{2-}$, but nevertheless serves as a rapid control method for the determination of total thio salts if there is no need to determine the individual thio salts. The method is very simple, hence it may be very useful for monitoring mining effluents, ponds or processes that are developed to destroy the thio salt before discharge to rivers, *etc.*, only the total thio salt content then being of importance.

In the absence of sulphite or weak-acid buffers a titration to a pH 4.30 end-point is excellent but in the presence of sulphite a titration to pH 8.20 is necessary, after addition of formaldehyde. If sulphite is present, we prefer to use formaldehyde to mask the sulphite rather than pretitration of sulphite and thiosulphate with iodine solution, because the results are more reliable.

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REFERENCES

1. L. Szekeres, *Talanta*, 1974, **21**, 1.
2. A. Hitchen and C. W. Smith, *Mineral Sciences Laboratories Rep.* MRP/MSL 76-208 (LS), August 1976, CANMET, Energy, Mines and Resources, Ottawa, Canada.
3. C. W. Smith and A. Hitchen, *Mineral Sciences Laboratories Rep.* MRP/MSL 76-223 (LS), August 1976, CANMET, Energy, Mines and Resources, Ottawa, Canada.
4. T. Mizoguchi and T. Okare, *Bull. Chem. Soc. Japan*, 1975, **48**, 1799.
5. E. Rolia, *Mineral Sciences Laboratories Rep.* MRP/MSL 77-21 (TR), January 1977, CANMET, Energy, Mines and Resources, Ottawa, Canada.
6. M. L. Cotton and N. D. Johnson, *Noranda Research Centre Information Memorandum, The Analysis of Thiocompounds in Solution*, 31 March 1976.
7. W. Feld, *Z. Angew. Chem.*, 1911, **24**, 290.
8. A. Kurtenacker and K. Bittner, *Z. Anorg. Allgem. Chem.*, 1925, **142**, 119.
9. R. R. Jay, *Anal. Chem.*, 1953, **25**, 288.
10. A. Hitchen *Mineral Sciences Laboratories, Rep.* MRP/MSL 76-279 (TR), December 1976, CANMET, Energy, Mines and Resources, Ottawa, Canada.
11. H. Stamm, M. Goehring and U. Feldman, *Z. Anorg. Allgem. Chem.*, 1942, **250**, 226, *Chem. Abstr.*, 1943, **37**, 2289.
12. I. M. Kolthoff, and R. Belcher, *Volumetric Analysis*, Vol. III, p. 295, Interscience New York, 1957.

Talanta, Vol. 25, pp. 85–89. Pergamon Press. 1978. Printed in Great Britain.

JOINT DETERMINATION OF FLUORINE AND CHLORINE IN GRANITIC ROCKS WITH ION-SELECTIVE ELECTRODES

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Summary—This enables both fluorine and chlorine in granitic rocks to be determined with a single sample. A rapid technique, using fusions in culture tubes, and a slower technique, employing fusions in platinum crucibles are described. The culture-tube technique is suitable for geochemical exploration and employs an oxidizing flux so that sulphide-bearing rocks can be analysed. The platinum-crucible technique yields fluorine and chlorine results for the standard rocks G-2 and GSP-1 that are comparable in value and precision to those obtained by other analytical methods. It is faster, easier to manipulate and yields higher fluorine values than the existing joint spectrophotometric method.

Classical techniques for the determination of chlorine and fluorine in rocks are time-consuming and photometric sulphide methods for chlorine require considerable chemical manipulation.[1] Modification of the ferric thiocyanate method[2] for chlorine, coupled to a zirconium–Cyanine R colorimetric method for fluorine, by Huang and Johns[3] is considerably faster, particularly with use of an autoanalyser,[4] because only a single sample fusion is employed.

Ion-selective electrodes have been used by Haynes and Clark[5] for chlorine by Edmond[6] and Ficklin[7] for fluorine. After experimentation with different fluxes, sample weights and buffers, the present technique for the joint determination of chlorine and fluorine in the same sample fusion was devised.

EXPERIMENTAL

Apparatus

An Orion 407 ion-selective meter was used in conjunction with Orion electrodes (90-02 double-junction reference electrode, 91-01 pH electrode, 94-09 fluoride electrode, 94-17 chloride electrode, and 94-16 silver sulphide electrode). A Metrohm E412 Dosimat automatic burette and Orion 10% volume-corrected Gran plot paper were also used.

Reagents

Doubly-distilled water is used throughout.

Fluoride solution, 1% F^-. Prepared from reagent grade sodium fluoride dried at 110° overnight and cooled in a desiccator; diluted as necessary.

Citric acid solution, 10%.

Chloride solution, 10%Cl^-. Prepared from reagent grade sodium chloride dried at 110° overnight and cooled in a desiccator; diluted as necessary.

Silver nitrate solution, (1 *ml* ≡ 1 *mg of* Cl^-). This solution is diluted tenfold, placed in the reservoir of the Dosimat and changed weekly.

Flux. Two parts, by weight, of reagent-grade sodium carbonate mixed with one part of potassium nitrate for use in culture tubes or one part of zinc oxide for use in platinum crucibles.

Sample dissolution

Weigh out 0.5 g of dried rock sample, ground finer than 100-mesh, and 2 g of the appropriate flux into a platinum crucible or a culture tube. Mix thoroughly.

Heat platinum crucibles in a muffle furnace for 30 min at 950°. Allow to cool. Add 20 ml of water and three drops of ethanol to reduce manganate. Boil gently on a hot-plate for 1 min and let stand for at least 1 hr to dissolve the soluble material.

Place culture tubes in the holders of an Optimus burner and heat for 15 min. Take each tube in turn from the burner (replacing it with a fresh sample) and fuse over a Méker burner for 3 min, swirling the tube to distribute the melt evenly on the walls. Let cool, add 20 ml of water, vibrate each tube with a vortex mixer, and gently simmer on a sand-tray for 30 min. Return the tubes to the vortex mixer during and after heating. Let the solution stand for 1 hr.

Filter the solution through a Whatman No. 5 filter paper into a clean polypropylene beaker (marked at 50 and 100 ml) by means of a Witt's apparatus. Crush and loosen the fusion cake with a clean glass rod and wash it into the filter with water. Wash the filter and residue several times with water and discard. Make up the solution in the beaker to the 100-ml graduation mark with water and mix thoroughly with a clean polypropylene rod. Tap into the beaker any drops remaining on the rod. Carefully pour 50 ml of this solution into a similar polypropylene beaker and cover both beakers. The solution in each beaker should be at the 50-ml mark (checked for accuracy previously). One aliquot is used for determination of fluorine, the other for chlorine.

Fluorine determination

Add 8 ml of the citric acid solution through the lip of the covered beaker to expel most of the CO_2 and slightly acidify the solution. Wash the cover and make up to about 90 ml with water. Swirl gently to mix and let stand for at least 1 hr to complete complexation of aluminium. Test the pH and adjust it to 5.5–6.5 (pH-meter) with citric acid or 10% sodium hydroxide solution. Rinse the electrodes into the beaker and make up the solution to 100 ml with water. Repeat for all samples.

Add a Teflon-coated magnet to each beaker, stir gently with a magnetic stirrer, and measure the fluoride activity. To calibrate the meter, pipette appropriate volumes of standard fluoride solution into polypropylene beakers containing 1 g of flux and 10 ml of citric acid solution, and

treat as for the samples. Adjust the meter to read 10, 100 and 1000 for 0.1, 1 and 10 μg/ml standards respectively. For solutions with fluoride activities greater than 10 μg/ml adjust the meter to read 10, 100 and 1000 for 10, 100 and 1000 μg/ml standards.

This procedure will give the fluoride *activity* which is suitable for geochemical exploration, with use of glass culture tubes in the field. The activity is usually lower than the *concentration*, because the activity coefficient is dependent on the total ionic strength and the specific composition of the solution.

The *concentration* can be obtained directly by the method of known additions.[8–10] This is achieved by pipetting into the sample 1 ml of standard solution having a concentration approximately 100 times the sample activity (usually 1000 μg/ml), stirring, and reading the value on the known-addition scale of the meter and calculating the concentration by simple proportion. The result can be checked by adding a further 1 ml of standard fluoride solution and taking a new reading on the known-addition scale (double known-addition method).

Chlorine determination

Add 1.5 ml of concentrated nitric acid through the lip of the beaker to expel most of the CO_2 and acidify the solution. Wash the cover then make up the volume to 100 ml with water.

Add a Teflon-coated magnet, stir gently, and measure the chloride activity. To calibrate the meter, add appropriate volumes of standard chloride solution to polypropylene beakers containing 1 g of flux. Make up to about 80 ml with water, cover and cautiously add 1.5 ml of nitric acid. The pH should be checked to ensure it is below 7 because OH^- ions interfere with the chloride electrode. Wash the cover, make up to 100 ml and adjust the meter to read 50, 100 and 1000 for 5, 10 and 100 μg/ml standards. Check the calibration with 8 and 15 μg/ml solutions.

If the chloride activity is greater than 5 μg/ml use the method of known additions described above. For sample solutions having activities less than 5 μg/ml perform a Gran plot potentiometric titration,[5,11] using the silver sulphide electrode. Record the potential after the addition of 3 ml of the 100-μg/ml standard silver nitrate solution from the automatic burette. Using the expanded mV scale of the meter, record the potential after each addition of silver nitrate solution (0.5-ml increments up to a total of 10 ml), stirring gently throughout the titration. Plot the readings on the Gran plot paper. Draw a straight line through the last 4–7 points and read the *concentration* (μg/ml) of the sample directly from the intercept of the line with the horizontal axis.[11]

The Gran plot paper is constructed on the assumption that the electrode response is 58 mV per decade. Check the slope by adding two drops of 1*M* potassium nitrate (to provide constant ionic strength) to 100 ml of doubly-distilled water and titrate as above. The resulting plot line will pass through the origin if the slope is correct. If not, subtract (algebraically) the intercept from the sample concentration.

The silver nitrate solution must be standardized at the start of each batch of samples. Add two drops of 1*M* potassium nitrate to 100 ml of 1-μg/ml standard chloride solution and titrate. The intercept should be at 1 μg/ml.

Blanks

Fuse several blanks, containing only the flux, at the same time as the samples, apply the procedure to them, and subtract the blank values from those for the samples. Check recovery by running a standard with each batch of samples.

RESULTS AND DISCUSSION

Separate fusions for fluorine and chlorine

Results for the U.S.G.S. standard rocks G-2 and GSP-1 obtained by various methods are compared in Tables 1 and 2. These determinations were made with separate fusions in platinum crucibles, using 0.25-g sample weights and 1 g of sodium carbonate–zinc oxide flux.

Fluoride. The mean fluoride values for G-2 by the present method are close to Flanagan's[13] and Abbey's[12] "usable values", the spectrophotometric results and those from the Kesler *et al.*[15] method. The value found for GSP-1 is comparable to Flanagan's and Abbey's values. However, the Huang and Johns[1] value appears to be in error since both Edmond and I obtained similar values when using their method. Also we both obtained comparable results, by ion-selective techniques, which are about 6% higher than the spectrophotometric results. Edmond used the same flux but acidified with nitric acid and added sodium citrate buffer. I consider that

Table 1. Comparison of the fluorine contents (in *ppm*) of U.S.G.S. standard rocks G-2 and GSP-1, by different analytical methods

	Previous results							This work							
	I	II	III	IV	V	VI	VII	Spectrophotometric*				Ion-selective electrode†			
Sample	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Found	Mean	*S*	*C*,%	Found	Mean	*S*	*C*,%
G-2	1300	1290	1350	1205	—	1120	1230	1220	1209	62	5	1200	1230	44	4
								1130				1280			
								1205				1190			
								1280				1250			
GSP-1	3800	3200	3850	1940	3200a	2400	—	3300	3270	26	1	3440	3430	22	1
					3400b			3280				3420			
								3240				3400			
								3260				3450			

S—standard deviation; *C*—relative standard deviation; I—Abbey,[12] "usable values"; II—Flanagan,[13] "recommended magnitudes"; III—Flanagan,[14] conventional distillation method; IV—Huang and Johns,[1] ferric thiocyanate spectrophotometric method; V—Edmond,[6] (*a*) spectrophotometric, (*b*) ion-selective electrode; VI—Ficklin,[7] ion-selective electrode; VII—Kesler *et al.*,[15] ion-selective electrode.

* Ferric thiocyanate spectrophotometric method, after Huang and Johns.[3]

† Using platinum crucibles and sodium carbonate–zinc oxide flux mixture.

Table 2. Comparison of the chlorine contents (in *ppm*) of U.S.G.S. standard rocks G-2 and GSP-1 by different analytical methods

	Previous results					This work							
	I	II	III	IV	V	Spectrophotometric*				Ion-selective electrode†			
Sample	Mean	Mean	Mean	Mean	Mean	Found	Mean	*S*	*C*,%	Found	Mean	*S*	*C*, %
G-2	100	50	53	120	192	90,80 95,70	84	11	13	80,112 104,108	101	14	14
GSP-1	400	300	311	365	342	365 330	347	25	7	375,312 340,390	354	35	10

S—standard deviation; *C*—relative standard deviation; I—Abbey,[12] "usable values"; II—Flanagan,[13] "recommended magnitudes"; III—Johansen and Steinnes,[16] neutron activation; IV—Sen Gupta (in Flanagan[17]), photometric; V—Huang and Johns,[1] ferric thiocyanate spectrophotometric method.

* Ferric thiocyanate spectrophotometric method, after Huang and Johns.[3]

† Using platinum crucibles and a sodium carbonate–zinc oxide flux mixture.

the direct addition of citric acid gives the same result, but is faster. Ficklin[7] reported low values for both G-2 and GSP-1. This is probably due to the use of glass culture tubes for fusions. I consider that the close agreement of the results obtained by Edmond[6] and Kesler *et al.*[15] with mine indicates that, among rapid methods, the ion-selective techniques are more accurate, because there is still a possibility that multivalent cations are present in the alkaline filtrate in the spectrophotometric method. The higher values of both G-2 and GSP-1 obtained with the conventional distillation method suggests that fluorine may not be *completely* liberated from interferents, present in rock samples, when non-distillation techniques are employed.

Chloride. The mean chloride values of G-2 and GSP-1 obtained by the method described here are similar to those quoted in Abbey[12] as "usable values" but higher than Flanagan's[13] "recommended magnitudes". The Huang and Johns[1] value for G-2 (192 ppm) would appear to be too high. By their method I obtained a mean chloride concentration of 84 ppm. This is in closer agreement with the Johansen and Steinnes[16] value of 53 ppm, Sen Gupta's value of 120 ppm (in Flanagan[17]) and the mean value for the present method of 101 ppm.

Single fusion for fluorine and chlorine

Values for the U.S.G.S. standards (G-2 and GSP-1) and a domestic standard (H121), obtained with a single fusion (0.5 g sample weight and 2 g of flux) are shown in Table 3. Comparison of Tables 1, 2 and 3 indicates that the higher sample weight for fusions in platinum crucibles has no significant effect.

With fusions in culture tubes the values were reasonably close for chlorine but low for fluorine. Even separate fusions with 0.25 g of sample and 1 g of flux gave consistently low fluorine results.

Interferences

Fluorine. The fluoride electrode is highly specific. The only serious interference is caused by OH^-, since it has a similar ionic size to F^- and can pass through the disc membrane. This is eliminated by making the solutions acid. However, at pH $\leq$ 5 hydrogen ions form fluoride species such as HF_2^- and undissociated HF. Therefore the pH of the sample solution is adjusted to 5.5–6.5.

Elements such as Al, Fe and Si form complexes with fluorine. The use of a sodium carbonate–zinc oxide flux allow their ions to be retained as an insoluble residue in the filter.[3,6,18] Any aluminium left in the filtrate is complexed by the citric acid added. However, Ross[19] has pointed out that citrate combines with the lanthanum of the sensing crystal of the disc membrane, and has the overall effect of raising the limit of detection. Errors resulting from other complexes in solution are reduced by the use of the known-addition technique.

The low values obtained by the culture-tube fusion method (no ZnO in the flux) appear to be due to the silicate ions in solution. Runs using known

Table 3. Joint analyses for fluorine and chlorine in standard rocks with a single sample fusion and the ion-selective electrode technique

		Platinum crucibles with sodium carbonate–zinc oxide flux						Culture tubes with sodium carbonate–potassium nitrate flux					
	No. of	Fluorine, *ppm*			Chlorine, *ppm*			Fluorine, *ppm*			Chlorine, *ppm*		
Sample	Replicates	Mean	*S*	*C*,%	Mean	*S*	*C*,%	Mean	*S*	*C*,%	Mean	*S*	*C*,%
G-2	6	1230	32	3	95	17	18	1050	60	6	85	45	53
GSP-1	6	3440	30	1	355	35	10	2380	40	2	360	49	14
H121	10	450	26	6	430	18	4	370	25	5	495	70	14

C—relative standard deviation.

amounts of fluoride only, or the standard rocks with and without added known amounts of fluoride, were checked by the known-addition technique. Although the results were higher than the activity values they were still lower and more erratic than values obtained by the platinum-crucible method. Runs with the standard rocks in platinum crucibles without zinc oxide flux were not significantly different from runs with zinc oxide at low fluorine levels. However, the values for GSP-I were about 5% lower. These results indicate that additional silicate is introduced from the glass walls of the culture tubes during fusion.

Chlorine. Iodide, bromide, cyanide and thiocyanate interfere because they are precipitated by silver nitrate. However, it is unlikely that they would be present in more than trace amounts (parts per milliard) in silicate rocks.

Carbonate forms a precipitate with silver nitrate, and hydroxide ions present in the basic sample filtrate interfere with the chloride electrode. Both interferences are suppressed by making the solution acid. A series of tests with 0.5–2.0 ml of concentrated nitric acid showed that though the pH of the sample solutions varied, it did not make a significant difference provided it was below 6.5.

Sulphide ions react with silver chloride in the sensing crystal of the chloride electrode and also form precipitates with silver nitrate. Therefore, an oxidizing agent is used for sulphide-rich samples. For fusions in platinum crucibles, hydrogen peroxide is added to the solution in the crucible and the excess removed by boiling. With culture tubes, an oxidizing flux is used anyway, because it melts at a lower temperature than the zinc oxide-sodium carbonate mixture. The efficiency of this oxidation was tested by fusing known amounts of anhydrous sodium sulphide with 1.0 g of flux containing 100 μg of chloride and applying the procedure described. The results[5] showed that 0.1 g of sodium sulphide (0.041 g of sulphide ion) is apparently successfully oxidized. This is approximately equivalent to 16% sulphide in a rock.

Reproducibility

Fluorine. With platinum crucibles the reproducibility is within 6%, but with culture tubes it is highly variable, although usually less than 10% (Table 3). The limit of detection is set at 40 ppm because a fluoride activity of less than 0.1 μg/ml cannot be easily measured on the meter, owing to the slow response time for very dilute fluoride solutions containing citrate.

Chlorine. Above the 400-ppm level the reproducibility of the platinum-crucible method is within 5% (Table 3). Below this level the precision is poorer because the Gran plot has an intrinsic measuring error of ±0.025 μg/ml, corresponding to ±10 ppm chlorine in the rock sample. The reproducibility of the culture-tube method is much poorer, being within 20% at the 500-ppm level and above. Below this level the method is only semi-quantitative. The major reason for this poor reproducibility is the high chloride values of the culture-tube blanks which, although clustering around 1.2 μg/ml, can vary by as much as 0.3 μg/ml. This variation is equivalent to a difference of 120 ppm in rocks. This uncertainty is somewhat reduced by analysing several blanks and domestic standard rocks with each batch of samples.

It was found that the Orion electrodes are not necessarily compatible with meters manufactured by other companies. Erroneous results will also occur with poor electrical connections (especially in some electrode jacks).

The double-junction reference electrode should be dismantled and cleaned regularly to prevent encrustation with salts, from the inner filling solution, at the connection of the electrode with the lead to the meter. If an encrustation is allowed to form it can insulate the electrode from the meter and may also cause corrosion of the connecting wires.

Tarnished or scratched electrode crystals caused problems in meter stabilization. Tarnish can easily be removed by polishing the crystal with alumina applied with an optical tissue. Scratches can be removed with coarser abrasives and a lot of patience, but the analyst, unfamiliar with polishing techniques, is cautioned about the use of this practice.

CONCLUSIONS

The method described is faster and requires less manipulation than other methods and gives results without reference to a standard curve. The precision for both chlorine and fluorine is comparable to that of other methods, provided sample fusions are performed in platinum crucibles. A more rapid method can be employed, using disposable culture tubes for the fusions, but the precision is poorer.

Values of fluorine and chlorine for the standard rocks G-2 and GSP-1 compare favourably with those from other methods although the ion-selective electrode methods for fluorine yield lower values for these standard rocks than methods employing classical distillation techniques.

The use of an oxidizing flux mixture, or the addition of hydrogen peroxide to the filtrate, enables sulphide-bearing samples to be analysed.

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REFERENCES

1. W. H. Huang and W. D. Johns, *Geochim. Cosmochim. Acta*, 1967, **31**, 597.
2. J. G. Bergmann and J. Sanik, *Anal. Chem.*, 1957, **29**, 241.
3. W. H. Huang and W. D. Johns, *Anal. Chim. Acta*, 1967, **37**, 508.
4. R. Fuge and G. M. Power, *Geochim. Cosmochim. Acta*, 1969, **33**, 888.

5. S. J. Haynes and A. H. Clark, *Econ. Geol.*, 1972, **67**, 378.
6. C. R. Edmond, *AMDEL Bull.*, 1969, **7**, 1.
7. W. H. Ficklin, *U.S. Geol. Surv. Prof. Pap.*, 1970, **700-C**, 186.
8. Orion Research Inc., *Newsletter*, 1969, **1**, 9.
9. *Idem*, *ibid.*, 1970, **2**, 5.
10. *Idem*, *Know-how on Known Addition*, Reprint, 1971.
11. *Idem*, *Newsletter*, 1970, **2**, 49.
12. S. Abbey, *Geol. Surv. Canada Pap.*, 1975, **74–41**, 1.
13. F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1973, **37**, 1189.
14. *Idem*, *ibid.*, 1967, **31**, 289.
15. S. E. Kesler, J. C. Van Loon and J. H. Bateson, *J. Geochem. Explor.*, 1973, **2**, 11.
16. O. Johansen and E. Steinnes, *Geochim. Cosmochim. Acta*, 1967, **31**, 1107.
17. F. J. Flanagan, *ibid.*, 1969, **33**, 81.
18. H. R. Shell and R. L. Craig, *Anal. Chem.*, 1954, **26**, 996.
19. J. W. Ross, Jr., in *Ion-selective Electrodes*, (R. A. Durst, ed.), p. 74, U.S. Natl. Bur. Stds. Spec. Publ. 314, 1969.

Talanta. Vol. 25. pp. 91–95. Pergamon Press, 1978. Printed in Great Britain.

ION-PAIR EXTRACTION OF Na^+, K^+ AND Ca^{2+} WITH SOME ORGANIC COUNTER-IONS AND DICYCLOHEXYL-18-CROWN-6 AS ADDUCT-FORMING REAGENT

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Summary—Extraction equilibria of ion-pairs formed by the Na^+, K^+ and Ca^{2+} complexes of dicyclohexyl-18-crown-6 and β- and γ-dinitrophenol, picric acid and dipicrylamine have been studied in the two-phase system H_2O/CH_2Cl_2. Extraction constants and dissociation constants for the ion-pairs in the organic phase are given and show that the efficiency of extraction increases with the hydrophobicity of the counter-ion. At the same time, the selectivity decreases.

Liquid–liquid extraction is one of the most important techniques in analytical chemistry. It finds extensive applications, both in chemical analysis and organic preparative chemistry. The substances are usually extracted either as uncharged molecules or as ion-pairs. Extraction as ion-pairs has the advantage that both the efficiency of extraction and the selectivity can be considerably increased in comparison with extraction as molecules. The degree of extraction is expressed in terms of the distribution coefficient, that is, the equilibrium distribution of a substance between the aqueous phase and the immiscible organic phase. The principle of ion-pair formation has long been employed in the extraction of a large number of metals, but not the alkali metals, because of the lack of complexing agents forming stable complexes with them.

During the last decade, however, the so-called "crown ethers", first prepared by Pedersen,[1] have gained considerable importance because of their ability to form stable complexes with a number of metal ions, particularly the alkali metal ions. These crown ethers are macrocyclic compounds containing 9–60 atoms, including 3–20 oxygen atoms, in the ring. The complexation is said to result mainly from electrostatic ion–dipole attraction between the metal ion sitting in the cavity of the ring and the oxygen atoms surrounding it. The stability of the complex so formed and its stoichiometry are related to the relative size of the metal ion and the "hole" of the ring. If the ionic diameter of the metal is such that it just fits into the hole of the cyclic ring, a stable 1:1 complex is formed. However, if the metal ion is too small to fit into the cavity of the ring, this may lead either to incomplete complexation or to the formation of 2:1 and even 3:2 (M:L) stable complexes. In a similar manner, a metal ion of relatively large size may form 1:2 or 2:3 complexes.

The work done on the macrocyclic polyethers has been reviewed comprehensively by Christensen *et al.*[2] A number of workers have studied the complexing of various macrocyclic polyethers with alkali metal ions, by different techniques. Among them are Danesi *et al.*,[3–6] Frensdorff[7,8] and Sadakane *et al.*[9] Frensdorff's work was aimed at clarifying the relationship between the complexation and the size of the cation, the structure of the polyether and the nature of the solvent. His results show that potassium is best complexed by dicyclohexyl-18-crown-6 because the potassium ion has about the same diameter (2.68 Å) as the size of the hole in the cyclic polyether (2.6–3.2 Å).

Partition between an aqueous phase and an immiscible organic phase has proved useful as an aid in the study of complexation. This technique was used by all three groups mentioned above in their work on the extraction of alkali metal ions, with different counter-ions and cyclic polyethers.

Since the efficiency of ion-pair extraction depends, in addition to other factors, on the nature of the counter-ion, the present work was undertaken to investigate the influence of ions of different nature, such as dinitrophenols, picrates and dipicrylamine on the extraction of certain alkali and alkaline earth metals. We also wanted to investigate the possibilities of separating the alkali metal ions, by a simple liquid–liquid extraction method. In order to enhance the selectivity of extraction it would seem possible to use DCTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid) as an auxiliary complexing agent. We chose to work with dicyclohexyl-18-crown-6 because this cyclic polyether has been thoroughly investigated and forms stable complexes with some alkali and alkaline earth metals. As organic solvent, dichloromethane was chosen because it is moderately polar and because the partition of dicyclohexyl-18-crown-6 between water and dichloromethane is extremely small. The use of nitrophenols, picrates and dipicrylamine is justified partly because they provide

a rather bulky anionic component and partly because they facilitate the spectrophotometric determinations.

EXPERIMENTAL

Reagents and materials

Dicyclohexyl-18-crown-6 (Fluka, purum grade). The reagent was used without further purification. This cyclic polyether exists in two isomeric forms. No attempts were made to separate the two isomers and the results reported are, therefore, valid only for the isomeric mixture of the substance.

Dinitrophenols. Since these substances are commercially available as a 50% mixture with water, they were assayed by photometric titration in acetone medium with tetrabutylammonium hydroxide in benzene–methanol mixture. 2,5-Dinitrophenol was titrated at 546 nm and 2,6-dinitrophenol at 509 nm.

Picric acid. Standardized potentiometrically with sodium hydroxide.

Dipicrylamine. This substance is also obtainable as a 50% mixture with water. The reagent content was therefore assayed by an extractive photometric titration procedure in presence of tetramethylammonium as the counter-ion and dichloromethane as the organic solvent. The water content was determined by the Karl Fischer method as modified by Johansson.[10]

Calcium hydroxide. A saturated solution was standardized with hydrochloric acid. The calcium content was determined by titration with EDTA.

Sodium and potassium hydroxides. The solutions were prepared in carbon dioxide-free water and standardized with hydrochloric acid.

Dichloromethane, water-saturated.

Apparatus

The spectrophotometric measurements were made with Zeiss Model PMQ II and Hitachi Model 100-20 Digital spectrophotometers. An Eppendorf flame photometer was used for the determination of alkali metal concentrations in the organic phase.

Procedures

Extraction. The aqueous solutions were prepared by adding a known amount of standard alkali solution to the acid so that the resulting solution had a pH of 9 or greater, in order to make sure that protonation of the counter-ion could be neglected. The organic phase was made by dissolving dicyclohexyl-18-crown-6 in dichloromethane. Equal volumes of the two phases were placed in stoppered glass tubes and shaken at constant room temperature (20 ± 1°). Equilibrium is established rapidly and the two phases separate easily. The use of a centrifuge is not necessary but may occasionally be desirable to facilitate the phase separation.

In each system, the concentrations of polyether and the counter-ion were varied so that sufficient data were obtained for evaluating the extraction and dissociation constants. The concentrations used are included in Figs. 1–7.

Determination of concentrations. The equilibrium concentrations of dinitrophenols, picrate and dipicrylamine in the aqueous phase, and in a few cases in the organic phase, were determined spectrophotometrically. Since the sum of the two concentrations thus measured was in good agreement with the total amount taken, within the limits of experimental error, the concentration measurements were made mostly on the aqueous phase and the concentrations in the organic phase were taken by difference.

In a few cases, especially in blank tests, the content of alkali metal ions in the organic phase was determined by flame photometry.

RESULTS AND DISCUSSION

Equilibrium reactions

When the aqueous phase containing a metal ion M^+ and the counter-ion L^- is brought into contact with the organic phase containing the cyclic polyether E, the following equilibrium reactions are possible. The free cyclic polyether is distributed between the aqueous and the organic phase. The partition coefficient, P_E, is given by

$$E_{aq} \rightleftharpoons E_0; \quad P_E = \frac{[E]_0}{[E]_{aq}} \tag{1}$$

the brackets indicating molar concentrations.

The metal ion M^+ is complexed by the polyether transferred to the aqueous phase. The formation constant, K_s, of the reaction can be written as

$$M^+_{aq} + E_{aq} \rightleftharpoons ME^+_{aq}; \quad K_s = \frac{[ME^+]_{aq}}{[M^+]_{aq}[E]_{aq}}. \tag{2}$$

The predominant reaction is one in which the metal ion M^+ in the presence of the counter-ion L^- in the aqueous phase is extracted by the cyclic polyether as an ion-pair into the organic phase. The extraction constant, K_{ext}, for the reaction is given by

$$M^+_{aq} + L^-_{aq} + E_0 \rightleftharpoons MEL_0;$$

$$K_{ext} = \frac{[MEL]_0}{[M^+]_{aq}[E]_0[L^-]_{aq}} \tag{3}$$

$[MEL]_0$ represents the molar concentration of the ion-pair extracted into the organic phase. Since the organic solvent is moderately polar and the concentrations of the components are quite low, the ion-pair may dissociate in the organic phase. The dissociation constant, K_d can be expressed as

$$MEL_0 \rightleftharpoons ME^+_0 + L^-_0; \quad K_d = \frac{[ME^+]_0[L^-]_0}{[MEL]_0}. \tag{4}$$

Evaluation of concentration of different components

To evaluate the concentration of different components, the following points must be taken into consideration.

(*a*) In blank experiments, no detectable extraction was observed in the absence of either the polyether or the counter-ion since the working pH was sufficiently high.

(*b*) The partition of the uncomplexed polyether between the two phases is extremely small when dichloromethane is used as the organic solvent,[8] so its concentration in the aqueous phase and the subsequent formation of the metal complexes can be neglected.

(*c*) A phase-volume ratio of unity was maintained for each experimental point to simplify the calculations.

(*d*) The 1:1(:1) stoichiometry of the ion-pairs formed between the metal, the polyether, (and the

counter-ion), as demonstrated by different workers,[8] has also been assumed in the present work, except for calcium where the stoichiometry was assumed to be 1:1:2.

If C_M, C_L and $C_{E(0)}$ are the total concentrations of the metal ion, the counter-ion and the polyether respectively, and D is the distribution ratio, then (neglecting the formation of HL) for a univalent metal ion

$$[M^+] = C_M - A \quad (5)$$

$$[L^-] = C_L - A \quad (6)$$

$$[E]_0 = C_{E(0)} - A \quad (7)$$

and

$$D = A/(\psi)C_L - A\psi \quad (8)$$

where

$$A = [MEL]_0 + [L^-]_0 = [MEL]_0 + [ME^+]_0 \quad (9)$$

(assuming that MEL dissociates into ME^+ and L^- in the organic phase).

From equation (9) we can obtain

$$\begin{aligned}[MEL]_0 &= A - [L]_0 \\ &= A - (K_d[MEL]_0)^{1/2} \\ &= 1/2[K_d + 2A - (K_d^2 + 4AK_d)^{1/2}] \end{aligned} \quad (10)$$

Substitution of (5), (6), (7) and (10) in equation (3) gives a single relationship containing two unknowns, K_{ext} and K_d, which can be easily evaluated. In our work, this was accomplished by non-linear regression.

With a bivalent ion, such as the calcium ion, the corresponding reactions will be

$$M_{aq}^{2+} + E_{aq} \rightleftharpoons ME_{aq}^{2+} \quad (1a)$$

$$M_{aq}^{2+} + 2L_{aq}^- + E_0 \rightleftharpoons MEL_{2(0)};$$

$$K_{ext} = \frac{[MEL_2]_0}{[M^{2+}][E]_0[L^-]^2} \quad (2a)$$

and

$$MEL_{2(0)} \rightleftharpoons MEL_0^+ + L_0^-;$$

$$K_d = \frac{[MEL^+]_0[L^-]_0}{[MEL_2]_0}. \quad (3a)$$

There exists a possibility for the charged species MEL^+ to dissociate further in the organic phase according to the reaction

$$MEL^+ \rightleftharpoons ME^{2+} + L^- \quad (4a)$$

However, dissociation leading to such highly charged species in a slightly polar solvent such as dichloromethane would not seem likely. Initially, therefore, only the first dissociation step was considered. The results seem to justify this assumption.

At low pH-values some HL may be extracted as such and should be taken into account. The formation of dimeric ion-pairs is also possible but not very likely and has not been reported by other workers concerned with the complexing properties of the crown ethers. No systematic deviations indicating dimerization were found in the concentration range studied in this work.

The concentrations of the different components may in this case be calculated as follows.

If C_M, C_L and $C_{E(0)}$ are, as before, the total concentrations of the metal ion, the counter-ion and the polyether respectively, and D is the distribution ratio, then if the protonation of L is again neglected for a bivalent metal ion

$$[M^{2+}] = C_M - A \quad (5a)$$

$$[L^-] = C_L - 2A \quad (6a)$$

$$[E]_0 = C_{E(0)} - A \quad (7a)$$

and

$$D = 2A/(\psi)C_L - 2A\psi \quad (8a)$$

where

$$\begin{aligned}2A &= 2[MEL_2]_0 + [L^-]_0 + [MEL^+]_0 \\ &= 2[MEL_2]_0 + 2[L^-]_0 \\ &= 2[MEL_2]_0 + 2[MEL^+]_0 \end{aligned} \quad (9a)$$

(assuming that MEL_2 dissociates only into MEL^+ and L^- in the organic phase). From equation (9a), we can obtain

$$[MEL_2]_0 = 1/2[K_d + 2A - (K_d^2 + 4AK_d)^{1/2}] \quad (10a)$$

Treatment of the data

LETAGROP[11] could not be used to handle the data because it cannot take into account the dissociation of the ion-pair extracted into the organic phase. A short computer program was therefore written, which, for the given values of the distribution coefficient and concentrations, adjusts the values of the extraction and dissociation constants so as to minimize the sum of the squares of the differences between the calculated and experimental values of the measured variable, *viz.* the equilibrium concentration of the counter-ion in the organic phase. This enables us to find the values of the extraction and dissociation constants that will give the best explanation of the experimental data.

DISCUSSION

The values of log K_{ext} and log K_d that best describe the experimental values of A have been collected in Table 1. The values given were obtained by treating

Table 1. Extraction and dissociation constants

Metal ion	Ligand	log K_{ext}	log K_d
K^+	2,5-dinitrophenol	3.98	−4.6
K^+	2,6-dinitrophenol	4.26	−4.7
Na^+	picric acid	4.20	−4.1
K^+	picric acid	6.36	−4.6
Na^+	dipicrylamine	7.81	−4.8
K^+	dipicrylamine	8.16	−4.9
Ca^{2+}	dipicrylamine	10.23	−5.5

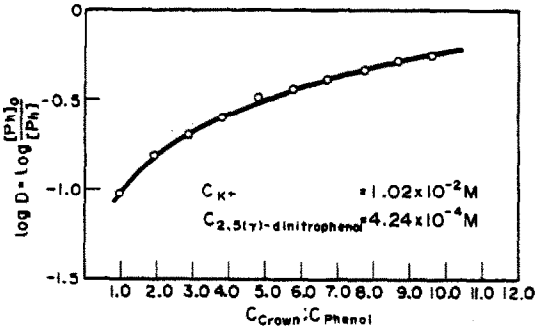


Fig. 1.

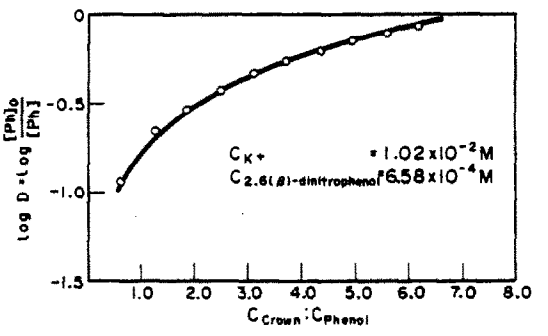


Fig. 4.

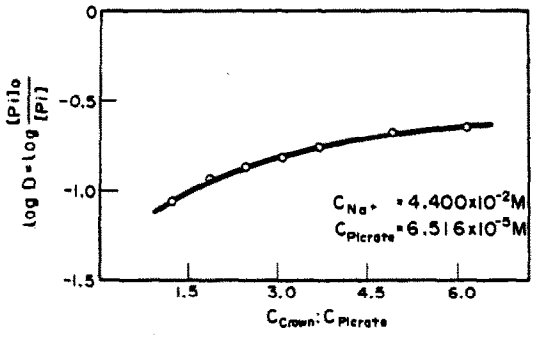


Fig. 2.

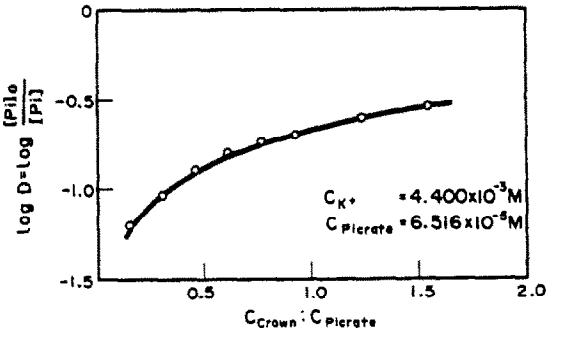


Fig. 5.

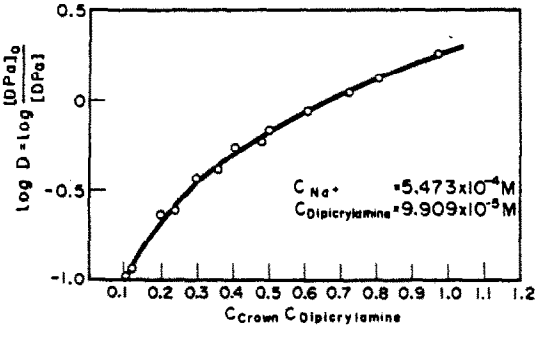


Fig. 3.

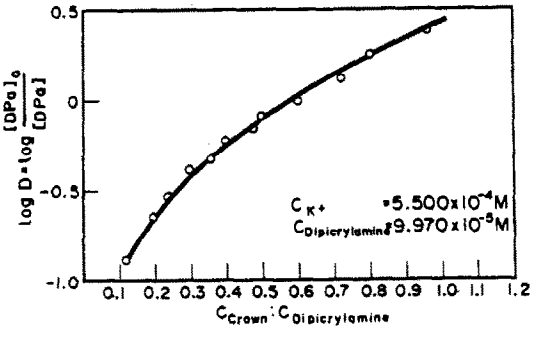


Fig. 6.

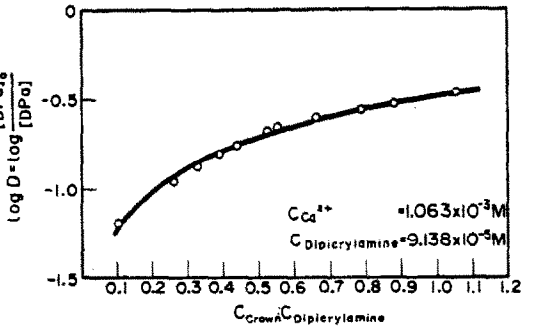


Fig. 7.

the data of 10–30 experimental points for each system at different polyether to counter-ion ratios in the manner described above. The picric acid–potassium constant is in good agreement with Frensdorff's value.[8]

In Figs. 1–7 the experimental *D*-values are plotted as functions of the concentration ratio of the crown ether to the ligand. The solid curves in the figures were calculated by using the constants yielded by the evaluation of the experimental data and show no evident systematic deviations. It is therefore concluded that the constants presented in Table 1 give a reasonable description of the data.

It is seen from Table 1 that, for the given conditions, the extraction increases in the order Ca < Na < K. This is consistent with the results

obtained by Izatt *et al.*,[12] and is due to increasingly strong complexation between the crown ether and the metal ion.

As may be expected, the bulkier ligands are less hydrophilic and therefore facilitate the extraction into an organic phase. For potassium ions, the extraction constant is about 1.8 logarithmic units higher for picric acid than for dinitrophenols and 2 logarithmic units higher still for dipicrylamine.

The selectivity for potassium in preference to sodium is greater when picric acid is used as the counter-ion instead of dipicrylamine. The separation factor is then well over 100. For dipicrylamine, it is only about 2. However, the selectivity is in no case great enough to make possible the separation of sodium and potassium by liquid–liquid extraction. Attempts to increase selectivity by using selective complexing agents such as DCTA will fail because both the conditional extraction constants will then be lowered to such an extent that neither of the ions can be extracted into an organic phase. It will, however, be possible to separate the ions by liquid chromatography and in that case a much shorter column will suffice if picric acid and not dipicrylamine is used as the counter-ion.

REFERENCES

1. C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
2. J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1973, **74**, 351.
3. P. R. Danesi, H. Meider-Gorican, R. Chiarigia and G. Scibona, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1479.
4. Lj. Tusek, H. Meider-Gorican and P. R. Danesi, *Z. Naturforsch.*, 1976, **31 b**, 330.
5. Lj. Tusek, P. R. Danesi and R. Chiarigia, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1538.
6. P. R. Danesi, R. Chiarigia, C. Fabiani and C. Domenichini, *ibid.*, 1976, **38**, 1226.
7. H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93**, 600.
8. *Idem, ibid.*, 1971, **93**, 4684.
9. A. Sadakane, T. Iwachido and K. Toei, *Bull. Chem. Soc. Japan* 1975, **48**, 60.
10. A. Johansson, *Sv. Papperstidn.*, 1974, **50**, 124.
11. P. Brauner, L. G. Sillén and R. Whiteker, *Arkiv Kemi*, 1969, **31**, 365, and references therein.
12. R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore and J. J. Christensen, *J. Am. Chem. Soc.*, 1971, **93**, 1619.

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THERMOMETRIC STUDIES ON THE Fe(III)–EDTA CHELATE

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Summary—A ΔH of -11.5 ± 0.5 kJ/mole has been determined for the formation of the Fe(III)–EDTA chelate at 25.0° and $\mu = 0.1$ ($= [HClO_4] + [NaClO_4]$) by a direct thermometric titration procedure. The entropy change, ΔS, has been calculated to be 440 $J.mole^{-1}.deg^{-1}$ by combining the result of the heat measurements with the free energy change obtained from the stability constant previously determined. A relationship between the ΔS values and the standard partial molal entropies of the tervalent metal ions is discussed. In addition, conditions for the thermometric titration of Fe(III) with Na_4EDTA at room temperature have been investigated. Iron(III) can be determined in the presence of fairly large amounts of phosphate, Cr(III), Mn(II) and Al(III).

The equilibrium of iron(III) with EDTA has been studied by many workers.[1] A log K_{FeY} value of 25.0 at 25° and $\mu = 0.1$ was selected by Martell and Smith.[2] Since the 1:1 Fe(III)–EDTA chelate is very stable, the enthalpy of formation is difficult to determine calorimetrically by the usual methods such as alkalimetry. In previous communications,[3,4] direct thermometric titrations giving a linear titration curve have been used for calculating the overall heat change of the reaction $MA_n + Y \rightleftharpoons MY + nA$. The enthalpy of formation of an EDTA chelate, ΔH_{MY}, can be obtained by correcting the observed overall heat changes for all the side-reactions accompanying formation of the EDTA chelate.

In this study we report the formation and protonation enthalpies of the Fe(III)–EDTA chelate at 25° and $\mu = 0.1$, obtained by means of a direct thermometric titration. The thermometric determination of iron(III) with Na_4EDTA is also described.

EXPERIMENTAL

Apparatus and procedures

The calorimetric measurements were made with a twin-type calorimeter composed of two identical 200-ml Dewar flasks, two 5-ml constant-rate burettes, a thermistor bridge circuit and a chart recorder.

Once thermal equilibrium was established (temperature drift less than 0.0002° in 15 min), titrant (1–5 ml) was added to 130.0 ml of titrand at a constant rate of 1.11 ml/min, and the temperature change was recorded as a function of time. Calibrations were performed before and after each titration by Joule heating; the potential drop (0.2–1.5 V) across an electric heater (9.032 ohm at 25.0°) was regulated with a potentiostat. The ΔT *vs.* time graphs obtained consisted of straight lines and the quantity of heat evolved in the titration was calculated by comparison of the slopes of the titration and calibration lines (mean value for calibrations before and after the titration, after correction for the volume change in the titration). To test the procedures and apparatus used, the heat of ionization of water was determined by titrating sodium hydroxide solution with perchloric acid, a value of $55.8_1 \pm 0.5$ kJ/mole at 25.0° being obtained.

Ultraviolet absorption spectra were measured with a Hitachi 124 recording spectrophotometer using 1-cm quartz cells, and accurate absorbance measurements were made with a Nippon Bunko UVIDEC-1 digital double-beam spectrophotometer.

Reagents

All iron(III) reagents used were of guaranteed grade except for ferric perchlorate, which was prepared from the chloride as usual. Approximately 0.1*M* solutions of ferric chloride, nitrate, sulphate and perchlorate were prepared so that the solutions were *ca.* 0.1*M* in the corresponding acid. The concentrations of iron(III) and free acid were determined by EDTA titration (Variamine Blue B as indicator) and by the method of Gustafson and Martell,[5] respectively.

The concentrations of sodium and free acid in the sodium perchlorate stock solution were determined by a method using cation-exchange and acid-base titration and by titration with standard alkali, respectively.

A solution of the tetrasodium salt of EDTA was prepared by dissolution of the disodium salt in CO_2-free distilled water containing the appropriate amount of sodium hydroxide and standardized with a standard zinc solution (Eriochrome Black T as indicator).

For the titration of iron(III) in phosphoric acid ferric phosphate was prepared by adding a solution of sodium dihydrogen phosphate to a ferric perchlorate solution and adjusting to the desired pH with perchloric acid, by use of a pH-meter calibrated with hydrochloric acid standards. In the other cases, the acidity of the iron(III) solutions was adjusted to the desired concentration with the corresponding acids.

Calculations

Formation constant and enthalpy of FeOH complex. It is well known that a solution of ferric perchlorate usually contains such species as Fe^{3+}, $FeOH^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$. In order to prevent the formation of the hydroxo-complexes other than $FeOH^{2+}$, the total iron(III) concentration was $4.8 \times 10^{-4}M$ and the total perchloric acid concentration above $4 \times 10^{-3}M$. In such conditions the absorption spectra of the solutions with various concentrations of perchloric acid had an isosbestic point at 272 nm as shown by Olson and Simonson.[10]

The formation of the $FeOH^{2+}$ complex may be described as follows:

$$Fe^{3+} + H_2O \overset{{}^*K_{FeOH}}{\rightleftharpoons} FeOH^{2+} + H^+ \quad \Delta^*H_{FeOH} \qquad (1)$$

and the equilibrium constant, ${}^*K_{FeOH}$, is defined as:

$${}^*K_{FeOH} = \frac{[FeOH^{2+}][H^+]}{[Fe^{3+}]} \qquad (2)$$

The total concentrations of perchloric acid and iron(III) are

$$\left.\begin{aligned} C_{HClO_4} &= [H^+] - [FeOH^{2+}] \\ C_{Fe} &= [Fe^{3+}] + [FeOH^{2+}] \end{aligned}\right\} \qquad (3)$$

and the apparent molar absorptivity at 300 nm, $\bar{\epsilon}$, is given by

$$\bar{\epsilon} = [\epsilon_{Fe}[Fe^{3+}] + \epsilon_{FeOH}[FeOH^{2+}]]/C_{Fe} \qquad (4)$$

where ϵ_{Fe} and ϵ_{FeOH} are the molar absorptivities at 300 nm of Fe^{3+} and $FeOH^{2+}$, respectively. There are three unknowns for this system, ${}^*K_{FeOH}$, ϵ_{Fe} and ϵ_{FeOH}. Suitable values of these unknowns are assumed, and the $\bar{\epsilon}$ value is calculated from equations (2)–(4) and expressed as $\bar{\epsilon}_{cal}$. The error square sum U is defined as:

$$U = \sum_i (\bar{\epsilon}_i - \bar{\epsilon}_{i,cal})^2 \qquad (5)$$

and the values ${}^*K_{FeOH}$, ϵ_{Fe} and ϵ_{FeOH} are refined by successive approximations by the least-squares method, which minimizes U.

Next 1.476M perchloric acid (1–4 ml) was added at constant rate to 130.0 ml of $2.5 \times 10^{-3}M$ ferric perchlorate at pH 1.8–2.1 with the ionic strength kept constant at 0.1M by addition of sodium perchlorate. The reaction of $FeOH^{2+}$ with perchloric acid is

$$FeOH^{2+}_2 + H^+ \rightarrow Fe^{3+} + H_2O - \Delta^*H_{FeOH} \qquad (6)$$

and therefore,

$$\Delta^*H_{FeOH} = Q_{corr}/\Delta n_{FeOH} \qquad (7)$$

where Δn_{FeOH} is the change in the number of moles of $FeOH^{2+}$ and Q_{corr} the observed effective heat corrected for the heat of dilution, and this can be calculated from equations (2) and (3) by using the ${}^*K_{FeOH}$ value.

Effective heat of dilution of Na_4EDTA

From 1 to 3 ml of 0.159M Na_4 EDTA, Y(Titrant), were added at constant rate to 130.0 ml of 0.1M acetic acid–sodium acetate buffer solution in the pH range from 4.0 to 4.5 at a total ionic strength of 0.1 (=[AcONa] + [$NaClO_4$]), or 130.0 ml of 0.1M perchloric, nitric or hydrochloric acid. The observed effective heat, Q_{obs}, is considered in terms of the effective heats of dilution of Na_4EDTA [equation ((8)], Q_D, and of protonation of the quadrivalent anion of EDTA, $Q_{Y'}$, which are expressed as follows:

$$Y(Titrant) \rightarrow Y^{4-}(Titrand) \qquad Q_D \qquad (8)$$

$$Y^{4-} + nH^+ \rightarrow (Y)' \qquad Q_{Y'} \qquad (9)$$

and in addition, in the case of acetic acid–sodium acetate buffer solutions, the heat effect of ionization of acetic acid, Q_{AcOH}, must be considered:

$$AcOH \rightarrow AcO^- + H^+ \qquad Q_{AcOH} \qquad (10)$$

and therefore,

$$Q_{obs} = Q_D + Q_{Y'} + Q_{AcOH} \qquad (11)$$

where (Y)′ is used to designate all the protonated EDTA species. The concentrations of the protonated EDTA species and acetic acid in the titrand can be calculated from the stoichiometry of the titration and the protonation constants of EDTA and acetic acid. Since

$$Q_{Y'} = \sum_n \Delta H_{H_nY}[H_nY]$$

and

$$Q_{AcOH} = -\Delta H_{AcOH} \cdot \Delta m_{AcOH},$$

the value of (Q_D) is calculated as follows:

$$-Q_D = -Q_{obs} + \sum_n \Delta H_{H_nY} \cdot [H_nY] - \Delta H_{AcOH} \cdot \Delta m_{AcOH} \qquad (12)$$

where ΔH_{H_nY} and ΔH_{AcOH} are the enthalpies of formation of the protonated EDTA species, H_nY, and acetic acid, respectively, and Δm_{AcOH} stands for the change in the acetic acid concentration during the titration.

The successive protonation enthalpies of EDTA used in this calculation are: $\Delta H_{HY} = -23.4$ kJ/mole, $\Delta H_{H_2Y} = -18.2$ kJ/mole, $\Delta H_{H_3Y} = +5.4$ kJ/mole and $\Delta H_{H_4Y} = +1.3$ kJ/mole at 25° and $\mu = 0.1$,[6,7] and further, $\Delta H_{H_5Y} = +2.1$ kJ/mole at 20° and $\mu = 0.1$.[4] The ΔH_{H_nY} values for n = 1–4 agree with the corresponding values determined at 20° and $\mu = 0.1$ by Anderegg,[8] within ± 0.5 kJ/mole. The corresponding protonation constants at 25° and μ = 0.1 selected by Martell[2] were used in the calculation.

These enthalpy values were mostly determined in 0.1M potassium nitrate medium. Knowledge of the protonation enthalpies of EDTA in various ionic media is required for calculating the heat effects of dilution of Na_4EDTA, but few reliable data for these enthalpies, except for the values of ΔH_{H_3Y} and ΔH_{H_4Y}, are available. Vasil'ev *et al.*[7] determined the ΔH_{H_3Y} and ΔH_{H_4Y} values in the presence of various electrolytes such as $NaClO_4$, $NaNO_3$, KNO_3 and $LiNO_3$, at ionic strengths 0.2–0.75. The ΔH_{H_3Y} values obtained by extrapolating their data to $\mu = 0.1$ are constant within ± 0.2 kJ/mole. A similar result is obtained for the ΔH_{H_4Y} values. In a solution of low ionic strength (*e.g.*, 0.1) the effect of supporting electrolytes on the heats of protonation of EDTA seems unimportant.

The K_{AcOH}[9] and ΔH_{AcOH} values of $10^{4.65}$ and -0.1_7 kJ/mole, respectively, were used in the calculation. The latter value was determined experimentally at 25° and $\mu = 0.1$ (= [AcONa] + [$NaClO_4$]).

Enthalpy of formation of Fe(III)–EDTA chelate

From 1 to 3 ml of 0.159M Na_4EDTA were added as before to 130.0 ml of *ca.* $5 \times 10^{-3}M$ ferric perchlorate containing free perchloric acid in the concentration range 0.02–0.1M, the total concentration of perchlorate being kept at 0.1M by addition of sodium perchlorate. The observed effective heat, Q_{obs}, is considered in terms of the effective heat of dilution of Na_4EDTA (Q_D), and heat of reaction of iron(III) with Y^{4-} ($Q_{FeY'}$), expressed as follows:

$$(Fe^{3+})'_b + Y^{4-} \rightarrow (FeY^-)'_a \qquad Q_{FeY'} \qquad (13)$$

and therefore,

$$Q_{obs} = Q_D + Q_{FeY'} \qquad (14)$$

$(Fe^{3+})'_b$ being the total ferric ion concentration in the titrand before the titration and $(FeY^-)'_a$ that of the 1:1 species involving Fe(III) and Y in the titrand after the titration. The solution equilibria involving in the titrand after the titration are as follows:

$$Fe^{3+} + Y^{4-} \overset{K_{FeY}}{\rightleftharpoons} FeY^- \qquad \Delta H_{FeY} \qquad (15)$$

$$Fe^{3+} + Y^{4-} + H^+ \overset{K_{FeHY}}{\rightleftharpoons} FeHY \qquad \Delta H_{FeHY} \qquad (16)$$

$$Fe^{3+} + H_2O \overset{{}^*K_{FeOH}}{\rightleftharpoons} Fe(OH)^{2+} + H^+ \quad \Delta^*H_{FeOH} \qquad (17)$$

where K_{FeY} and ΔH_{FeY} are the formation constant and the enthalpy of formation, respectively, of the Fe(III)–EDTA chelate, and K_{FeHY} and ΔH_{FeHY} are the overall formation

constant and the enthalpy of formation, respectively, of the monoprotonated Fe(III)–EDTA chelate. Since iron(III) is present in excess under the experimental conditions, the following stoichiometric relations hold:

$$\left.\begin{aligned} C_{HClO_4} &= [H^+] - [FeOH^{2+}] + [FeHY] \\ C_{Fe} &= [Fe^{3+}] + [FeOH^{2+}] + [FeY^-] + [FeHY] \\ C_Y &= [FeY^-] + [FeHY] \end{aligned}\right\} \quad (18)$$

where C_{HClO_4}, C_{Fe} and C_Y are the total concentrations of perchloric acid, iron(III) and EDTA, respectively. The concentration of each species is calculated from equation (18) by using the values for K_{FeHY}[2] and $^*K_{FeOH}$. Since the concentration of each species in the titrand before the titration is calculated in a similar manner as above [*cf.* equations (1)–(3)], the changes in the number of moles of each species during the titration can be obtained from the results. From a consideration of equations (14)–(17), we obtain:

$$\begin{aligned} Q_{corr} &= Q_{obs} - Q_D \\ &= Q_{FeY} \\ &= Q_{FeY} + Q_{FeHY} - Q_{FeOH} \\ &= \Delta H_{FeY} \cdot \Delta m_{FeY} + \Delta H_{FeHY} \cdot \Delta m_{FeHY} \\ &\quad + \Delta H^*_{FeOH} \cdot \Delta m_{FeOH} \end{aligned} \quad (19)$$

where Q_{FeY}, Q_{FeHY} and Q_{FeOH} stand for the effective heats of reactions (15), (16) and (17), respectively, and Δm_{FeY}, Δm_{FeHY} and Δm_{FeOH} stand for the changes in the number of moles of the FeY, FeHY and FeOH complexes, respectively. Two unknown values in this system, *i.e.*, ΔH_{FeY} and ΔH_{FeHY}, can be refined by means of a successive approximation using a least-squares method in a similar manner as above [*cf.* equations (4)–(5)].

RESULTS AND DISCUSSION

Few values of the first hydrolysis constant of iron(III) in the ionic medium 0.1*M* ($[HClO_4] + [NaClO_4]$) at 25° have been obtained.[1] Therefore, this constant was determined spectrophotometrically for these conditions. Measurements were made with ferric solutions ranging in perchloric acid concentration from 4.0×10^{-3} to 0.1*M*. The results obtained are $-\log^*K_{FeOH} = 2.50 \pm 0.03$; $\epsilon_{Fe} = 126 \pm 51$. $mole^{-1}.cm^{-1}$ (300 nm); $\epsilon_{FeOH} = 2020 \pm 50$ (300 nm). Olson and Simonson[10] obtained a value of 2.55 for $-\log^*K_{FeOH}$ at relatively low perchloric acid concentration ($1.5–5.5 \times 10^{-3}M$) at an ionic strength of 0.046*M*, and showed that the degree of hydrolysis of ferric ion increases as the perchlorate ion concentration decreases. The value obtained in this study is somewhat lower than theirs, presumably because of the difference in perchloric acid concentration.

The Δ^*H_{FeOH} value of 42.3 ± 6 kJ/mole was obtained at an ionic strength of 0.1*M*. The calorimetric Δ^*H_{FeOH} value at an ionic strength of 3*M* ($NaClO_4$), recalculated by Arnek,[11] is 46.0 ± 7.5 kJ/mole. Milburn[12] reports a Δ^*H_{FeOH} value of 42.7 kJ/mole for an ionic strength of 1*M* ($NaClO_4$), calculated from the temperature dependence of $^*K_{FeOH}$ values determined spectrophotometrically. Since all the present study was carried out at an ionic strength of 0.1*M*, the Δ^*H_{FeOH} value obtained cannot be directly compared with the others.

The effective heats of dilution of Na_4EDTA (0.159*M*), ΔH_D (kJ/mole of EDTA), in various media are as follows: 3.8 ± 0.2 at $\mu = 0.1$ (= [AcONa] + $[NaClO_4]$); 3.8 ± 0.4 at $\mu = 0.1$ ($HClO_4$); 4.2 ± 0.4 at $\mu = 0.1$ (HNO_3); 5.0 ± 0.3 at $\mu = 0.1$ (HCl). The observed ΔH_D values (except for hydrochloric acid medium) are in fairly good agreement with each other, and 3.8 kJ/mole was therefore used in the subsequent calculations. These heats of dilution probably include not only the heat of dilution for each ionic EDTA species in the titrant but also the heat of dissociation of the sodium–EDTA complex, and therefore are much greater than those of common electrolytes.

Small changes in hydrogen ion concentration were observed in the titrations of iron(III) with Na_4EDTA. Therefore, the values of Q_{FeY} were plotted (Fig. 1) against the averaged pH values, pH_{av}, of the titrands during the titrations, and the best fit was calculated by using the values $\Delta H_{FeY} = -11.6$ kJ/mole and $\Delta H_{FeHY} = -11.7$ kJ/mole. Repeated measurements at various initial concentrations of iron(III) gave a ΔH_{FeY} value of -11.5 ± 0.5 kJ/mole and a ΔH_{FeHY} value of -11.6 ± 0.5 kJ/mole. The broken lines in Fig. 1 show the curves for Q_{FeY}, Q_{FeHY} and Q_{FeOH}, calculated from these results. It is seen from this figure that the heats evolved in the formation of Fe(III)–EDTA chelates, *i.e.*, Q_{FeY} and Q_{FeHY}, are nearly constant and thus the Q_{FeY} values increase as the averaged pH values increase because of heat of dissociation of the $FeOH^{2+}$ complex.

A ΔG value for formation of the Fe(III)–EDTA chelate was calculated from $\Delta G = -RT \ln K$ and the K_{FeY} value[2] at 25° and $\mu = 0.1$, and then a ΔS value was obtained from $\Delta G = \Delta H - T\Delta S$. The results thus obtained are $\Delta G = -143$ kJ/mole; $\Delta S = 440$ $J.mole^{-1}.deg^{-1}$.

Charles[13] pointed out that a plot of ΔS°_{MY} for the formation of EDTA chelates of uni- and bivalent

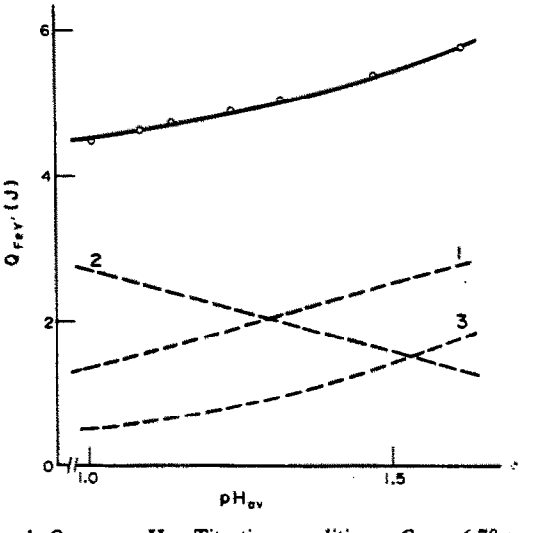


Fig. 1. Q_{FeY} *vs.* pH_{av}. Titration conditions: $C_{Fe} = 6.78 \times 10^{-3}$ *M*, final concentration of EDTA = 2.67×10^{-3} *M*. Solid line is the best fit calculated from the enthalpies ΔH_{FeY} and ΔH_{FeHY}. The broken lines represent: (1) Q_{FeY}; (2) Q_{FeHY}; (3) Q_{FeOH}.

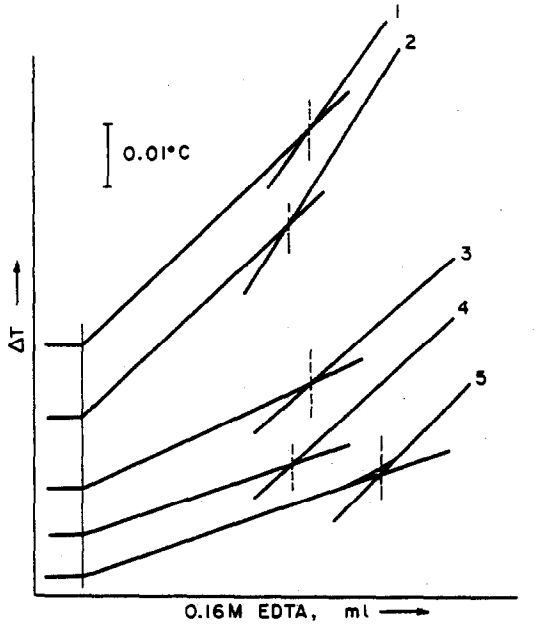


Fig. 2. Thermometric titrations of Fe(III) with Na_4EDTA in various mineral acids. $C_{Fe} = 5 \times 10^{-3}M$, $C_{acid} = 0.05M$. (1) H_3PO_4; (2) H_2SO_4; (3) HCl; (4) HNO_3; (5) $HClO_4$. (-----) End-point.

metal ions *vs.* the standard partial molal entropy, $\bar{S}^{\circ}_{M}$, for the corresponding metal ions gave a straight line of unit slope. The ΔS_{MY} values[2] for tervalent metal ions were therefore plotted against the $\bar{S}^{\circ}_{M}$ values.[14] An approximately linear relationship was obtained, with a slope of *ca.* 1.7. This shows that the ΔS_{MY} value is not governed by only the $\bar{S}^{\circ}_{M}$ value. Furthermore, the large value of the slope suggests that the normal partial molal entropy values[15] for the M(III)Y chelates, that is, $(\bar{S}^{\circ}_{MY} + x\bar{S}^{\circ}_{H_2O})$, are not constant throughout the series. The ΔS_{FeY} value obtained in this study agrees with that expected from the $\bar{S}^{\circ}_{Fe(III)}$ value, and is nearly equal to the ΔS_{AlY} value[2] of 494 J.mole.deg^{-1} at 25°. Thus, in analogy with the Al(III)–EDTA chelate,[16] the stability of the Fe(III)–EDTA chelate is determined largely by the entropy change associated with its formation. Moreover, the ΔH_{FeY} value is more exothermic by 60–70 kJ/mole than the ΔH_{AlY} value of 52.7 kJ/mole at 20° and $\mu = 0.1$. The large difference between the formation enthalpies of the EDTA chelates of Fe(III) and Al(III) means that the Fe(III)–EDTA chelate is much more stable than the Al(III)–EDTA chelate. Radmacher and Schmitz[17] showed that Fe(III) can be determined in presence of Al(III) by titration with EDTA, salicylic acid being used as indicator.

ANALYTICAL APPLICATION

Typical thermograms for titrations of iron(III) with Na_4EDTA in various mineral acids at room temperature are shown in Fig. 2. For hydrochloric, sulphuric or phosphoric acid media, the curves give well-defined inflection points, whereas those for perchloric or

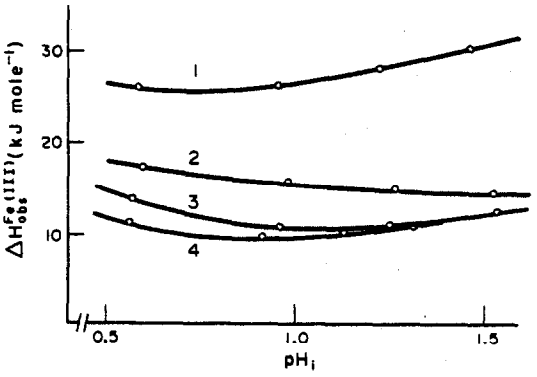


Fig. 3. Observed heat effect $\Delta H^{Fe(III)}_{obs}$ as a function of pH_i. Titration conditions: $C_{Fe} = 5 \times 10^{-3}M$, EDTA concentration of titrant = 0.159*M*. (1) H_2SO_4; (2) HCl; (3) HNO_3; (4) $HClO_4$.

nitric acid media have rounded inflection points. Determination of iron(III) in nitric acid medium by extrapolating the portions of the titration curve before and after the end-point results in an error of about 3%. This is consistent with the result reported by Priestley.[18] The difference in the titration curves seems to be due to the difference in the rate of the formation of the Fe(III)–EDTA chelate in the presence of complex-forming anions because the equilibrium conditions for the titrations of Fe(III) in the presence of perchlorate and nitrate ions are more advantageous than those for the titrations in the presence of chloride, sulphate and phosphate ions.

The good linearity of all the thermograms obtained makes it possible to calculate the heat evolved in the titration from the slope of the thermogram. The heats evolved before and after the equivalence point in the titration are expressed by $\Delta H^{Fe(III)}_{obs}$ [kJ/mole of Fe(III)] and ΔH^{Y}_{obs} (kJ/mole of EDTA), respectively. If the acid concentration of the ferric solution to be titrated is denoted by $[Acid]_i$, plots of $-\log[Acid]_i$ ($= pH_i$) *vs.* $\Delta H^{Fe(III)}_{obs}$ and ΔH^{Y}_{obs} have the appearances shown in Figs. 3 and 4, respectively. The larger the difference between $\Delta H^{Fe(III)}_{obs}$ and ΔH^{Y}_{obs} at the same pH_i value, the more readily can the end-point be judged. In the titration of Fe(III) in hydrochloric acid medium, the difference is approximately constant over

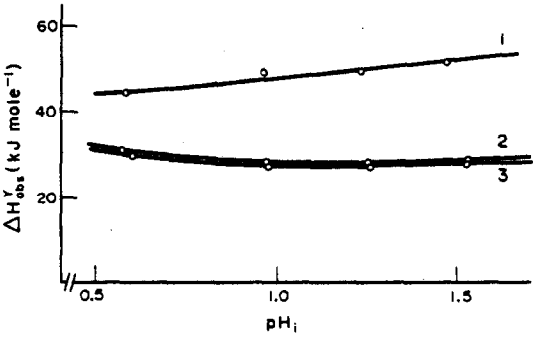


Fig. 4. Observed heat effect ΔH^{Y}_{obs} as a function of pH_i. Titration conditions as for Fig. 3. (1) H_2SO_4; (2) HNO_3 or $HClO_4$; (3) HCl.

Table 1. Determination of iron(III) with Na_4EDTA in the presence of other ions

Fe taken, *mg*	Other ion taken, *mg*	Fe found, *mg*
18.2		18.3
36.5		36.4
36.5		36.7
54.7		54.6
	Cr(III)	
36.5	338	36.6
36.5	676	36.8
54.7	338	54.7
54.7	676	55.1
	Mn(II)	
36.5	182	36.7
36.5	363	36.8
	Al(III)	
36.5	35	36.8
36.5	88	36.9
54.7	88	55.0
	PO_4^{3-}	
36.5	615	36.5
36.5	1230	36.8

Conditions: $C_H = 0.05M$; $C_{Cl} = 0.1$–$0.3M$; temperature 25°C.

the concentration range shown in the figures, but for sulphuric acid medium the difference becomes smaller with increasing pH_i. Therefore, the recommended titration medium is 0.01–0.1*M* hydrochloric acid or 0.03–0.1*M* sulphuric acid. For a ferric solution containing only perchloric or nitric acid, the hydrogen ion concentration of the solution should be adjusted to 0.01–0.1*M* and enough sodium chloride should be added to give a final chloride concentration of 0.1–0.3*M*.

Typical analytical results for the titration of Fe(III) with Na_4EDTA in the presence of various ions are shown in Table 1. Ions such as Cr(III) which are kinetically inert to substitution do not interfere. Mn(II) and the alkaline-earth metal ions, which do not form chelates with EDTA under the experimental conditions, also cause no interference. It is very interesting that Al(III) did not interfere even when present in 5-fold molar ratio to Fe(III). However, Cu(II), Ni(II) and Co(II) interfere by formation of their EDTA chelates in the course of the titration.

REFERENCES

1. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, 1964 and 1971.
2. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 1: Amino Acids, Plenum Press, New York, 1974).
3. K. Doi and M. Tanaka, *Anal. Chim. Acta*, 1974, **71**, 464.
4. K. Doi, *ibid.*, 1975, **74**, 357.
5. R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, 1963, **67**, 576.
6. G. C. Kugler and G. H. Carey, *Talanta*, 1970, **17**, 907.
7. V. P. Vasil'ev, L. A. Kochergina and T. D. Yastrebova, *Zh. Obshchei Khim.*, 1973, **43**, 975.
8. G. Anderegg, *Helv. Chim. Acta*, 1967, **50**, 2333.
9. A. Ringbom, *Complexation in Analytical Chemistry*, Wiley, New York 1963.
10. A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, 1949, **17**, 1322.
11. R. Arnek and K. Schlyter, *Acta Chem. Scand.*, 1968, **22**, 1327.
12. R. M. Milburn, *J. Am. Chem. Soc.*, 1957, **79**, 537.
13. R. G. Charles, *ibid.*, 1954, **76**, 5854.
14. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, NBS Circular 500, U.S. Dept. of Commerce, Washington, D.C., 1952.
15. J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1443, 1446, 1451.
16. T. Moeller and Shu-Kung Chu, *J. Inorg. Nucl. Chem.*, 1966, **28**, 153.
17. W. Radmacher and W. Schmitz, *Brennstoff. Chem.*, 1959, **40**, 161.
18. P. T. Priestley, *Analyst*, 1963, **88**, 194.

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ION-EXCHANGER COLORIMETRY—II MICRODETERMINATION OF CHROMIUM IN NATURAL WATERS

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Summary—Ion-exchanger colorimetry for chromium(VI) with 1,5-diphenylcarbohydrazide has been developed for the determination of chromium at μg/l. concentrations in natural water samples. About 90% of the chromium(VI) in a 1-litre sample solution is concentrated in 200–400 mesh Dowex 50W-X4 resin within half an hour. It is possible to obtain higher sensitivity by employing a larger amount of sample solution. Total chromium can be determined by oxidizing chromium(III) to chromium(VI) with ceric sulphate.

Chromium is known to occur widely in nature and to be present at μg/l. levels (or lower) in natural waters. However, the concentration of chromium in the environment is becoming higher from industrial waste materials, which result from many processes in industry such as electroplating. Even minute trace amounts of chromium, especially sexivalent chromium, do harm to animals and plants. Consequently, attention must be paid to environmental pollution by chromium. For this purpose, trace analytical methods have been developed by many investigators.[1–7] Almost all of them require some time-consuming preconcentration steps.

In our previous work, light-absorption by an ion-exchange resin phase, which sorbed the coloured sample complex species, was measured and employed for microdetermination of chromium(VI), iron(II) and (III), copper(II), and cobalt(II) in water.[8] The advantages of this method are that concentration and colour development for the metal concerned take place simultaneously and that sensitivity and selectivity are higher than those of the conventional colorimetric method.

The aim of the present paper is to develop ion-exchanger colorimetry for chromium(VI) with 1,5-diphenylcarbohydrazide in order to determine chromium at the μg/l. level in natural water samples.

EXPERIMENTAL

Chemicals

Dowex 50W-X4 (200–400 mesh) in the hydrogen form was used. It was conditioned, air-dried, and stored in a polyethylene container.

Standard chromium(VI) stock solution was prepared by dissolving an appropriate amount of potassium dichromate in demineralized water and standardized cerimetrically.

Standard chromium(III) stock solution in 1*M* sulphuric acid was prepared by reducing standard chromium(VI) solution with sodium sulphite.

1,5-Diphenylcarbohydrazide (analytical grade) was used as a 0.25% solution in acetone.

All other chemicals used were of analytical grade.

Spectrophotometric measurements

Spectrophotometric measurements were performed with the same instrument and the same procedure as those described in the previous paper,[8] except for the sample cell. The quartz cell with a small hole at the bottom (Fig. 1) makes the packing of the coloured resin beads easier, because the equilibrated solution flows out through the small hole and the beads settle down in a shorter time.

Procedure for the determination of chromium(VI)

To a 1-litre water sample containing 0.01–0.3 μmole of chromium(VI), concentrated sulphuric acid was added to make the concentration of the acid approximately 0.05*M*. Then 15 ml of 0.25% acetone solution of the reagent and 0.50 g of the resin were added. The mixture was stirred for 30 min, the coloured resin collected, and the resin slurry transferred to the cell. The absorbances at 550 and 700 nm were measured.

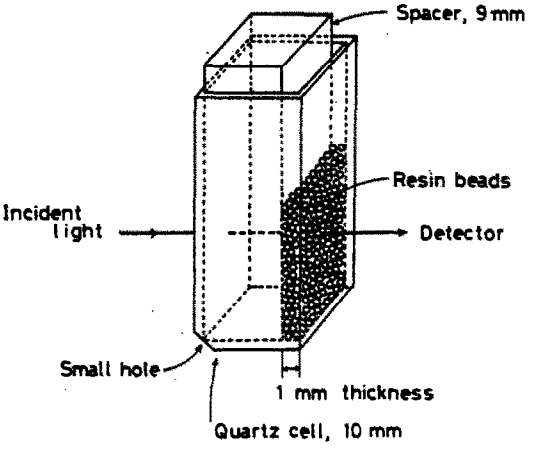


Fig. 1. The resin-holder for colorimetric determination.

Procedure for the determination of total chromium

To a 1-litre water sample were added sulphuric acid to make the concentration of the acid approximately 0.05*M* and 5 ml of 0.005*M* ceric sulphate. The solution was kept at 100° for 5 min, then cooled to about 20°. The colour reagent and the resin were added and the mixture was treated by the procedure described above.

Distribution measurements

To a 200-ml water sample containing 0.30 μmole of chromium(VI), 2 ml of 2.5*M* sulphuric acid, 5 ml of the colour reagent, and then 0.50 g of Dowex 50W-X2 (100–200 mesh) in the hydrogen form were added. After a 15-min equilibration, the chromium concentration, *C* (mole/l.) of the equilibrated solution separated from the resin was determined by ion-exchanger colorimetry.[8] The distribution ratio, *D*, was calculated from

$$D = \frac{\text{mmole of Cr sorbed per g of resin}}{\text{mmole of Cr per ml of solution}}$$

$$= \frac{(3{\cdot}0 \times 10^{-4} - 200\,C)/0.50}{200\,C/207}$$

$$= (6.2 \times 10^{-4}/C) - 4.1 \times 10^{2}$$

RESULTS AND DISCUSSION

Volume effect on the sensitivity

In ion-exchanger colorimetry the sensitivity should be increased if a larger amount of sample solution is taken for equilibration with the resin. The increase in sensitivity can be estimated from the distribution ratio *D*. If *m* g of the resin be added to *V* ml of sample solution, the amount of sorbed complex, M_R, is estimated by

$$M_R = \frac{mDV}{mD + V} \cdot C_i \qquad (1)$$

where C_i is the initial concentration of the sample solution. This value of M_R can be related to the value of A_{RC} [see equation (1) in the previous paper[8]]. When V_2 ml, instead of V_1 ml, of the sample solution is equilibrated with the resin, the sensitivity ratio, S_{V_2}/S_{V_1}, is calculated as follows:

$$S_{V_2}/S_{V_1} = \frac{(mD + V_1)}{(mD + V_2)} \cdot \frac{V_2}{V_1}. \qquad (2)$$

In Table 1, the relations between the sensitivity and sample volume are listed with respect to the reference volume of 200 ml. In the case of chromium, the distribution ratio found was 1.2×10^4, promising a much higher sensitivity by use of a larger amount of sample solution. Optimum conditions were established for the use of a 1-litre sample solution.

Time-dependence of colour development

Amount of the resin. A large amount of the resin may lower the concentration of the complex species sorbed, whereas too small an amount may result in slow sorption and difficulty in operation. For all measurements 0.50 g of the resin was used.

Particle size of the resin. With a 200-ml sample solution and 100–200 mesh resin it took about 15 min for the sorption of chromium.[8] As shown in Fig. 2, equilibrium with a 1-litre sample solution and Dowex 50W-X2 50–100 or 100–200 mesh resin took more than 1 hr to reach. Use of 200–400 mesh Dowex 50W-X4, which makes it possible to sorb almost all the chromium within 30 min, may be recommended for large sample volumes, even though the separation and packing of the resin are somewhat difficult.

Acid concentration of a sample solution. As a suitable acidity (mineral acid) for the chromium–1,5-diphenylcarbohydrazide reaction, 0.025–0.1*M* has been recommended.[9] For the ion-exchanger colorimetry, the colour development was almost complete even at an acidity as low as 0.0025*M*.

Table 1. Volume effect on the sensitivity with respect to that with a reference volume of 200 ml (m = 0.50 g)

D	S_{100}/S_{200}	S_{500}/S_{200}	S_{1000}/S_{200}	S_{5000}/S_{200}	S_{10000}/S_{200}
10^2	0.83	1.14	1.19	1.24	1.24
10^3	0.58	1.75	2.33	3.18	3.33
10^4	0.51	2.36	4.33	13.0	24.8
10^5	0.50	2.49	4.92	22.8	41.8

Table 2. Reproducibility of measurements

[Cr(VI)] *M*	$A_{RC(550\,nm)}$†	Relative standard deviation, %
0	0.069 ± 0.002 (A_R^*)‡	3.5
1.5×10^{-8}	0.061 ± 0.004	6.5
1.0×10^{-7}	0.384 ± 0.013	3.5
2.0×10^{-7}	0.753 ± 0.024	3.2

Resin: Dowex 50W-X4 (200–400 mesh, H^+ form), 0.50 g. Solution: 1 litre + 3 ml of conc. H_2SO_4. Stirring time: 30 min.

† $A_{RC(550\,nm)} = A_{(550\,nm)} - A_{(700\,nm)} - A_R^*$.

‡ $A_R^* = A_{(550\,nm)} - A_{(700\,nm)}$ (for blank).

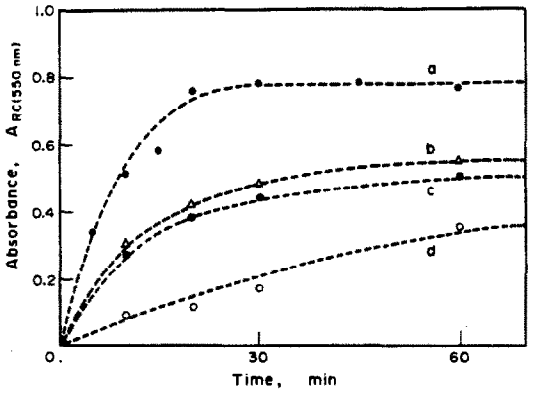


Fig. 2. Colour development of the chromium–1.5-diphenylcarbohydrazide complex in the cation-exchange resin phase. Resin: a, b; Dowex 50W-X4 (200–400 mesh, H^+ form), 0.50 g. c; Dowex 50W-X2 (100–200 mesh, H^+ form), 0.50 g. d; Dowex 50W-X2 (50–100 mesh, H^+ form), 0.50 g. Solution: a, c, d; 0.2 μmole of Cr(VI) + 1 litre of water + 3 ml of conc. H_2SO_4. b; 0.2 μmole of Cr(VI) + 1 litre of 0.6M NaCl + 3 ml of conc. H_2SO_4.

The reagent concentration. The effect of the reagent concentration on the colour development at the $2 \times 10^{-7}M$ chromate level was studied over the range 1×10^{-6}–$2.5 \times 10^{-4}M$. Colour development was complete when the reagent concentration was higher than $1 \times 10^{-4}M$, and 15 ml of 0.25% reagent solution was adequate in the standard procedure for a 1-litre sample, *i.e.*, the final concentration of the reagent was $1.5 \times 10^{-4}M$.

Calibration and precision

The calibration curves are reasonably linear in the concentration ranges 1×10^{-8}–$3 \times 10^{-7}M$ for 1-litre samples and 1.5×10^{-8}–$5 \times 10^{-7}M$ for 1-litre samples with a 0.6*M* concentration of sodium chloride.

Precision was measured with 1-litre samples with chromium(VI) concentrations of 1.5×10^{-8}, 1.0×10^{-7} and $2.0 \times 10^{-7}M$. For 10 determinations, the relative standard deviations were 6.5, 3.5 and 3.2% respectively, as shown in Table 2.

Sensitivity

The sensitivity was compared with that obtained previously for 200-ml samples. It was improved by a factor of 4.8 (to $1.2 \times 10^{-7}M$) for 1-litre samples and a factor of 2.7 (to $2.5 \times 10^{-7}M$) for 1-litre samples that were 0.6*M* in sodium chloride.

The relative detection limit may be defined as the concentration that produces an absorbance equal to twice the magnitude of the fluctuation in the background absorbance, A_R^* (Table 2). In this case the limit was $2.1 \times 10^{-9}M$, *i.e.*, 0.11 μg/l.

Effect of the concentration of background electrolyte

The presence of sodium chloride as background electrolyte at the concentration level found in seawater had no effect on the sorption rate of the complex from 200-ml samples. As shown in Fig. 3, the presence of sodium chloride resulted in a lower absorbance than that in the absence of the salt for 1-litre samples, because of both the lower distribution ratio and the lower sorption rate of the sample species (Fig. 2, curves a and b). A competition between these two factors and a volume contraction of the resin beads, which leads to increased concentration of the coloured species in the resin and hence to an increased effective light-path, may occur in the system. For the determination of chromium by this method it is recommended to use a calibration curve prepared at the same concentration of background electrolyte as that in the sample solution, particularly in the case of a high electrolyte concentration. Alternatively the standard addition method can be applied.

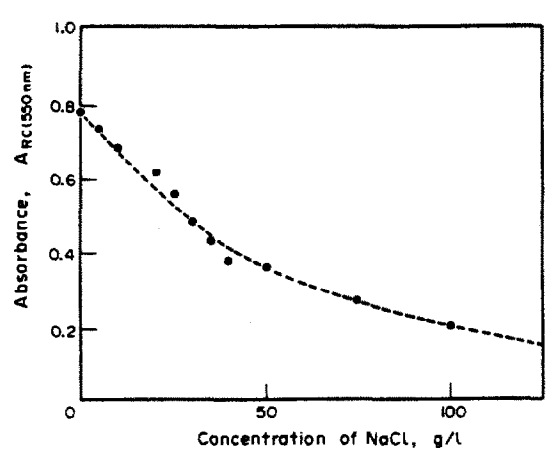


Fig. 3. Dependence of the colour development on concentration of sodium chloride. Resin: Dowex 50W-X4 (200–400 mesh, H^+ form), 0.50 g. Solution: 0.2 μmole of Cr(VI) + 1 litre of NaCl solution + 3 ml of conc. H_2SO_4. Stirring time: 30 min.

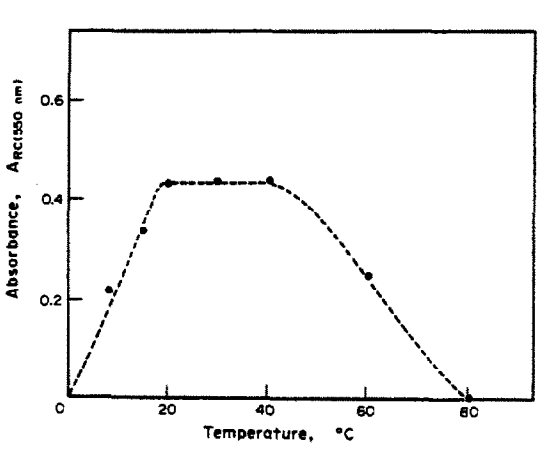


Fig. 4. Temperature-dependence of the resin colour development. Resin: Dowex 50W-X4 (200–400 mesh, H^+ form), 0.50 g. Solution: 0.1 μmole of Cr(VI) + 1 litre of water + 3 ml of conc. H_2SO_4. Stirring time: 30 min.

Table 3. Effects of foreign ions on the determination of chromium(VI)

	Concentration, $10^{-7}M$	Cr taken, $10^{-7}M$	$A_{RC(550\,nm)}$	Cr found, $10^{-7}M$	Relative error, %
		0.92	0.370	0.98	+6.5
		1.83	0.664	1.76	−3.8
		2.75	1.059	2.81	+2.2
		3.66	1.376	3.65	−0.3
V(V)	200	1.83	0.771	1.86	+1.6
	2000	1.83	0.618	1.64	−10.4
Cr(III)	200	1.83	0.686	1.82	−0.5
	2000	1.83	0.689	1.83	0
Mn(II)	200	1.83	0.695	1.84	+0.5
	2000	1.83	0.733	1.94	+6.0
Fe(III)	200	1.83	0.683	1.81	−1.1
	2000	1.83	0.666	1.76	−3.8
Co(II)	200	1.83	0.699	1.85	+1.1
	2000	1.83	0.714	1.89	+3.3
Ni(II)	200	1.83	0.721	1.91	+4.4
	2000	1.83	0.678	1.80	−1.6
Cu(II)	2	1.83	0.663	1.76	−3.8
	20	1.83	0.531	1.41	−23.0
	200	0.92	0.223	0.59	−35.9
	200	1.83	0.473	1.25	−31.7
	200	2.75	0.697	1.85	−32.7
Zn(II)	200	1.83	0.698	1.85	+1.1
	2000	1.83	0.728	1.93	+5.5
Mo(VI)	200	1.83	0.725	1.92	+4.9
	2000	1.83	0.682	1.81	−1.1
Cd(II)	200	1.83	0.656	1.74	−4.9
Sn(IV)	200	1.83	0.728	1.93	+5.5
	2000	1.83	0.722	1.91	+4.4
Ce(III)	2000	1.83	0.656	1.74	−4.9
Ce(IV)	2000	1.83	0.701	1.86	+1.6
Hg(II)	200	1.83	0.712	1.89	+3.3
Pb(II)	200	1.83	0.720	1.91	+4.4

Effect of temperature

The absorbance of the sorbed complex was nearly constant in the temperature range 20–40°. At temperatures lower than 20°, the absorbance was lowered because of the lower sorption rate of the chromium species on the resin. At temperature higher than 40°, the absorbance was again lowered because of decomposition of the coloured complex (Fig. 4).

Effect of foreign ions

In Table 3, the effects of many metals are listed. Almost all metals, except for copper, did not interfere when present in up to 1000 times the concentration of chromium(VI). The presence of copper(II) at ten times that of chromium(VI) (or more) caused fading of the purple colour. This effect could be eliminated by use of the standard addition method. According to equation (1) and Table 1, it can be expected that the metals with a distribution ratio lower than that for chromium(VI) will give less interference when a large amount of sample solution is used. Similar results were obtained for the 1-litre samples that were 0.6*M* in sodium chloride.

Oxidation of Cr(III) to Cr(VI)

For the oxidation of chromium(III) to chromium(VI), Osaki *et al.* have reported that good results were obtained by use of ammonium ceric nitrate in 0.05*M* sulphuric acid.[7] This oxidation method with cerium(IV) is of advantage in the ion-exchanger colorimetry for chromium, because neither cerium(III) nor cerium(IV) interferes (Table 3). The oxidation of chromium(III) was found to be complete if the sample solution was boiled for 5 min in the presence of $2.5 \times 10^{-5}M$ ceric sulphate.

Determination of chromium in sea-water and river water

The method was applied to the determination of chromium in natural water samples from Hakata Bay and the Muromi River in Fukuoka Prefecture. On sampling, 3 ml of concentrated sulphuric acid per litre of sample solution were added immediately after filtration of the sample. For the sea-water, the total concentration of chromium was $9.6 \times 10^{-8}M$, *i.e.*, 4.9 μg/l. Addition of chromium(III) or chromium(VI) gave the same result, which indicates that the oxidation of chromium(III) with cerium(IV) is complete. For the river water, a 1-litre sample gave too low an absorbance and it was necessary to employ a still larger amount of sample. By use of 3 litres of the sample solution, the total chromium was found to be $5.7 \times 10^{-9}M$, *i.e.*, 0.30 μg/l. With a 3-litre sample and 200–400 mesh resin, it took more than 30 min for the sorption of chromium. A linear calibration

curve was. however, obtained at a fixed equilibration time (30 min, *cf.* Fig. 2), even though sorption equilibrium was not attained.

REFERENCES

1. L. Chuaecas and J. P. Riley, *Anal. Chim. Acta*, 1966, **35**, 240.
2. F. Lima and C. Silva, *J. Radioanal. Chem.*, 1968, **1**, 147.
3. Y. K. Chau, S. S. Sim and Y. H. Wong, *Anal. Chim. Acta*, 1968, **43**, 13.
4. T. R. Gilbert and A. Clay, *ibid.*, 1973, **67**, 289.
5. W. R. Seitz, W. W. Suydam and D. M. Hercules, *Anal. Chem.*, 1972, **44**, 957.
6. J. F. Pankow and G. E. Janauer, *Anal. Chim. Acta*, 1974, **69**, 97.
7. S. Osaki, T. Osaki, S. Shibata and Y. Takashima, *Bunseki Kagaku*, 1976, **25**, 358.
8. K. Yoshimura, H. Waki and S. Ohashi, *Talanta*, 1976, **23**, 449.
9. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959.

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SHORT COMMUNICATIONS

SOLVENT EXTRACTION OF GALLIUM(III) AS THE MONOTHIODIBENZOYLMETHANE COMPLEX

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Summary—Gallium(III) can be quantitatively extracted at trace levels with monothiodibenzoylmethane in benzene at pH 5.0. It is then determined spectrophotometrically as its Rhodamine B complex in the organic phase, at 570 nm. The system conforms to Beer's law at 570 nm, in the range 1.4–26 μg of gallium. The absorbance is stable for 24 hr. Gallium can be extracted and determined in the presence of several elements with which it is generally associated in minerals and other products.

Several β-diketones have been used for the solvent extraction of gallium.[1] Although some of them are good extractants, others such as acetylacetone are inefficient, as the extraction is not quantitative. Amongst thiosubstituted β-diketones, thiothenoyltrifluoroacetone[2] has been used for the extraction of gallium. The extension of our studies with thiosubstituted β-diketones has shown that monothiodibenzoylmethane (HSDBM) can also be used for the solvent extraction of gallium. Gallium in the organic phase is equilibrated with 6*M* hydrochloric acid containing Rhodamine B and the tetrachlorogallate–Rhodamine B complex in benzene is measured spectrophotometrically at 570 nm.

EXPERIMENTAL

Reagents

Gallium chloride solution. Gallium chloride (0.723 g) dissolved in 250 ml of distilled water containing 1% of hydrochloric acid; standardized complexometrically[3] and diluted as required.

Monothiodibenzoylmethane (HSDBM) solution in benzene, 0.001*M*. The reagent is synthesized as described earlier.[4]

Rhodamine B solution 0.05% *in* 6*M hydrochloric acid.*

General procedure

A suitable volume of dilute gallium solution (~6 μg/ml) is diluted to 25 ml with water and adjusted to pH 5.0 with 0.01*M* hydrochloric acid and 0.01*M* ammonia, then shaken in a separatory funnel for about 10 min with 10 ml of 0.001*M* HSDBM in benzene. After settling, the aqueous phase is withdrawn. The coloured organic layer is then shaken for 2 min with 10 ml of the Rhodamine B solution in 6 *M* hydrochloric acid. The organic layer is transferred to a 10-ml standard flask, made up to the mark with benzene, and its absorbance measured at 570 nm against a reagent blank, in matched 10-mm cells.

RESULTS AND DISCUSSION

Mechanism of complex formation

The chelate of gallium(III) with monothiodibenzoylmethane is formed at pH 4.8–5.2, in the following manner:

$$HSDBM \rightleftharpoons H^+ + SDBM^-$$

$$Ga^{3+} + 3(SDBM^-) \rightarrow Ga(SDBM)_3$$

On equilibration with 6*M* hydrochloric acid, the complex splits to form $GaCl_4^-$, which in association with RH^+ (R = Rhodamine B or tetraethyl rhodamine) is extracted as an ion-pair complex. Other protonated species of the dye are RH_2^{2+} and RH_3^{3+}, but in 6*M* hydrochloric acid only RH^+ exists.[5]

Spectral properties

The gallium–Rhodamine B complex (A) in benzene containing HSDBM shows strong absorbance at 570 nm (Fig. 1). The HSDBM has its absorption maximum at 410 nm and very little absorbance at 570 nm (B). Hence, all measurements were made at 570 nm. Beer's law is obeyed over the gallium range of 1.4–26 μg and the absorbance of the complex remains constant for at least 24 hr.

The apparent molar absorptivity found by us was 2.68×10^4 l.mole^{-1}.cm^{-1} which is low compared with

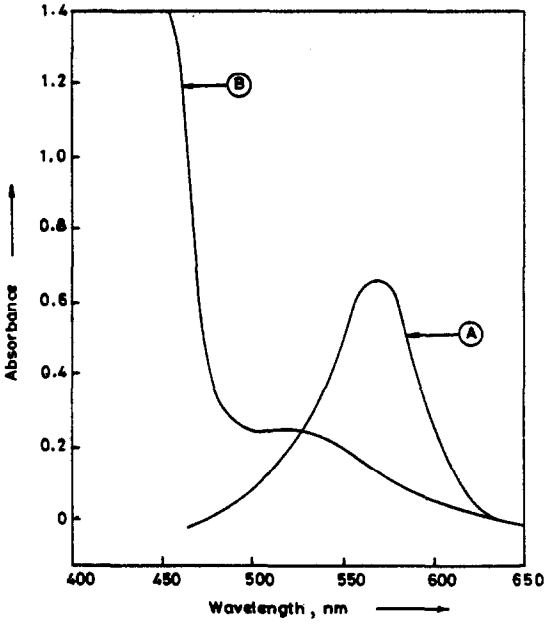


Fig. 1. Absorption spectra of Ga(III)–Rhodamine B complex. Ga(III) = $2.461 \times 10^{-5}M$; [*HSDBM*] = $1.0 \times 10^{-3}M$ in benzene. (A) Ga(III)–Rhodamine B complex in HSDBM–benzene *vs.* reagent blank. (B) Reagent blank *vs.* benzene.

Table 1. Effect of foreign ions [Ga(III) = 11.44 μg; pH = 5.0; 0.001*M* HSDBM in C_6H_6]

Tolerance limit *mg*	Foreign species
50	NH_4^+, Na^+, Li^+, K^+, NO_3^-, SO_4^{2-}, Cl^-
30	NO_2^-, SO_3^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, Br^-, SCN^-, CN^-, ascorb$^-$, thiourea$^-$
10	Rb^+, Cs^+, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, $Mo_7O_{24}^{6-}$, AsO_2^-, ReO_4^-
5	Be^{2+}, VO_3^-, SeO_3^{2-}
1	In^{3+}, Zn^{2+}, Mn^{2+}, Ge^{4+}, Co^{2+}, Rh^{3+}, Ni^{2+}, Pt^{4+}, Os^{6+}, Ir^{3+}, Fe^{3+}, Cd^{2+}, Sn^{4+}, Ag^+, UO_2^{2+}, WO_4^{2-}, TeO_3^{2-}
0.5	Th^{4+}, Zr^{4+}, Au^{3+}, Pd^{2+}, Cu^{2+}, Sc^{3+}
0.25	Sb^{3+}, Ti^{4+}, Hg^{2+}, Ru^{3+}
None	Pb^{2+}, Bi^{3+}, F^-, CH_3COO^-, cit^{3-}, tart^{3-}, $C_2O_4^{2-}$, mal^{2-}, EDTA^{4-}

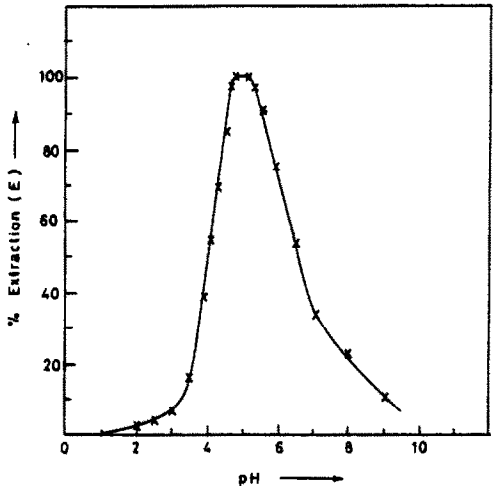


Fig. 2. Extraction as a function of pH. Ga(III) = 3.28 × $10^{-5}M$; [HSDBM] = 1 × $10^{-3}M$ in C_6H_6.

the 6.0 × 10^4 observed by Onishi and Sandell.[6] This is attributed to a difference in degree of extraction of the Rhodamine B complex, the volume ratio of aqueous to organic phase being 1:1 in our method and 1:2 in the other. The initial extraction with HSDBM was shown to be complete, there being no change when a double extraction was used. Extraction of the Rhodamine B complex is dependent on the volumes of the two phases, hence it is important that these volumes should be accurately controlled. Culkin and Riley[7] used a mixture of chlorobenzene and carbon tetrachloride for the extraction of the gallium–Rhodamine B complex. The molar absorptivity in this medium was 7.89 × 10^4 l.mole^{-1}.cm^{-1}. The molar absorptivity is thus dependent on the nature of the solvent used for extraction. It is lowest (1.1 × 10^3) with xylene as extractant.[1]

Effect of pH and other parameters

The extraction was studied over the pH range 1.0–9.0 (Fig. 2). The results showed that the optimum pH was 4.8–5.2.

All other factors being kept constant, the concentration and the volume of the reagent were varied. The extraction of up to approximately 26 μg of gallium was quantitative in a single stage, with 10 ml of 0.001*M* HSDBM in benzene. This was confirmed by performing a second extraction. It was incomplete with concentrations of reagent less than 0.00075*M*. There was no significant increase when the concentration of the reagent was increased to 0.002*M*. The use of varying volumes of 0.001*M* reagent showed that the extraction was quantitative with 10 ml of the reagent.

The period of equilibration was varied from 2 to 20 min. The extraction was quantitative after 9 min of equilibration. It is therefore recommended that the mixture be shaken for 10 min.

Effect of foreign ions

Several ions were tested for their effect on the extraction of gallium. The tolerance limit was taken as the amount required to cause an error of ±2% (Table 1). The ions showing strong interference were anions of sequestering agents, such as EDTA, citrate, tartrate, oxalate and malonate, and cations such as lead and bismuth. The ions likely to be precipitated at pH 5.0 were kept in solution by masking them with ascorbic acid, *e.g.*, tin(IV), tungstate, tellurium(IV), thorium, zirconium and scandium (this masking forms the basis for their separation by anion-exchange chromatography in ascorbate media at pH ~5.0).[8] Ions which formed coloured complexes with HSDBM and interfered in the extraction were masked with cyanide, *e.g.*, zinc, cobalt(II), nickel, cadmium, palladium(II), gold(III), copper(II), silver and mercury. Iron was masked with ascorbic acid.

The proposed method possesses several advantages, as it is possible to separate gallium from indium, thallium and aluminium, with which it is usually associated. The method is selective, as it is possible to separate gallium from large amounts of other elements.

The method is fast, taking only 30 min. Gallium concentrations as low as 0.03 μg/ml can be determined. The results are reproducible. The relative standard deviation is ±1.2%.

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REFERENCES

1. P. V. Dhond and S. M. Khopkar, *Talanta*, 1976, **23**, 51.
2. *Idem*, *Indian J. Chem.*, 1977, **15A**, 334.
3. F. J. Welcher, *Analytical Applications of Ethylenediaminetetraacetic Acid*, pp. 165, 178. Van Nostrand, London, 1958.
4. H. S. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shannon, *Australian J. Chem.*, 1965, **18**, 673.
5. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., p. 210. Interscience, New York, 1959.
6. H. Onishi and E. B. Sandell, *Anal. Chim. Acta*, 1955, **13**, 159.
7. F. Culkin and J. P. Riley, *Analyst*, 1958, **83**, 208.
8. J. Korkisch, *Modern Methods for the Determination of Rare Metal Ions*, Pergamon, Oxford, 1970.

Talanta, Vol. 25, pp. 111–112. Pergamon Press, 1978. Printed in Great Britain.

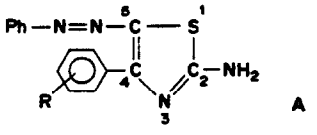
QUANTITATIVE TREATMENT OF SUBSTITUENT EFFECTS IN THE POLAROGRAPHIC INVESTIGATIONS OF SOME POTENTIAL ANTINEOPLASTIC 2-AMINO-4-ARYL-5-PHENYLAZOTHIAZOLES

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Summary—Polarographic reduction of 2-amino-4-aryl-5-phenylazothiazoles takes place in a single 2-electron transfer, giving a diffusion-controlled irreversible wave in the pH range 2.0–10.0. Substituents in the 4-position of the thiazole moiety shift the half-wave potential through conjugation of the system. A correlation of $E_{1/2}$ with the Brown and Hammett substituent constant has also been established.

The information available on the polarography of thiazoles is surprisingly scarce[1–3] in spite of their use as chemotherapeutic agents for the treatment of bacterial infections.[4] The present communication deals with polarographic studies done on 2-amino-4-aryl-5-phenylazothiazoles (A) in order to investigate (*a*) the mechanism involved in the reduction process, and (*b*) the relationship of the half-wave potential to the Brown substituent constant (σ^+) and Hammett substituent constant (σ), when the substituents are remote from the site of reduction. Only *p*-substituted phenyl groups were considered in these studies as they offer no steric hindrance to coplanarity.



A

EXPERIMENTAL

2-Amino-4-aryl-5-phenylazothiazoles, *viz.* the 4-phenyl, 4-chlorophenyl, 4-bromophenyl, 4-methylphenyl, 4-hydroxyphenyl, 4-methoxyphenyl and 4-ethyxophenyl compounds, were synthesized in the laboratory by the method of Garg and Sharma[5,6] and purified by repeated recrystallization from ethanol. Britton–Robinson buffers (0.2*M*) in the pH range 2.0–10.0 were prepared from analytical-grade chemicals. Stock solutions (2.0×10^{-3} *M*) of the thiazoles were prepared in pure methanol.

Apparatus

A Cambridge pen-recording polarograph was used. All measurements were made at 30 ± 0.1°. All potentials were with reference to the SCE.

Procedure

Britton-Robinson buffer (5.0 ml), methanol (3.0 ml, necessary to keep the compounds in solution), 1*M* potassium chloride (1.0 ml) and 2-amino-4-aryl-5-phenylazothiazole solution (1 ml) were mixed thoroughly. Oxygen in the solution was removed by passage of purified hydrogen for about 10 min and the polarograms were recorded. The conventional method of Devries and Kroon,[7] using a mercury pool cathode, was employed for determining the value of *n*, the number of electrons involved in the reduction. The temperature coefficient was determined by Nejedly's method.[8]

RESULTS AND DISCUSSION

For all the compounds tested a single 2-electron reduction wave was observed in the pH range 2.0–10.0. The wave-heights were practically independent of pH over the entire range studied.

The diffusion-controlled nature of the waves was shown by the linearity of plots of *i vs.* $\sqrt{h}$ and of *i vs.* depolarizer concentration, and from the low value of the temperature coefficient (1.2–1.6%/deg). The diffusion-current constants were practically identical (range 0.21–0.23) (Table 1). The irreversible nature of the waves was confirmed by the shift of $E_{1/2}$ towards more negative potential with increasing concentration of the depolarizer. The half-wave potential of these thiazoles was found to become more negative with increase in pH and the plots of $E_{1/2}$ *vs.* pH were linear.

The number of protons involved per molecule of reactant in the rate-determining step (*b*) and αn (product of the transfer coefficient and the number of electrons involved per molecule of the reactant in the rate-determining step) were calculated by means of the following equation.[9,10]

$$\frac{dE_{1/2}}{dpH} = \frac{0.059p}{\alpha n}$$

where

$$\alpha n = \frac{0.0517}{E_{1/4} - E_{3/4}}.$$

The values of *p* were 1.1–1.2, and of αn 1.55–1.60.

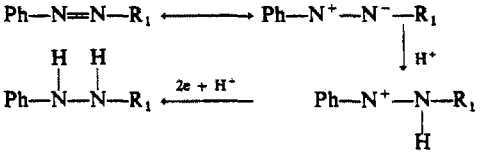
As two electrons are involved in the reduction of the azo group, and one proton is involved in the rate-determining step, a mechanism similar to that proposed by other workers[11–13] can be proposed for the reduction of these azothiazoles.

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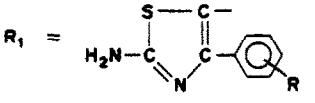
Table 1. Characteristics of some 2-amino-4-substituted-5-phenylazothiazoles ($2 \times 10^{-4}M$, pH 6.40)

No.	R	$-E_{1/2}$ V	$\Delta E^{*}_{1/2}$, V	i_d, μA	$dE_{1/2}/dpH$ mV/pH	σn	σ	σ^+
1	H	0.56	0.00	1.35	53	1.60	0.00	0.00
2	4Cl	0.52	0.04	1.28	57	1.58	0.23	0.11
3	4-Br	0.53	0.03	1.40	55	1.55	0.23	0.15
4	4-CH_3	0.58	−0.02	1.28	55	1.58	−0.17	−0.31
5	4-OH	0.60	−0.04	1.40	55	1.60	−0.37	−0.92
6	4-OCH_3	0.59	−0.03	1.40	53	1.56	−0.27	−0.78
7	4-OC_2H_5	0.59	−00.03	1.40	55	1.55	−0.25	—

* Relative to compound 1.



where



Effect of substituents

Reduction of azo compounds reportedly[11] takes place at the –N=N– group; giving hydrazo derivatives. As such a reduction depends on the electron density at –N=N–, electron-donating groups would facilitate reduction. As the azo group is not directly attached to the phenyl ring, reduction of the 4-hydroxyphenyl derivative takes place in a two-electron step and not the four-electron process observed[13] for 4-hydroxyazobenzene.

For evaluation of the substituent effects on the half-wave potentials, all the members of the series must undergo reduction by the same mechanism.[14] As all these thiazoles show almost the same value of the transfer coefficient (α) and of $dE_{1/2}/dpH$, the conditions for applying the Brown constants and Hammett constants are fulfilled.[15,16] The values of these constants are taken[17–19] from the literature. For Hammett substituent constants all the derivatives examined fit a straight line and the value of the specific reaction constant (ρ) was found to be 0.12 V which is in good agreement with the reported values for similar systems.[15,20] The magnitude of ρ, which agrees with $E_{1/2} = -0.56$ V, nevertheless indicates that transmission of substituent effects through the thiazole ring is easy, as in the present case the substituent effect must be transmitted through both the benzene and the thiazole rings (substitution on the benzene, electroactive —N=N— on the thiazole ring). The positive value of ρ points to a nucleophilic mechanism for the electrode process (electron uptake as the potential-determining step). This also enabled us to decide that $\Delta E_{1/2} = \rho\sigma$ gives a better fit than $\Delta E_{1/2} = \rho\sigma^+$.

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REFERENCES

1. J. Tirouflet and E. Laviron, *Compt. Rend.*, 1957, **244**, 2063.
2. J. Tirouflet, E. Laviron, J. Metzger and J. Biochard, *Collection Czech. Chem. Commun.*, 1960, **25**, 3277.
3. W. U. Malik, R. N. Goyal and M. R. Bhavikatti, *Indian J. Chem.*, 1975, **13**, 955.
4. R. J. Fosbinder and L. A. Walter, *J. Am. Chem. Soc.*, 1939, **61**, 2032.
5. H. G. Garg and R. A. Sharma, *J. Pharm. Sci.*, 1970, **59**, 348.
6. *Idem, Can. J. Pharm. Sci.*, 1971, **6**, 215.
7. T. DeVries and J. L. Kroon, *J. Am. Chem. Soc.*, 1953, **73**, 2484.
8. V. Nejedly, *Collection Czech. Chem. Commun.*, 1922, **1**, 319.
9. B. Janik and P. J. Elving, *J. Electrochem. Soc.*, 1969, **116**, 1087.
10. L. Meites, *Polarographic Techniques*, Wiley, New York, 1965.
11. C. R. Castor and H. J. Saylor, *J. Am. Chem. Soc.*, 1953, **75**, 1427.
12. W. U. Malik, V. K. Mahesh and R. N. Goyal, *J. Electroanal. Chem.*, 1974, **54**, 411.
13. T. M. Florence, *ibid.*, 1974, **52**, 115.
14. P. Zuman, *Collection Czech. Chem. Commun.*, 1960, **25**, 3225.
15. *Idem, Substituent Effects in Organic Polarography*, p. 39. Plenum Press, New York, 1967.
16. L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1940.
17. H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191.
18. M. Kozeny and V. Velich, *Collection Czech. Chem. Commun.*, 1960, **25**, 1031.
19. H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 1958, **80**, 4979.
20. I. F. Vladimirtsev and I. Postovski, *Dokl. Akad. Nauk SSSR*, 1952, **83**, 855.

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DETERMINATION OF FLUORIDE WITH THORIUM NITRATE BY CATALYTIC TITRATION

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Summary—Amperometry, constant-current potentiometry and spectrophotometry were used to follow the course of catalytic titrations of fluoride and silicofluoride with thorium nitrate. The hydrogen peroxide–iodide system was used as the indicator reaction. Titrations were performed in 50% ethanolic acetate buffer, pH 3.6. Amounts of 3.70–6.85 mg of ammonium fluoride, 5.53–10.79 mg of potassium fluoride and 4.34–8.41 mg of sodium silicofluoride were determined with a maximum average deviation of 0.9%. The results obtained are in good agreement with those of comparable methods.

It has been shown that catalytic indicator reactions can be used for end-point determination in volumetric and coulometric titrations.[1–18] The use of thermometric, spectrophotometric, and visual methods has been described in the literature, but the potential use of electroanalytical methods for end-point detection has not yet been fully explored. The amperometric method has been applied to chelatometric titrations,[8] and the biamperometric method to chelatometric, argentometric and fluoride titrations.[4,8–10] Zero-current potentiometry has been used in argentometric and chelatometric titrations,[11–18] and constant-current potentiometry has been used for chelatometric titrations.[8]

In our previous methods for titration of fluoride with thorium nitrate, the end-points were determined biamperometrically, thermometrically and visually[9] by using a Landolt-type reaction (hydrogen peroxide–iodide–ascorbic acid). Two different techniques were used. In the first, a discontinuous catalytic-titration procedure, the end-point of the titration was determined from the intersection of the kinetic curves of the activity of free thorium ions before and after the equivalence point. The second method was based on plotting a calibration curve of the decrease of catalytic activity of a fixed amount of thorium *vs.* increasing amount of fluoride, and this was found to be more suitable. Both procedures were subject to large errors, however, and the determinations were time-consuming.

The present paper describes continuous catalytic titrations of fluoride and silicofluoride with thorium nitrate in 50% ethanolic acetate buffer, pH 3.6. The indicator reaction was the oxidation of iodide with hydrogen peroxide; this reaction is catalysed by the first excess of titrant. The indicator reaction rate was followed amperometrically, potentiometrically (at a small constant current) and spectrophotometrically. The effect of the concentrations of alcohol and the indicator-reaction components on the shape of the catalytic titration curve was studied.

EXPERIMENTAL

Chemicals and solutions

All chemicals used were of analytical purity. Solutions were prepared with doubly distilled water and stored in plastic vessels.

Potassium fluoride and ammonium fluoride solutions, 0.05*M*. Prepared by dissolving the necessary amounts of the solid substances.

Sodium silicofluoride solution, 0.01*M*. Prepared by steam distillation (Willard and Winter method[19]).

Thorium nitrate standard solution, 0.02*M*. Standardized against a known amount of fluoride by potentiometric titration, with the fluoride-selective electrode as end-point detector.

Potassium iodide solutions, 2.5×10^{-2} and 2.5×10^{-4}*M*.

Hydrogen peroxide solutions, 3.7×10^{-2} and 3.7×10^{-4}*M*.

Acetate buffer, pH 3.6. Prepared by mixing 0.2*M* acetic acid and 0.2*M* sodium acetate in the appropriate ratio.

Zirconium–alizarin complex. Prepared in the usual way.[20]

When two identical indicator eletrodes (Pt+/Pt−) were used for amperometric end-point location, the polarization voltage was 70 mV; when only one indicator electrode was used, the polarization voltage was 160 mV for cathodic polarization (Pt−/SCE+), and 350 mV for anodic polarization (Pt+/SCE−), both *vs.* the SCE. For potentiometry at a small constant current (2 μA), two identical indicator eletrodes or one indicator electrode (polarized cathodically or anodically) coupled with the SCE were used.

The platinum indicator electrodes for amperometric titrations were needle-shaped, 6 mm long and 0.6 mm in diameter. Square platinum electrodes, 0.80 cm^2 in area, were used for potentiometric measurements. The electrodes were washed with doubly distilled water after each measurement. The influence of the surface properties of the indicator electrode was investigated, and it was established that the end-point is less pronounced if the electrode surface is pretreated by heating in an alcohol flame or by electrolysis in dilute sulphuric acid.

A Carl Zeiss Spekol spectrophotometer was used for catalytic spectrophotometric titrations at 430 nm and for reference determinations (zirconium–alizarin complex as indicator) at 550 nm. For potentiometric end-point detection, a fluoride-selective electrode (Radiometer type F-1052F) and an SCE (Iskra) were used. The potential changes were followed by means of a Radiometer pH-meter type PHM 26. Conductivity measurements were carried out with a Radiometer type CDM 3 conductivity meter.

The titrant was added continuously from an automatic piston-burette (Radiometer type ABU 12) at 0.36 ml/min. Amperometric, constant-current potentiometric, spectrophotometric and conductometric titration curves were recorded by means of a chart recorder (Goerz-Electro Servogor S type RE 541).

Procedure

Aliquots of 2.00 or 4.00 ml of potassium fluoride, ammonium fluoride or sodium silicofluoride solutions were placed in a 50-ml glass vessel (or, for spectrophotometric determinations, in a 30-ml cell), then 4 ml of acetate buffer, 0.5 ml of hydrogen peroxide, 0.5 ml of potassium iodide solution and 11 ml of ethanol were added and the solution was diluted with water so that the alcohol concentration at the equivalence point would be 50%. This solution was titrated with 0.02*M* thorium nitrate. To investigate the effect of the concentrations of the components of the indicator reaction on the shape of the catalytic titration curve, the volumes of solutions of hydrogen peroxide and potassium iodide added were varied. Reference titrations were performed in the absence of the components of the indicator reaction, and for the conductometric titrations no buffer was added either.

The end-points of the catalytic titrations were determined graphically from the intersection of the straight segments of the curve occurring before and after the equivalence point. A blank titration was carried out, and the results were corrected accordingly.

RESULTS AND DISCUSSION

It is possible to determine the end-points in the titration of fluoride and silicofluoride with thorium nitrate (in 50% ethanolic acetate buffer, pH 3.6) by amperometry and constant-current potentiometry, with the aid of the indicator reaction between hydrogen peroxide and iodide. Also, the evolution of iodine after the equivalence point allows spectrophotometric end-point location.

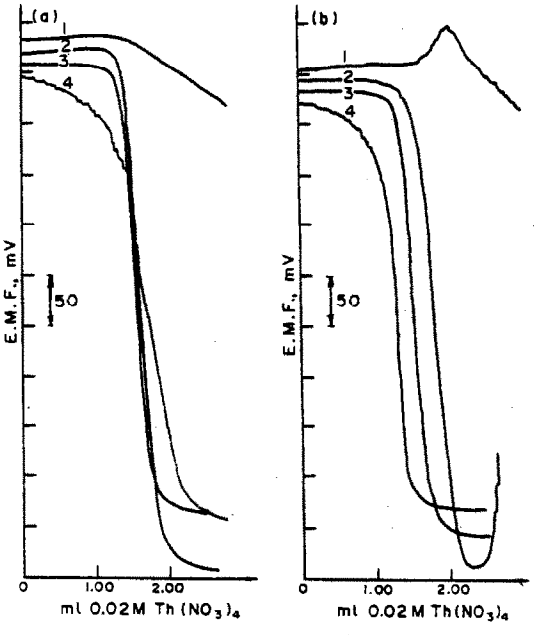


Fig. 1. Effect of various concentrations of H_2O_2 (*a*) and KI (*b*) on the shapes of constant-current potentiometric titration curves (Pt+/Pt−) of NH_4F with $Th(NO_3)_4$ (50% ethanol, in the presence of acetate buffer pH 3.6). (*a*) 1—$1.8 \times 10^{-5}M$; 2—$1.8 \times 10^{-4}M$; 3—$8.8 \times 10^{-4}M$; 4—$4.4 \times 10^{-3}M$; (*b*) 1—$1.2 \times 10^{-5}M$; 2—$1.2 \times 10^{-4}M$; 3—$6.0 \times 10^{-4}M$; 4—$3.0 \times 10^{-3}M$. (Concentrations of H_2O_2 and KI refer to the final dilution.)

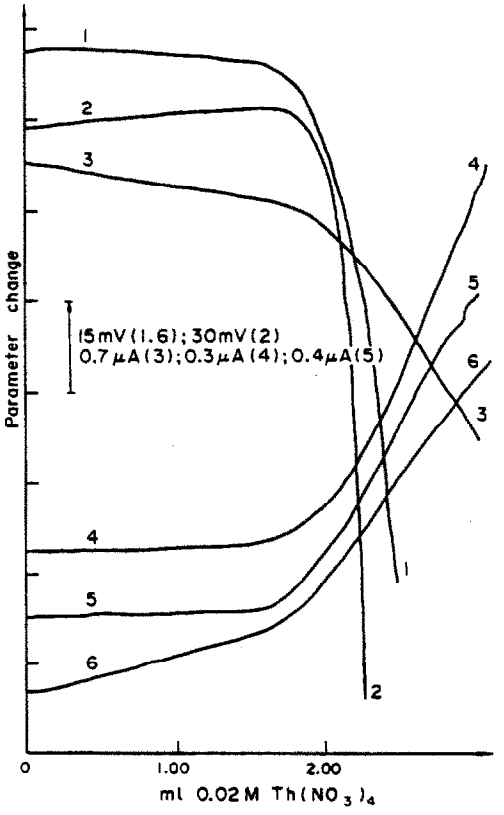


Fig. 2. Catalytic titration curves of 4.34 mg of Na_2SiF_6 with 0.02*M* $Th(NO_3)_4$ (50% ethanol, in the presence of acetate buffer pH 3.6; 0.5 ml of $2.5 \times 10^{-2}M$ KI and 0.5 ml of $3.7 \times 10^{-2}M$ H_2O_2 added). 1—constant-current potentiometry (Pt−/SCE+); 2—constant-current potentiometry (Pt+/Pt−); 3—amperometry (Pt+/SCE−); 4—amperometry (Pt−/SCE+); 5—amperometry (Pt+/Pt−); 6—constant-current potentiometry (Pt+/SCE−).

In order to determine the best conditions for catalytic determination of fluoride and silicofluoride with thorium nitrate, the effects of the concentrations of alcohol and of the components of the indicator reaction on the results of titrations were investigated.

An increase in the ethanol concentration decreases the solubility of thorium fluoride, and allows a sharper end-point to be obtained. On the other hand, an increase in the alcohol concentration causes low results to be obtained. This can probably be explained by assuming that a 1:4 Th:F precipitate is no longer formed.[21] If the same amount of fluoride is titrated after dilution of the initial solution by, for example, a factor of 2.5, correct results are obtained. Further dilution (5-fold) may cause high results.

The effect of hydrogen-ion concentration on the shape of the catalytic titration curve in the pH range 2.5–5.1 was investigated. The sharpest end-points were found at pH 3.6. The influence of pH on the shape of the titration curve can be explained in terms of the different catalytic behaviour of the various thorium complex ions present at the various pH values. It was also established that the indicator reaction rate does not depend on the pH of the solution in the range considered, and this agrees with literature data.[22]

The greatest influence on the reaction rate of oxidation of iodide by hydrogen peroxide, apart from the catalytic

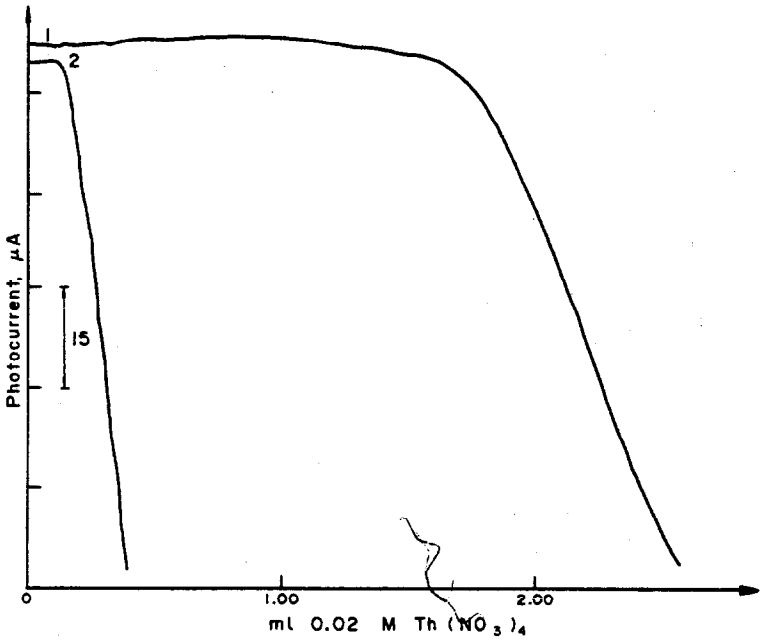


Fig. 3. Catalytic spectrophotometric titration curves of 4.34 mg of Na_2SiF_6 with 0.02*M*$Th(NO_3)_4$ (50% ethanol, in the presence of acetate buffer pH 3.6; 0.5 ml of 2.5 × 10^{-2}*M* KI and 0.5 ml of 3.7 × 10^{-2}*M* H_2O_2 added). 1—titration curve. 2—blank titration (Na_2SiF_6 omitted).

effect of thorium, is that of the concentrations of the two reactants. Figure 1 illustrates the influence of the concentrations of hydrogen peroxide (*a*) and potassium iodide (*b*) on the shape of the constant-current potentiometric titration curve (Pt+/Pt−). At higher concentrations of hydrogen peroxide and potassium iodide, iodine evolution commences before the end-point, but the rate of evolution increases greatly at the end-point (curves 4). Lower concentrations of hydrogen peroxide and potassium iodide result in slower iodine evolution (curves 1 and 2). For our investigations, we used the following concentrations: 8.8 × 10^{-4}*M* hydrogen peroxide and 6.0 × 10^{-4}*M* potassium iodide, both referring to the final dilution (Fig. 1, curves 3).

Catalytic amperometric titration curves for sodium silicofluoride, obtained with two identical indicator electrodes and with one indicator electrode polarized cathodically or anodically *vs.* the SCE, are shown in Fig. 2 (curves 3, 4 and 5). Curves of a similar shape are obtained for titration of potassium and ammonium fluoride.

Table 1. Determination of potassium fluoride, ammonium fluoride and sodium silicofluoride by various methods (6 titrations carried out in each case)

Method of end-point determination		NH_4F				KF				Na_2SiF_6			
		*a**	*b**	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Catalytic amperometric titration	Pt+/Pt−	3.63	0.6	6.89	0.2	5.56	0.7	10.82	0.6	4.37	0.0	8.36	0.2
	Pt+/SCE−	3.64	0.3	6.89	0.5	5.57	0.4	10.84	0.3	4.34	0.7	8.34	0.5
	Pt−/SCE+	3.63	0.4	6.91	0.3	5.53	0.4	10.85	0.1	4.34	0.6	8.32	0.5
Catalytic potentiometric titration at a small constant current	Pt+/Pt−	3.63	0.4	6.88	0.3	5.57	0.4	10.86	0.5	4.37	0.9	8.38	0.5
	Pt+/SCE−	3.63	0.2	6.89	0.3	5.57	0.3	10.84	0.4	4.35	0.7	8.38	0.4
	Pt−/SCE+	3.62	0.4	6.89	0.3	5.54	0.1	10.84	0.3	4.36	0.9	8.36	0.3
Catalytic spectrophotometric titration		3.63	0.5	6.90	0.3	5.56	0.4	10.82	0.4	4.37	0.3	8.40	0.6
Spectrophotometric titration		3.51	0.4	7.01	0.5	5.43	0.7	10.89	0.3	4.24	0.2	8.46	0.2
Potentiometric titration	F^-/SCE	3.70	0.4	6.85	0.4	5.53	0.4	10.79	0.5	4.34	0.5	8.41	0.6
Conductometric titration		3.51	0.1	6.70	0.6	5.44	0.6	10.62	0.7	4.18	0.3	8.26	0.1

* *a* quantity found (mg); *b* average deviation (%).

The same figure shows the catalytic constant-current potentiometric titration curves obtained with two identical indicator electrodes (Pt+/Pt−), and with one cathodically (Pt−/SCE+) or anodically (Pt+/SCE−) polarized indicator electrode (Fig. 2, curves 1, 2 and 6). Similar titration curves are obtained for titration of potassium and ammonium fluoride.

The catalytic spectrophotometric titration curve obtained for titration of sodium silicofluoride with thorium nitrate is shown in Fig. 3. Similar titration curves can be obtained for titration of potassium and ammonium fluoride.

Some results of determinations of ammonium fluoride, potassium fluoride and sodium silicofluoride are presented in Table 1. Ammonium fluoride (3.70–6.85 mg), potassium fluoride (5.53–10.79 mg) and sodium silicofluoride (4.34–8.41 mg) were determined with a maximum average deviation of 0.9%. The results were in good agreement with those obtained by zero-current potentiometry.

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REFERENCES

1. H. A. Mottola, *Talanta*, 1969, **16**, 1267.
2. V. J. Vajgand, F. F. Gaál and S. S. Brusin, *ibid.* 1970, **17**, 415.
3. H. Weisz, *Allgem. Prakt. Chem.*, 1971, **22**, 98.
4. H. Weisz and S. Pantel, *Anal. Chim. Acta*, 1972, **62**, 361.
5. *Idem*, *Z. Anal. Chem.*, 1973, **264**, 389.
6. H. A. Mottola, *Crit. Rev. Anal. Chem.*, 1975, **4**, 228.
7. F. Gaál and L. Bjelica, *Chem. Anal. (Warsaw)*, 1976, **21**, 227.
8. F. F. Gaál, B. F. Abramović, F. B. Szebenyi and V. D. Canić, *Z. Anal. Chem.*, 1977, **286**, 222.
9. F. F. Gaál, V. I. Sörös and V. D. Canić, *Mikrochim. Acta*, 1975 II, 689.
10. S. Pantel and H. Weisz, *Z. Anal. Chem.*, 1976, **281**, 211.
11. T. P. Hadjiioannou, E. A. Piperaki and D. S. Papastathopoulos, *Anal. Chim. Acta*, 1974, **68**, 447.
12. V. Vajgand and F. Gaál, *Proc. 2nd Conf. on Some Appl. of Phys. Chem.*, Vol. 1, p. 683. Veszprém, 1971.
13. V. Vajgand, F. Gaál, Lj. Zrnić-Zeremski and V. Sörös, *Thermal Analysis, Proc. 3rd ICTA*, Vol. II, p. 437. Davos, 1971.
14. H. Weisz and D. Klockow, *Z. Anal. Chem.*, 1967, **232**, 321.
15. H. Weisz, S. Pantel and H. Ludwig, *ibid.*, 1972, **262**, 269.
16. T. P. Hadjiioannou and M. M. Timotheou, *Mikrochim. Acta*, 1977 I, 61.
17. T. P. Hadjiioannou, M. A. Koupparis and C. E. Efstathiou, *Anal. Chim. Acta*, 1977, **88**, 281.
18. T. P. Hadjiioannou and E. A. Piperaki, *ibid.*, 1977, **90**, 329.
19. H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7.
20. L. Erdey, *A kémiai analízis súlyszerinti módszerei III*, p. 87. Akadémiai Kiadó, Budapest, 1960.
21. J. J. Lingane, *Anal. Chem.*, 1967, **28**, 881.
22. G. Svehla and L. Erdey, *Microchem. J.*, 1963, **7**, 206.

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Summary—Vanadium in different oxidation states in a sample of mixed oxides can be determined by a voltammetric method without the need for decomposition of the sample. The oxide is mixed into a paste with graphite and 1-bromonaphthalene, and packed into the electrode holder. Current maxima on the polarization curves give a measure of the amount of vanadium present in each oxidation state.

When some inorganic compounds are to be analysed, it may be desirable to eliminate the usual chemical decomposition of the sample in order to exclude the possibility of a change in oxidation state of one of the components. One non-destructive method which may be useful is voltammetry at a graphite paste electrode, with the sample material mixed into the graphite paste and remaining in the solid state. This electrode, proposed by us,[1] has recently been used for the determination of vanadium in different oxidation states in samples of vanadium oxides. The electrode differs from Adams' paste electrode[2] in that the electrode contains a known amount of material to be analysed (mineral, oxide, metal, salt, *etc.*) as a powdered solid. When such an electrode is polarized cathodically or anodically (the polarization limits being −0.4 and +1.4 V *vs.* NHE), the electroactive substances in the paste are reduced or oxidized, giving characteristic current maxima on the current–voltage curve. The electrode is shown in Fig. 1 and some typical curves in Fig. 2.

These maxima can have several origins: depletion of the electroactive substance on the surface of the paste, surface passivation by products of electrode reactions or by adsorption of sparingly soluble products of chemical reaction in solution, and diffusion. But in all cases the position of the maximum on the potential axis depends on the nature of the electroactive substance and the composition of the electrolyte. The value of the maximum current depends in its turn on the amount of the substance present in the paste. In other words, there exists the same dependence as in classical polarography, $i = KC$, and the technique becomes useful for quantitative analysis.

The constant K has been shown[3–6] to depend on both

The same figure shows the catalytic constant-current potentiometric titration curves obtained with two identical indicator electrodes (Pt+/Pt−), and with one cathodically (Pt−/SCE+) or anodically (Pt+/SCE−) polarized indicator electrode (Fig. 2, curves 1, 2 and 6). Similar titration curves are obtained for titration of potassium and ammonium fluoride.

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REFERENCES

1. H. A. Mottola, *Talanta*, 1969, **16**, 1267.
2. V. J. Vajgand, F. F. Gaál and S. S. Brusin, *ibid.* 1970, **17**, 415.
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7. F. Gaál and L. Bjelica, *Chem. Anal. (Warsaw)*, 1976, **21**, 227.
8. F. F. Gaál, B. F. Abramović, F. B. Szebenyi and V. D. Canić, *Z. Anal. Chem.*, 1977, **286**, 222.
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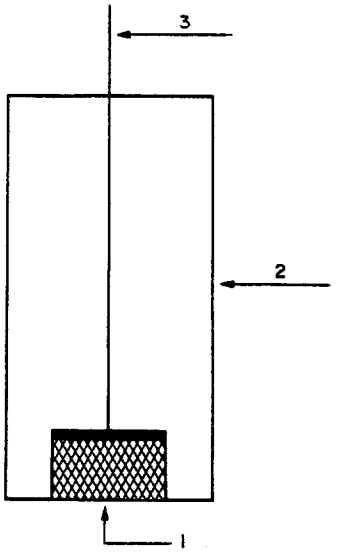


Fig. 1. Mineral graphite paste electrode; *1*—mineral graphite paste; *2*—Teflon rod, $d = 10$ mm, with a cavity for the paste, $d = 5$ mm; *3*—platinum or copper wire contact.

then does not exceed 5% ($n = 25$) and decreases by only 1% when the mixing is prolonged for a further 15 min. Prolonging the mixing time too much, or grinding the sample too finely can, however, give rise to larger errors, especially with sulphide minerals, which may be partly oxidized during this mechanical procedure. The particle size of the graphite powder is of no great importance, but it is preferable that it should be about the same as that of the sample, *i.e.* ~0.06 mm, to make for efficient mixing.

A technique for preparing mineral paste electrodes has been developed on the basis of these findings. It is applicable to a wide range of samples—minerals, oxides, salts, and others.

EXPERIMENTAL

Preparation of the electrode

Mix carefully 10–50 mg of the sample, already ground, with 1 g of graphite powder and 0.7 ml of binding liquid (preferably 1-bromonaphthalene as suggested by Adams[2] the chemical and physical properties of the substance, as well as on the method of preparing the paste and on the polarization scanning rate. The particle size is of great importance, as a decrease in the particle diameter leads to an increase in the working area of the paste electrode and thereby to an increase in the current. In other words the "sensitivity" of the method is enhanced. A systematic study of the dependence of the current on the particle diameter has supplied the data shown in Table 1. These results show that for practical purposes the 0.04–0.06 mm fraction should be used. The average error of 5% can be lowered to 2–3% by taking larger quantities of the material to be analysed, since the current is proportional to the amount of sample.

We have also shown[3] that adequate mixing of the paste components can be achieved in 5 min: the average error for the graphite paste electrode) for 5 min, then pack it into the end of the electrode body (Fig. 1). The paste surface must be smoothed by rubbing it lightly on writing paper, or some other paper which does not absorb liquids too readily. The diameter of the paste electrode is usually 5 mm, but if the concentration of the element to be determined in the sample is very small, a bigger electrode, up to 10 mm in diameter, can be used. The polarization scanning rate should be about 200–300 mV/min.

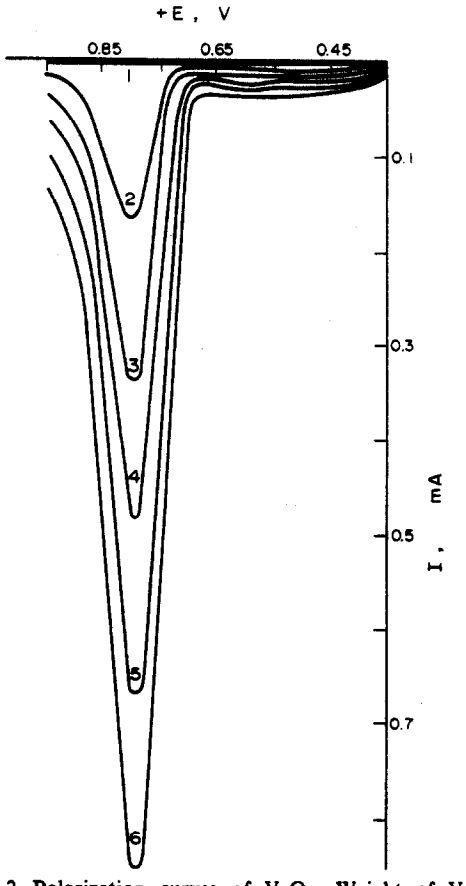


Fig. 2. Polarization curves of V_2O_3. Weight of V_2O_3 in paste, mg: *1*—0; *2*—10; *3*—20; *4*—30; *5*—40; *6*—50.

RESULTS

The behaviour of all three oxides of vanadium has been studied with the paste electrode.[7,8] Figure 2 shows curves recorded for V_2O_3 in 1*M* sulphuric acid. The height of the maximum is proportional to the amount of oxide taken. The potential of the maximum depends on the electrolyte, and shifts to more positive values as the acidity decreases, but the current maximum remains proportional to the amount of vanadium in all cases.

The maximum is associated with the depletion of V_2O_3 on the surface of the paste electrode as a result of anodic oxidation of V(III). No insoluble products are formed, and consequently the electrode process is not hampered by passivation. Because V_2O_3 is soluble in acids, the height of the maximum depends on the length of time the electrode has been in contact with the solution before the polarization curve is recorded. The same is also true for alkaline solutions, but as the oxide does not dissolve in water, this time factor is not important for neutral solutions. When acid or alkaline solutions are used, the electrode must be polarized immediately after immersion in the solution.

The height of the current-peak depends on the nature of the electrolyte: the reaction rate is higher in more concentrated acid or alkaline solutions.

The oxide V_2O_3 is oxidized in acid solution to V(IV), forming the vanadyl ion, VO^{2+}. In neutral and alkaline solution the oxidation proceeds to V(V). In neutral solutions VO^{3-} or its polymers are formed, and in alkaline solution, the orthovanadate ion, VO_4^{3-}.

Vanadium(IV) oxide V_2O_4 is oxidized anodically only in neutral or very dilute acid solution (pH not less than 3). The same behaviour is also demonstrated by the VO^{2+} ion at a platinum electrode.[9]

The pentoxide V_2O_5 cannot, of course, be oxidized, but

Table 1. Effect of particle size on the current and the average error for a copper/sulphide electrode (bornite, Cu_5FeS_4)

Particle size, *mm*	Mean current, μA	Average error, %
0.098–0.149	1.67	19.2
0.074–0.098	2.12	10.4
0.057–0.074	2.56	6.7
0.044–0.057	3.15	5.4
<0.044	4.00	4.7

it can be reduced cathodically at potentials around +0.5 V (NHE). It should be noted that V(V) ions can be reduced at a platinum electrode only in rather concentrated acid solutions[10] (8–10*M*) whereas solid V_2O_5 is also reduced in 1*M* hydrochloric or sulphuric acid.

The potentials of the current maxima for all three vanadium oxides are given in Table 2. It can be seen that if the right electrolyte is chosen, V_2O_3 can be determined in the presence of V_2O_4 as well as of V_2O_5. Such a selective determination of V_2O_3 in an oxide mixture is not possible by the usual chemical methods because it would be oxidized immediately in solution by any vanadium(V) from the sample, resulting in more V(IV) and less V(III) and V(V) than there should be.

For the determination of V_2O_3 we recommend 1*M* hydrochloric acid as electrolyte. V_2O_4 cannnot be determined directly in the presence of V_2O_3 because V_2O_4 is oxidized only in potassium nitrate solutions, and at nearly the same potential as V_2O_3, but it can be determined in the presence of V_2O_5 in potassium nitrate solution. When all three oxides are present, V_2O_4 must be determined in the following way: V_2O_3 is first determined in hydrochloric acid, the potential being swept in the anodic direction from 0.6 to 0.95 V *vs.* NHE. The electrode surface is then wiped on paper as in the preparation of the electrode, and the same electrode is polarized again, being swept in the opposite direction from 0.6 V to lower potentials. The amount of the pentoxide is then obtained from the height of the cathodic peak. Another portion of the sample is polarized similarly in 1*M* potassium nitrate and the peak-height gives the amount of V_2O_3 plus V_2O_4. The amount of V_2O_4 is then calculated by difference.

The oxide content can be checked by the standard addition method: two batches of paste are prepared, each containing 50 mg of sample, 1 g of graphite, and 0.7 ml of 1-bromonaphthalene, and to one of them is added a 10-mg portion of standard oxide. The peak-heights are compared after the samples have been run under the same conditions. The limit of determination is about 1 mg of oxide in 1 g of graphite.

CONCLUSION

This communication has been restricted to the determination of oxides of vanadium, but the technique can be applied to various products—commercial vanadium pentoxide, catalysts *etc.* This electrode has proved to be a useful tool which can be applied not only to the study of oxides, but also to that of various sulphide minerals, salts, *etc.* For example, polarization curves can be obtained for the mineral bornite (Cu_5FeS_4) by using a 0.05*M* solution of thiourea in 1*M* hydrochloric acid, and taking advantage of the very sharp cathodic maximum of the copper ion reduction. Correct choice of electrolyte allows analysis of materials containing several elements, which can be determined selectively, or consecutively.

REFERENCES

1. V. G. Barikov and O. A. Songina, *Khim. i Khim. Tekhnol. Alma-Ata*, 1967, **6**, 105.
2. R. N. Adams, *Anal. Chem.*, 1958, **30**, 1570.
3. O. A. Songina, Z. B. Roszdestvenskaya and E. P. Medvedeva, *Zavodsk. Lab.*, 1976, **42**, 379.
4. E. P. Medvedeva and Z. B. Roszdestvenskaya, *Vestn. Akad. Nauk Kaz. SSR*, 1976, No. 3, 61.
5. H. S. Brainina and R. P. Lessunova, *Zh. Analit. Khim.*, 1974, **29**, 1302.
6. E. P. Medvedeva, Z. B. Roszdestvenskaya and A. K. Kulikovski, *Iv. Akad. Nauk. Kaz. SSR, Ser. Khim.*, 1976, 801.
7. O. A. Songina, G. B. Bekturova, Z. T. Yarkesheva and V. A. Zakharov, *Vestn. Akad. Nauk. Kaz. SSR*, 1976, No. 10, 50.
8. O. A. Songina, V. A. Zakharov, G. B. Bekturova and Z. T. Yarkesheva, Summaries of papers, *Interan-76*, 1976, Prague, 126.
9. O. A. Songina, I. S. Savizkaya and Z. B. Roszdestvenskaya, *Izv. Vusshykh. Uchebn. Zavedinii. Khim. i Khim. Technol.*, 1969, 12, 7, 858.
10. O. A. Songina, G. B. Bekturova, V. A. Zakharov, Z. T. Yarkesheva, *Izv. Akad. Nauk Kax. SSR, Ser. Khim.*, 1973, No. 6, 78.
11. O. A. Songina, *ibid.*, 1975, No. 6, 73.

Table 2. Potentials of the current maxima in different electrolytes

Oxide	Electrode process	Peak potentials (*V vs.* NHE) 1*M* HCl	1*M* H_2SO_4	1*M* KNO_3	1*M* NaOH
V_2O_3	anodic	0.80	0.80	0.90	0.30
V_2O_4	anodic	not oxidized		0.85	not oxidized
V_2O_5	cathodic	0.40	0.45	not reduced	

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COMPORTEMENT ELECTROCHIMIQUE DES ANTIIMFLAMMATOIRES DERIVES DE LA PYRAZOLONE: APPLICATION AU DOSAGE DANS LES MEDICAMENTS

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Résumé—Le comportement électrochimique de quelques dérivés de la pyrazolone pharmacologiquement actifs, est étudié en milieux aqueux et éthanolique. Il est montré que les composés β-dicétoniques possédant un hydrogène mobile en -4 sont directement réductibles dans l'éthanol en milieu neutre, alors que les dérivés de la phénazone doivent être préalablement nitrosés. Une application au dosage dans les médicaments est proposée en polarographie à impulsion.

Les dérivés de la pyrazolone ont été relativement peu étudiés du point de vue électrochimique, probablement en raison de la non-électroactivité de ces composés en d.c. polarographie dans les solvants utilisés jusqu'alors.[1]

Adam et Joslin[2] ont étudié l'oxydation électrochimique de ces composés en milieu alcalin et quelques travaux concernant le comportement de la phénazone et de la phénylbutazone en oscillopolarographie ont été décrits.[3,4]

Ce travail fait apparaître un comportement électrochimique différent selon la nature des substituants: nous distinguerons les dérivés de la pyrazolidine-3,5 dione possédant deux fonctions carbonyle, qui, dans certaines conditions, peuvent être électrochimiquement actifs et les dérivés de la pyrazolidine-5 one qui ne sont réductibles électrochimiquement qu'aprés transformation de la molécule.

Cette méthode permet le dosage de ces composés en trés faible quantité. Elle peut être appliquée aux dosages dans les liquides biologiques.

PARTIE EXPERIMENTALE

Matériel électrochimique, électrodes, électrolytes support

Les potentiels sont imposés à l'aide d'un potentiostat Tacussel type PRG 5. Les électrodes utilisées sont les suivantes:

—électrode de travail: électrode à goutte de mercure à temps de goutte imposé Tacussel type MPO;

—électrode de référence: électrode au calomel aqueux;

—électrode auxiliaire: électrode de platine poli.

L'électrolyte indifférent est constitué de solution de perchlorate de lithium 0.2*M* (Merck pour analyse) pour les études effectuées dans l'éthanol et de solution 0.2*M* d'acide chlorhydrique pour les études effectuées en milieu aqueux.

La coulométrie à potentiel imposé est réalisée sur une nappe de mercure en employant une électrode de platine de grande surface comme électrode auxiliaire; le potentiel est imposé à l'aide d'un potentiostat Tacussel type PRT202X, le courant est intégré à l'aide d'un intégrateur Tacussel type IGS.

La polarographie impulsionnelle est réalisée à l'aide d'un potentiostat Tacussel PRG5 en imposant des impulsions constantes de 20 mV. Les voltampérogrammes sont enregistrés sur un enregistreur Tacussel type EPL1.

Les cellules sont thermostatées à 25 ± 0.5°.

Solvants

Eau bidistillée pour les composés nitrosés dérivés de la phénazone.

Ethanol (Merck pour analyse) préalablement distillé pour les dérivés de la pyrazolidine-3,5 dione.

Transformation en dérivé nitrosé

Dissoudre 5.10^{-6} mole de substance dans 10 ml d'eau bidistillée; ajouter 1 ml de solution de nitrite de sodium à 0.25% dans l'acide chlorhydrique 0.2*M*, préparée extemporanément, et 30 ml d'acide chlorhydrique 0.2*M*; porter à ébullition pendant environ 10 mn afin d'éliminer l'excés d'acide nitreux, laisser refroidir et compléter à 50 ml à l'aide d'acide chlorhydrique 0.2*M*. Les mesures sont effectuées sur 20 ml de solution.

Dans le cas de la phénazone il apparaît immédiatement une coloration verte qui évolue vers le jaune par chauffage; l'aminophénazone ne donne pas de couleur verte mais seulement une couleur jaune aprés chauffage.

Méthode des ajouts dosés

Dans une cellule de polarographie, introduire une prise d'essai exactement pesée, voisine de 10^{-6} mole de substance a doser, soit p mg, ajouter 20 ml d'électrolyte support dans l'éthanol, agiter sous courant d'azote pendant environ 10 mn puis enregistrer le voltampérogramme par polarographie à impulsion; mesurer la hauteur du palier de diffusion soit i_a.

Ajouter dans la cellule 5.10^{-6} mole de substance étalon (q mg), agiter sous courant d'azote pendant environ 10 mn, enregistrer à nouveau le voltampérogramme et mesurer la hauteur du palier de diffusion, soit i_b.

La quantité de substance à doser, exprimée en g pour 100 g est donnée par l'expression

$$\frac{100\, i_a q}{(i_b - i_a)p}.$$

Application au dosage dans des comprimés ou des dragées

Pulvériser finement 10 comprimés ou dragées. Dans une fiole jaugée de 50 ml, introduire une prise d'essai de poudre éxactement pesée correspondant à $2{,}5.10^{-5}$ mole de substance, compléter à 50 ml à l'aide d'électrolyte support dans l'éthanol, agiter pendant environ 10 mn, filtrer en rejetant les premiers millilitres de filtrat. Effectuer la méthode des ajouts dosés sur 20 ml de filtrat.

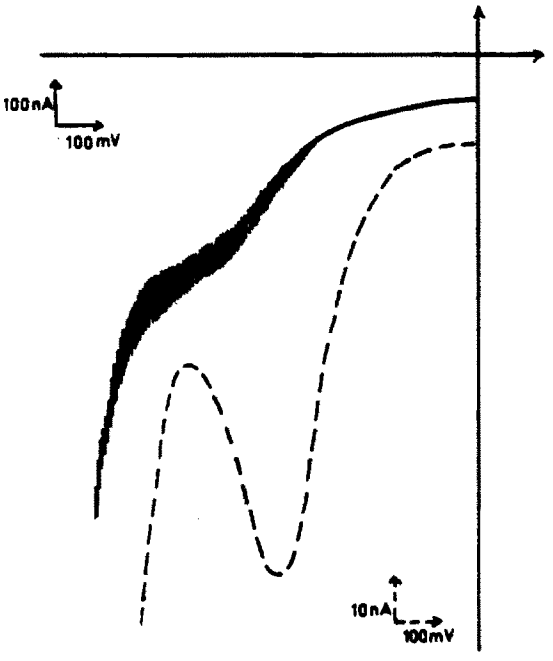


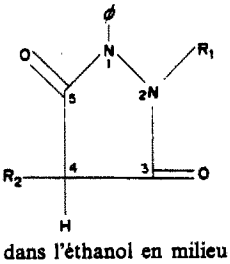
Fig. 1. Voltampérogramme de l'oxyphenbutazone dans l'éthanol: (——) d.c. polarographie; (– – –) polarographie impulsionnelle.

Si P est le poids moyen des comprimés ou dragées, p la prise d'essai de poudre, q la prise d'essai de substance étalon, la quantité de principe actif exprimée en g par comprimé ou dragée est donnée par l'expression

$$\frac{i_a q P}{(i_b - i_a)p}.$$

RESULTATS ET DISCUSSION

Les dérivés de la pyrazolidine-3,5 dione de formule générale:

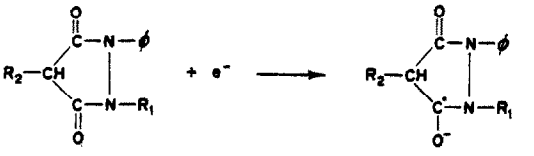


sont électroactifs dans l'éthanol en milieu neutre, en utilisant une électrode de mercure comme électrode de travail; un voltampérogramme est représenté sur la figure I; il apparait pour chacun des dérivés étudiés une vague de réduction. Les potentiels de demi-vague, mesurés par rapport à une électrode au calomel aqueux sont rassemblés dans le tableau 1.

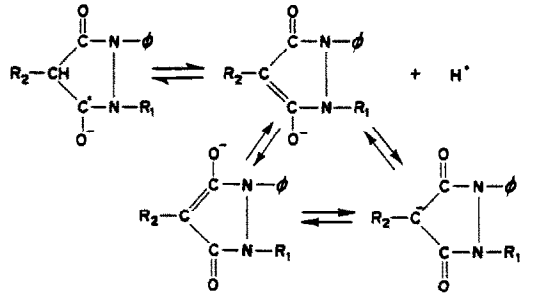
L'analyse mathématique des courbes intensité–potentiel obtenues, en appliquant la méthode des moindres carrés, avec un risque d'erreur à 5%, aux droites $E = f[\log(I_d - I)/I]$ montre que les valeurs des pentes trouvées s'écartent d'une manière significative des valeurs théoriques correspondant aux systèmes réversibles (58 mV pour une réaction électrochimique monoélectronique rapide), *cf.* tableau 1. Les systèmes électrochimiques mis en jeu sont donc irréversibles.

Le nombre d'électrons échangés lors de la réduction électrochimique est déterminé par coulométrie à potentiel constant en utilisant une nappe de mercure comme électrode de travail. L'intégration du courant d'électrolyse met en évidence la consommation d'un Faraday par molécule transformée; la réaction de réduction est donc monoélectronique. L'étude de l'évolution des courbes intensité–potentiel au cours de la coulométrie confirme l'irréversibilité des systèmes électrochimiques; en effet, les composés réduits, formés lors de la coulométrie, ne sont pas oxydables dans le domaine d'électroactivité du solvant.

La réaction électrochimique peut être schématisée de la manière suivante:



La présence de deux groupements carbonyle confère à la molécule un caractère acide et de ce fait augmente la mobilité de l'hydrogène situé en position -4. Le composé réduit est en équilibre selon les réactions:



L'existence de différentes formes mésomères déplace l'équilibre vers la droite et favorise ainsi la réaction électrochimique. Cette hypothèse est confirmée par le fait que les dérivés qui ne possédent pas d'hydrogène mobile en −4

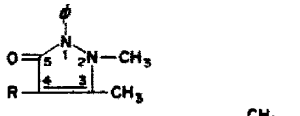
Tableau 1. Potentiel de demi-vague de réduction des dérivés de la pyrazolidine-3,5 dione dans l'éthanol

Composé étudié (D.C.)	Nature des substituants	$E_{1/2}$, V	Pente de la droite $E = f[\log(I_d - I)/I]$
Phénylbutazone	$R_1 = -C_6H_5$ $R_2 = -C_4H_9$	−1,540	0,137 ± 0,006
Oxyphenbutazone	$R_1 = -C_6H_4OH$ $R_2 = -C_4H_9$	−1,510	0,142 ± 0,012
Cétophénylbutazone	$R_1 = -C_6H_5$ $R_2 = -CH_2CH_2COCH_3$	−1,535	0,124 ± 0,003
Sulfinpyrazone	$R_1 = -C_6H_5$	1 ère vague −1,250	1 ère vague 0,089 ± 0,018
	$R_2 = -CH_2CH_2SOC_6H_5$	2 ème vague −1,490	2 ème vague 0,165 ± 0,010

ne sont pas directement réductibles à une électrode de mercure dans les mêmes conditions: c'est en particulier le cas de la suxibuzone qui posséde en −4, un groupement butyl $-C_4H_9$ et un groupement succinyl $-CH_2-O-CO-CH_2-COOH$.

La sulfinpyrazone se réduit en deux étapes monoélectroniques, le courant de diffusion correspondant à $E_{1/2} = -1{,}25$ V provient de la réduction de la fonction sulfoxyde (tableau 1).

Les dérivés de la pyrazolidine-5 one de formule:



Phénazone (R : H); Aminophénazone (R : $N(CH_3)_2$)

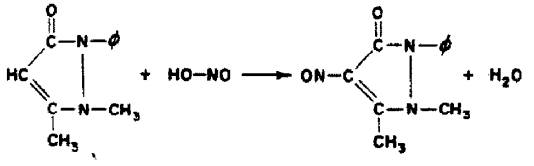
possédant un seul groupement carbonyle ne sont pas directement réductibles en milieu alcoolique. Cependant ces composés sont susceptibles de réagir avec l'acide nitreux à chaud, pour former des espèces stables et électroactives en milieu aqueux à une électrode de mercure.[5]

Les potentiels de demi-vague de réduction de la phénazone et de l'aminophénazone nitroses, mesurés par rapport à une électrode de réference au calomel aqueux sont rassemblés dans le tableau 2.

Tableau 2. Potentiel de demi-vague de réduction des dérivés nitrosés de la pyrazolidine-5 one en milieu aqueux

Composé étudié	$E_{1/2}$, V	Pente de $E = f[\log(I_d - I)/I]$
Phénazone	−0,900	0,130 ± 0,007
Amino-phénazone	−0,875	0,090 ± 0,008

Pour la phénazone la nitrosation doit avoir lieu en −4 selon la réaction:



Dans le cas de l'aminophénazone qui ne posséde pas d'hydrogène en −4, il se forme par action de l'acide nitreux à chaud un dérivé réductible à une électrode de mercure; le potentiel de demi-vague étant voisin de celui correspondant à la phénazone nitrosée. Il est possible que dans ce cas la nitrosation ait lieu en para sur le noyau benzénique; une réaction similaire a été décrite dans le cas d'une nitration par de l'acide nitrique concentré.[6]

Les courants de diffusion observés sont du à la réduction électrochimique de la fonction nitrosée selon la réaction:

$$-NO + 4e^- + 4H^+ \rightarrow -NH_2 + H_2O$$

L'analyse mathématique des courbes intensité–potentiel montre que les pentes des droites $E = f[\log(I_d - I)/I]$ correspondent à des systèmes électrochimiques irréversibles.

Les potentiels de demi-vague observés sont proches de ceux décrits par Roushdi *et al.*[7] lors de l'étude de la nitrosation d'un dérivé voisin, la noramidopyrine méthanesulfonate de sodium (Méthampyrone), qui posséde en −4 aprés hydrolyse un groupement $-N(CH_3)H$

APPLICATION ANALYTIQUE

Nous avons vérifié que dans les deux séries étudiées, les courants de diffusion respectaient la relation d'Ilkovič et qu'en particulier, les intensités des courants limites étaient reliées au temps de goutte de l'électrode selon la relation:

$$i = f(K\tau^{1/6})$$

(K = constante; τ = temps de goutte de l'électrode).

Les courants sont donc limités par la diffusion des espèces à l'électrode et sont proportionnels aux concentrations des composés en solution.

Dans le but d'améliorer la sensibilité de la méthode nous avons tracé les voltampérogrammes des différents composés en polarographie impulsionnelle à tension constante de 20 mV; un voltampérogramme de l'oxyphenbutazone est représenté sur la figure 1. Nous obtenons des pics bien définis dont la hauteur reste proportionnelle à la concentration.

Les valeurs des courants limites de réduction de l'oxyphenbutazone, en polarographie impulsionnelle dans l'éthanol, sont une fonction linéaire des quantités de substance introduites dans la cellule de mesure. Nous obtenons des droites d'étalonnage identiques avec la phénylbutazone, la cétophénylbutazone et la sulfinpyrazone. La sensibilité de la méthode permet de doser 2.10^{-6} mole de substance avec une précision voisine de 3%.

Cette méthode peut être appliquée au dosage des dérivés de la pyrazolidine-3,5 dione, possédant un hydrogène mobile en −4, dans des comprimés ou des dragées, après une simple extraction par l'éthanol. La présence d'excipients tels que amidon, gélatine, gomme arabique, gomme laque, cire blanche, stéarate de magnésium, acide stéarique, silice colloïdale et talc n'interfère pas lors du dosage; il en est de même pour les colorants tels que bleu patenté, indigotine, jaune orangé S et tartrazine. Cette méthode particulièrement simple et rapide permet l'analyse directe de ces molécules sans modification de structure et sans apport de réactif chimique.

Les valeurs des courants limites obtenus en polarographie à impulsion sont une fonction linéaire des quantités de phénazone et d'aminophénazone nitrosées utilisées.

Cette méthode permet de doser 10^{-6} mole de composé préalablement nitrosé et présente une meilleure sensibilité que les méthodes électrochimiques proposées jusqu'alors, telles que l'analyse en d.c. polarographie aprés nitration ou nitrosation[5,6] ou la bromation ou chloration par génération coulométrique.[8,9] Les courbes d'étalonnage tracées à partir de la méthode des moindres carrés donnent une précision de l'ordre de 3%.

CONCLUSION

La sensibilité des méthodes d'analyse proposées pour les principes actifs et les médicaments terminés, permet d'envisager le dosage des dérivés de la pyrazolone dans le cadre de l'étude du métabolisme de ces médicaments.

Contrairement aux travaux antérieurs, une réduction électrochimique directe des dérivés de la pyrazolidine-3,5 dione est proposée. Une étude approfondie des mécanismes de réduction mis en jeu en fonction du pH est actuellement en cours.

LITTERATURE

1. R. Kalvoda et J. Zýka, *Chem. Listy*, 1952, **46**, 56.
2. H. H. Adam et T. A. Joslin, *J. Electroanal. Chem.*, 1976, **72**, 197.
3. L. Molnàr, B. Proska et H. Szöcsovà, *Chem. Zvesti*, 1974, **28**, 366.

4. E. Szyszko et W. Weglowska, *Acta Pol. Pharm.*, 1974, **31**, 195.
5. K. Matsumoto, *J. Pharm. Soc. Japan*, 1955, **75**, 1001.
6. H. Oelschläger et D. Hamel, *Arch. Pharm. Ber. Dtsch. Pharm. Ges.*, 1969, **302**, 847.
7. I. M. Roushdi, S. A. Soliman et M. H. Sadek, *J. Pharm. Sci. U.A.R.*, 1971, **13**, 347.
8. A. A. Inkin et V. T. Kharlamov, *Zh. Analit. Khim.*, 1973, **28**, 2037.
9. K. Kalinowski et J. Fecko, *Acta Pol. Pharm.*, 1964, **21**, 247.

Summary—The electrochemical behaviour of some pyrazolone derivatives has been studied in aqueous and ethanolic media. β-Diketone compounds with a labile hydrogen atom on carbon atom 4 are directly reducible in neutral ethanol; phenazone derivatives have to be diazotized. Pulse polarography is suggested for determination of these derivatives in pharmaceutical preparations.

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SELECTIVITY OF CATALYTIC METHODS OF DETERMINATION*

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Summary—By means of catalytic analytical methods, extremely low levels can be determined at low cost and with a high sensitivity that is equal to that of physical methods of trace analysis. The selectivity of the catalytic determinations, is, however, usually rather lower than that of other methods of trace analysis. The selectivity can sometimes be improved by modification of the indicator reaction through variation of the reagents and their concentrations, or by use of masking reagents or activators, or by combination with a separation method. Modification of the indicator reaction can be exemplified by the selective determination of osmium and ruthenium by their catalysis of the nitrate oxidation of 1-naphthylamine. By variation of the nitrate concentration and the use of 1,10-phenanthroline and 8-hydroxyquinoline as complexing agents it is possible to determine these two elements simultaneously. An especially significant increase in the selectivity is made possible by use of a preliminary separation step. If the ion to be determined is separated by solvent extraction and then catalytically determined directly in the extract, a very specific determination is possible; this technique has been called "extractive catalytic determination". This method has been used for determination of molybdenum (0.5 ng/ml) in sea-water, iron (5 ng/ml) in heavy metal salts, and copper (3 ng/ml) in the presence of numerous elements.

The selectivity/specificity of analytical procedures based on chemical reactions results from the selectivity both of the chemical reaction and of the monitoring technique.

A specific determination is possible if either the monitoring system or the chemical reaction is specific (or if both are). The specific photometric determination of iron(II) in organic materials,[1] for example, by means of the well-known reaction with 1,10-phenanthroline, is feasible because of the possibility of specific monitoring of the tris(1,10-phenanthroline)iron(II) complex at 512 nm, where complexes of copper, cobalt, nickel, zinc, *etc.* do not absorb. On the other hand, the determination of copper with cuproins is a specific extractive photometric method resulting from the high selectivity of the reaction between copper and these ligands. In these reagents substituents in the *o*-position to nitrogen hinder the formation of extractable tris-complexes such as would be formed, for example, by iron(II).

Selective determinations require either a selective monitoring system—in an absorption-spectrometric method the component to be determined can be selected by changing the wavelength—or the conditions for the chemical reaction may be chosen to make the reaction at least partially specific for the relevant species.

Thus, the selectivity/specificity of catalytic methods of determination should be characterized by the selectivity of the catalytic reaction as well as by the selectivity of the monitoring technique used.

The general rate equation for the "indicator reaction"

$$A + B \rightarrow P \qquad (1)$$

in the presence of a catalyst C, determined by monitoring the increase of concentration of the reaction product P, is expressed as follows:

$$v = (d[P]/dt) = k'[A]^{p'}[B]^{q'} + k[A]^{p}[B]^{q}[C] \qquad (2)$$

in which A, B are the reactants, k', k represent the rate constants of the uncatalysed and catalysed reactions, respectively, p', q', p, q refer in simple cases to coefficients resulting from the reaction equation.

In the presence of different catalysts, the expressions for the rate of the catalysed reaction under various conditions are as follows:

$$\begin{aligned} v_1 - v_{10} &= k_{11}\pi_{11}[C_1] + k_{12}\pi_{12}[C_2] + \cdots + k_{1n}\pi_{1n}[C_n] \\ v_2 - v_{20} &= k_{21}\pi_{21}[C_1] + k_{22}\pi_{22}[C_2] + \cdots + k_{2n}\pi_{2n}[C_n] \\ &\vdots \\ v_n - v_{n0} &= k_{n1}\pi_{n1}[C_1] + k_{n2}\pi_{n2}[C_2] + \cdots + k_{nn}\pi_{nn}[C_n] \end{aligned} \qquad (3)$$

where $v_1 \ldots v_n$ characterize the rates of the (total) catalytic reaction, $v_{i0} = k'[A]^{p'i}[B]^{q'i}$ is the rate of the uncatalysed reaction, and $\pi_{ik} = [A]^{pik}B]^{qik}$ with $i, k = 1 \ldots n$.

Spectrophotometric methods are usually used for monitoring, but amperometric, potentiometric, enthalpimetric, and other techniques are also applied.[2] These techniques do not require expensive

* Paper presented at the International Symposium on Microchemical Techniques, Davos, May 1977.

For definitions see: H. Kaiser, *Z. Anal. Chem.*, 1972, **260**, 252.

or complicated apparatus, and this is one of the main advantages of catalytic methods of determination (in addition to their extremely high sensitivity and low limits of detection) over other methods of trace analysis.

The selectivity of such monitoring systems is sufficient to allow the rate of the indicator reaction to be followed specifically enough to avoid complications from side-reactions (complex formation, additional reaction products, *etc.*) resulting from foreign ions. Almost without exception the selectivity/specificity of a catalytic method is determined by the selectivity of the catalytic reaction.

A catalytic determination will be selective [*cf.* equation(3)] if either the individual catalysts show, under different reaction conditions, very different catalytic activities ($k_{ii} > k_{ik}$) or the catalysts present react according to different reaction mechanisms (p_{ii}, $q_{ii} > p_{ik}$, q_{ik},). Unfortunately, not much is known about the reaction mechanisms of different catalysts in one and the same indicator reaction, so, in most cases, only the sum of the two effects may be considered.

When the catalyst species are not chemically similar, the selectivity of catalytic reactions is usually high. For instance, the catalytic determination of molybdenum in the presence of alkali and alkaline earth metals, cobalt, nickel, and manganese[3] or the determination of platinum metals in the presence of copper, iron, and main group elements[4] is relatively easy. Catalytic reactions are much less selective when the determinant and interferent are closely related chemical species. Table 1 lists some indicator reactions which are influenced in a similar way by more than one catalyst (inhibitor).

Most of the catalytic determinations described in the literature are highly sensitive and reproducible, but their selectivity has not been considered. Because of this, they are not likely to be very useful for application to routine analysis. Change of pH, reagent concentrations and temperature, use of suitable complexing agents, and selection of the best monitoring technique may greatly increase the selectivity of such catalytic reactions. Sometimes, it will not be possible to obtain good enough selectivity by changing the conditions for the catalytic reaction, and in such cases, a preliminary separation step is necessary. Such combination of separation procedure with a catalytic determination is another means of increasing the selectivity of a catalytic procedure.

INCREASE OF SELECTIVITY OF CATALYTIC DETERMINATIONS

Influencing the catalyst–reactant interaction

The different activities of individual catalysts result from their individual reactivities toward the substrate, the oxidant, the buffer, and other species in the reaction mixture. The degree of interaction of a catalyst with the reactants depends on its tendency to form complexes, its oxidation potential, *etc.*

Unfortunately, not all the methods which are known to increase the selectivity can be discussed in terms of the mechanism of the catalytic reaction. Therefore, the examples which follow will be classified according to the sources of the changes in the catalyst–reactant interaction (*e.g.*, pH, concentration of reagents, temperature, co-ordination sphere of the catalyst, complexing agents).

Variation of pH, reagent concentration and temperature

The catalytic activity of chemical species is observed only in a narrow pH range, and this can confer some specificity. A typical case, studied by Yatsimirskii and Raizman,[10] was the reaction between iodide and hydrogen peroxide. The catalytic activities for zirconium and hafnium in this indicator reaction did not have the same pH-dependence.

Zirconium showed highest activity at pH 1.1 and hafnium at a pH near 2. This difference arises because only certain of the possible hydroxo-complexes of the metals cause catalytic acitivity, and these complexes are formed at different pH-values. By working at two pH-values, zirconium and hafnium could be determined in the same sample.[10]

Another effect of change of pH is to influence the formation of complexes with the substrate, the oxidant or an activator. It is well known that copper catalyses the oxidation of arylamines and phenols in alkaline medium, but that, because of the low stability of the copper complexes of ligands containing oxygen as donor atoms, only the oxidation of arylamines is catalysed in acidic medium. Therefore, by use of phenolic substrates, other metals such as iron can be determined catalytically in acidic medium in the presence of a relatively large excess of copper.[11]

The usefulness of temperature changes for increasing the selectivity of catalytic reactions was demonstrated by Wolff and Schwing[12] who studied the catalytic oxidation of iodide by bromate. At temperatures

Table 1. Non-specific indicator reactions

Species to be determined	Indicator reaction	Ref.
Ti, Zr, Hf, Th, Nb, Ta, Cr, Mo, W, Fe	$H_2O_2 + I^-$	5
Os, Ir, Ru	As(III) + Ce(IV) + ferroin	6
Pd, Pt, Ru, Ir	Lucigenin + N_2H_4	7
8-Hydroxyquinoline derivatives	Alizarin + H_2O_2 + Mn(II)	8
20 metals	Luminol + H_2O_2	9

between 0° and 40° the reaction is catalysed to varying extents by molybdenum(VI), tungsten(VI), and chromium(VI). The authors utilized this to develop methods for determination of mixtures of Mo(VI) with W(VI) and Mo(VI) with Cr(VI), by determining catalytic activities at two temperatures. However, the temperature dependences of the catalytic activities are rather similar, so the error in simultaneous determinations is about 20%.

The selectivity of a catalytic reaction can be changed by altering the reagent concentrations, because different catalysts give rise to different kinetic dependences in the indicator reaction. An example of this, given by Worthington and Pardue[13] was the catalytic determination of osmium and ruthenium by the Ce(IV)–As(III) reaction. With high As(III) concentrations and low concentrations of Ce(IV) the reaction is catalysed mainly by osmium. The indicator reaction is relatively specific for ruthenium with low As(III) concentrations and high Ce(IV) concentrations. Thus, if two different ratios of As(III) to Ce(IV) are used, osmium and ruthenium may be determined in the same sample at the nanogram level.

Selection of a defined co-ordination sphere of the catalyst

The co-ordination sphere of the catalyst metal plays an important part in its catalytic action. Where the metal easily undergoes ligand-exchange reactions with the reagents, the co-ordination sphere of the catalyst in the sample to be analysed is of little importance. However, if the metal (*e.g.*, a platinum metal) forms inert complexes, the co-ordination sphere of the catalyst must be defined.

For example, Lukovskaya and Kushchevskaya[14] found that the catalytic activities of iridium and rhodium solutions in the luminol–periodate reaction depended significantly on their history. Rhodium could be determined only in sulphate solutions because rhodium chloride solutions hydrolysed, with loss of catalytic activity. On the other hand, the catalytic action of iridium is not affected by chloride and sulphate, so this reaction allows the catalytic determination of the sum of these elements in sulphate solutions, whereas, in chloride solutions, iridium alone may be determined in the presence of rhodium.

A similar effect was observed by Mueller *et al.*[15] in the reaction of Mn(III) pyrophosphate with *p*-benzoquinone, catalysed by ruthenium and palladium. The chloro-complexes of these elements catalyse the indicator reaction similarly, but sulphate solutions increase the catalytic action of ruthenium and decrease that of palladium. This allows a relatively specific determination of ruthenium.

Modification of the substrate

The first step in the (catalytic) reaction of a metal with organic substrate is, in most cases, the formation of a complex between the metal and the substrate.

Bontchev[16] proposed the use of this complex formation for regulation of the selectivity of catalytic reactions. By introducing suitable substituents into the substrate, it may be possible to make it specific for some particular ion, and thus make the catalytic interaction specific.

Such tailor-made substrates have not yet been developed for catalytic analysis. However, some selectivity of substrates towards individual catalysts may be observed in the catalytic oxidation of various substituted phenols with hydrogen peroxide. These reactions are catalysed by copper, nickel and cobalt.[17] The catalytic action of copper is especially high if the phenol contains hydroxyl-groups in the *para*-position, whereas *meta*- or *ortho*-substituted phenols are less suitable as substrates (Table 2). Conversely, nickel and, particularly, cobalt strongly catalyse the oxidation of *ortho*-substituted phenols (Table 2).

Masking and activation

A common method for increasing the selectivity of catalytic reactions is the use of suitable masking agents, *e.g.*, organic ligands such as EDTA, 2-nitroso-1-naphthol, diethylamine and sulphosalicylic acid, or halides, *etc.* Some typical applications are listed in Table 3.

Besides the intentional introduction of complexing agents into the reaction, masking effects are often produced by reagents of the indicator reaction. Thus, the catalytic determination of copper based on its inhibitory effect on the *m*-thioammeline-catalysed iodine–azide reaction[25] is relatively specific, because the reagent sodium azide masks several foreign ions. Hydrogen peroxide acts in similar manner in the niobium- and tantalum-catalysed iodide–H_2O_2 reaction.[26] If the sample is reacted with the hydrogen peroxide before the catalytic determination, niobium is masked and tantalum may be determined in the presence of niobium.

Table 2. Substituted phenols as substrates in the metal catalysed oxidation with hydrogen peroxide

Substrate	Position of OH-group	Detectable concentration, μg/ml Cu(II)[17]	Ni(II)[17]	Co(II)[18]
Quinol	*para*	0.005	Inactive	0.02
Resorcinol	*meta*	0.01	Inactive	0.002
Pyrocatechol	*ortho*	0.05	0.1	0.0002
Pyrogallol	*ortho*	0.05	0.1	0.002
Tiron	*ortho*	—	0.01	0.00002

Table 3. Masking in catalytic analysis

Species of interest	Indicator reaction	Masking agent	Ref.
Mn	H_2O_2 decomposition	Sulphosalicylic acid	19
V	$I^- + BrO_3^-$	Citrate for Cu, Fe, Mo, Ti	20
Cu	$I^- + S_2O_8^{2-}$	F^- for Fe	21
Zn, Cd, Pb	$Ni(trien)^{2+} + Cu(EDTA)^{2-}$	CN^- for Fe, Co, Cu, Ni	22
Os	Lucigenin + H_2O_2	EDTA for Co, Cu, Ni, Pb, Fe	23
Cr	Bromopyrogallol Red + H_2O_2	EDTA for Fe, Co, Ni	24

The choice of suitable buffers may increase the selectivity of a catalytic reaction. For example, the oxidation of Alizarin S by hydrogen peroxide in the presence of sodium hydrogen carbonate buffer is a rather unselective reaction,[27] because cobalt and manganese can both act as catalysts. In ammonium carbonate buffer, however, the reaction becomes specific for manganese because cobalt forms very stable ammine complexes which are catalytically inactive. Thus, in an ammonium carbonate buffer, manganese may be determined in the presence of cobalt by catalytic titration[27] or by photometric monitoring of the indicator reaction[28] in presence of a 1000-fold excess of cobalt.

There are cases where it is not possible to find a masking agent which influences only the interfering elements. The catalytic activity of osmium would be lowered strongly by use of such ligands as CN^-, NH_3, salicylaldoxime or 1,10-phenanthroline,[4] which are therefore of no use as masking agents in the catalytic determination of osmium. An analogous inhibitory effect was shown by EDTA, in the catalytic determination of tin based on the ascorbic acid–molybdate reaction,[29] and so this ligand could not be used for masking. Likewise, in the catalytic determination of chromium(VI) in the presence of chromium(III), by use of the oxidation of *o*-dianisidine with hydrogen peroxide, no suitable masking agent was found. Kneebone and Freiser[30] tested EDTA, NTA, citrate and oxalate as masking agents for chromium(III) but these ligands were not applicable, because they either decreased the catalytic activity of chromium(VI) or masked chromium(III) too slowly.

The elimination of interfering ions by masking agents is only one way of increasing the allowable excess of metal ions. Another way is to use activators.[31] These reagents, in most cases organic complexing agents, increase the rate of a given catalytic reaction in the presence of certain catalysts. In general, the activator increases the catalytic action of only one catalyst (the metal to be determined) and for that reason the permissible ratio of interferent to determinant is increased. Very often the activator also acts as masking agent for some of the interfering ions.

Bontchev, who was the first to propose the use of activation and masking for regulation of the selectivity of catalytic reactions, used this variant as a means of increasing the selectivity of the *p*-phenetidine–chlorate reaction. The indicator reaction is catalysed by vanadium(V), iron(III), and copper(II). By use of citric acid as an activator the sensitivity of the vanadium(V)-catalysed reaction is increased about 15-fold, while the catalytic action of copper and iron is completely suppressed.

This author considers that the catalytic behaviour of vanadium(V) in the presence of citric acid is due to the formation of free radicals from the activator, so that the citric acid does not quench the catalytic activity of vanadium(V) even when present in large excess. The complexes of iron(III) and copper(II) with citric acid, however, are co-ordinatively saturated and therefore no complex formation with the substrate is possible.

Other examples are the catalytic determinations of silver and again vanadium. In the first case,[33] 2,2′-bipyridyl and ethylenediamine cause activation of the silver-catalysed sulphanilic acid–persulphate reaction and at the same time mask copper and iron. The second example[34] is the determination of vanadium by means of the *p*-phenetidine–bromate reaction with a high sensitivity in presence of the activator sulphosalicylic acid which acts simultaneously as masking agent for iron.

Combinations of effects

Combinations of masking and activation have already been mentioned, but there are some other possible combinations of effects influencing the selectivity of catalytic reactions.

By choice of suitable reaction conditions, masking agents and activators, we were able to improve the selectivity of the catalytic oxidation of 1-naphthylamine by nitrate[35] so much that the closely related platinum metals osmium and ruthenium could be determined in each other's presence. Study of the Os- and Ru-catalysed indicator reaction in the presence of various organic complexing agents showed that the catalytic activity of osmium is influenced by these ligands, but that the activity of ruthenium is not. Use of 1,10-phenanthroline to suppress the catalytic effect of osmium allows ruthenium to be determined in the presence of osmium. Osmium may be determined in the presence of ruthenium if 8-hydroxyquinoline is

used as activator for osmium, and the concentration of the nitrate oxidant is changed. This reaction enables osmium and ruthenium to be determined in the same sample in the concentration range 5–20 ng/ml. This method is more selective than the Ce(IV)–As(III) method[13] discussed previously.

COMBINATION OF CATALYTIC DETERMINATIONS WITH SEPARATION PROCEDURES

The common trace-analytical separation techniques such as liquid–liquid extraction, chromatographic methods (ion-exchange procedures, paper and thin-layer chromatography) and co-precipitation may also be used in combination with catalytic determinations. Table 4 gives some typical applications.

Liquid–liquid extraction is the technique most often used, because it is advantageous in that smaller amounts of sample are required and less time is needed for the separation step than for other techniques (*e.g.*, ion-exchange). Again, extraction reagents and solvents are available in higher purity than ion-exchange resins.[52] Chromatographic techniques such as paper or thin-layer chromatography are seldom preferred, because the separation matrix often interferes with the catalytic determination.[53]

Indeed, the influence of the separation matrix is also a problem with extraction methods. After an extraction, the metal is usually in an organic solvent in the presence of an excess of the extracting ligand. Because direct determination in the organic extract is not easy, the metal is often stripped into an aqueous medium. In many cases the metal can be back-extracted into water by changing the pH. However, very often the excess of ligand is also stripped from the organic phase, and it can interfere in the catalytic reaction. An additional treatment of the back-extract is then needed.[54,55] Furthermore, in the back-extraction, some of the organic solvent may be introduced into the aqueous phase, where it may cause inhibitory effects.[56] The metal complex may alternatively be transferred to an aqueous phase by oxidative destruction of the organic extract (*cf.* Table 4).

Unfortunately, both back-extraction of the metal and destruction of the organic extract make the combination of extraction with catalytic methods less attractive. The necessary work-up of the extract extends the analysis time and introduces the possibility of contamination or loss of sample. It seems much more attractive to determine the extracted species directly in the organic extract, but this is not simple.

Kneebone and Freiser,[30] for example, tried to determine chromium(VI), after extracting it from hydrochloric acid medium, directly in the extract by use of the Cr(VI)-catalysed *o*-dianisidine–H_2O_2 reaction, but without success. The extraction solvents (methyl isobutyl ketone, methyl n-propyl ketone, and decanol) strongly increased the uncatalysed reaction, and therefore the sensitivity of the method of determination was considerably decreased.

Sheikh and Townshend[56] observed a similar effect in the determination of indium by its inhibitory action on isocitrate dehydrogenase, after separation of indium by extraction with *N*-benzylaniline into chloroform. The extractant completely suppressed the enzyme reaction and therefore no inhibitory effect of indium could be detected.

Table 4. Combination of catalytic methods of determination with separation procedures

Element or compounds	Indicator reaction	Separation system or technique	Matrix	Ref.
		Liquid–liquid extraction		
Ni	diphenylcarbazone + tiron + H_2O_2	1-benzyldioxime/$CHCl_3$	oxides of La, Y, P	37
Co	Alizarin S + H_2O_2	2-nitroso-1-naphthol	P	38
Au	Hg(I) + Ce(IV)	HCl/ethyl acetate	ores	39
V	phenylhydrazine-*p*-sulphonic acid + ClO_3^-	oxine/$CHCl_3$	blood, urine	40
Cr	*o*-dianisidine + H_2O_2	HCl/MIBK	$AlCl_3$	41
Mn	H_2O_2 decomposition, 1,10-phenanthroline as activator	PAN/$CHCl_3$	alkali metal halides	42
		Ion-exchange		
Mo	Fe(III) + $SnCl_2$	Dowex 1, X-8	sea-water	43
Se	Methylene Blue + S^{2-}	Dowex 50W-X2		44
Cr	*o*-dianisidine + H_2O_2	Dowex 50W-X8	industrial atmosphere	30
Mn	Malachite Green + IO_4^-	Amberlite CG-120	Ta, Nb	46
		Chromatographic and other methods		
F	zirconium-catalysed reaction between perborate + I^- (inhibiting action)	microdiffusion	biological material	45
Ru	benzidine + H_2O_2	paper chromatography	aqueous solutions	47
Ir	Mn(II) + BrO^-	thin-layer chromatography		48
Cu	$Fe(SCN)_3$ + $S_2O_3^{2-}$	co-precipitation on Hg_2S	Me(II, III) salts	49
Ru	*o*-dianisidine + IO_4^-	distillation as RuO_4	ores	50
dithiocarbamates	N_3^- + I_2	high-voltage electrophoresis	aqueous solutions	51

The successful combination of extraction with catalytic determination in the organic extract will be discussed below. By analogy with extraction photometric methods we propose to call the new technique "extractive catalytic methods of determination".

Extractive catalytic methods of determination

For catalytic determination of a species (in most cases, a metal ion) in an organic extract the following conditions must be fulfilled:

(*a*) the metal species extracted must be catalytically active in the indicator reaction when this is carried out in mixtures of water and organic solvents or in purely organic solvents;

(*b*) the extraction system should enable the metal of interest to be separated specifically without co-extraction of interfering extracting agents.

As the first condition is the more difficult to achieve, it will be discussed in detail.

The catalytic activity of metal complexes in homogeneous indicator reactions

As a rule, the catalytic activity of metals (metal complexes) results from complex formation with the reagents for the indicator reaction—the substrate, oxidants, activators, *etc.* Complexed metals can catalyse an indicator reaction if either the co-ordination sphere of the metal is not completely saturated (apart from solvent molecules), or if a co-ordinatively saturated complex reacts according to an inner-sphere mechanism.

The second mechanism is seldom observed in catalytic analysis, but there are many examples in which the catalytically active metal complex still contains free co-ordination sites.

The tris(1,10-phenanthroline)manganese(II) complex, for instance, does not show any catalytic activity in the iodide–periodate reaction[57] nor in the oxidation of tiron by hydrogen peroxide.[58] Complexes of manganese with one or two 1,10-phenanthroline molecules, however, do catalyse these indicator reactions.[57,58]

On the other hand, an extraction step usually requires a co-ordinatively saturated metal complex, so the metal complex cannot be extracted in its catalytically active form. Thus for the extractive catalytic determination of silver, based on the reaction of Bromopyrogallol Red and persulphate with 1,10-phenanthroline as activator, the metal could not be separated as the catalytically active 1:1 metal–activator complex, but had to be extracted as the silver–1,10-phenanthrolinc 1:2 complex (in the presence of Bromopyrogallol Red).[59]

The catalytically active complex is then formed only in the reaction mixture, by ligand-exchange reactions or by irreversible changes of the complex.

The extraction of inert or extremely stable co-ordinatively saturated metal complexes is unsuitable because ligand-exchange reactions are slow or impossible. For example, an extractive catalytic determination of iron based on the extraction of the inert tris(1,10-phenanthroline)iron(II) complex is impossible because the dissociation of the catalytically inactive tris-chelate occurs too slowly.[60]

Thus, the first step in the development of an extractive catalytic procedure is to choose a suitable metal complex for extraction. For example, in the study of the extractive catalytic determination of molybdenum, we tested the catalytic activities of the molybdenum complexes of 8-hydroxyquinoline, 8-mercaptoquinoline, diethyldithiocarbamate and dithiolate, in the indicator reaction based on the oxidation of 1-naphthylamine by bromate.[61] The reaction was carried out in acidic mixtures of water, ethanol and chloroform. Spectrophotometric measurements showed that the catalytic activity of the complexes is proportional to their stabilities in the reaction solution.[62] The most suitable system was extraction of molybdenum(VI) into chloroform, with 8-hydroxyquinoline and it was found to offer high specificity and sensitivity, and to be simple to operate.[61]

Catalytic reactions in mixed and pure organic solvents

In extractive catalytic determinations the organic extract is usually introduced into mixed solvents. Mixtures of water, ethanol and chloroform,[61] water, dioxan and nitrobenzene,[59] water, ethanol and methyl isobutyl ketone,[63] and water, acetone and n-butanol[64] are commonly used.

When these organic solvents are used, the catalytic reactions are scarcely affected, and determinations are as precise and accurate as in aqueous solutions. However, mixtures of organic solvents and water have some disadvantages. First, because of the relatively low solubility of common extracting solvents in polar media such as water, ethanol or dioxan, the organic extract can be dissolved in the reaction mixture only to a small extent, and this limits the amount of the species of interest which can be determined. Secondly, some mixtures of water with organic solvents tend to separate.

For these reasons, it seems preferable to carry out the indicator reaction in a purely organic phase, since the solubility of the organic extract will be high and no separation ought to occur.

Of course, there are still problems with indicator reactions in organic media, in the present state of development of catalytic analysis. There are few indicator reactions in which both the substrate and the other reagents are organic. Also, it is not easy to find substances suitable for pH-adjustment in organic reaction mixtures. Most of the organic acids and bases available contain oxygen or nitrogen as donor atoms (in addition they may be chelating agents) and therefore interfere in the catalytic determination by complex formation with the metal to be determined.

An example of a catalytic indicator reaction in organic medium, suitable for an extractive catalytic procedure, is the method developed for determination

Table 5. Extractive catalytic determinations

Species to be determined	Indicator reaction	Extraction system	Ref.
Ag	Bromopyrogallol Red (BPR) + $S_2O_8^{2-}$ + 1,10-phenanthroline	1,10-phenanthroline, BPR/nitrobenzene	59
Mo	1-naphthylamine + BrO_3^-	oxine/$CHCl_3$	61
Fe	*p*-phenetidine + H_2O_2 + 1,10-phenanthroline	chloride/MIBK	63
Cu	sulphanilic acid + H_2O_2 + pyridine	pyridine, salicylate/$CHCl_3$	65
dimethylglyoxime	pyrocatechol + H_2O_2 + Co(II)	n-butanol	64

of copper based on the oxidation of sulphanilic acid by hydrogen peroxide.[65] The indicator reaction proceeds in neutral medium, so there is no need to add organic acids or bases, and all the reagents can be prepared as ethanolic solutions. Copper was extracted into chloroform as a ternary complex with pyridine and salicylate.[66] About 65% of the chloroform extract could be introduced into the ethanolic reaction solutions. The extractive catalytic procedure is rapid, selective, and enables copper to be determined with the same sensitivity as in aqueous solution.

Other extractive catalytic methods of determination are shown in Table 5.

Applications

The proposed extractive catalytic procedure for molybdenum (Table 5) could be used for its determination in sea-water,[69] whereas the normal catalytic method (without extraction) suffered from strong interferences from the salt content of the sample.

The attraction of extractive catalytic methods is illustrated by a method for the determination of iron. The selectivity of the indicator reaction used—the *p*-phenetidine–H_2O_2 reaction—is rather low because cobalt, nickel, and copper interfere.[67] An extractive catalytic procedure based on the same indicator reaction, and extraction of iron from 7*M* lithium chloride by methyl isobutyl ketone, allowed iron to be determined in salts of cobalt, nickel and copper in the range 5×10^{-6}–5×10^{-3}% of Fe with relative errors of about 2–10%.[63]

The first method for determination of a non-metallic species by means of an extractive catalytic method was developed by Antonov and Kreingold.[64] They determined dimethylglyoxime, by use of the oxidation of pyrocatechol with hydrogen peroxide, after extraction of the ligand with n-butanol. The method was used for determination of dimethylglyoxime in cadmium chloride.

REFERENCES

1. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, Springer-Verlag, Berlin, 1974.
2. H. Mueller and G. Werner, *Z. Chem.*, 1976, **16**, 304.
3. K. B. Yatsimirskii and A. P. Filippov, *Zh. Analit. Khim.*, 1965, **20**, 815.
4. V. I. Shlenskaya, V. P. Khvostova and G. P. Kadyrova, *ibid.*, 1973, **28**, 779.
5. K. B. Yatsimirskii, *MTP Int. Rev. Sci.*, **12**, T. S. West, ed., 1973, 193.
6. A. G. Gillet, *Mikrochim. Acta*, 1970, 855.
7. A. T. Pilipenko and A. V. Terletskaya, *Zh. Analit. Khim.*, 1973, **28**, 1135.
8. T. J. Janjić and G. A. Milovanović, *Anal. Chim. Acta*, 1976, **85**, 169.
9. A. Hartkopf and R. Delumyea, *Anal. Lett.*, 1974, **7**, 79.
10. K. B. Yatsimirskii and L. P. Raizman, *Zh. Analit. Khim.*, 1963, **18**, 29.
11. E. A. Bozhevolnov, S. U. Kreingold, R. P. Lastovskii and V. V. Sidorenko, *Dokl. Nauk SSSR*, 1963, **153**, 97.
12. C. M. Wolff and J. P. Schwing, *Bull. Soc. Chim. France*, 1976, 679.
13. I. B. Worthington and H. L. Pardue, *Anal. Chem.*, 1970, **42**, 1157.
14. N. M. Lukovskaya and N. F. Kushchevskaya, *Ukr. Khim. Zh.*, 1976, **42**, 87.
15. H. Mueller, L. P. Tichonova, K. B. Yatsimirskii and S. N. Borkovets, *Zh. Analit. Khim.*, 1973, **28**, 2012.
16. P. R. Bontchev, *Talanta*, 1970, **17**, 499.
17. I. F. Dolmanova, G. A. Zolotova, N. M. Ushakova, T. N. Tchernyavskaya and V. M. Peshkova, *Uspekhi Analiticheskoi Khimii*, Nauka, Moscow, 1974.
18. J. Bognar, *Mikrochim. Acta*, 1961, 901.
19. S. U. Kreingold, V. A. Komarova, V. I. Martsokha and E. M. Yutal, *Zh. Analit. Khim.*, 1974, **29**, 2324.
20. A. Thompson and G. Svehla, *Microchem. J.*, 1968, **13**, 576.
21. A. Páll, G. Svehla and L. Erdey, *Talanta*, 1970, **17**, 211.
22. R. H. Stehl, D. W. Margerum and J. J. Latterell, *Anal. Chem.*, 1967, **39**, 1346.
23. A. K. Babko and A. V. Terletskaya, *Zavodsk. Lab.*, 1969, **35**, 1046.
24. J. M. Ottaway, *Proc. Soc. Anal. Chem.*, 1974, **11**, 63.
25. Z. Kurzawa and M. Zietkiewicz, *Chem. Anal. Warsaw*, 1976, **21**, 13.
26. I. I. Alekseeva, L. P. Ruzinov, L. M. Chernysheva and E. G. Kachaturyan, *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1973, **16**, 1445; *Chem. Abstr.*, 1974, **80**, 33563r.
27. H. Weisz and T. Janjić, *Z. Anal. Chem.*, 1967, **227**, 1.
28. T. J. Janjić, G. A. Milovanović and M. B. Čelap, *Anal. Chem.*, 1970, **42**, 27.
29. V. I. Rigin and G. I. Alekseeva, *Zh. Analit. Khim.*, 1975, **30**, 2372.
30. B. M. Kneebone and H. Freiser, *Anal. Chem.*, 1975, **47**, 595.
31. P. R. Bontchev, *Talanta*, 1972, **19**, 675.
32. *Idem, Mikrochim. Acta*, 1964, 79.
33. A. A. Aleksiev and P. R. Bontchev, *ibid.*, 1970, 13.
34. V. M. Zyatkovskii, *Ph.D. Thesis*, Kiev, 1972.
35. H. Mueller and M. Otto, *Mikrochim. Acta*, 1975 I, 519.

36. *Idem, Z. Chem.*, 1974, **14**, 159.
37. L. V. Yurikova and A. Dzhumatev, *Zavodsk. Lab.*, 1974, **40**, 1197.
38. V. M. Peshkova, I. F. Dolmanova and N. N. Semenova, *Zh. Analit. Khim.*, 1963, **18**, 1228.
39. B. G. Zhelyazkova, P. R. Bontchev and A. A. Alexiev, *Mikrochim. Acta*, 1972, 896.
40. G. D. Christian, *Anal. Lett.*, 1971, **4**, 187.
41. I. F. Dolmanova, G. A. Zolotova, L. V. Tarusova and V. M. Peshkova, *Zh. Analit. Khim.*, 1969, **24**, 1035.
42. R. P. Pantaler, L. D. Alfimova and A. M. Bulgakova, *ibid.*, 1975, **30**, 1584.
43. R. Kuroda and T. Tarui, *Z. Anal. Chem.*, 1974, **269**, 22.
44. P. W. West and T. V. Ramakrishna, *Anal. Chem.*, 1968, **40**, 966.
45. D. Klockow and J. Auffarth, *Anal. Chim. Acta*, 1977, **89**, 37.
46. T. Fukasawa and T. Yamane, *Bunseki Kagaku*, 1975, **24**, 120.
47. G. M. Varshal, I. Y. Koshcheeva, R. P. Moiozova and O. N. Konopleva, *Zh. Analit. Khim.*, 1971, **26**, 939.
48. M. P. Volynets, R. P. Morozova, A. N. Ermakova, I. V. Pankratova and T. V. Dubrova, *ibid.*, 1973, **28**, 555.
49. H. Hesselbarth, *Z. Anal. Chem.*, 1969, **248**, 167.
50. V. E. Kalinina and O. I. Boldyreva, *Zh. Analit. Khim.*, 1973, **28**, 720.
51. Z. Kursawa and A. Krzyminsa, *II. Natl. Conf. on Anal. Chem.*, 20–24.9. 1976, Varna (Bulgaria).
52. R. Kucharkowski, *Ph.D. thesis*, Dresden, 1971.
53. G. H. Varshall, L. P. Tichonova, V. A. Sychkova and L. S. Shulik, *Zh. Analit. Khim.*, 1970, **25**, 2427.
54. Yu. I. Grosse and A. D. Miller, *Metody Anal. Redkometal. Miner., Rud. Gorn. Porod*, 1971, No. 2, 52; *Chem. Abstr.*, 1974, **80**, 33485s.
55. S. J. L. Hainberger and R. N. Damascenko, *Mikrochim. Acta*, 1975 II, 267.
56. R. A. Sheikh and A. Townshend, *Talanta*, 1974, **21**, 401.
57. Y. D. Tiginyanu and V. I. Oprya, *Zh. Analit. Khim.*, 1973, **28**, 2206.
58. Y. A. Tiginyanu, *Koord. Khim.*, 1976, **2**, 809.
59. H. Mueller, H. Schurig and G. Werner, *Talanta*, 1974, **21**, 581.
60. M. Otto and H. Mueller, *Z. Chem.*, 1977, **17**, 148.
61. *Idem, Talanta*, 1977, **24**, 15.
62. *Idem, Z. Chem.*, 1977, **17**, 232.
63. *Idem, Anal. Chim. Acta*, 1977, **90**, 159.
64. V. N. Antonov and S. U. Kreingold, *Zh. Analit. Khim.*, 1976, **31**, 193.
65. M. Otto, P. R. Bontchev and H. Mueller, *Mikrochim. Acta*, 1977 I, 193.
66. E. Papp and J. Inczédy, *Acta Chim. Acad. Sci. Hung.* 1974, **82**, 133.
67. E. E. Kriss, Y. S. Savichenko and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1969, **24**, 875.

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SPECTROPHOTOMETRIC DETERMINATION OF BISMUTH IN CONCENTRATES AND NON-FERROUS ALLOYS BY THE IODIDE METHOD AFTER SEPARATIONS BY DIETHYLDITHIO-CARBAMATE AND XANTHATE EXTRACTION

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Summary—A method for determining 0.0001–1% of bismuth in copper, molybdenum, lead, zinc and nickel sulphide concentrates is described. After sample decomposition, bismuth is separated from matrix and other elements, except lead and thallium(III), by chloroform extraction of its diethyldithiocarbamate complex, pH 11.5–12.0, from a sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. Following back-extraction of bismuth into 12*M* hydrochloric acid and reduction of thallium to the univalent state, bismuth is separated from co-extracted lead and thallium by chloroform extraction of its xanthate from a 2.5*M* hydrochloric acid–tartaric acid–ammonium chloride medium. Bismuth is then determined spectrophotometrically, at 337 or 460 nm, as the iodide. Interference from lead, which is co-extracted in μg-amounts as the xanthate and causes high results at 337 nm, is eliminated by washing the extract with a hydrochloric acid solution of the same composition as the medium used for extraction. The proposed method is also applicable to lead-, tin- and copper-base alloys.

In support of the Canadian Certified Reference Materials Project at CANMET, the author has developed spectrophotometric methods for the determination, at the ppm-level, of tellurium,[1] arsenic[2] and selenium[3] in copper, lead, zinc, nickel and molybdenum sulphide concentrates. The present work was undertaken to develop a method for minor and trace amounts of bismuth in such concentrates.

Probably the most common method for determining small amounts of bismuth is that based on its extraction as the diethyldithiocarbamate (DDTC) complex from an alkaline medium, followed by a spectrophotometric finish.[4–10] Bismuth has also been determined by an atomic-absorption method involving the direct aspiration into the flame of the methyl isobutyl ketone extract of the pyrrolidinedithiocarbamate complex.[11] However, this and other methods involving atomic-absorption finishes, after separation of bismuth by co-precipitation[12–14] or hydride-evolution[15] techniques, were not considered in the present work because they are usually less sensitive than spectrophotometric methods and are generally subject to numerous interferences. Because of the apparent simplicity and relatively high specificity of the DDTC-extraction procedure—when bismuth is extracted at pH ≥ 11 in the presence of citric or tartaric acid and EDTA and cyanide as masking agents [5,8,9,16,17]—the applicability of this separation procedure to the determination of bismuth in diverse sulphide concentrates was investigated. The direct measurement of the absorbance of the extract, advocated by many investigators, was not feasible for the present work because of the low sensitivity and reported instability.[5,8,10] Other investigators have used dithizone[9] or the iodide method,[6,7,9] in which spectrophotometric measurement is made at ~460 nm, for the indirect determination of bismuth after its separation by extraction as the DDTC complex. However, the sensitivity of the iodide method can be increased ~threefold, *i.e.*, to 3.05×10^3 l.mole^{-1}.mm^{-1}, by measuring the absorbance at 337 nm, the wavelength of maximum absorption.[18] Therefore, because of its sensitivity and overall simplicity the iodide method was chosen for use in the present work.

This paper describes the successful determination of bismuth in copper, molybdenum, lead and zinc concentrates and in non-ferrous alloys, after its separation from most of the matrix elements by chloroform extraction as the DDTC complex from a strongly alkaline (pH 11.5–12.0) sodium hydroxide medium containing both citric and tartaric acids, and EDTA and potassium cyanide as masking agents. Bismuth is subsequently separated from co-extracted lead and thallium by chloroform extraction as the xanthate from a 2.5*M* hydrochloric acid–tartaric acid–ammonium chloride medium. Interference from molybdenum and zinc, which results in incomplete back-extraction of bismuth into 12*M* hydrochloric acid after the DDTC–chloroform extraction, is avoided by adding lead before the extraction.

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EXPERIMENTAL

Reagents

Standard bismuth solutions, 5 and 50 μg/ml. Dissolve 0.2500 g of pure bismuth metal in 20 ml of concentrated nitric acid, cool and dilute to 500 ml with water. Transfer a 5-ml aliquot of this stock solution to a 500-ml standard flask, then transfer a 20-ml aliquot to a 200-ml flask. Add 5 ml of concentrated nitric acid to each flask and dilute the solutions to volume with water. Prepare fresh as required.

Lead, 0.5% w/v solution. Dissolve ~2.5 g of pure lead metal by heating gently with 150 ml of 50% nitric acid, cool and dilute to 500 ml with water.

Sodium hypophosphite, 15% w/v solution. Prepare fresh as required.

Potassium iodide, 20% w/v solution. Prepare fresh as required.

Citric acid–tartaric acid solution, 25% each, w/v.

EDTA, disodium salt–sodium hydroxide solution, 12% each, w/v.

Sodium hydroxide, 50% w/v solution.

Potassium cyanide, 20% w/v solution. Prepare fresh as required.

Sodium DDTC, 1% w/v solution. Prepare fresh as required.

Tartaric acid, 20% w/v solution.

Sulphurous acid. Water saturated with sulphur dioxide.

Ammonium chloride, 25% w/v solution.

Potassium ethyl xanthate, 20% w/v solution. Prepare fresh as required.

Hydrochloric acid–tartaric acid–ammonium chloride wash solution. Add 215 ml of concentrated hydrochloric acid to approximately 500 ml of water, then add 25 ml of 20% tartaric acid solution and 200 ml of 25% ammonium chloride solution and dilute the resultant solution to 1 litre with water.

Sulphuric acid, 50% v/v.

Nitric acid, 50% v/v.

Chloroform. Analytical-reagent grade.

Procedures

Calibration. Add 3 ml of 50% sulphuric acid and 1 ml of concentrated nitric acid to each of thirteen 100-ml beakers; then, from a burette, add to the first five beakers 1, 2, 4, 6 and 8 ml respectively, of standard 5-μg/ml bismuth solution. From a burette, add to the next seven beakers 1, 2, 3, 4, 6, 8 and 10 ml respectively, of standard 50-μg/ml bismuth solution. The last beaker contains the blank. Evaporate each solution to fumes of sulphur trioxide and cool to room temperature. Add 2 ml of freshly prepared 15% sodium hypophosphite solution to each beaker and mix. Add 5 ml of freshly prepared 20% potassium iodide solution, mix thoroughly, then transfer each solution to a 25-ml standard flask and dilute to volume with water. Allow the solutions to stand for 5 min, then determine the absorbance, at 337 nm, of the blank and each of the five solutions in the first series against water as the reference solution, using 40-mm cells. Determine the absorbance of the blank and each of the seven solutions in the second series in a similar manner, at 460 nm, using 10-mm cells, then determine that of the blank and the four solutions of lowest bismuth content in the second series, using 20-mm cells. Correct the absorbance value obtained for each bismuth iodide solution by subtracting the corresponding blank value. Plot μg of bismuth *vs.* absorbance for each series of measurements.

Concentrates. Depending on the expected bismuth content, transfer 0.2–0.5 g of powdered sample (Note 1) to a 60-ml zirconium crucible, add 3 g of sodium peroxide and mix thoroughly (Note 2). Cautiously fuse the mixture over an open flame and maintain it in the molten state for ~30 sec to ensure complete sample decomposition. Allow the melt to cool, then transfer the crucible to a covered 400-ml Teflon beaker containing ~80 ml of water and 25 ml of 50% sulphuric acid. When the melt has dissolved, remove the crucible after washing it thoroughly with water. If necessary, add sufficient 0.5% lead solution for ~25 mg of lead to be present, then cover the solution (Note 3) and evaporate it to ~75 ml. Remove the cover, add 5 ml of concentrated hydrofluoric acid and evaporate the solution to fumes of sulphur trioxide to remove silica and hydrogen peroxide. Cool, wash down the sides of the beaker with water and evaporate the solution until ~10 ml of sulphuric acid remain. Cool to room temperature, add ~40 ml of water and 5 or 10 g of sodium chloride (Note 4) and heat gently to dissolve the sodium salts and lead sulphate. Add 20 ml of 25% citric acid–25% tartaric acid solution, mix (Note 5) and add 50 ml of 12% EDTA–12% sodium hydroxide solution. With the aid of a pH meter, if necessary (Note 6), or a small piece of red litmus paper added to the solution, make the solution alkaline (pH 7–11) by adding 50% sodium hydroxide solution. Cool to room temperature in a water-bath, then adjust the pH to 11.5–12.0 with 50% sodium hydroxide solution. Carry a blank through the whole procedure.

Transfer the blank and sample solutions to 250-ml separating funnels, add 30 ml of freshly prepared 20% potassium cyanide solution and mix thoroughly. Add 5 ml of freshly prepared 1% sodium DDTC solution, mix, then add 10 ml of chloroform (Note 7), stopper and shake for 1 min. Allow several minutes for the layers to separate, then drain the chloroform phase into a 125-ml separating funnel marked at 75 ml (Note 8). Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform, then wash it by shaking it for ~30 sec with 5 ml of chloroform. Add 16 ml of concentrated hydrochloric acid to the combined extracts, stopper and shake for 2 min. Allow several minutes for the layers to separate, then drain off and discard the chloroform layer. Add 2 ml of 20% tartaric acid solution, 2 ml of sulphurous acid and 15 ml of 25% ammonium chloride solution to the resultant solution, dilute to the 75-ml mark with water and mix throughly. Add 10 ml of chloroform followed by 1 ml of freshly prepared 20% potassium ethyl xanthate solution, stopper and extract immediately (Note 9) by shaking for 1 min. Allow several minutes for the layers to separate.

If the sample contains 40 μg or less of bismuth, drain the sample and blank extracts into 125-ml separating funnels. Extract the aqueous phase three more times, in a similar manner, with 10-, 5- and 5-ml portions of chloroform and 1, 0.5 and 0.5 ml of xanthate solution, respectively. Add 30 ml of hydrochloric acid–tartaric acid–ammonium chloride wash solution to the combined extracts, stopper and shake for 1 min. After the layers have separated, drain the chloroform phase into a 150-ml beaker. Add 5 ml of chloroform and 0.5 ml of xanthate solution to the aqueous phase and shake for 1 min. Allow the layers to separate and drain the chloroform phase into the beaker containing the initial extract. Extract the aqueous phase once more in a similar manner, then wash it by shaking it for ~30 sec with 5 ml of chloroform. Add 10 ml of 50% nitric acid and 1 ml of concentrated perchloric acid to the combined extracts and heat in a hot water-bath to remove the chloroform. Cover the beaker until the evolution of brown oxides of nitrogen ceases, then remove the cover, wash down the sides of the beaker with water and evaporate the solution to fumes of sulphur trioxide or almost to dryness (Note 10). Cool, add 1 ml of 50% nitric acid and 3 ml of 50% sulphuric acid and evaporate the solution to fumes of sulphur trioxide again. Cool to room temperature, then proceed with the additions of sodium hypophosphite and potassium iodide solutions and the subsequent determination of bismuth as described above, using 40-mm cells and a wavelength of 337 nm.

If the sample contains between 40 and 500 μg of bismuth, drain the sample and blank extracts into 150-ml beakers. Extract the aqueous phase three more times as described above, then add 10 ml of 50% nitric acid and 1 ml of concentrated perchloric acid to the combined extracts and proceed with the removal of chloroform and the ultimate determination of bismuth as described above, using either 10- or 20-mm cells as required and a wavelength of 460 nm.

If the sample contains more than 500 μg of bismuth, treat the combined sample and blank extracts with 10 ml of 50% nitric acid and 1 ml of concentrated perchloric acid as described above and evaporate the solution to fumes of sulphur trioxide or almost to dryness (Note 10). Cool, add 10 ml of 50% nitric acid and heat gently to dissolve the salts. Cool to room temperature, then transfer both the sample and blank solutions to standard flasks of appropriate size (50–200 ml) and dilute to volume with water. Transfer suitable aliquots (up to 40 ml) of both solutions to 150-ml beakers and add 3 ml of 50% sulphuric acid. Evaporate the solutions to fumes of sulphur trioxide, then proceed with the determination of bismuth as described above, using a wavelength of 460 nm.

Non-ferrous alloys. Depending on the expected bismuth content, transfer 0.2–0.5 g of sample to a 400-ml beaker, cover and add ~5 ml of water and 10 ml of concentrated nitric acid. When the dissolution of the sample is complete, add 20 ml of 50% sulphuric acid and, if necessary, sufficient 0.5% lead solution for ~25 mg of lead to be present and heat until the evolution of brown oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool to room temperature, add ~40 ml of water and, depending on the amount of lead sulphate present, 5 or 10 g of sodium chloride (Note 4). Heat to dissolve the salts, then proceed with the additions of citric acid–tartaric acid and EDTA–sodium hydroxide solutions, the pH adjustment, the extractions of bismuth DDTC and xanthate and the subsequent determination of bismuth as described above.

Notes

1. Larger samples should not be used unless the volume of EDTA–sodium hydroxide solution that is employed subsequently for masking purposes is increased correspondingly.

2. If the sample contains little, or no, acid-insoluble material, it can be decomposed with acids in a Teflon beaker as follows. Add 10 ml of 20% v/v bromine–carbon tetrachloride solution, cover and add 15 ml of concentrated nitric acid. Allow the solution to stand for ~15 min, then heat gently to remove the bromine and carbon tetrachloride. Add 20 ml of 50% sulphuric acid, heat gently until the evolution of brown oxides of nitrogen ceases, then remove the cover and add 5 ml of concentrated hydrofluoric acid and, if necessary, sufficient 0.5% lead solution to give a total of ~25 mg of lead. Evaporate the solution to fumes of sulphur trioxide, then proceed as described.

3. The solution should be kept almost completely covered during the initial evaporation to avoid loss by spray.

4. Approximately 10 g of sodium chloride should be used if more than ~250 mg of lead are present.

5. If the subsequent DDTC and xanthate extractions cannot be performed the same day, allow the solution to stand overnight at this point. Addition of the EDTA–sodium hydroxide solution is not harmful except that the EDTA will precipitate from the acidic solution during prolonged standing.

6. A pH meter is only necessary for highly coloured copper and nickel solutions of low iron content. If an appreciable amount of iron is present, add 50% sodium hydroxide solution until the solution changes colour owing to the formation of the reddish-brown iron(III)–EDTA complex.

7. Carbon tetrachloride is not recommended for the extraction of bismuth from solutions containing an appreciable amount of lead. Lead DDTC, which is less soluble in this solvent, precipitates in the organic phase and may interfere mechanically with the extraction of bismuth.

8. The separating funnel should be drained thoroughly after washing, to prevent dilution of the concentrated hydrochloric acid used for the subsequent back-extraction of bismuth.

9. Because of the known instability of many metal xanthate complexes, extraction immediately after the addition of chloroform and xanthate solution is recommended.

10. The small amount of sulphuric acid that is present is formed during the nitric acid oxidation of xanthate in the extract.

RESULTS

Separation of bismuth by extraction of its DDTC and ethyl xanthate complexes

The extraction of bismuth, as its DDTC complex, from a strongly alkaline solution containing citrate or tartrate and EDTA and cyanide as masking agents, is relatively specific[5,8,9,16,17] and is quantitative up to pH ~12.[6–8,17] Bode[16,17] reported that lead is not precipitated or extracted as the DDTC complex at pH ≥ 7 in the presence of EDTA, and that only thallium(III) is co-extracted from EDTA or cyanide solutions at pH ~11. Both of these elements interfere in the determination of bismuth by the iodide method[19] because of the formation of insoluble coloured iodides. However, the co-extraction of thallium(III) can be avoided by reducing it to the univalent state before the extraction of bismuth.[17] Contrary to Bode,[16,17] later workers[5,10,20] found that lead is also partially extracted from an alkaline EDTA–cyanide medium. This was also confirmed in the present work in tests in which bismuth–DDTC was extracted into chloroform, under the proposed extraction conditions, from solutions containing 500 mg of lead. The lead that is co-extracted interferes in the subsequent determination of bismuth by the formation of lead iodide and also by the formation of lead sulphate before the complex formation. Furthermore, bismuth is lost by occlusion[20] during the removal of lead sulphate by filtration, either before or after complex formation. Shaking the extract with 2*M* hydrochloric acid[21] was found to be ineffective for the removal of large amounts of co-extracted lead. Bismuth can be separated from large amounts of lead by chloroform extraction of its cupferronate from 0.1*M* nitric acid medium.[22] However, tests showed that this was not practicable in the present work because a strongly acidic (~50% v/v) nitric acid solution is required for the prior back-extraction of the bismuth and lead DDTC complexes from the chloroform phase. Consequently, the addition of an inordinately large volume of water would be required to adjust the acid concentration to 0.1*M*. Conversely, nitric acid cannot be removed by evaporation, followed by the dissolution of the salts in ≥0.1*M* nitric acid, because lead sul-

phate is formed by reaction with the small amount of sulphuric acid that is produced during the nitric acid oxidation of DDTC in the extract. Previous work by the author[23] showed that bismuth can be quantitatively extracted into chloroform as the xanthate from ~0.1–3*M* hydrochloric acid, and that lead is not appreciably extracted from ~2.5–3*M* hydrochloric acid. Furthermore, thallium(I) is essentially not extracted from ≥0.5*M* hydrochloric acid media. Xanthate–chloroform extraction of bismuth from a dilute hydrochloric acid–tartaric acid–ammonium chloride medium has been used earlier[24] for its separation from lead. Therefore, it was considered that this might be a simple and effective means of separating bismuth from large amounts of co-extracted lead DDTC and also from thallium after its reduction to the univalent state.

Preliminary experiments with 2.5 and 3*M* hydrochloric acid solutions of bismuth and lead containing tartaric acid and ammonium chloride showed that, although the co-extraction of lead into chloroform as the xanthate is lower from the 3*M* medium, moderately large amounts of bismuth (2 mg) are more readily extracted from 2.5*M* medium. The lead (less than 100 μg) that is co-extracted from a 2.5*M* medium does not interfere in the subsequent determination of bismuth as the iodide when absorbance measurements are made at 460 nm, but does cause high results if measurements are made at 337 nm. Further work showed that the co-extracted lead can be removed by washing the chloroform extract with a 2.5*M* hydrochloric acid solution of the same composition as the medium used for extraction. Although μg-amounts of bismuth enter the aqueous phase under these conditions, they can be recovered by adding xanthate to the wash solution and re-extracting the bismuth. The xanthate–chloroform extraction procedure was also found to be a simple and effective method for separating bismuth from up to at least 1 mg of co-extracted thallium after it is reduced with sulphurous acid. Subsequent work showed that, after extraction as the DDTC complex, up to at least 2 mg of bismuth can be quantitatively back-extracted from the chloroform phase into 12*M* hydrochloric acid by shaking for two minutes or more.

Complete recovery of bismuth (500 μg) was

Table 1. Recovery of bismuth from synthetic concentrate samples

Matrix and nominal composition, %	Total Bi present, %	Bi found, %
Cu concentrate (33.5 Cu, 30.0 Fe, 34.2 S)	0.0006_5	0.0008_0
	0.0011_5	0.0011_8
	0.0051_5	0.0052_0
	0.0102	0.009_9
	0.0502	0.049_0
	0.1002	0.101_3
	0.500	0.50_4
	1.000	1.00_0
Mo concentrate, NBS 333 (93 MoS_2, 1.0 Cu, 1.2 Fe)	0.0007_9	0.0007_6
	0.0012_9	0.0012_8
	0.0052_9	0.0052_2
	0.0103	0.010_1
	0.0503	0.050_4
	0.1003	0.099_8
	0.500	0.50_4
	1.000	0.99_9
Pb concentrate (~82 Pb, 0.3 Fe)	0.0007_2	0.0008_0
	0.0012_2	0.0014_2
	0.0052_2	0.0050_0
	0.0102	0.009_7
	0.0502	0.500_0
	0.1002	0.100_5
	0.500	0.50_1
	1.000	1.00_2
Zn concentrate, NBS 113 (61.1 Zn, 1.2 Fe)	0.0005_0	0.0004_2
	0.0010_0	0.0010_4
	0.0050_0	0.0050_4
	0.0100	0.010_1
	0.0500	0.049_6
	0.1000	0.100_8
	0.500	0.50_4
	1.000	0.99_7

Duplicate determinations of bismuth in the Cu, Mo, Pb and Zn concentrates by the proposed method gave 0.0001_4 and 0.0001_6, 0.0003_0 and 0.0002_8, 0.0002_8 and 0.0001_6, and none detected and none detected, respectively.

Table 2. Determination of bismuth in N.B.S. and B.C.S. non-ferrous alloys and in reference ores MP-1 and PR-1

Sample	Nominal composition, %	Certified value and range, % Bi	Bi found, %
NBS-C1100 Cartridge brass	67.4 Cu, 32.2 Zn, 0.1 Pb	0.0010	0.0011
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn, 0.05 Pb	0.0004	0.0004
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn, 0.02 Pb	0.0005	0.0006
NBS-53d Lead-base bearing metal	9.9 Sb, 4.9 Sn	0.135 (0.12–0.143)	0.141
NBS-54D Tin-base bearing metal	88.6 Sn, 7.1 Sb, 3.6 Cu, 0.6 Pb	0.044 (0.037–0.050)	0.048
NBS-127A Solder	30.0 Sn, 0.8 Sb, 0.1 As	0.036 (0.031–0.04)	0.039
BCS-178 White metal "B"	84.0 Sn, 7.5 Sb, 4.1 Cu, 3.9 Pb	0.005* (0.003–0.008)	0.0030
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni	0.008 (0.007–0.010)	0.0072
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn, 0.7 Pb	0.04 (0.039–0.048)	0.042
MP-1-Zinc–tin–copper–lead ore	16.3 Zn, 2.5 Sn, 2.2 Cu, 1.9 Pb, 5.7 Fe, 0.8 As, 19.4 Si, 3.6 Al, 3.4 Ca	0.025 (0.023–0.027)†	0.022‡, 0.022§
PR-1 Molybdenum ore	39.2 Si, 1.3 Fe, 0.6 Mo, 2.4 Al, 1.4 Ca, 2.0 K	0.111 (0.107–0.114)†	0.107‡, 0.107§

* Certified value based on the 2 results shown.
† 95% Confidence limits of the recommended mean value.
‡ Mean of 4 values after sample decomposition by fusion.
§ Mean of 2 values after sample decomposition with acids (described in Note 2).

obtained when the proposed procedure (except for the addition of lead) was applied to synthetic (0.5-g samples) copper and lead concentrates after sample decomposition by fusion with sodium peroxide. However, low and erratic results, especially in the presence of molybdenum, were obtained for synthetic molybdenum and zinc concentrates (compositions given in Table 1). Similarly, even lower and more erratic results were obtained for the reference ore PR-1 (composition given in Table 2) which contains considerably less molybdenum than the molybdenum concentrate employed. Ultimately, tests showed that this was not due to incomplete extraction of bismuth as the DDTC complex in the presence of molybdenum or zinc, but to the subsequent failure of the complex to be quantitatively back-extracted from the chloroform phase into 12*M* hydrochloric acid. It is not yet understood how molybdenum and zinc interfere, because tests showed that neither of these elements is co-extracted under the conditions chosen. Further tests, with the reference ore MP-1, (composition given in Table 2), yielded consistent and reproducible results for bismuth, even when molybdenum was added to the sample solution before the extraction of bismuth DDTC. Consequently, some element in MP-1 seems to obviate the interference of molybdenum. A comparison of the two reference ores[25,26] shows that PR-1 contains very little copper (0.01%), lead (0.04%) or tin (none detected) compared to MP-1 (Table 2). Because lead is the only one of these elements that is co-extracted as a DDTC complex under the proposed conditions, it was considered that it may be responsible for eliminating interference from the added molybdenum in the test with MP-1. This was proved in subsequent tests with PR-1 and synthetic molybdenum and zinc concentrates, in which quantitative and reproducible results were obtained when 25 mg of lead were added to the solutions before the extraction of bismuth DDTC. No explanation can be seen for the remedial effect of lead.

Effect of diverse ions

Tests showed that bismuth is not extracted as the DDTC complex in the presence of 500 mg of iron(III)—even in the presence of a large excess of potassium cyanide—unless a considerable excess of EDTA (>6 g) is present. It was also found that citric acid is not a good complexing agent for iron(III) because it does not completely prevent formation of the hydrous oxide precipitate during pH adjustment to 11.5–12.0. The precipitate dissolves when potassium cyanide is added but bismuth is not extracted under these conditions. Although tartaric acid is an effective complexing agent for iron(III), a mixture of citric and tartaric acids was used in this work because citric acid is a more effective complexant than tartaric acid in alkaline media. Tests—in which lead was not added and in which the bismuth DDTC extract was treated with nitric and perchloric acids as described in the proposed method for the xanthate extract—showed that, in the presence of ~6 g of EDTA and ~7 g of potassium cyanide, up to 500 mg of copper (II), molybdenum(VI), zinc and nickel, and 250 mg of iron(III) will not interfere in the DDTC extraction or subsequent determination of bismuth. Also, up to at least 200 mg of tin(IV), 100 mg of cadmium, anti-

mony(V), manganese(II), aluminium, zirconium and calcium, and 50 mg of arsenic(V) and phosphorus(V) will not interfere.

Applications

The proposed method was applied to the analysis of a series of four synthetic concentrates (200-mesh commercial-grade sulphide concentrates) in which bismuth, added to the samples in the form of a standard solution after dissolution of the sodium peroxide melt, was varied from 0.0005 to 1%. It was also applied to certified reference lead-, tin- and copper-base alloys and to two reference ores, MP-1 and PR-1, that have been certified for bismuth by the Canadian Certified Reference Materials Project. The results of these analyses are given in Tables 1 and 2.

DISCUSSION

Table 1 shows that the results obtained for the synthetic copper, molybdenum, lead and zinc concentrates agree favourably with the calculated amount of bismuth present. Unfortunately, a nickel concentrate of low bismuth content could not be obtained for test purposes. However, the proposed method is applicable to nickel concentrates because, as stated previously, nickel (up to 500 mg) does not interfere in the determination of bismuth. The results (Table 2) for the National Bureau of Standards and British Chemical Standards non-ferrous alloys are also in good agreement with the certified values. The results obtained for the certified reference molybdenum ore, PR-1, after sample decomposition both by fusion and with acids, are in good agreement with the recommended mean value.[25] However, those obtained for the zinc–tin–copper–lead ore, MP-1, are lower than the recommended mean value[26] and also lower than the lower 95% confidence limit. MP-1 was certified by a scheme in which participants used mostly atomic-absorption methods. Details of most of these methods are not available, but it is probable that many have not been examined for bias as closely as the one proposed here.

The proposed method is suitable for samples containing $\geq 0.0001\%$ of bismuth. Probably, samples containing $\sim 0.01\%$ or more can be analysed by flame atomic-absorption spectroscopy. This would involve the direct treatment of the bismuth–DDTC extract with nitric and perchloric acids, followed by the evaporation of the solution to dryness, dissolution of the residue in sufficient concentrated hydrochloric acid to dissolve lead sulphate and maintain bismuth in solution, and dilution of the resulting solution to an appropriate volume (25 ml or more) with water. To eliminate possible error from the co-extracted lead, an equivalent amount should be added to the bismuth calibration solutions.

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REFERENCES

1. E. M. Donaldson, *Talanta*, 1976, **23**, 823.
2. *Idem, ibid.*, 1977, **24**, 105.
3. *Idem, ibid.*, 1977, **24**, 441.
4. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1954, **43**, 88.
5. K. L. Cheng, R. H. Bray and S. W. Melsted, *Anal. Chem.*, 1955, **27**, 24
6. N. P. Strel'nikova and G. G. Lystsova, *Zavodsk. Lab.*, 1962, **28**, 659.
7. N. P. Strel'nikova, *Tr. Komis. po Analit. Khim. Akad Nauk SSSR, Inst. Geokhim. i Analit. Khim.*, 1963, **14**, 305; *Chem. Abstr.*, 1963, **59**, 13332d.
8. H. Pohl, *Metall.*, 1964, **18**, 113.
9. N. A. Filippova, V. A. Korosteleva and S. B. Yurovskaya, *Spektral'n. Khim. Metody Analiza Materialov, Sb. Metodik*, 1964, 176; *Chem. Abstr.*, 1965, **62**, 3384d.
10. A. I. Busev, V. M. Bry'ko and R. G. Zhukova, *Vestn. Mosk. Univ., Ser. II*, 1966, **21**, 72; *Chem. Abstr.*, 1967, **66**, 72126f.
11. H. K. Y. Lau, H. A. Droli and P. F. Lott, *Anal. Chim. Acta*, 1971, **56**, 7.
12. K. E. Burke, *Anal. Chem.*, 1970, **42**, 1536.
13. W. Reichel and B. G. Bleakley, *ibid.*, 1974, **46**, 59.
14. S. J. Royal and K. Dixon, *NIM Rept. No. 1795*, 1976.
15. A. E. Smith, *Analyst*, 1975, **100**, 300.
16. H. Bode, Z. *Anal. Chem.*, 1955, **144**, 165.
17. *Idem, ibid.*, 1954, **143**, 182.
18. N. M. Lisicki and D. F. Boltz, *Anal. Chem.*, 1955, **27**, 1722.
19. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., pp. 332–334. Interscience, New York, 1959.
20. J. H. Thompson and B. W. Peters, *Analyst*, 1959, **84**, 180.
21. D. Weiss, Z. *Anal. Chem.*, 1964, **204**, 102.
22. H. Bode and G. Henrich, *ibid.*, 1952, **135**, 98.
23. E. M. Donaldson, *Talanta*, 1976, **23**, 411.
24. *Idem, ibid.*, 1976, **23**, 163.
25. The Staff of the Mineral Sciences Division, *Technical Bulletin TB 139*, Department of Energy, Mines and Resources, Ottawa, 1971.
26. G. H. Faye, *Technical Bulletin TB 155*, Department of Energy, Mines and Resources, Ottawa, 1972.

Talanta, Vol. 25, pp 137–141. Pergamon Press, 1978. Printed in Great Britain.

TITRATION OF CYANIDE AND HEXACYANOFERRATE(II) WITH SILVER NITRATE—I

CALCULATION OF TITRATION CURVES FOR POTENTIOMETRIC AND CONDUCTOMETRIC TITRATION

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Summary—Stepwise potentiometric titration of cyanide and hexacyanoferrate(II) with silver nitrate is possible in the absence of potassium ions. At an initial concentration below $5.00 \times 10^{-4}M$, cyanide can be titrated with silver nitrate (Ag:CN = 1:2) and the end-point indicated by precipitation of silver hexacyanoferrate(II); hexacyanoferrate(II) can be titrated with silver nitrate (Ag:$Fe(CN)_6$ = 4:1) and the end-point indicated by precipitation of silver dicyanoargentate. The hexacyanoferrate(II) reacts with silver to form two poorly soluble salts, $Ag_4Fe(CN)_6$, $KAg_3Fe(CN)_6$. The formation of these salts has been confirmed by conductometric titration of hexacyanoferrate(II) with silver nitrate in solutions containing varying concentrations of potassium nitrate.

Cyanide ions react with silver ions in two steps. First, dicyanoargentate is formed [reaction (1)]:

$$2\ CN^- + Ag^+ \rightleftharpoons Ag(CN)_2^- \qquad (1)$$

When more silver ions are added, a precipitate of silver dicyanoargentate is formed [reaction (2)]:

$$Ag(CN)_2^- + Ag^+ \rightleftharpoons Ag[Ag(CN)_2] \qquad (2)$$

These reactions can be used for titration of cyanide ions with silver nitrate; the precipitation of silver dicyanoargentate is used to indicate the end-point of reaction (1).

Formation constants of dicyanoargentate and solubility products of silver dicyanoargentate found in the literature[1–7] are shown in Table 1.

At the start of the titration, if the cyanide concentration is greater than $1.60 \times 10^{-4}M$, tricyanoargentate, $Ag(CN)_3^{2-}$, ($\log \beta_3 = 21.3$) is formed.[5] As the titration proceeds, dicyanoargentate begins to predominate and the influence of tricyanoargentate on the titration can be neglected.

The hexacyanoferrate(II) ion forms a number of compounds with different metal ions. The compounds are often coloured and poorly soluble in water and sometimes they have a tendency to form colloidal solutions. The type of hexacyanoferrate(II) compound formed depends on the other ions in the solution. The existence of both "normal" and "mixed" hexacyanoferrates(II) (the latter contain a univalent cation such as K^+, Rb^+, Cs^+, Tl^+, NH_4^+ in a constant ratio to the other cation) is reported in the literature.[8–13]

Table 1. Values for the solubility product of silver dicyanoargentate, $K_{sp,Ag[Ag(CN)_2]}$ and the stability constant of dicyanoargentate, β_2, from the literature

$K_{sp,Ag[Ag(CN)_2]}$	β_2	Reference
$10^{-11.30}$		1
$10^{-11.29}$	$10^{21.4}$	2
$10^{-11.4}$		3
$10^{-11.3}$	$10^{20.7}$	4
$10^{-11.23}$	$10^{20.44}$	5
$10^{-11.35}$	$10^{20.85}$	6
$10^{-11.37}$		7

Silver ions react with hexacyanoferrate(II) to form the poorly soluble silver hexacyanoferrate(II). Another poorly soluble salt, potassium trisilver hexacyanoferrate(II) [$KAg_3Fe(CN)_6$] is also likely to be formed, since the ionic radii of Ag^+ and K^+ are almost the same (0.133 and 0.126 nm respectively). Kolthoff[14] showed by conductometric titration of silver nitrate with potassium hexacyanoferrate(II) that both $Ag_4Fe(CN)_6$ and $KAg_3Fe(CN)_6$ are formed. Formation of these salts was also demonstrated by Streyer[15] by potentiometric titration and by Kleibs[16] by amperometric titration. At the start of a titration of silver nitrate with potassium hexacyanoferrate(II) a precipitate of silver hexacyanoferrate(II) is formed. When an excess of potassium hexacyanoferrate(II) is present, the following reaction takes place:

$$3\ Ag_4Fe(CN)_6 + K_4Fe(CN)_6 \rightarrow 4\ KAg_3Fe(CN)_6 \qquad (3)$$

Bellomo[12] showed that $Ag_4Fe(CN)_6$ is formed in titrations of potassium hexacyanoferrate(II) with silver nitrate, when the initial concentration of $K_4Fe(CN)_6$ is 8.0×10^{-5}–$5.0 \times 10^{-4}M$, and that $KAg_3Fe(CN)_6$ is formed when the initial concentration of $K_4Fe(CN)_6$ is greater than $5.0 \times 10^{-4}M$.

Solubility products found in the literature[12,17,18] for $Ag_4Fe(CN)_6$ and $KAg_3Fe(CN)_6$ are given in Table 2. There is some uncertainty concerning that of $Ag_4Fe(CN)_6$.

Table 2. Values for the solubility product of silver hexacyanoferrate(II), $K_{sp,Ag_4Fe(CN)_6}$, and of potassium trisilver hexacyanoferrate(II), $K_{sp,KAg_3Fe(CN)_6}$, from the literature

$K_{sp,Ag_4Fe(CN)_6}$	$K_{sp,KAg_3Fe(CN)_6}$	Reference
$10^{-40.8}$		17
$10^{-44.1}$		18
$10^{-19.2}$	$10^{-19.3}$	12

THEORY

The following reactions can be written for a stepwise titration of cyanide and hexacyanoferrate(II) with silver in a potassium-free solution:

$$Ag^+ + 2\,CN^- \rightarrow Ag(CN)_2^- \quad (1)$$

$$4\,Ag^+ + Fe(CN)_6^{4-} \rightarrow Ag_4Fe(CN)_6 \quad (4)$$

$$Ag^+ + Ag(CN)_2^- \rightarrow Ag[Ag(CN)_2] \quad (2)$$

The titration ratio, a, is defined as:

$$a = \frac{c_{Ag}}{c_{CN}} \quad (5)$$

and the ratio r is defined as:

$$r = \frac{c_{Fe(CN)_6}}{c_{CN}} \quad (6)$$

Simple equations can now be derived for calculation of the titration curve, with a as a function of the silver ion concentration $[Ag^+]$.

The following equation is valid for the titration curve for reaction (1):

$$[Ag^+] = \frac{a\alpha_{CN(H)}^2}{c_{CN}(1 - 2a)^2\beta_2} \quad (7)$$

where $\alpha_{CN(H)}$ is the side-reaction coefficient for the reaction of cyanide with hydrogen ions. It is assumed that silver ions do not participate in any side-reactions ($\alpha_{Ag(X)} = 1$). Equation (7) applies when $a < 0.5$. Because the complex is a strong one, the following approximations are made:

$$[CN'] = c_{CN} - 2c_{Ag} = c_{CN}(1 - 2a)$$

and

$$[Ag(CN)_2^-] = c_{Ag} = ac_{CN},$$

where $[CN']$ is the conditional concentration of cyanide.

The silver ion concentration at the equivalence point of reaction (1) is given by equation (8):

$$[Ag^+] = \frac{1}{2}\sqrt[3]{\frac{c_{CN}\alpha_{CN(H)}^2}{\beta_2}} \quad (8)$$

The silver ion concentration at which $Ag_4Fe(CN)_6$ begins to precipitate is given by equation (9):

$$[Ag^+] = \sqrt[4]{\frac{K_{sp,Ag_4Fe(CN)_6}}{rc_{CN}}}. \quad (9)$$

In titration of hexacyanoferrate(II) [reaction (4)] the titration curve is given by equation (10):

$$[Ag^+] = \sqrt[4]{\frac{K_{sp,Ag_4Fe(CN)_6}}{c_{CN}(r - a/4 + 1/8)}}. \quad (10)$$

Equation (10) applies when $0.5 < a < 0.5 + 4r$. Because a precipitate is formed, the following approximation is made:

$$[Fe(CN)_6^{4-}] = c_{Fe(CN)_6} - (c_{Ag} - c_{CN}/2)/4$$
$$= c_{CN}(r - a/4 + 1/8).$$

The silver ion concentration at the equivalence point for reaction (4) is given by equation (11):

$$[Ag^+] = \sqrt[5]{4K_{sp,Ag_4Fe(CN)_6}}. \quad (11)$$

In titration of dicyanoargentate [reaction (2)] the titration curve is given by equation (12):

$$[Ag^+] = \frac{K_{sp,Ag[Ag(CN)_2]}}{c_{CN}(1 + 4r - a)}. \quad (12)$$

Equation (12) applies when $0.5 + 4r < a < 1.0 + 4r$. The following approximation is made:

$$[Ag(CN)_2^-] = c_{CN}/2 - (c_{Ag} - 4c_{Fe(CN)_6} - c_{CN}/2)$$
$$= c_{CN}(1 + 4r - a)$$

This approximation is not valid in the region of the 1:1 equivalence point, because of the relatively high solubility of silver dicyanoargentate.

Figure 1 shows the calculated curve for titration of 100.0 ml of a solution $5.00 \times 10^{-4}M$ in sodium cyanide and $1.25 \times 10^{-4}M$ in sodium hexacyanoferrate(II) with silver nitrate at pH 9.80. The constants used were: $\log \beta_2 = 21.1$, $-\log K_{sp,Ag[Ag(CN)_2]} = 11.3$, $-\log K_{sp,Ag_4Fe(CN)_6} = 40.8$ and $\log \alpha_{CN(H)} = 0.1$. A compilation of silver ion concentrations calculated for the equivalence points and the end-points in a stepwise titration of cyanide and hexacyanoferrate(II) is given in Table 3.

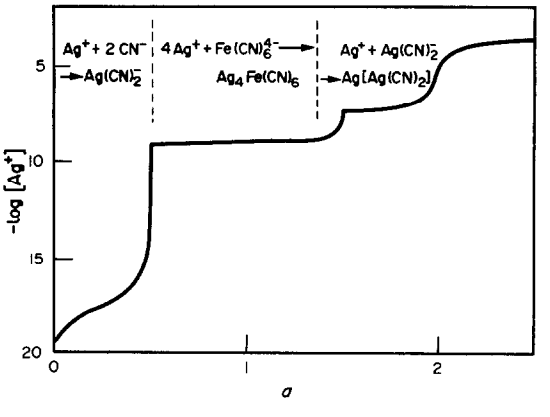


Fig. 1. Calculated titration curve for the titration of 100.0 ml of solution $5.00 \times 10^{-4}M$ in NaCN and $1.25 \times 10^{-4}M$ in $Na_4Fe(CN)_6$ with $AgNO_3$ at pH 9.80. The constants used in the calculations were $\log \beta_2 = 21.1$, $-\log K_{sp,Ag[Ag(CN)_2]} = 11.3$, $-\log K_{sp,Ag_4Fe(CN)_6} = 40.8$, $\log \alpha_{CN(H)} = 0.1$.

Table 3. Values calculated for the silver ion concentrations at the equivalence points and the end-points in the stepwise titration of cyanide and hexacyanoferrate(II) with $AgNO_3$ at pH 9.80 in a solution $5.00 \times 10^{-4}M$ in NaCN and $1.25 \times 10^{-4}M$ in $Na_4Fe(CN)_6$

Reaction	$-\log [Ag^+]$	Titration ratio a
$Ag_4Fe(CN)_6$ begins to precipitate.	9.22	$0.499 < a < 0.5$
End-point in the titration of CN^- to $Ag(CN)_2^-$.		
Equivalence point in the titration of CN^- to $Ag(CN)_2^-$.	8.37	$a = 0.5$
$Ag[Ag(CN)_2]$ begins to precipitate.	7.70	$1.499 < a < 1.5$
End-point in the titration of $Fe(CN)_6^{4-}$ to $Ag_4Fe(CN)_6$.		
Equivalence point in the titration of $Fe(CN)_6^{4-}$ to $Ag_4Fe(CN)_6$.	8.04	$a = 1.5$

Thus, in a potentiometric titration of free cyanide (CN^-) and the complex cyanide [$Fe(CN)_6^{4-}$] with silver nitrate, the free cyanide can be titrated (Ag:CN = 1:2) and the end-point indicated by precipitation of $Ag_4Fe(CN)_6$. The value $-\log[Ag^+] = 8.37$ gives the calculated silver ion concentration at the equivalence point ($a = 0.5$) of reaction (1). At the end-point of reaction (1) $-\log [Ag^+] = 9.22$, and at this point in the titration curve $0.499 < a < 0.5$. Thus the equivalence point and the end-point are in good agreement.

The complex cyanide can also be titrated [$Ag:Fe(CN)_6 = 4:1$] and the end-point indicated by precipitation of $Ag[Ag(CN)_2]$. The value $-\log[Ag^+] = 8.04$ gives the calculated silver ion concentration at the equivalence point ($a = 0.5 + 4r$) of reaction (4). At the end-point of reaction (4), $-\log [Ag^+] = 7.70$, and at this point in the titration curve $1.499 < a < 1.5$. This means that the equivalence point and the end-point are again in good agreement.

The concentration of silver ion at which $Ag_4Fe(CN)_6$ begins to precipitate depends on the concentration of the hexacyanoferrate(II) ion [equation (9)]. Since precipitation begins very near to the equivalence point for reaction (1), and the silver ion concentration here depends on the fourth root of the concentration of hexacyanoferrate(II), titration of free cyanide is possible for a very wide range of concentration of cyanide and hexacyanoferrate(II).

The titration of hexacyanoferrate(II) gives an unsymmetrical potential jump and the equivalence point is located on the steep part of the curve. The silver ion concentration at the equivalence point is independent of the hexacyanoferrate(II) ion concentration [equation (11)].

The point on the titration curve at which silver dicyanoargentate begins to precipitate can, within a certain concentration range, be used to indicate the end-point of the titration of hexacyanoferrate(II) ions, since this point is very near the equivalence point. The silver ion concentration at which $Ag[Ag(CN)_2]$ begins to precipitate depends on the initial concentration of cyanide in the solution:

$$[Ag^+] = \frac{2K_{sp,Ag[Ag(CN)_2]}}{c_{CN}}. \qquad (13)$$

To illustrate the possibility of using this for end-point detection, the titration curve was calculated, using various values for the solubility product of $Ag_4Fe(CN)_6$ from the literature. Figure 2 shows calculated titration curves for 100.0 ml of $1.25 \times 10^{-4}M$ $Na_4Fe(CN)_6$ solution. The silver ion concentrations at which silver dicyanoargentate begins to precipitate are marked on the curves for different initial cyanide ion concentrations. The curves are plotted as a function of a', defined as:

$$a' = \frac{c_{Ag}}{c_{Fe(CN)_6^{4-}}}. \qquad (14)$$

It is seen that the end-point of a titration of a $1.25 \times 10^{-4}M$ solution of hexacyanoferrate(II) can thus be indicated when the initial cyanide ion concentration in the test solution is lower than $10^{-3}M$, provided the value of the solubility product of $Ag_4Fe(CN)_6$ is in fact lower than $10^{-40.8}$. In more and less concentrated hexacyanoferrate(II) solutions, slightly higher and slightly lower concentrations, respectively, of cyanide allow indication of the end-point in this way.

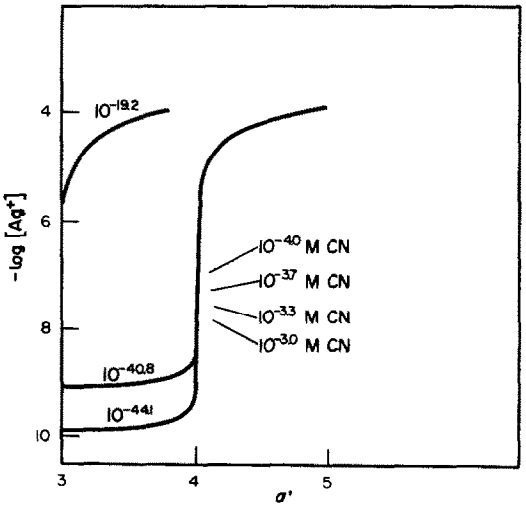


Fig. 2. Calculated titration jump in the titration of 100.0 ml of $1.25 \times 10^{-4}M$ $Na_4Fe(CN)_6$ with $AgNO_3$ at pH 9.80, using the various values for the solubility product of silver hexacyanoferrate(II) found in the literature. The silver ion concentrations at which silver–dicyanoargenate begins to precipitate at different initial cyanide ion concentrations are marked on the curves.

EXPERIMENTAL

Apparatus

A digital pH/mV meter (Orion 801), and a digital printer (Orion 751), were used for potential measurements. An Ag/Ag_2S electrode was used as indicator electrode (silver sulphide deposited electrolytically on a silver wire electrode). The saturated calomel electrode used as reference was isolated from the sample solution by an agar-agar bridge (1*M* in sodium nitrate) to prevent contamination from potassium and chloride ions. The potential was taken as stable when the drift was less than ± 0.2 mV/min. The titration vessel was maintained at 25°. A Metrohm Conductoskop E 365 (50 Hz), a Metrohm Potentiograph E 336 and a Metrohm EA 608 cell were used for conductometric titrations.

All experiments were performed in dark vessels, to minimize problems caused by the sensitivity of the silver and hexacyanoferrate(II) ions to light.

Reagents

Analytical grade reagents were used throughout. The solution of sodium hexacyanoferrate(II) was prepared from the potassium salt, by ion-exchange of protons for potassium ions (batch technique, Dowex 50 × 8) followed by neutralization with sodium hydroxide solution.

The pH of the sample solution was adjusted to 9.80 with sodium tetraborate and sodium hydroxide solutions.

RESULTS

The stepwise titration of cyanide and hexacyanoferrate(II) with silver is influenced by pH and potassium concentration. Hydrocyanic acid is a weak acid ($pK = 9.2$) so it is important to do the titration at high pH, where the free cyanide is not protonated ($\alpha_{CN(H)} = 1$). A suitable pH is 9.8 or higher.

As stated above, in a solution containing potassium ions, both $Ag_4Fe(CN)_6$ and $KAg_3Fe(CN)_6$ may be formed. The influence of potassium ions on the titration of hexacyanoferrate(II) with silver can be shown by conductometric titration.

The overall reaction for the titration in a potassium-free solution is:

$$4\,Ag^+ + Fe(CN)_6^{4-} \rightarrow Ag_4Fe(CN)_6 \qquad (15)$$

If the potassium concentration is high enough for $KAg_3Fe(CN)_6$ to be formed exclusively, the overall

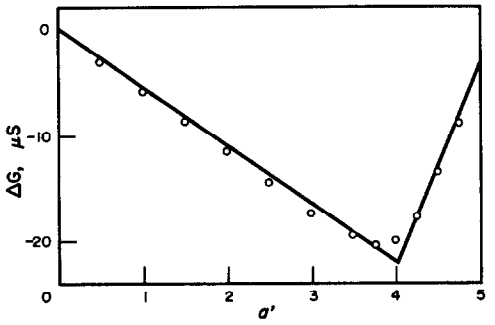


Fig. 3. Conductometric titration curves of 90.0 ml of $1.17 \times 10^{-4}M$ $Na_4Fe(CN)_6$ with $AgNO_3$. Experimental titration curve: O, calculated titration curve: ——. The cell constant $K = 0.82$ cm^{-1}.

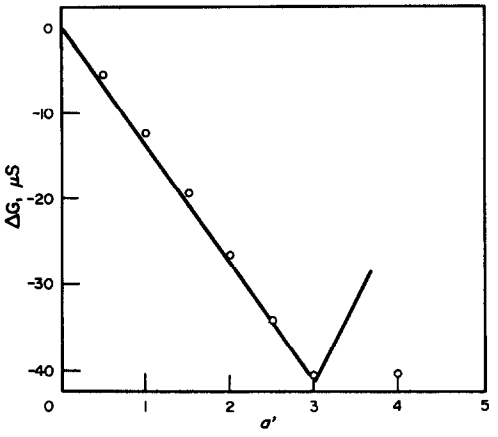


Fig. 4. Conductometric titration curves of 100.0 ml of solution $1.25 \times 10^{-4}M$ in $Na_4Fe(CN)_6$ and 0.10*M* in KNO_3, with $AgNO_3$. Experimental titration curve: O, calculated titration curve: ——. The cell constant $K = 0.82$ cm^{-1}.

reaction is:

$$K^+ + 3\,Ag^+ + Fe(CN)_6^{4-} \rightarrow KAg_3Fe(CN)_6 \qquad (16)$$

Figure 3 shows calculated and observed conductometric titration curves for titration of 90.0 ml of $1.17 \times 10^{-4}M$ sodium hexacyanoferrate(II) with 0.010*M* silver nitrate. Titration curves for a solution which is also 0.010*M* in potassium nitrate are shown in Fig. 4.

The conductometric titration curves were calculated from:

$$\Delta G = \frac{1}{K}\sum \Delta c_i \Lambda_i^0 \qquad (17)$$

where ΔG is the change in the conductance and Δc_i is the change in the concentration of the *i*th ion. The molar conductivities of the ions at infinite dilution used were: $\Lambda^0_{(Ag^+)} = 61.9$ cm^2.Ω^{-1}.mole^{-1}, $\Lambda^0_{(NO_3^-)} = 71.46$ cm^2.Ω^{-1}.mole^{-1}, $\Lambda^0_{(Fe(CN)_6^{4-})} = 440.4$ cm^2.Ω^{-1}.mole^{-1} and $\Lambda^0_{(K^+)} = 73.51$ cm^2.Ω^{-1}.mole^{-1}.

To allow comparison between the calculated and the observed curves it is useful to define ΔG as zero at the start of the titration ($a' = 0$). Figure 3 shows that hexacyanoferrate(II) reacts with silver in 1:4 ratio in absence of potassium, and Fig. 4 that the reaction ratio is 1:3 with hexacyanoferrate(II) ions in presence of excess of potassium. Once a' has reached 3, no further change in the conductance of the solution occurs, probably because of the high total salt concentration and/or formation of colloids. However, it is obvious that potassium trisilver hexacyanoferrate(II) is formed. At lower potassium nitrate concentrations the break point on the conductometric titration curve moves towards $a' = 4$, indicating that $Ag_4Fe(CN)_6$ and $KAg_3Fe(CN)_6$ are both formed.

A 0.010*M* sodium nitrate solution containing hexacyanoferrate(II) and no potassium was also titrated conductometrically. No mixed-salt formation was observed (as expected, since the ionic radii for Na^+ and Ag^+ are 0.095 and 0.126 nm respectively).

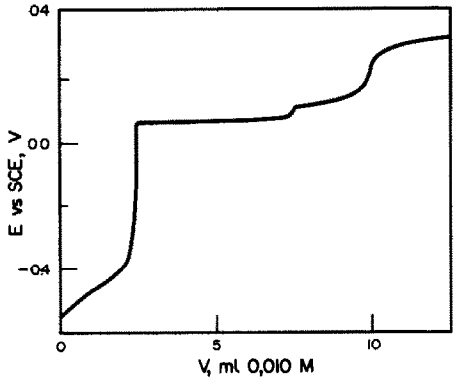


Fig. 5. Potentiometric titration curve of 100.0 ml of solution $5.00 \times 10^{-4}M$ in NaCN and $1.25 \times 10^{-4}M$ in $Na_4Fe(CN)_6$, with $AgNO_3$ at pH 9.80 and $\mu = 0.10$ ($NaNO_3$).

Figure 5 shows the titration curve for the potentiometric titration of 100.0 ml of a solution $5.00 \times 10^{-4}M$ in sodium cyanide and $1.25 \times 10^{-4}M$ in sodium hexacyanoferrate(II) at pH 9.80, with $0.010M$ silver nitrate.

Figure 6 shows the titration jump in the potentiometric titration of 100.0 ml of $1.25 \times 10^{-4}M$ sodium hexacyanoferrate(II) solution containing varying concentrations of sodium cyanide at pH 9.80, with $0.010M$ silver nitrate. The sample solutions were $0.10M$ in sodium nitrate.

The results show that free cyanide (CN^-) and complex cyanide [$Fe(CN)_6^{4-}$] can be titrated potentiometrically with silver nitrate when the concentration of the free cyanide, $c_{CN'}$ is less than $5.00 \times 10^{-4}M$. The end-point of the titration of the free cyanide is indicated with the aid of the complex cyanide and that in the titration of the complex cyanide can be indicated with the aid of the free cyanide. An application of the method is given in Part II.[20]

If the sample solution contains potassium ions, the potassium ion concentration can be increased to such a high level that only potassium trisilver hexacyanoferrate(II) is formed. If, however, the sample solution contains iodide, bromide or chloride ions, it can be calculated from the solubility products that silver iodide will precipitate quantitatively before $Ag_4Fe(CN)_6$ begins to precipitate, silver chloride will precipitate after quantitative precipitation of silver dicyanoargentate, and silver bromide precipitates at the same time as silver hexacyanoferrate(II). Thus only bromide ions prevent the stepwise titration of cyanide and hexacyanoferrate(II) with silver nitrate.

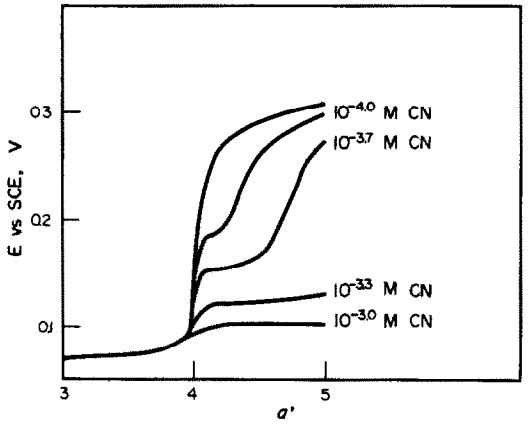


Fig. 6. Titration jump in the potentiometric titration of 100.0 ml of $1.25 \times 10^{-4}M$ $Na_4Fe(CN)_6$ containing varying concentrations of NaCN, with $AgNO_3$ at pH 9.80 and $\mu = 0.10$ ($NaNO_3$).

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REFERENCES

1. R. Lucas, *Z. Anorg. Allgem. Chem.*, 1904, **41**, 193.
2. H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 192, 1940.
3. R. Gauguin, *J. Chim. Phys.*, 1945, **42**, 28.
4. *Idem.*, *Ann. Chim. (Paris)*, 1949, **4**, 832.
5. A. M. Azzam and I. A. W. Shimi. *Z. Anorg. Allgem. Chem.*, 1963, **321**, 284.
6. J. Zsakó and E. Petri, *Rev. Roumaine Chim.*, 1965, **10**, 571.
7. B. Ungerer, R. Jurio and R. J. Manuele, *J. Chem. Educ.*, 1972, **49**, 434.
8. H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1933, 1543.
9. E. L. Nimer, R. E. Hamm and G. L. Lee, *Anal. Chem.*, 1950, **22**, 790.
10. D. F. Swinehart, *ibid.*, 1951, **23**, 381.
11. K. L. Cheng, *ibid.*, 1955, **27**, 1594.
12. A. Bellomo, *Talanta*, 1970, **17**, 1109.
13. A. Bellomo, D. de Marco and A. Casale, *ibid.*, 1971, **19**, 1256.
14. I. M. Kolthoff, *Z. Anal. Chem.*, 1923, **62**, 209.
15. W. Streyer, *ibid.*, 1928, **74**, 108.
16. G. A. Kleibs, *Zh. Analit. Khim.*, 1955, **10**, 244; *Chem. Abstr.* **50**, 110g.
17. J. N. Pearce and L. D. Ough, *J. Am. Chem. Soc.*, 1939, **60**, 80.
18. P. A. Rock and R. E. Powell, *Inorg. Chem.*, 1964, **3**, 1593.
19. A. Ringbom, *Complexation in Analytical Chemistry*, Wiley-Interscience, New York, 1963.
20. J. Asplund, *Talanta*, 1978, **25**, 143.

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TITRATION OF CYANIDE AND HEXACYANOFERRATE(II) WITH SILVER NITRATE—II

DETERMINATION OF SODIUM CYANIDE AND SODIUM HEXACYANOFERRATE(II) IN A COMPLEXING AGENT

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Summary—Cyanide and hexacyanoferrate(II) can be titrated with silver nitrate in the presence of a complexing agent masked with a suitable metal ion. A method for determination of sodium cyanide and sodium hexacyanoferrate(II) in the presence of sodium nitrilotriacetate masked with magnesium ions is given as an example.

Cyanide is usually titrated with silver nitrate, to form dicyanoargentate. The end-point of the titration can be indicated by precipitation of silver dicyanoargentate. At pH values lower than 10, the cyanide participates in a side-reaction with hydrogen ions, the influence of which can be described in terms of the side-reaction coefficient,[1] $\alpha_{CN(H)}$. In titration of cyanide ions in the presence of a complexing agent, L, the silver ions may also participate in side-reactions, which can be described by the side-reaction coefficient $\alpha_{Ag(L)}$.

Generally, $\alpha_{Ag(L)}$ denotes $[Ag']/[Ag^+]$, where $[Ag']$ is the sum of the concentrations of all species containing Ag except the complex formed in the main reaction. The conditional constant for the 1:2 complex of Ag^+ with CN^- is

$$\beta'_2 = \frac{[Ag(CN)_2]}{[Ag'][CN']^2} \quad (1)$$

or

$$\beta'_2 = \frac{\beta_2}{\alpha_{Ag(L)} \cdot \alpha^2_{CN(H)}} \quad (2)$$

In the titration of a cyanide solution of concentration c_{CN} with silver nitrate in the presence of a complexing agent, L, the equivalence point can be calculated from the equation:

$$[Ag']_{eq} = \frac{1}{2}\sqrt[3]{\frac{c_{CN} \cdot \alpha^2_{CN(H)} \cdot \alpha_{Ag(L)}}{\beta_2}}. \quad (3)$$

In a potentiometric titration the silver-ion concentration, $[Ag^+]$, (or rather the silver-ion activity, $\{Ag^+\}$), is measured, and for that reason it is better to calculate $[Ag^+]$ than $[Ag']$. The silver-ion concentration at the equivalence point for the silver–cyanide reaction can be calculated from

$$[Ag^+]_{eq} = \frac{[Ag']_{eq}}{\alpha_{Ag(L)}}. \quad (4)$$

When the end-point is indicated by precipitation of silver dicyanoargentate the silver-ion concentration at the end-point, $[Ag^+]_{end}$, can be calculated from

$$[Ag^+]_{end} = \frac{2K_{sp,Ag[Ag(CN)_2]}}{c_{CN}}. \quad (5)$$

The small amounts of cyanide present as impurity in a complexing agent can exist in various forms such as free cyanides (HCN, KCN, NaCN) and as relatively stable cyano-complexes such as hexacyanoferrates(III). Cyanide and hexacyanoferrate(II) ions can be titrated potentiometrically with silver nitrate[2] when the initial concentration of free cyanide is lower than $5.00 \times 10^{-4} M$. The end-point for the 2:1 reaction between cyanide ions and silver ions can be indicated by precipitation of silver hexacyanoferrate(II). The silver-ion concentration at this point can be calculated from

$$[Ag^+]_{end} = \sqrt[4]{\frac{K_{sp,Ag_4Fe(CN)_6}}{c_{Fe(CN)_6^{4-}}}}. \quad (6)$$

Equations (5) and (6) can also be used for calculation of the silver-ion concentration at the end-points when the solutions do not contain the complexing agent L.

The titration error, $\Delta[Ag]$, can be defined as

$$\Delta[Ag] = [Ag^+] - [Ag'] \quad (7)$$

and it is evident that $|\Delta[Ag]|$ has the lowest value when $\alpha_{Ag(L)} = 1$. In the titration of cyanide with silver nitrate the complexing agent L can be masked with metal ions which do not form strong cyano-complexes.

The optimal conditions for masking of the complexing agent with the metal ion can be investigated as follows (charges are omitted).

$$\alpha_{Ag(L)} = 1 + [L]K_{AgL} \quad (8)$$

Table 1. The metal ion concentration, [M], for complete masking of ethylenediaminetetra-acetate, EDTA, and nitrilotriacetate, NTA, with lead, calcium and magnesium ions in the titration of cyanide ions with silver nitrate. Values of constants are as given by Ringbom.[1] The value used for K_{AgNTA} was that given by Starý[3]

Metal ion	EDTA		NTA	
	$\log K_{ML}$	$-\log [M]$	$\log K_{ML}$	$-\log [M]$
Lead	18.0	11.7	11.8	7.6
Calcium	10.7	4.4	6.4	2.2
Magnesium	8.7	2.4	5.4	1.2

In the presence of an excess of metal ions the concentration of free complexing agent can be calculated from:

$$[L] = \frac{[ML]}{[M]K_{ML}}. \quad (9)$$

From (8) and (9)

$$\alpha_{Ag(L)} = 1 + \frac{[ML]K_{AgI}}{[M]K_{ML}}. \quad (10)$$

The metal-ion concentrations necessary for complete masking of ethylenediaminetetra-acetate and nitrilotriacetate with lead, calcium and magnesium ions in the titration of cyanide ions with silver nitrate are given in Table 1. The values in the table were calculated for $[ML] = 0.1M$.

Sodium cyanide is best titrated at a pH high enough for none of the cyanide to be protonated ($\alpha_{CN(H)} = 1$). In masking of a complexing agent with a metal ion, the precipitation of metal hydroxide usually determines the highest possible metal-ion concentration at any pH-value.

Titration of cyanide ions with silver nitrate is possible even when $\alpha_{Ag(L)} > 1$, but the conditions for the titration should be chosen so that the value $\alpha_{Ag(L)}$ is as low as possible.

Other complexing agents can also be masked by metals. Complete masking of ethylene glycol bis(2-aminoethyl ether)tetra-acetate, EGTA, in the titration of cyanide is possible with $[Pb^{2+}] > 10^{-7.2}M$, $[Ca^{2+}] > 10^{-5.20}M$ or $[Mg^{2+} > 10^{0.68}M$, so lead and calcium are suitable for masking EGTA. The influence of the formation of $Pb(CN)_4^{2-}$ ($\log \beta_4 = 10$) can be neglected.

The potentiometric titration of cyanide and hexacyanoferrate(II) with silver nitrate in the presence of nitrilotriacetate masked with magnesium ions is discussed here. A suitable pH for the titration is ~9.8 and a magnesium concentration $[Mg^{2+}]$ of $10^{-2}M$ is used. Log $\alpha_{Ag(L)}$ is 0.83 when $[MgNTA] = 0.1M$. A titration curve was calculated for a solution $10^{-4}M$ in sodium cyanide and $1.5 \times 10^{-5}M$ in sodium hexacyanoferrate(II). Table 2 shows calculated silver ion concentrations at the equivalence points and end-points.

The value $-\log[Ag^+] = 8.85$ gives the calculated silver-ion concentration at the equivalence point of the 1:2 reaction between silver ions and cyanide ions ($a = 0.5$). The value $-\log[Ag^+] = 8.99$ when $Ag_4Fe(CN)_6$ begins to precipitate gives the calculated silver-ion concentration at the end-point of this reaction. At this point, a has a value very close to 0.5, so the equivalence point and the end-point are in good agreement.

The value $-\log[Ag^+] = 8.04$ gives the calculated silver-ion concentration at the equivalence point of the 4:1 reaction between silver and hexacyanoferrate(II) ($a = 1.1$).

[If the titration ratio, a, is defined by

$$a = \frac{c_{Ag}}{c_{CN}}$$

and the ratio r is defined as

$$r = \frac{c_{Fe(CN)_6}}{c_{CN}},$$

then in this case the ratio r has the value 0.15 ($r = 1.5 \times 10^{-5}/10^{-4}$), and $a = 0.5 + 4r = 1.1$.]

The value $-\log[Ag^+] = 7.00$, when $Ag[Ag(CN)_2]$ begins to precipitate, gives the calculated silver-ion concentration at the end-point of the 4:1 reaction between silver and hexacyanoferrate(II). At this point, a again has a value very close to 1.1, so the equivalence point and the end-point are in good agreement.

The silver-ion concentration at the equivalence point in the titration of hexacyanoferrate(II) was cal-

Table 2. Values calculated for the silver-ion concentrations at the equivalence points and the end-points in the stepwise titration of cyanide and hexacyanoferrate(II) ions, in the presence of nitrilotriacetate, with $AgNO_3$ at pH 9.80 in a solution $10^{-4}M$ in NaCN and $1.5 \times 10^{-5}M$ in $Na_4Fe(CN)_6$ (the NTA was masked with magnesium nitrate)

Reaction	$-\log [Ag^+]$	$-\log [Ag']$
$Ag_4Fe(CN)_6$ begins to precipitate. End-point in the titration of CN^- to $Ag(CN)_2^-$	8.99	8.16
Equivalence point in the titration of CN^- to $Ag(CN)_2^-$	8.85	8.02
Equivalence point in the titration of $Fe(CN)_6^{4-}$ to $Ag_4Fe(CN)_6$	8.04	7.21
$Ag[Ag(CN)_2]$ begins to precipitate. End-point in the titration of $Fe(CN)_6^{4-}$ to $Ag_4Fe(CN)_6$	7.00	6.17

culated from the equation:

$$[Ag^+] = \sqrt[5]{4K_{sp,Ag_4Fe(CN)_6}}. \quad (11)$$

EXPERIMENTAL

Reagents

Sodium cyanide and sodium hexacyanoferrate(II) were determined in technical-grade sodium nitrilotriacetate. Nitrilotriacetic acid of analytical grade was used as reference substance. The complexing agent was masked with $Mg(NO_3)_2 \cdot 6H_2O$ (Merck Suprapur with a maximum iron content of 5×10^{-6}%). All other reagents were of analytical quality. The pH of sample solutions was adjusted to 9.80 with sodium tetraborate and sodium hydroxide.

RESULTS

The total concentration of cyanide in different substances can be determined after steam distillation of hydrogen cyanide from acid solution. The hydrogen cyanide is absorbed in sodium hydroxide solution and the cyanide concentration is measured with an ion-selective cyanide electrode. This method was used to determine the total concentration cyanide in the reagents used. Cyanide was not detected in the analytical grade nitrilotriacetic acid used as reference.

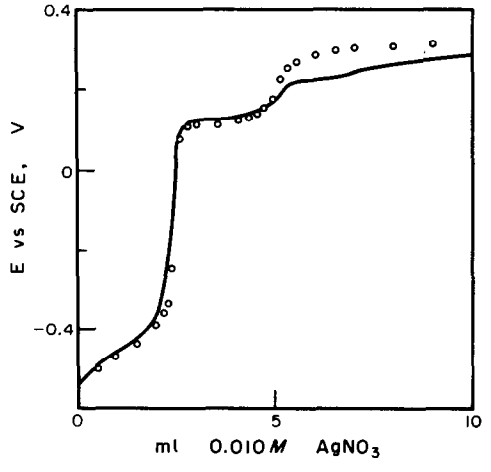


Fig. 1. Titration curve for the potentiometric titration (——) of 100.0 ml of $5.00 \times 10^{-4}M$ NaCN in the presence of analytical-grade nitrilotriacetate at pH 9.80 with $AgNO_3$. The NTA was masked with magnesium nitrate. The titration curve (○) for titration of NaCN in $0.10M$ $NaNO_3$ medium is also shown.

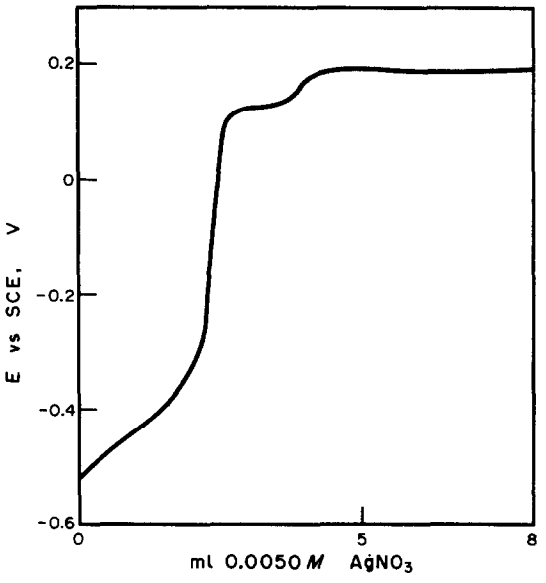


Fig. 2. Titration curve for the potentiometric titration of 100.0 ml of a solution of technical-grade sodium nitrilotriacetate containing NaCN and $Na_4Fe(CN)_6$ at pH 9.80 with $AgNO_3$ (2.12 mg of NaCN added to the solution). The NTA was masked with magnesium nitrate.

Figure 1 shows the observed titration curve for the potentiometric titration of sodium cyanide in the presence of analytical grade nitrilotriacetate at pH 9.80 with silver nitrate. The nitrilotriacetate was masked with magnesium nitrate. The corresponding titration curve for titration of sodium cyanide in $0.10M$ sodium nitrate medium at the same pH is also shown. The two titration curves coincide up to the equivalence point for the reaction between silver and dicyanoargentate ions. A difference of 6–7 mV can be explained by the fact that the ionic strength in the titrations is not the same.

For determination of sodium cyanide and sodium hexacyanoferrate(II) in technical-grade sodium nitrilotriacetate five 2.5-g samples were taken, 15.0 ml of $1.0M$ magnesium nitrate were added, the solutions were diluted to 100 ml and the pH was adjusted to 9.80. To four of the sample solutions various known amounts of sodium cyanide were added. The results of the determinations are given in Table 3. Figure 2 shows the potentiometric titration curve for the sample solution containing 2.12 mg of sodium cyanide.

Table 3. Results of determinations of free and complex cyanide in technical-grade sodium nitrilotriacetate

Solution CN^- Sample, *mg*	added, *mg*	CN^- found in solution, *mg*		CN^- found in NTA, *mg/kg*			Deviation from mean value, *mg/kg*		
		Free	Complex	Free	Complex	Total	Free	Complex	Total
2500		0.197	0.259	78.8	103.6	182.4	+3.8	+3.1	+6.9
2500	0.256	0.455	0.244	79.6	97.6	177.2	+4.6	−2.9	+1.7
2500	0.511	0.707	0.255	78.4	102.0	180.4	+3.4	+1.5	+4.9
2500	0.767	0.939	0.244	68.8	97.6	166.4	−6.2	−2.9	−9.1
2500	1.022	1.196	0.254	69.6	101.6	171.2	−5.2	+1.1	−4.3
		Mean value		75.0	100.5	175.5			

Table 4. Results of determinations of total cyanide in technical-grade sodium nitrilotriacetate

Sample, *mg*	CN^- found, *mg/kg*	Deviation from the mean value, *mg/kg*
100.0	180	+4
150.0	178	+2
250.0	173	−3
500.0	173	−3
Mean value:	176	

The technical-grade sodium nitrilotriacetate used contains on average 0.0075% of free cyanide and 0.0101% of cyanide complexed with iron(II), or, on average, a total of 0.0176% CN^-. The results of determinations of the total cyanide by steam-distillation are given in Table 4. The values are in good agreement with the values obtained by titration with silver nitrate.

Tetrasodium ethylenediaminetetra-acetate was also examined. For the titration with silver nitrate it was masked with magnesium nitrate, and it was found that the technical-grade material did not contain detectable amounts of cyanides.

DISCUSSION

The technical-grade sodium nitrilotriacetate examined contained only small amounts of cyanides, so large amounts of reagents had to be used. This means that comparatively high concentrations of impurities may have been introduced into the sample solutions by the reagents. Magnesium nitrate of analytical grade contains at most 5×10^{-4}% of iron. When 3.85 g of it are used to mask 2.50 g of the Na_3NTA, the iron content of the sample solution will increase by about 20% because the Na_3NTA contains 3.75×10^{-3}% of iron [as $Fe(CN)_6^{4-}$]. With magnesium nitrate of Suprapur grade containing at most 5×10^{-6}% of iron, the iron content of the sample solution will increase by only about 0.2%. If iron(II) or iron(III) ions are added to a solution containing cyanide ions, hexacyanoferrate(II) or hexacyanoferrate(III) ions are formed.

The nitrilotriacetate examined contained small amounts of sodium cyanide and sodium hexacyanoferrate(II). When both are to be determined a super pure reagent with a low iron content must be used. $Mg(NO_3)_2 \cdot 6H_2O$ of Merck Suprapur grade is suitable.

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REFERENCES

1. A. Ringbom, *Complexation in Analytical Chemistry*, Wiley-Interscience, New York. 1963.
2. J. Asplund, *Talanta* 1978, 1978 **25**, 137.
3. J. Starý, *Anal. Chim. Acta*, 1963, **28**, 132.

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HYDROXIDE COMPLEXES OF CERIUM(III)

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Summary—From the experimentally determined borderline of precipitation in the pM′–pH diagram, the stability constants of the mononuclear and polynuclear species of cerium hydroxide have been determined graphically. The stability constants found are $\log^*\beta_1 = -8.1$, $\log^*\beta_2 = -16.3$, $\log^*\beta_3 = -26.0$, $\log^*\beta_{5,3} = -32.8$ and $\log^*K_{s0} = 20.1$. These values refer to freshly prepared precipitates, at room temperature and an ionic strength of 1, and are precise to about 0.2 log units.

The behaviour of Ce^{3+} ions in aqueous solution is of increasing interest because cerium(III) is an excellent back-titrant in complexometry, with Xylenol Orange as indicator, especially for titrations at low concentration levels. For selection of optimum conditions for these titrations insight into cerium–hydroxide complex formation is necessary.

Limited reliable information about the hydrolysis of Ce^{3+} ions and precipitation of cerium hydroxide is available. Moeller[1] investigated the composition and stability of the hydroxide complexes in 0.01–0.3*M* cerous sulphate. He supposed $CeOH^{2+}$ to be formed, the stability constant being $\log^*\beta_1 = -9.0$. Biedermann and Newman[2] measured the pH change in a series of cerous perchlorate solutions (concentration range 0.05–1*M*; medium 3*M* perchlorate) when the hydrogen ions were reduced electrochemically by constant-current coulometry. They found strong evidence for the formation of $Ce_3(OH)_5^{4+}$ with stability constant $\log^*\beta_{5,3} = -35.7$ at the pH just before the start of precipitation. Stepanov and Shvedov[3] investigated the hydrolysis of cerous nitrate solutions at low concentrations (10^{-4}–$10^{-6}M$) by studying the electromigration of radioactive tracers. From the dependence of the migration on pH in the range 2–5 it was deduced that mononuclear hydroxide complexes predominate in acid solutions at pCe > 5. Although it was suggested that at low pH polynuclear complexes are formed at slightly higher concentrations, definite conclusions cannot be drawn from their experiments. Buchenko *et al.*[4] studied the hydrolysis of cerous sulphate solutions (3.7×10^{-4} and $9.75 \times 10^{-4}M$) by means of an oscillopolarographic method. Cerium(III) hydroxide was precipitated in the pH range 6–7.6; a value of 19.1 was obtained for $\log^*K_{s0}$ (extrapolated to $I = 0$). The identity of the soluble hydroxide complexes was not investigated.

Kumok and Serebrennikov[5] proposed the relationship $\log^*K_{LnL} = a \log^*K_{LaL} + b$, and tabulated *a* and *b* for the lanthanide cations. Baes and Mesmer[6] applied this relationship to Ce(III) and calculated $\log^*K_1 = -8.3$ ($I = 0$), -8.6 ($I = 0.05$) and -9.7 ($I = 3$). The solubility product of Ce(III) hydroxide is also given as $\log^*K_{s0} = 19.9$ ($I = 0$).

Up till now there is no information about the stability of $Ce(OH)_2^+$ and higher hydroxides and the solubility of $Ce(OH)_3$(s) over the pH range 6–14 has not been determined.

Kragten[7] showed that the borderline of precipitation in a pM′-pH diagram can be considered as composed of separate straight-line segments, each holding for a distinct pH region in which a specific hydroxide species predominates. When this theory is applied to an experimentally determined borderline, in principle the identity and stability constants of the various hydroxide species can be determined. In this paper the application to the precipitation of cerium(III) hydroxide will be described.

THEORY

The stability constant of the complex $M_p(OH)_q$ can be defined according to IUPAC notation as

$$^*\beta_{q,p} = \frac{[M_p(OH)_q]}{[M]^p} \cdot [H]^q$$

(note the reversal of *p* and *q*). If this complex predominates, the following equation can be derived for the α-coefficient for the side-reaction of the metal ion with hydroxide:[7,8]

$$\log \alpha_{M(OH)} = \left(\frac{q}{p}\right)pH + \left\{\frac{\log {}^*\beta_{q,p} + \log p}{p}\right\} + \left(\frac{p-1}{p}\right)\log[M'] \quad (1)$$

where [M'] is the total concentration of the metal present in solution. For a given [M'] every complex (p,q) gives rise to a straight line on the log α *vs.* pH diagram.

The maximum solubility of $M(OH)_n(aq)$ in equilibrium with its precipitate may be expressed as

$$[M(OH)_n]_{max} = {}^*K_{sn} = {}^*\beta_n \cdot {}^*K_{s0}. \qquad (2)$$

Combined with

$${}^*\beta_n = \frac{[M(OH)_n][H]^n}{[M^{n+}]} \quad \text{and} \quad \frac{[M']}{\alpha_{M(OH)}} = [M^{n+}]$$

this leads to the following formula for the borderline of the precipitation region:

$$pM'_{max} = -\log {}^*K_{s0} + n\,pH - \log \alpha_{M(OH)} \qquad (3)$$

Substitution of (1) in (3) finally gives the general formula for the straight-line approximation to the borderline of precipitation:

$$pM'_{max} = (np\text{-}q)pH - (p \log {}^*K_{s0} + \log {}^*\beta_{q,p} + \log p) \qquad (4)$$

The different (p,q) combinations lead to a set of straight lines in the pM'–pH diagram. The true curve is the envelope of the line segments corresponding to the lowest pM' values.

When the precipitation region in the pM'–pH diagram has been experimentally established, the straight-line segments, each with its distinct slope $(nq - q)$, can be shifted so that the envelope curve fits the experimental points. From the final position of the lines the stability constants and probable composition of the hydroxide complexes can be deduced.

EXPERIMENTAL

The experiments were done with cerous nitrate in 1*M* perchlorate as indifferent medium under constant ionic strength conditions. The tervalent form is the stable oxidation state of cerium in solution. A cerous hydroxide precipitate, once formed, becomes easily oxidized to the yellowish $CeO_2 \cdot nH_2O$ when exposed to the air. This process lowers the pH, as it gives rise to the formation of hydrogen ions. There is also evidence that the solution absorbs CO_2, with further release of H_3O^+ ions. In order to prevent these phenomena all experiments were performed under nitrogen.

It is difficult to define a state of equilibrium adequate for practical applications where formation of a metal hydroxide precipitate in contact with solution is concerned. Typical phenomena obscuring the equilibrium are supersaturation, dependence of the solubility on particle size, slow reactions in dilute solution and recrystallization. The first two phenomena are especially important in studies of the lanthanides. Our experiments were done with unbuffered solutions and although only very small amounts of H_3O^+ ions were released in comparison with the amount of precipitate present, the phenomena mentioned could cause a shift of several pH units because the system was near neutrality (pH 7), resulting in a non-equilibrium situation. The reaction proceeds to equilibrium very slowly or not at all.

It was found that reproducibility of the results improved remarkably when they were obtained under "fresh precipitate" conditions. To what extent we were then dealing with equilibrium conditions is of minor importance.

Table 1. Initial Ce(III) concentration

Final pCe'	Initial pCe'
0–0.4	0
0.4–0.75	0.3
0.75–2.0	0.7
1.0–3.0	1.0
2.1–6.0	2.0
>5.0	3.0

Reproducible and comparable circumstances for precipitation over the whole pH region of interest (pH 6–12) were achieved in the following way.

1. The ionic strength was kept constant at 1 (within a few per cent).
2. The initial Ce(III) concentration was matched to the final pCe' values to limit the amount of precipitate formed (see Table 1).
3. The precipitate was removed from solution after about 30 min by filtration (Schleicher and Schüll, Blue-Band paper no. 589/3). The adsorption of Ce(III) on this paper has been tested and found to be less than $5 \times 10^{-7}M$.

Apparatus

Precipitation and filtration were done in a glove-box flushed with nitrogen at a rate of 0.2–0.5 l./sec, starting at least 1 hr beforehand.

Procedure

A 50% sodium hydroxide solution was added dropwise to 200–300 ml of cerous nitrate solution (in 1*M* perchloric acid) with vigorous stirring, until a pH of 1 was reached. Then dilute alkali was added carefully until precipitation just began. About 25 ml of the solution were removed and dilute alkali was added to the remaining solution until the pH had increased by about 0.2. This step was then repeated until the desired pH range had been covered. After being aged for about 30 min all the fractions were filtered and the pH of the filtrates was determined. Finally the pH of the filtrates was adjusted to 1 with 5*M* perchloric acid. pCe' was determined by complexometric titration, with Xylenol Orange as indicator.

Filtrates with cerium concentrations $>10^{-4}M$ were diluted (with 0.01*M* perchloric acid), so that the metal ion concentration was 10^{-4}–$10^{-5}M$. Then 5-ml portions of the solution were placed in the titration cell, 1 ml of the indicator solution ($10^{-4}M$, pH 2) and 5 ml of the buffer solution (0.5*M* hexamine, pH 5.8) were added, and the solution was titrated with $10^{-4}M$ EDTA at a wavelength of 575 nm.

RESULTS AND CONCLUSIONS

The experimental results are presented as points in Fig. 1.

The slope of the nearly straight part in the region pH 7.12–7.75 and pCe' 0.74–3.11 has been determined by regression analysis; a value of 4.0 ($\pm$0.2) was found. The theoretical value of the slope being $(np–q)$, it can be concluded that either $Ce_3(OH)_5^{4+}$ or $Ce_2(OH)_2^{4+}$ predominates in this region. The formation of higher complexes such as $Ce_4(OH)_8^{4+}$ and $Ce_5(OH)_{11}^{4+}$ is most unlikely.[2]

If only $Ce_2(OH)_2$ and/or $Ce_3(OH)_5^{4+}$ are present, the following system of linear equations, representing a set of lines in the pM'–pH diagram, can be introduced (Table 2).

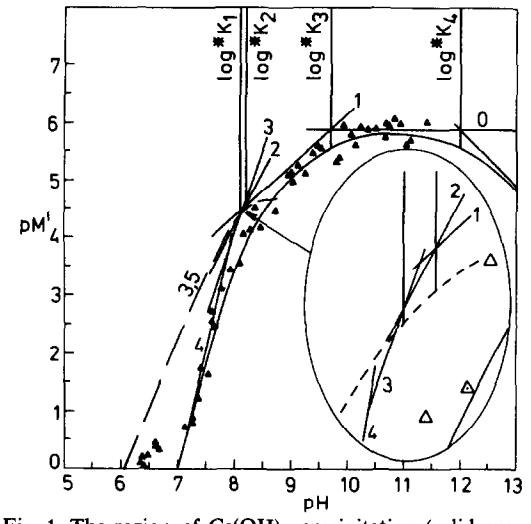


Fig. 1. The region of $Ce(OH)_3$ precipitation (solid curve), the region for the $Ce_3(OH)_5^{4+}$ complex (dashed curve) and the experimentally determined points. The curves are constructed with the constants $\log^*\beta_1 = -8.1$; $\log^*\beta_2 = -16.3$; $\log^*\beta_3 = -26.0$; $\log\ ^*\beta_4 = -38.0$; $\log^*\beta_{5,3} = -32.8$; $\log^*K_{s0} = 20.1$. The straight lines 0, 1, 2, 3 and 4 relate to the approximation of the borderline of precipitation [equations (4f), (4e), (4d), (4c), (4b) respectively]. The numbering gives the slope of the lines.

The experimental points in Fig. 1 corresponding to concentrations below $pCe' = 0.74$ obviously deviate from the best fit with slope 4. This is evidently caused by the high ionic strengths ($I = 4$–7), at which precipitate formation necessarily has to take place. These points are not taken into consideration, as theoretical corrections can only be made qualitatively.

From our experimental results it directly follows that

(1) the extrapolated steep part of the precipitation borderline intersects the pH axis at pH = 7.0; substitution of this value in the straight-line formulae (4b) and (4a) gives:

$$3\log^*K_{s0} + \log^*\beta_{5,3} = 27.5 \qquad (5)$$

and

$$2\log^*K_{s0} + \log^*\beta_{2,2} = 27.7 \qquad (6)$$

(2) from the horizontal part of the precipitation curve in the pH region 10.2–11.5 a mean value of $pCe' = 5.9 \pm 0.15$ can be estimated. Substitution in equation (4f) leads to:

$$\log^*K_{s3} = \log^*K_{s0} + \log^*\beta_3 = -5.9 \qquad (7)$$

It will be clear that the lines with slopes of 0 and 4 certainly contribute to the envelope. As a first approximation, straight lines with definite slopes of 1, 2 and 3 can be drawn as tangents to the experimental curve. The line with slope 1 definitely contributes to the envelope. This line intersects the horizontal line at $pM' = 5.9$ [equation (7)]. Substituting the pH value of this point of intersection in equation (4e) and using (7) gives the value for $\log^*K_3$ ($=\log^*\beta_3 - \log^*\beta_2$).

In principle, from the points of intersection of the other lines—1 and 2, 2 and 3, respectively—we can obtain values for $\log^*K_2$ and $\log^*K_1$. In this area the points of intersection are close together; the different mono-complexes all contribute to the envelope. The straight lines must be shifted upwards—compared with the true tangents—about 0.25 units, as otherwise the exactly calculated envelope will lie too low.

The line with slope 2 contributes in a small region (see Fig. 1) and $\log^*K_2$ ($=\log^*\beta_2 - \log^*\beta_1$) can be deduced from equations (4d) and (4e) by substitution of the pH value of the point of intersection. The line with slope 3 may also contribute to the envelope and must be placed to the left of the point of intersection of the lines with slopes 2 and 1, corresponding to equations (4d) and (4e). If the line with slope 3 is placed to the right of the position indicated in Fig. 1, it will certainly contribute to the envelope, which will then change its shape and no longer give the best fit to the experimental points. If the line is chosen left of the position indicated in Fig. 1, it does not contribute to the envelope. The position in Fig. 1 can be regarded as an extreme position. It suggests that a minimum value of -8.1 for $\log^*\beta_1$ is reasonable.

It is generally agreed by Biedermann and Newman[2] and many others that polycomplexes of Ce(III) are formed only in a small region just before precipitation starts. Support for fixing $\log^*\beta_1$, at -8.1 is given by the fact that this value minimizes the area of polycomplex formation.

We introduce the 1% polycomplex borderline[7] as a measure for defining the extent of the polycomplex region. The following equations can be derived for the straight-line approximation to the steep left-hand-side of this region, concerning the two possible Ce(III) polycomplexes:

$$pM'_{2,2} = 2\,pH + \log^*\beta_{2,2} + 2.3 \qquad (8)$$

Table 2.

Equation	p	q	Slope ($np-q$)	
4a	2	2	4	$pM' = 4\ pH - (2\log^*K_{s0} + \log^*\beta_{2,2} + 0.3)$
4b	3	5	4	$pM' = 4\ pH - (3\log^*K_{s0} + \log^*\beta_{5,3} + 0.5)$
4c	1	0	3	$pM' = 3\ pH - \log^*K_{s0}$
4d	1	1	2	$pM' = 2\ pH - (\log^*K_{s0} + \log^*\beta_1)$
4e	1	2	1	$pM' = pH - (\log^*K_{s0} + \log^*\beta_2)$
4f	1	3	0	$pM' = -\log^*K_{s3} = -(\log^*K_{s0} + \log^*\beta_3)$

and

$$pM'_{5,3} = 2.5\,pH + \tfrac{1}{2}(\log^*\beta_{5,3} + 2.5) \qquad (9)$$

When $\log^*\beta_1$ is assumed to be less negative it can be proved easily, by using equations (5)–(7), that $\log^*\beta_{2,2}$ and $\log^*\beta_{5,3}$ become less negative, which according to equations (8) and (9) shifts the corresponding polycomplex borderlines to lower pH values, thus increasing the polycomplex region. This is not consistent with a minimum region of polycomplexation, so again we may assume $\log^*\beta_1 = -8.1$.

From the graphically estimated values the envelope has been calculated by a computer program. Some minor adjustments turned out to be necessary. (This program is available on request.)

The following values can be regarded as giving the best fit:

$$\log^*\beta_1 = -8.1 \qquad \log^*\beta_3 = -26.0$$
$$\log^*\beta_2 = -16.3 \qquad \log^*K_{s0} = 20.1$$

and $\log^*\beta_{2,2} = -12.4$ or $\log^*\beta_{5,3} = -32.8$, depending on which species prevails.

Substitution of the appropriate values in (8) and (9) gives two borderlines, of which that for $Ce_3(OH)_5^{4+}$ leads to the smallest polycomplex region. It makes $Ce_3(OH)_5^{4+}$ the more likely of the two to be present in solution, in agreement with the evidence of Biedermann and Newman.[2]

Baes and Mesmer[6] reported the possibility of the formation of $M(OH)_4^-$ hydroxides when various lanthanide hydroxides dissolve in concentrated sodium hydroxide solution. In the case of Ce(III) no data have been reported for $^*\beta_4$. As we did not observe an increase in solubility below pH = 12, we can only state that $\log {}^*K_4 < -12$.

DISCUSSION

The accuracy of the calculated constants can be assessed only qualitatively. The error in $\log^*K_{s3}$ (7) may be taken as equal to the standard deviation of the horizontal part of the approximated precipitation curve: $S_{yx} = 0.15$.

When all the approximated straight lines are shifted by such a distance, the points of intersection also shift. The resulting uncertainty in the constants can be estimated to be about ± 0.2 units in this way, except for $\log\beta_{5,3}$ for which the uncertainty is about ± 1 unit. Another approach to the determination of the stability constants uses matrix calculus. Formulae (4d), (4e), (4f) and (4b) can be written as a system of four linear equations with $^*\beta_1$, $^*\beta_2$, $^*\beta_3$ and $^*\beta_{5,3}$ as the unknown variables and $^*K_{s0}$ as the independent variable. This system has also been solved by standard numerical methods. In this way we found for the best fit: $\log^*K_{s0} = 20.1$; $\log^*\beta_1 = -8.2$; $\log^*\beta_2 = -16.4$; $\log^*\beta_3 = -26.3$ and $\log^*\beta_{5,3} = -32.8$, in good agreement with the values found graphically.

When the pCe' values of the experimental points are changed by ± 0.15, the logarithms of the constants vary by up to ± 0.2, which agrees with the graphically estimated uncertainty.

For a comparison of our constants with values reported by other investigators, the constants should be referred to the same ionic strength. This can be done in principle by using the equations of Pitzer and Brewer.[9] However, as the values for the interaction coefficient B_{CeX} (X = anion) are not available, only approximate corrections can be calculated.

Moeller[1] neglected the interaction of Ce(III) ions with sulphate and his value of $\log^*\beta_1$ may be regarded as too low for this reason. Stepanov and Shvedov[3] reported $\log^*\beta_1 = -4.3$ ($I = 0.005$), a value much higher than those found by other investigators for lanthanide hydroxides. The statistical method of Kumok and Serebrennikov[5] used by Baes and Mesmer[6] results in values for $\log^*\beta_1$, which are in agreement with those of Moeller. The statistical method is based on the use of $\log^*\beta_1$ values of lanthanides with a great variety of ligands other than OH^-; the compilation by Baes and Mesmer seems reliable. Our values for $\log^*\beta_1 = 8.1$ ($I = 1$) and $\log^*\beta_{5,3} = -32.8 \pm 1$ ($I = 1$) fit very well in this compilation.[2,6]

Small differences can be attributed to different working conditions; the determinations by Biedermann and Newman took 12–15 hr, for instance.

Correcting our value for $\log^*K_{s0}$ by using the formulae of Pitzer and Brewer[9] we obtain $\log^*K_{s0} = 21.0$ ($I = 0$). This value does not agree well with that obtained by Buchenko *et al.*,[4] but these authors kept the heterogeneous system for 24 hr at room temperature, before the filtration.

The higher value found by us is in agreement with the fact that fresh precipitates consist of relatively fine particles, for which $\log^*K_{s0}$ will be higher, compared with aged precipitates.

Finally we conclude that, in so far as our constants were comparable to those found in the literature, the agreement is sufficiently good. The method described in this paper seems very promising for the determination of the hydrolysis constants of lanthanides under "freshly precipitated" conditions. Further experiments are in preparation for the other lanthanides.

REFERENCES

1. T. Moeller, *J. Phys. Chem.*, 1946, **50,** 242.
2. G. Biedermann and L. Newman, *Arkiv Kemi*, 1964, **22,** 303.
3. A. V. Stepanov and V. P. Shvedov, *Russ. J. Inorg. Chem.*, 1965, **10,** 541.
4. L. I. Buchenko, P. N. Kovalenko and M. M. Evstifeev, *ibid.*, 1970, **15,** 1666.
5. V. N. Kumok and V. V. Serebrennikov, *ibid.*, 1965, **10,** 1095.
6. C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976.
7. J. Kragten, *Talanta* 1977, **24,** 483.
8. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
9. K. S. Pitzer and L. Brewer, *Thermodynamics*, (G. N. Lewis and M. Randall revised edition), McGraw-Hill, New York, 1961.

Talanta, Vol. 25, pp. 151-155 Pergamon Press, 1978. Printed in Great Britain.

BEHAVIOUR OF SOLID ELECTRODES IN NORMAL AND DIFFERENTIAL PULSE VOLTAMMETRIC METHODS

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Summary—In order to investigate the behaviour of solid electrodes in normal and differential pulse voltammetry, step functions have been applied to the electrochemical cell containing the electrodes to be tested, in the absence of electroactive species. The large residual current observed could be attributed to electrochemical reactions of the electrode material.

Normal pulse voltammetry and differential pulse voltammetry are useful techniques for the determination of low concentrations of electroactive species. In both techniques, which have a limit of detection lower than that for ordinary d.c. voltammetry, the current is measured during a time interval of the pulse when the ratio of the faradaic current and the charging current has a maximum value. This charging current is supposed to decay relatively quickly according to an exponential function because the electrochemical cell may be considered as an RC-circuit.

Although a wide range of electrode materials is available, pulse techniques in voltammetry have mainly employed mercury as the electrode material. However, mercury cannot be used at potential values larger than +0.4 V *vs.* SCE because of its dissolution as mercury ions. As more positive potentials are of interest for the determination of a wide range of oxidizable compounds attention must be paid to the use of solid electrodes. Adams[1] has given an extensive survey of the use, prepration and applicability of solid electrodes in d.c. voltammetry.

Information about the behaviour of solid electrodes in pulse voltammetry can be obtained from measurements of the electrode response after the application of a potential step. Meyers and Osteryoung[2] used this method for investigating the dependence of the faradaic current on the rotation rate of disc electrodes. Swartzfager[3] has carried out similar experiments to obtain a relationship between current and flow-rate in the case of a detector for high-performance liquid chromatography, the indicator electrode being a carbon paste electrode.

The present communication deals with the behaviour of different kinds of electrode materials in pulse voltammetry, and more particularly with a study of the residual current. Therefore a stepwise change in the potential was applied and the current studied. The measurements were performed under ordinary voltammetric conditions in the absence of electroactive species in the solution. From the shape of the current–time curves information could be obtained about the nature of the large residual currents found in normal pulse voltammetry with solid electrodes. The consequences with respect to the limit of detection for differential pulse voltammetry have also been considered.

EXPERIMENTAL

Apparatus

The block diagram of the apparatus for the experiments in which a step function is applied across the electrochemical cell containing the electrode to be tested, is shown in Fig. 1. It consists of the following items.

A function generator (Philips PM 5168) which delivers the step function. The generator was used in the single shot mode.

A precision voltage source (Knick S16) was used in order to adjust the d.c. level of the e.m.f. more precisely than can be achieved by using the function generator.

A digital voltmeter (DATA Precision 3500) was used to verify the e.m.f. of the step function.

The electrochemical cell, a Metrohm glass polarographic vessel with the solid electrode to be tested. If not stated otherwise a pool of mercury at the bottom of the cell was used as a reference electrode to ensure a minimum resistance R_1 between the working and the reference electrode.

A resistance R_2 approximately a tenth of R_1.

The gain circuit of a PAR model 113.

A Textronic T564 oscilloscope.

The normal pulse and differential pulse as well as the current-sampled d.c. voltammograms were obtained by means of a PAR 174. All potentials in the voltammograms were referred to the SCE. The counter-electrode was a coil of platinum wire. The scan-rate was 2 mV/sec and the time between two successive pulses was 0.5 sec throughout.

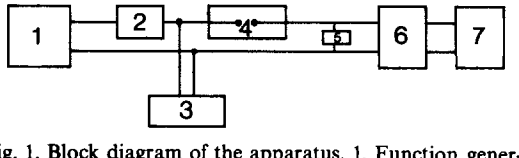


Fig. 1. Block diagram of the apparatus. 1, Function generator (Philips PM 5168). 2, Precision voltage source (Knick S16). 3, Digital voltmeter (DATA Precision 3500). 4, Electrochemical cell. 5, Resistance. 6, PAR model 113. 7, Textronic T564 oscilloscope.

Reagents

Quartz-distilled water was used in all experiments. The potassium chloride was of suprapure quality. If necessary, oxygen was removed from solutions by passage of nitrogen for 15 min.

Electrodes

A Metrohm hanging mercury drop electrode (HMDE).

A PAR glassy carbon electrode (GCE).

A home-made GCE, made of a glassy carbon rod (GC-20, Tokai Electrode Manufacturing Co., Ltd., Tokyo), sealed into a glass tube. Electrical contact was made by means of a small amount of mercury inside the tube, and a platinum wire.

A home-made GCE, made of a disc of glassy carbon (V-10, Le Carbone Lorraine) was sealed to a glass tube with UHU-plus adhesive. The contact between the adhesive and the supporting electrolyte was kept as small as possible, care being taken to avoid contamination of the surface with adhesive and the electrical contact being made as described above.

A carbon paste electrode (PAR).

A platinum foil electrode (home-made).

A gold foil electrode (home-made).

A paraffin-impregnated graphite electrode (PAR) coated with a mercury film.

A GCE (Tokai) coated with a mercury film.

The GCEs were polished with a diamond paste (Diaplast SS, Winter & Sohn, Hamburg) which can be removed with water and alcohol. Successive polishings were carried out by means of diamond pastes of decreasing particle size (30–7–1–0.25 μm), until the surface had a black, lustrous mirror-like appearance. Under the microscope (magnification 100×) some holes were seen. These holes can be removed by polishing thoroughly, but new holes become visible on other parts on the surface, indicating the presence of defects in the material. The platinum and gold electrodes were treated with *aqua regia* for 3 min and were subsequently kept in 10*M* nitric acid for about 1 hr and rinsed with water. The electrodes were stored in a solution containing a redox buffer of Fe(II) and Fe(III) in sulphuric acid medium (pH 2). Before use the electrode was rinsed with water. The paraffin-impregnated graphite electrode and the GCE (Tokai) were coated with mercury by electrolytic deposition for 20 min from $2 \times 10^{-5}M$ mercury(II) in acetic acid medium (pH 3) at a potential of −0.5 V, just before the electrode was tested. After the experiment the mercury film was wiped off with wet paper tissue. Before each experiment the GCEs to be tested were polished with diamond paste.

Selection of the potential range

Step functions were applied to the electrochemical cell containing supporting electrolyte only (pH 6–7). The measurements were restricted to those potential ranges in which no currents due to electrochemical reactions of the electrode material or solutions in d.c. voltammetry were expected.

RESULTS AND DISCUSSION

Figure 2a shows a current-sampled d.c. voltammogram obtained with a GCE (Tokai) in $5 \times 10^{-2}M$ potassium chloride. The residual current has a considerable value over a large potential range. This may be caused by the following reactions:

$$Cl_2 + 2e \rightleftharpoons 2Cl^- \quad E^0 = 1.12\,V \text{ vs. SCE}^4$$

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O \quad E^0 = 0.99\,V \text{ vs. SCE}^4$$

or by the oxidation of the electrode material. To establish which reaction occurs it is necessary to know the overvoltage of oxygen and chlorine on glassy carbon but these values have not been reported. In order to investigate whether the oxidation of chloride is responsible for the residual current, sampled d.c. voltammograms were obtained for nitrate as well as sulphate media. Similar voltammograms were observed, so the residual current cannot be attributed to the oxidation of chloride.

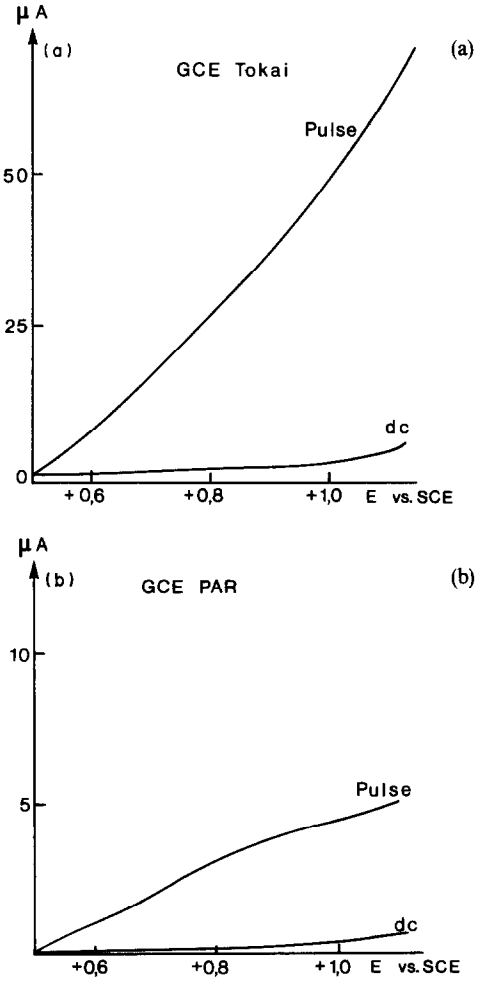


Fig. 2a. Current-sampled d.c. voltammogram and normal pulse voltammogram obtained with (a) a Tokai GCE and (b) a PAR GCE in $5 \times 10^{-2}M$ KCl.

The normal pulse voltammogram for the same electrode in the same solution also shows a considerable residual current (Fig. 2a). Replacing the Tokai GCE by the PAR GCE results in a lower current (Fig. 2b). Both electrodes give similar current-sampled d.c. voltammograms. Obviously the behaviour of apparently similar electrode materials of different origin is not similar and this is important in pulse voltammetry. According to Adams[1] the residual current in d.c. voltammetry is composed of three components: the charging current, currents due to chemical reactions of the electrode surface and currents due to traces of electroactive impurities in the solution. In order to investigate the nature of the residual current in pulse voltammetry, step functions were applied to

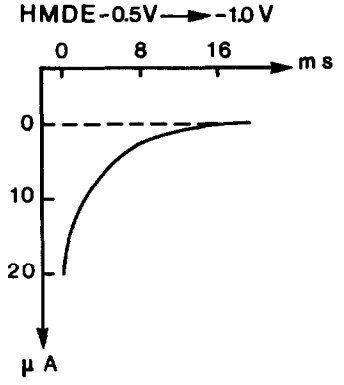


Fig. 3. Current–time relationship after the application of a potential step at an HMDE from −0.5 to −1.0 V.

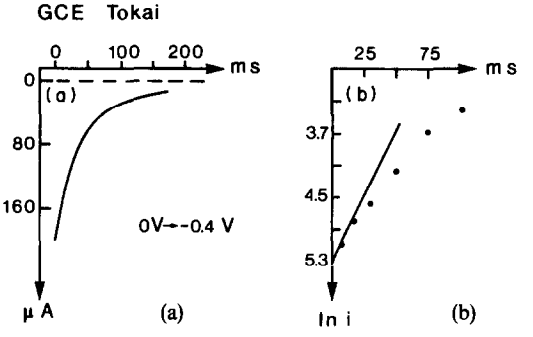


Fig. 5(a) Current–time relationship after the application of a potential step at a Tokai GCE from 0 to −0.4 V. (b) Plot of ln(i) *vs.* time (Tokai GCE).

the electrochemical cell. At first an HMDE was used. A potential step was applied to the HMDE from −0.5 to −1.0 V. As the very small time interval during which the current decays is difficult to measure, the RC-time was increased by replacement of the reference electrode by an SCE with a salt-bridge of high resistance (5 kΩ). The current–time relation is given in Fig. 3. A plot of ln(i) *vs.* time was made, in order to determine whether the current measured was due to the decay of the charging current, and was found to be linear. The RC-time of 6 msec obtained from Fig. 3 is in agreement with that of 5 msec calculated from the area of the HMDE (3.4 mm^2) and an assumed mean value of 30 μF/cm^2 for the differential capacity at a mercury surface.[5] This agreement is an indirect proof of the absence of electroactive impurities in the solution. Figure 4a shows the current–time relationship obtained for the Tokai GCE after the application of a potential step from 0 to +0.4 V. Within the period of observation the current does not reach the initial level. The plot of ln(i) *vs.* time does not yield a straight line (Fig. 4b). A similar behaviour was observed in the cathodic direction (Fig. 5). Although these observations might lead to the conclusion that the charging of the double layer is not the main factor responsible for the large residual current, the non-linearity of the ln(i) *vs.* time plot may be due to a continuously changing value of the differential capacity during the charging process. To check this possibility, the resistance in the

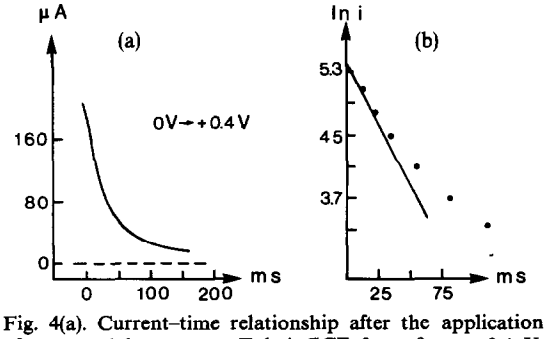


Fig. 4(a). Current–time relationship after the application of a potential step at a Tokai GCE from 0 to +0.4 V. (b) Plot of ln(i) *vs.* time (Tokai GCE).

circuit was varied. In the case of a constant capacity, the dependence of the charging current on the value of the resistance R is given by $i = \Delta E/R \exp(-t/RC)$. For a variable capacity such a simple expression cannot be given, but there will be a strong dependence on R. These experiments were performed on the PAR 174 with a 3-electrode system. A precision variable resistance was connected in series with the counter-electrode. The resistance between the counter-electrode and working electrode without the precision resistance was 70 Ω. The potential was changed stepwise from 0 to +0.4 V and the hold-button was then pressed. The sampled current was displayed on an X–Y recorder. For values up to 1 kΩ a constant residual current was obtained; a further increase up to 20 kΩ resulted in a decrease of the residual current from 50 to 48 μA. As no strong dependence of the residual current on the resistance is observed, it seems that the capacity does not form the most essential contribution to the residual current and the oxidation or reduction of the electrode material has to be considered.

In order to explain the behaviour of solid electrodes in normal pulse voltammetry it is important to know how the current decays after a block pulse is applied. This was investigated by applying a block pulse instead of a step function to the Tokai GCE. The start potential of +0.2 V was changed in one step to +0.8 V and was kept at this value for 100 msec. The block pulse was applied with the same equipment by modifying the frequency. Figure 6 shows the resulting current decay. Near the end of the block pulse the current still has a considerable value, as expected from Fig. 4a. About 400 msec after the end of the block pulse the current is negligible. When this electrode is used in normal pulse voltammetry the time interval between two successive pulses should therefore not be less than 0.5 sec.

From Fig. 2a it can be seen that in the case of normal pulse voltammetry the residual current increases linearly with increasing amplitude.

The use of solid electrodes results in a considerable residual current in pulse voltammetry, caused primarily by electrochemical reactions of the electrode material and cannot be recommended. Step functions

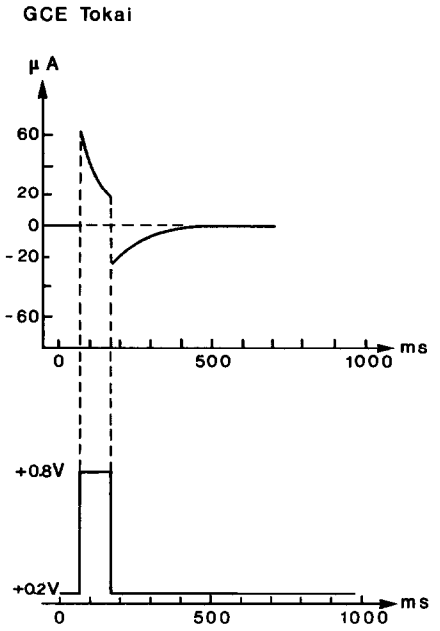


Fig. 6. Current–time relationship after the application of a block pulse at the Tokai GCE.

were therefore applied to other electrodes and the decaying current was sampled after about 60 msec (as in the PAR 174). The values of the current are in fairly good agreement with the values obtained from the corresponding normal pulse voltammograms, scanned over the same potential range as the step function, as can be seen from Tables 1 and 2. The values from the normal pulse voltammograms are obtained by subtracting the current at the initial potential from the value at the end of the normal pulse voltammogram. To give an idea of the residual current for different kinds of electrodes in normal pulse voltammetry Fig. 7a gives the results in the potential range from 0 to +0.4 V and Fig. 7b from 0 to −0.4 V. Although the relationship between the residual current and the amplitude of the block pulse is not completely linear for every electrode, the curves are represented schematically as being linear. As can be seen from Fig. 8b no difference was observed for the Tokai GCE with and without a mercury film. Štuliková[6] has reported that mercury on the electrode surface is not present as a film but as discrete small particles. The electrode surface exposed between these particles of mercury may be responsible for the residual current. Several GCEs of the same make were investigated in order to illustrate the difference in the residual current. Large differences were observed for the Tokai GCEs. The gold and platinum electrodes cannot be recommended, owing to the extremely high residual cuurents, which have also been observed in d.c. voltammetry.[7] Generally it can be said that the lower the residual current, the better the behaviour of the electrode in normal pulse voltammetry.

Differential pulse voltammetry (d.p.v.)

The pulse amplitudes in d.p.v. are smaller than those in normal pulse voltammetry and the residual

Table 1. Current values from a step function and a norn. ıal pulse voltammogram in the potential range from 0 to +0.4 v [7]

Electrode	Area of electrode surface, mm^2	i* from step function after 60 msec, μA	i from pulse voltammogram, μA
GCE (PAR)	32	10	4
Carbon paste (PAR)	55	2	1
GCE (Le Carbone Lorraine)	167	25	16
GCE (Tokai)	7	50	55

* The error in these values of the current may be about 10%

Table 2. Current values from a step function and a normal pulse voltammogram in the potential range from 0 to −0.4 V

Electrode	Area of electrode surface, mm^2	i* from step function after 60 msec, μA	i from pulse voltammogram, μA
Paraffin-impregnated graphite (PAR) + Hg film	30	28	25
GCE (Tokai) + Hg film	7	48	50
Carbon paste (PAR)	55	4	1
Pt	160	350	300
Au	225	450	625
GCE (PAR)	32	7	6
GCE (Tokai)	7	40	64
GCE (Le Carbone Lorraine)	30	40	30

* The error in these values of the current may be about 10%

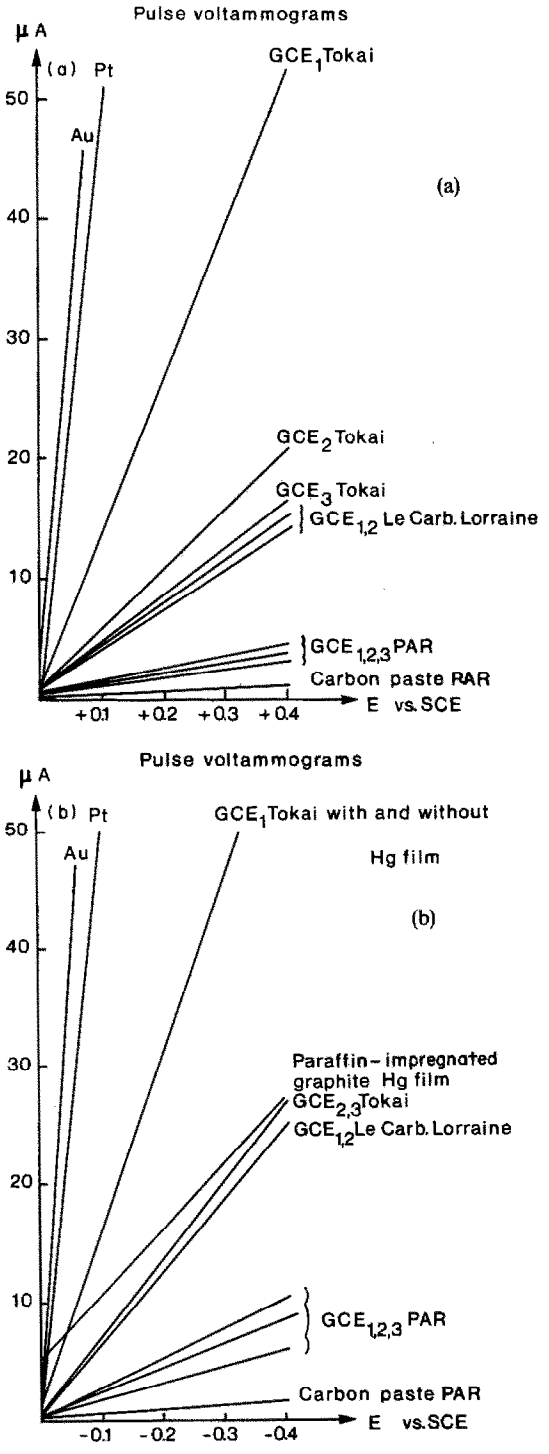


Fig. 7. Smoothed normal pulse voltammograms of different kinds of electrodes in the potential range (a) from 0 to +0.4 V, (b) from 0 to −0.4 V.

current is therefore also smaller. Although a constant amplitude is used in d.p.v., the residual current is not linear over the working range for every electrode, as shown in Fig. 8a for the PAR GCE and in Fig. 8b for the platinum electrode, (for several different pulse amplitudes). Electrodes with large residual currents are also not recommended for application in d.p.v.

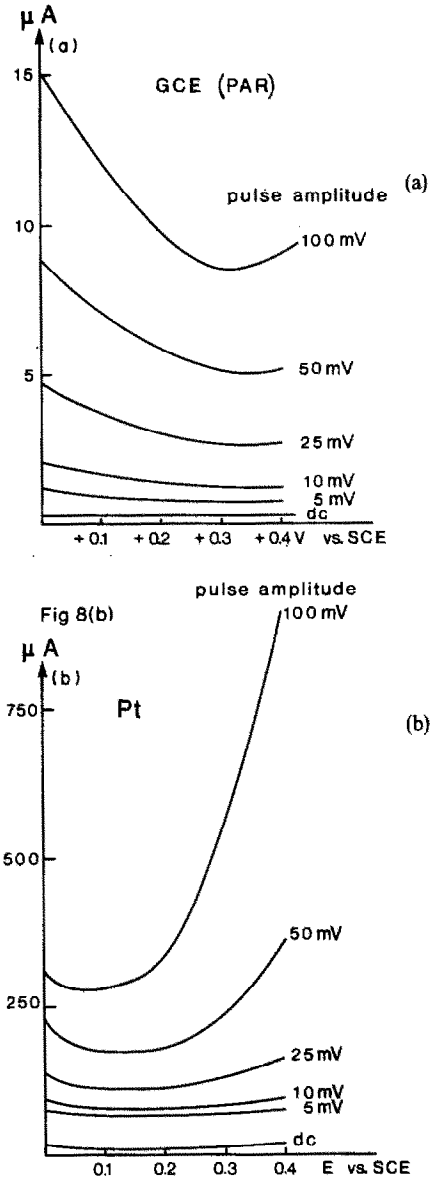


Fig. 8. Differential pulse voltammograms with varying pulse amplitudes obtained with (a) a PAR GCE, (b) a platinum electrode.

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REFERENCES

1. R. N. Adams, *Electrochemistry at Solid Electrodes*, Dekker, New York, 1969.
2. D. J. Meyers and R. A. Osteryoung, *Anal. Chem.*, 1974, **46**, 2089.
3. D. G. Swartzfager, *ibid.*, 1976, **48**, 2189.
4. *CRC Handbook of Chemistry and Physics*, 47th Ed. 1966–1967, The Chemical Rubber Co., Cleveland, Ohio.
5. B. E. Conway, *Theory and Principles of Electrode Processes*, Ronald Press, New York, 1965.
6. M. Štuliková, *J. Electroanal. Chem.*, 1973, **48**, 33.
7. I. M. Kolthoff and N. Tanaka, *Anal. Chem.*, 1954, **26**, 632.

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SHORT COMMUNICATIONS

STUDIES WITH INORGANIC ION-EXCHANGE MEMBRANES

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Summary—The pyridinium molybdoarsenate membrane shows a response to pyridinium ions and can be used to determine the concentration of these ions in the range 10^{-3}–1M. The potentials generated across the membrane are reproducible and the response time is less than 1 min. There is no interference from certain inorganic and organic ions. The electrode can be used in the pH range 3–6 as well as in non-aqueous medium. Small additions of cetyltrimethylammonium bromide cause large shifts in the membrane potentials. A membrane, after being treated with this surfactant, shows a wider range of response to pyridinium ions. Precipitation titration of pyridinium nitrate has been monitored by using this membrane electrode.

The wide range of ion-selective electrodes may be extended by the use of membranes of new chemically and thermally stable inorganic ion-exchangers. We have earlier described the selectivity and performance of some inorganic ion-exchange membranes.[1,2] This paper reports investigations with molybdoarsenate membranes, which are found to be highly selective for pyridinium ion over a fairly wide concentration range.

EXPERIMENTAL

Reagents

Ammonium molybdate and arsenic pentoxide were reagent grade chemicals. All other reagents used were of analytical grade. Solutions were prepared in doubly distilled water. The pyridinium nitrate used in the preparation of the heteropoly salt was obtained as a white crystalline compound, by mixing nitric acid and distilled pyridine in equimolar quantities. It was crystallized from water and alcohol.

Preparation of pyridinium molybdoarsenate

Ammonium molybdate was dissolved in sodium hydroxide and the solution was heated to remove ammonia. It was then cooled, and acidified with nitric acid, and arsenic pentoxide was added with stirring. Pyridinium nitrate was then added and the precipitate formed was left overnight. It was then washed with distilled water and dried at 90°. This compound was analysed (spectrophotometrically for pyridine and molybdenum) and the values obtained for pyridine, molybdenum and arsenic compare well with the theoretical values calculated on the basis of the formula $(C_5H_5NH)_3Mo_{12}AsO_{40}$. Found; Mo 54.4%, Py 11.4%, As 3.7%: calculated; Mo 54.67%, Py 11.40%, As 3.56%. Thermogravimetric analysis confirmed that the salt does not contain water.

Preparation of the membranes

The membranes were prepared by mixing 0.65 g of the heteropoly acid salt with 0.35 g of "Araldite". The mixture was spread thinly (about 0.5 mm) on filter paper and left to dry. The hardened membrane was cut into a circular disc 2.5 cm in diameter. It was then equilibrated with 0.1M pyridinium nitrate for 3–4 days. Between measurements the electrodes were washed with distilled water to prevent cross-contamination.

Procedure

The electrode assembly consisted of the membrane cemented between the two arms of a U-tube which formed the two compartments of a cell. The reference solution was 0.1M pyridinium nitrate. Saturated calomel electrodes were used as reference electrodes. The emf readings were taken when they became steady. All measurements were made at a constant temperature of 30°.

RESULTS AND DISCUSSION

The potentials observed with the pyridinium molybdoarsenate membrane interposed between solutions of pyridinium nitrate are shown in Fig. 1(*a*). The plots show the variation of electrode potential *vs.* log concentration (or activity) of pyridinium ion. Activity coefficients in dilute solutions were calculated by the extended form of the Debye–Hückel equation, while at appreciable concentrations the complete Hückel equation[3] was used. The values of the membrane potentials are smaller than the expected Nernstian value. The deviation from Nernstian behaviour may be due either to co-ion transfer or H^+ or OH^- competition with the electrolyte counter-ions.[4] In spite of deviations from Nernstian behaviour, these membranes are suitable for determining the pyridinium ion concentration from 1 to $10^{-3}M$ [Fig. 1(*a*)].

The precision was determined, the potential being repeatedly measured in test solutions containing pyridinium ions in the range 10^{-3}–$10^{-1}M$. The results show a standard deviation of 0.52 mV in the higher concentration range and 0.65 mV in the low concentration range. Thus good reproducibility is shown over a working range of 3 orders of magnitude of pyridinium ion activity.

The response time (static) is about 1 min in dilute solutions and a little less in concentrated solutions. The potentials remain constant for 2–3 hr, after which a drift of 0.1 mV/min takes place. These membranes can be used for 2 months, after which a decrease in potential of 4–8 mV/decade is observed. This does not affect the response of the membrane and the range of validity remains almost the same. The drift in potential is due to a shift in E_0.

The pH-dependence of the electrode has been investigated in the range 1–7; pH-values higher than this could not be used owing to depolymerization of the heteropoly

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salt. The useful pH-range for the electrode is 3–6. A drift in potential, at low pH-values, is observed at all concentrations of pyridinium ions from 1 to $10^{-3}M$.

The performance of the electrode has been assessed in the presence of various interfering ions in terms of the selectivity coefficient, K_{ij}, defined by the following equations. For an electrode responding to the primary ion i of activity a_i and charge z, in the presence of an interfering ion j of activity a_j and charge y, the potential E is

$$E = \text{constant} + (2.303\,RT/F)\log[a_i + K_{ij}(a_j)^{z/y}] \quad (1)$$

The potential in the presence of the primary ion i at activity a_i is

$$E' = \text{constant} + (2.303\,RT/zF)\log a_i \quad (2)$$

From equations (1) and (2)

$$K_{ij} = (10^{(E-E')zF/2\,303\,RT} - 1)a_i^{z/y}/a_j \quad (3)$$

In the case of inorganic cations and anions as interfering ions, the selectivity coefficients, K_{ij}, have been evaluated from cell potentials with $10^{-4}M$ pyridinium ion and with $10^{-4}M$ pyridinium + $10^{-2}M$ interfering ion. The results are reported in Table 1. Selectivity coefficients of the organic ions picolinium, lutidinium and collidinium have been evaluated from the potentials of solutions having $0.01M$ concentration of the interfering cation along with varying concentrations of pyridinium ion, and the data are given in Table 2. The electrode preferentially responds to the primary ion if $K_{ij} < 1$. The K_{ij} values of various univalent and bivalent inorganic ions (Table 1) show that these ions do not interfere. The organic cations picolinium, lutidinium and collidinium do not interfere (Table 2) unless the pyridinium ion concentration is too low.

The response of the membrane electrode in a partially non-aqueous medium has been investigated. The potential *vs.* activity plots (not shown here) are linear in the concentration range 10^{-3}–$1M$ in 10% alcohol or acetone solutions, and in 25% alcohol or acetone are linear down to $10^{-4}M$. The slopes of the curves are higher than those obtained in aqueous solution (Table 3). Thus the membrane shows a better response in 25% alcohol solution and this can be attributed to the low colloidal dispersion of molybdo and tungstoarsenates in aqueous media.[5] This dispersion effect vanishes in non-aqueous media of low dielectric constant. The response time rises to 4 min and the drift in potential increases considerably in solutions containing 35% or more of alcohol.

The electrode exhibits interesting behaviour in the presence of surfactant cations. A small addition of the cationic surfactant cetyltrimethylammonium bromide (CTAB) causes a shift in the membrane potential (in the presence of low concentrations of pyridinium ion) to a more negative value and extends the range of linear response. The effect can be made permanent by treating the membrane with the surfactant solution ($10^{-4}M$) for 1 hr. There is a slight change in the potential from that observed with the untreated electrode, and also a slight change in the slope of the response curve (Fig. 1*b*). A similar effect has been reported[6] for the calcium-selective membrane electrode, which is affected by the presence of an anionic surfactant, but becomes immune to the effect after conditioning for about an hour. The effect is attributed to initial adsorption of surfactant at the interface and subsequent extraction into the membrane phase. In the present case the ion-exchanger in the membrane is negatively charged and thus

Table 1. Selectivity coefficients (K_{ij}) values for various interfering ions ($10^{-2}M$) in the presence of pyridinium ion ($10^{-4}M$)

Interfering ion	K_{ij}
Na^+	7.50×10^{-3}
K^+	4.90×10^{-3}
Rb^+	2.64×10^{-3}
NH_4^+	4.56×10^{-3}
Ag^+	10.0×10^{-3}
Tl^+	3.48×10^{-3}
Sr^{2+}	1.65×10^{-3}
Ca^{2+}	2.19×10^{-3}
PO_4^{3-}	1.20×10^{-3}
AsO_4^{3-}	2.41×10^{-2}
MoO_4^{2-}	3.52×10^{-3}

Table 2. Selectivity coefficient (K_{ij}) values for organic cations ($0.01M$) at varying pyridinium ion concentrations

Concentration of pyridinium ion, M	K_{ij}		
	α-Picolinium	Lutidinium	Collidinium
0.20	~0	~0	~0
0.02	~0	~0	~0
0.001	0.185	0.161	0.183

Table 3. Effect of solvent composition on calibration curves

Solvent composition, *v/v*%	Slope $dE/dpPy^+$
Water	40.0
Methanol 10%	33.0
Methanol 25%	34.0
Ethanol 10%	40.0
Ethanol 25%	45.0
Acetone 10%	40.0
Acetone 25%	42.0

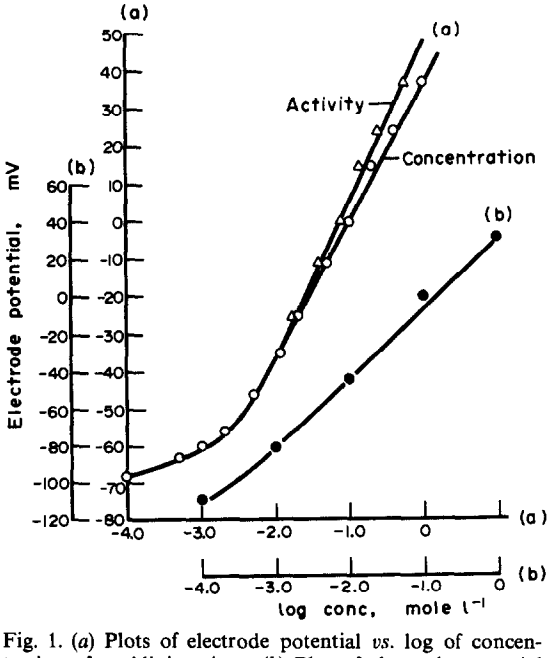


Fig. 1. (*a*) Plots of electrode potential *vs.* log of concentration of pyridinium ions. (*b*) Plot of electrode potential *vs.* log of pyridinium ion concentration, in the presence of $2 \times 10^{-4}M$ CTAB.

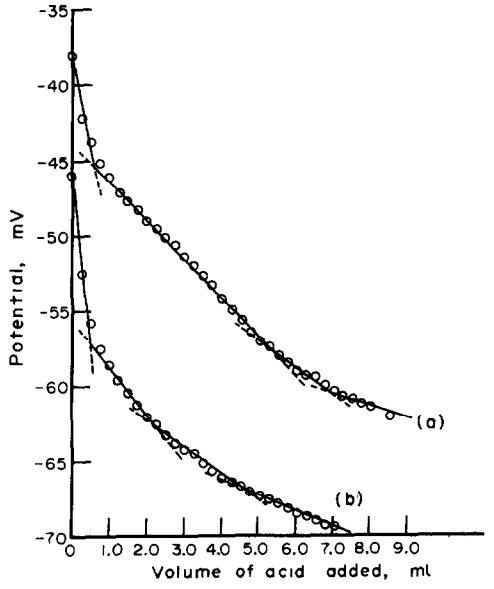


Fig. 2. (*a*) Titration of 25 ml of 0.01*M* pyridinium nitrate in aqueous solution, with molybdophosphoric acid (0.037*N*). (*b*) Titration of 25 ml of 0.005*M* pyridinium nitrate in 25% ethanol solution, with molybdophosphoric acid (0.027*N*).

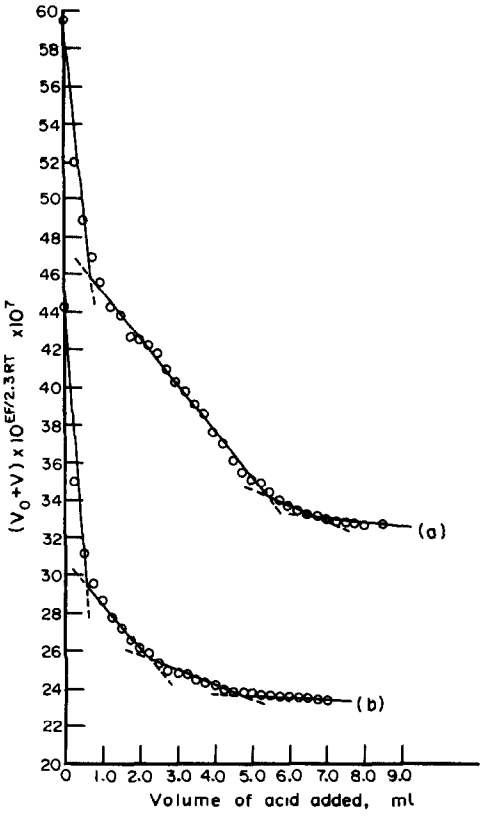


Fig. 3. (*a*) Gran plot of the titration data for aqueous medium. (*b*) Gran plot of the titration data for ethanolic medium.

there is a possibility of exchange of surfactant cations with the pyridinium ions at the membrane. However, it is thought that in this case only the adsorption at the interface takes place and that there is no uptake of surfactant cations by the membrane phase. This view is supported by the fact that the behaviour of the treated membrane towards surfactant cations at various concentrations is erratic. Also, in an earlier paper[5] on the ion-exchange properties of some heteropoly salts we observed that the crystal lattice of such compounds is not sufficiently open to permit the exchange of very large cations such as the cetyltrimethylammonium ion. Membranes treated with a more concentrated solution of the surfactant ion ($>10^{-3}M$) gave noisy signals and non-reproducible potentials, probably because of formation of micelles and their binding at the interface.

This electrode has also been used as an end-point indicator in potentiometric titrations in aqueous and alcoholic media. The titration of aqueous 0.01*M* pyridinium nitrate with 12-molybdophosphoric acid (0.037*N*) and the same titration in 25% ethanol (pyridinium nitrate 0.005*M* and molybdophosphoric acid 0.027*N*) is illustrated in Fig. 2. There should be three breaks corresponding to the three stages of precipitation:

$$Py^+ + H_3PMo_{12}O_{40} \rightarrow PyH_2PMo_{12}O_{40} + H^+$$

$$Py^+ + PyH_2PMo_{12}O_{40} \rightarrow Py_2HPMo_{12}O_{40} + H^+$$

$$Py^+ + Py_2HPMo_{12}O_{40} \rightarrow Py_3PMo_{12}O_{40} + H^+$$

The breaks in the titration curve (in aqueous media) are not very sharp. A Gran plot[7] of the data was constructed for both titrations, $10^7(V_0 + V)10^{EF/2.3RT}$ *vs.* V ml of the acid added (V_0 = initial solution volume) being plotted. Breaks in the Gran plot (Fig. 3) are quite sharp and easily detected, but the first two breaks do not correspond to stoichiometric ratios and it is only for the third step, that is, the complete precipitation of the salt as pyridinium molybdophosphate, that the correct stoichiometric ratio is realized. This, however, does not affect the utility of this electrode as an indicator electrode in precipitation titrations involving pyridinium ions.

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REFERENCES

1. W. U. Malik, S. K. Srivastava, V. M. Bhandari and S. Kumar, *J. Colloid Interface Sci.*, 1974, **1**, 47.
2. W. U. Malik, S. K. Srivastava, P. Razdan and S. Kumar, *J. Electroanal. Chem.*, 1976, **72**, 111.
3. S. Glasstone, *Electrochemistry of Solutions*, p. 145. Van Nostrand, New York, 1965.
4. G. J. Moody and J. D. R. Thomas, *Talanta*, 1972, **19**, 623.
5. W. U. Malik, S. K. Srivastava and S. Kumar, *ibid.*, 1976, **23**, 323.
6. R. A. Llenado, *Anal. Chem.*, 1975, **47**, 2243.
7. G. Gran, *Analyst*, 1952, **77**, 661.

Talanta, Vol. 25, pp. 160–162. Pergamon Press, 1978 Printed in Great Britain.

ELECTROTHERMAL ATOMIC-ABSORPTION SPECTROMETRY OF ARSENIC AND ITS APPLICATION TO ENVIRONMENTAL SAMPLES

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Summary—Electrothermal atomization of arsenic with a metal micro-tube atomizer has been studied. Thiourea and thionalide were found to give effective atomization of arsenic. A method involving extraction of the thionalide complex for determining traces of arsenic in water and soil is described.

Flame atomic-absorption spectrometry of arsenic presents some difficulties because of absorption by the flame in the ultraviolet region where the most sensitive resonance lines of arsenic lie. Flameless methods have been investigated with the object of avoiding these difficulties. Chu *et al.*[1] described a flameless atomic-absorption method for arsenic determination which involved the chemical conversion of arsenic into arsine. However, Smith[2] pointed out the significant interference of various metals in the hydride system.

The atomization of arsenic with the carbon rod or graphite furnace has also been studied. However, problems caused possible interaction with the carbon were reported by Robinson *et al.*[3]

This paper describes the atomic-absorption spectrometry of arsenic with a metal atomizer and its application to environmental samples.

EXPERIMENTAL

Apparatus

Atomic-absorption measurements were made with a JASCO CT-25N grating monochromator coupled to an R431 photomultiplier tube (Hamamatsu TV Co.) and JEOL AA-HMA signal-control unit as a signal-amplifier. The monochromator was purged with nitrogen to remove atmospheric oxygen, which absorbs strongly at the wavelength used for arsenic. The output signal from the signal-control unit was displayed on an Iwatus MS-5021 Memoriscope and on a Hitachi 056-1001 recorder.

The atomizer was a molybdenum micro-tube (25 mm long and 1.5 mm bore)[4] mounted in the absorption chamber (300 ml volume) which was purged with argon at a flow-rate of 480 ml/min and hydrogen at a flow-rate of 20 ml/min.

The source of resonance radiation was an arsenic electrodeless discharge lamp operated by a 27-MHz microwave generator (Hamamatsu C977 power supply).

The light-path between the light-source and the absorption chamber, and between the chamber and the monochromator was also purged with nitrogen.

The analytical wavelengths used were 188.99 and 193.70 nm. Background absorption was compensated for. The tube temperature was measured as already described.[5]

Reagents

A stock solution of arsenic(III) was prepared by dissolving arsenic trioxide in dilute sodium hydroxide solution, and a solution of arsenic(V) by dissolving potassium arsenate in water. These solutions were used as the basis for all the dilute arsenic solutions, which were freshly prepared immediately before use.

All reagents were of analytical grade.

RESULTS AND DISCUSSION

Atomization characteristics of arsenic

In order to ascertain the atomization characteristics of arsenic, attempts were made to atomize arsenic from arsenite and arsenate. Figure 1 shows the Memoriscope traces; the micro-tube atomizer was heated for 2 sec, reaching 2200° in about 2 sec after the power had been switched on.

The arsenic compounds were dried at 200° and ashed at 300–800° before atomization. As can be seen in Fig. 1, atomization of arsenic from arsenite was easier than that from arsenate. This is understandable because the heat of formation of arsenate is higher than that of arsenite ($-\Delta H°$ = 156.6 kcal/mole for As_2O_3 and 219.4 kcal/mole for As_2O_5). Sturgeon *et al.*[6] demonstrated the atomization mechanism in the graphite furnace by means of the activation energy, obtained by plotting the logarithm of the absorbance as a function of the inverse of the absolute temperature. We have calculated the activation energy for arsenic, and found it to be nearly identical to the dissociation energy of AsO. Therefore, the most likely path to formation of gaseous arsenic atoms involves thermal dissociation of the oxide. Contributions to arsenic atomization from reduction by the molybdenum atomizer and the hydrogen in the absorption chamber may not be predominant. It was decided to try adding a sulphur-containing complexing agent, because the arsenic–sulphur bond was expected to dissociate at a lower temperature (on the basis

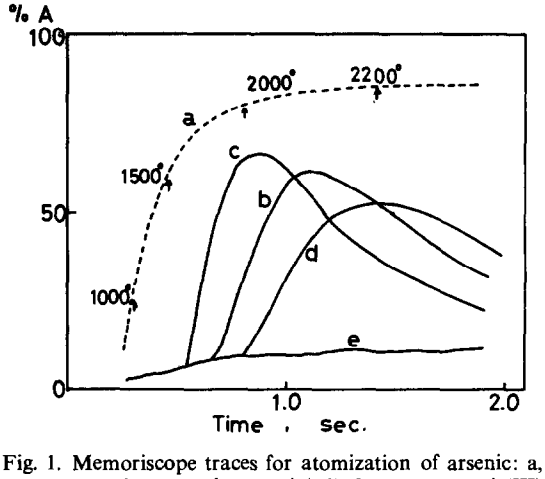


Fig. 1. Memoriscope traces for atomization of arsenic: a, temperature increase; b, arsenic(III) 2 ng; c, arsenic(III) 2 ng and thiourea 4 μg; d, arsenic(V) 2 ng; e, background (tube heated without sample).

of its heat of formation). Atomization of arsenic was found to start at lower temperature in the presence of thiourea. The times required for the attainment of the absorption maximum were 1.1 sec for pure arsenic and 0.86 sec for arsenic in the presence of thiourea. The atomization characteristics of arsenic from arsenate were similar to those for arsenite in the presence of thiourea. Urea showed no effect on arsenic atomization. The same phenomena were observed with thioacetamide. Therefore, it seems reasonable to assume that the major pathway leading to gaseous arsenic atoms by atomization in the presence of thiourea is thermal dissociation of arsenic sulphide, which has a lower heat of formation than the oxide ($-\Delta H^\circ = 35$ kcal/mole). Robinson *et al.*[3] reported the molecular absorption of arsenic resonance lines by As_4 and As_2. However, no molecular absorption was observed when a deuterium lamp was used as source. Arsenic molecules may dissociate into atoms at the temperature applied in the present work. The ashing temperature for the sample had little effect on arsenic absorption up to about 1200°.

Sensitivity and reproducibility

The absolute sensitivity under optimized conditions was found to be 1.4×10^{-11} g. The addition of thiourea improved the sensitivity by about 10%.

The precision of the determination with the micro-tube atomizer was evaluated by making repeated measurements on 2 ng of arsenic. The coefficient of variation was found to be 5%.

Interferences

The possible interference of fourteen elements was examined (Table 1). All samples were checked for background effects and absorption due to the heated micro-tube, and reagent blanks were run. The cations tested were added as their nitrates, except for antimony, selenium, tin and sodium. Tin and sodium were added as their chlorides, and the antimony solution was prepared from potassium antimonyl tartrate. The selenium solution was prepared from selenium dioxide. Enhancements or depressions of less than 5% were regarded as insignificant and are reported as zero. Only cobalt and antimony showed significant interference when present in 10-fold w/w ratio to arsenic. Interference was observed with 100-fold amounts of aluminium, bismuth, germanium, magnesium, lead and tin. The interference was reduced by the addition of thiourea, except in the case of antimony. Figure 2 shows the effects of thiourea on the interference from germanium and bismuth. Although thiourea generally reduced the interferences, it introduced interference in the case of chromium and selenium. Interference was pronounced at the 1000-fold level of added element.

Table 1. Interferences in determination of arsenic (2 ng)

Interfering element	Change in arsenic signal, %		
	10-fold amount	100-fold amount	
		Without thiourea	With thiourea
Ag	0	+6	0
Al	0	−8	0
Bi	0	−44	−8
Co	+10	0	+8
Cr	0	0	−10
Cu	0	0	0
Fe	0	0	0
Ge	0	−12	0
Mg	+9	+9	0
Na	+7	0	−6
Pb	−1	−11	0
Sb	+19	+10	−16
Se	+6	0	−6
Sn	0	−10	0

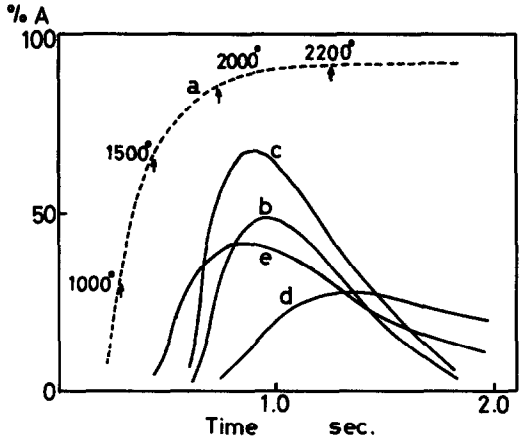


Fig. 2. Memoriscope traces for atomization of arsenic: a, temperature increase; b, arsenic(III) 2 ng and 100-fold germanium; c, arsenic(III) 2 ng, 100-fold germanium and thiourea 4 μg; d, arsenic(III) 2 ng and 100-fold bismuth; e, arsenic(III) 2 ng, 100-fold bismuth and thiourea 4 μg.

Measurement combined with extraction

Solvent extraction of arsenic was effective for elimination of interferences from matrix elements. The following extraction systems for arsenic were compared: diethyldithiocarbamate,[7] thionalide[8] and iodide.[9] Figure 3 shows the Memoriscope traces for arsenic atomized from these complexes. Arsenic was atomized at lower temperature from the thionalide complex than from the dithiocarbamate complex. The iodide complex also showed higher atomization temperature. Atomization from the thionalide complex was analogous in absorption profile to that from arsenite in the presence of thiourea. Therefore, the effect of thionalide on arsenic atomization may be identical to that of thiourea. At the ashing temperature, the metal dithiocarbamate complexes decompose to their sulphides, which give free metal atoms at the atomization temperature.[10] However, the absorption profile for arsenic from the dithiocarbamate complex resembled that for arsenite

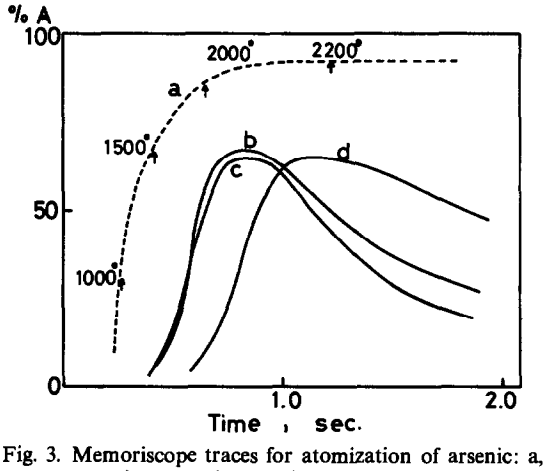


Fig. 3. Memoriscope traces for atomization of arsenic: a, temperature increase; b, arsenic(V) 2 ng and thiourea 4 μg; c, thionalide complex; d, diethyldithiocarbamate complex.

Table 2. Determination of arsenic in environmental samples

Sample	Sample taken, *ml*	Arsenic, *ppM** Added	Found
River water	50	—	1.3
	100	—	1.5
	50	2.5	4.1
Sea-water	100	—	2.6
	50	2.5	5.0
	50	5.0	7.5
Soil	0.8 (g)	—	3.5†
	0.8	0.9†	5.1†

* Parts per milliard.
† ppm.

instead of that for the thionalide. This may show insufficient formation of the sulphide at the ashing temperature. Thionalide itself dissolves in the organic solvent, whereas dithiocarbamic acid shows poor solubility. Therefore, the excess of thionalide may serve to increase formation of arsenic sulphide. Arsenic can be selectively extracted as the thionalide complex from 4*N* sulphuric acid and separated from other elements such as antimony, bismuth and copper which form their thionalide complexes at different acidity.

Application to environmental samples

Procedure for water. Transfer 25–100 ml of the sample to a separatory funnel, and add sulphuric acid and potassium iodide solution (2*M*) to give an acid concentration of 4*N* and an iodide concentration of 0.1–0.2*M* on dilution to 150 ml. After 20 min reduce the liberated iodine with the minimal amount of 0.1*M* sodium thiosulphate, add 1.5 ml of thionalide solution (1% in ethanol), then let stand for 15–20 min. Extract the arsenic thionalide complex with 5 ml of di-isopropyl ether. Separate the phases and use 50 μl of the organic phase for analysis. Prepare standards by extracting arsenic from standard solutions in distilled water by the method described.

Procedure for soil. Shake the soil sample containing 1–5 μg of arsenic with 10 ml of 1*M* hydrochloric acid at 20° for 30 min. After centrifuging, take 5 ml of the clear supernatant liquid and proceed as for water samples. Use 1 μl of the organic phase for analysis.

Some results for water and soil samples are listed in Table 2. A recovery study, through addition of known quantities of arsenic to the samples, has indicated good recovery. Because arsenic(V) is not extracted as the thionalide complex, arsenic(III) can be determined selectively, and total arsenic if iodide is used to reduce arsenic(V).

This method may be useful for the determination of traces of arsenic in biological and geological samples.

Conclusions

Effective atomization of arsenic in a metal micro-tube atomizer is expected to be achieved by the addition of thiourea to the arsenic solution or preliminary extraction of the arsenic thionalide complex. Thionalide complex extraction is recommended for environmental samples because of elimination of interference from diverse elements.

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REFERENCES

1. R. C. Chu, G. P. Barron and P. A. W. Baumgarner, *Anal. Chem.*, 1972, **44**, 1476.
2. A. E. Smith, *Analyst*, 1975, **100**, 300.
3. J. W. Robinson, R. Garcia, G. Hindman and P. Slevin, *Anal. Chim. Acta*, 1974, **69**, 203.
4. K. Ohta and M. Suzuki, *Talanta*, 1975, **22**, 465.
5. *Idem, ibid.*, 1976, **23**, 560.
6. R. E. Sturgeon, C. L. Chakrabarti and C. H. Langford, *Anal. Chem.*, 1976, **48**, 1792.
7. P. F. Wyatt, *Analyst*, 1955, **80**, 368.
8. S. Nakaya, *Bunseki Kagaku*, 1963, **12**, 241.
9. K. Tanaka, *ibid.*, 1961, **10**, 612.
10. S. Gomišček, Z. Lengar, J. Černetič and V. Hudnik, *Anal. Chim. Acta*, 1974, **73**, 97.

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EXTRACTION OF GOLD, PALLADIUM AND PLATINUM FROM CHLORIDE, BROMIDE AND IODIDE SOLUTION WITH DI-n-OCTYL SULPHIDE (DOS) IN CYCLOHEXANE

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Summary—The extraction of gold, palladium and platinum from hydrochloric acid, hydrobromic acid and iodide media by solutions of di-n-octyl sulphide in cyclohexane was examined. From distribution data it was concluded that the monosolvates $AuX_3 \cdot DOS$ and disolvates $PdX_2 \cdot 2DOS$ are extracted. Extraction of platinum was efficient only from iodide solutions; a disolvate $PtI_4 \cdot 2DOS$ was formed. The possibility of separation of gold and palladium from platinum by extraction from bromide or chloride solutions and simultaneous extraction of palladium and platinum from an iodide medium was demonstrated.

Alkyl sulphides are among the most promising extractants for the separation of noble metals. Complexes of noble metals with organic sulphides have been known for a long time, but it is only in the last decade that these reagents have been used as extractants. Nikolaev and co-workers[1–3] have shown that gold(III) and palladium(II) may be extracted from nitric and hydrochloric acid solutions with alkyl sulphides, R_2S (where R is an alkyl group of the series C_4H_9–$C_{10}H_{21}$), in benzene and other organic solvents. Silver and mercury(II) are extracted effectively from a nitric acid medium.[1,4,5] Extraction of platinum(IV) and with dialkyl sulphides is poor and that of iridium(III) and palladium (IV) very poor. Other metals are not extracted by dialkyl sulphides.

The production of organic sulphides from crude oil has facilitated their technological application as extractants and stimulated interest in this group of reagents.[3,6–9]

It is the purpose of the present investigation to obtain data concerning the extraction of noble metals with di-n-octyl sulphide (DOS) in cyclohexane from bromide (or iodide) solutions and to compare them with those for chloride solutions.

EXPERIMENTAL

Reagents

Di-n-octyl sulphide was prepared from n-octyl bromide and dehydrated sodium sulphide as described previously.[9] The crude product was distilled under reduced pressure (b.p. 137–139°/0.3 mm-g, the distillate having a refractive index of 1.463 at 20° and giving an infrared spectrum which matched that of a standard sample.

Standard $10^{-2}M$ gold(III) and platinum(IV) solutions in $4M$ hydrochloric acid (or $4M$ hydrobromic acid) were obtained by dissolving the pure metals in *aqua regia*. The solutions were evaporated several times with concentrated hydrochloric acid (hydrobromic acid) and the residue was dissolved in $4M$ hydrochloric acid ($4M$ hydrobromic acid).

Palladium(II) solutions ($10^{-2}M$ in $4M$) hydrochloric acid (or $4M$ hydrobromic acid were prepared from suitable salts by dissolving them in the appropriate acid, evaporating to dryness and redissolving in the appropriate $4M$ acid. The solutions were standardized gravimetrically with dimethylglyoxime.

Palladium(II) and platinum(IV) solutions ($10^{-2}M$) in $1M$ potassium iodide–$0.5M$ sulphuric acid were prepared from suitable salts. The solutions were standardized gravimetrically with dimethylglyoxime (Pd) and reduction with formic acid (Pt) after removal of iodide by successive evaporation with concentrated nitric and hydrochloric acids.

Other reagents used throughout this work were of analytical purity grade.

Procedure

Equal volumes of the aqueous and organic solutions were shaken for 15 min for extraction of gold and 60 min for extraction of platinum and palladium. A $10^{-3}M$ metal solution in the acid of known concentration was used as the aqueous phase, while a DOS solution of known concentration in cyclohexane was used as the organic phase. The phases were separated and the concentration of the metal was determined in one or both of them by spectrophotometric methods[10] after evaporation and mineralization (if necessary). Gold was determined by the bromide or the Brilliant Green method, and palladium by the iodide or α-furildioxime method. Platinum was determined with stannous chloride or *p*-nitrosodimethylaniline. On the basis of the results obtained the distribution coefficients of the metals, defined in terms of the ratio of total metal concentration in the organic phase to total metal concentration in the aqueous phase, were calculated. All experiments were carried out at $20 \pm 2°$.

RESULTS AND DISCUSSION

The results for the extraction of gold(III), palladium(II) and platinum(IV) from hydrochloric acid with a $0.1M$ DOS solution in cyclohexane are shown in Fig. 1. The extraction of gold is more efficient than that of palladium. Platinum is extracted from hydrochloric acid to a negligible extent. Variation of the concentration of hydrochloric acid in the range 1–$8M$ has little effect on the efficiency of the extraction. The distribution coefficients obtained for the extraction of palladium with $0.1M$ DOS in cyclohexane from hydrobromic acid are ten times those for hydrochloric acid media but the extraction of platinum and gold is similar in both media (Fig. 2.). The extraction of gold diminishes with hydrobromic acid concentration. The distribution coefficients are approximately 82 and 13 for $1M$ and $6M$ hydrobromic acid respectively. The extraction of platinum from hydrobromic acid is negligible.

It can be seen from the dependence of the distribution coefficients of palladium and platinum on the sulphuric acid concentration, at a constant concentration of potassium iodide of $1M$ (Fig. 3), that the effectiveness of the extraction increases in this medium, particularly in the case

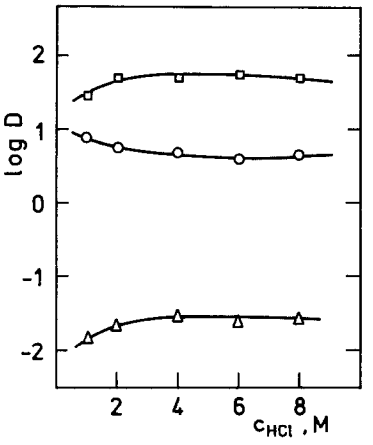


Fig. 1. Dependence of the distribution coefficients of gold (□), palladium (○) and platinum (△) on hydrochloric acid concentration for 0.1*M* DOS in cyclohexane.

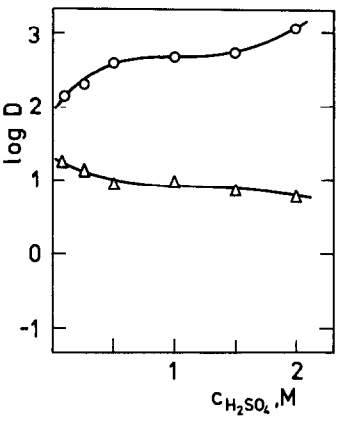


Fig. 3. Dependence of the distribution coefficients of palladium (○), and platinum (△) on acid concentration at a constant potassium iodide concentration of 1*M* for 0.1*M* DOS in cyclohexane.

of platinum. The distribution coefficients of platinum from an iodide medium are higher by a factor of 100 than those from chloride and bromide solutions. However, in this system, platinum can also be extracted as a sulphate complex (because of the mixed iodide–sulphate medium).

The dependence of the distribution coefficients of gold and platinum on the DOS equilibrium concentration in the organic phase was determined, the concentration of hydrochloric or hydrobromic acids in the aqueous phase being 2*M* . As mineral acids are practically non-extractable with DOS, the equilibrium concentration of the reagent was calculated from its initial concentration, taking into account the fraction bound to the metal. In both systems the slope of the plot of the logarithm of the distribution coefficient *vs.* the logarithm of the DOS equilibrium concentration was approximately 1 and 2 for gold and palladium, respectively, at DOS concentrations higher than 0.01*M*. In the case of the iodide medium (1*M* iodide–0.5*M* sulphuric acid) the slopes of the plots of log D *vs.* log [DOS] were approximately 2.

It has been found that at a constant DOS concentration in the organic phase (0.1*M*) the distribution coefficients of gold, palladium and platinum are nearly constant for initial metal concentrations in the range 5×10^{-3}–$1 \times 10^{-4}M$.

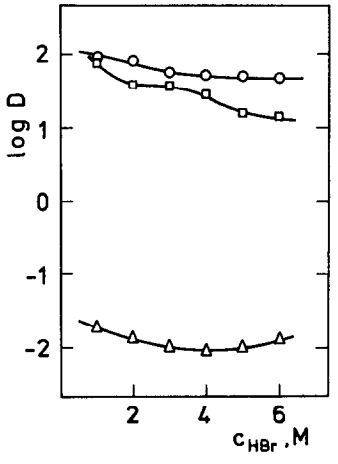


Fig. 2. Dependence of the distribution coefficients of gold (□), palladium (○) and platinum (△) on hydrobromic acid concentration for 0.1*M* DOS in cyclohexane

These results suggest that gold and palladium are extracted from hydrochloric and hydrobromic acid media as the monosolvate $AuX_3 \cdot DOS$, and disolvate $PdX_2 \cdot 2DOS$, respectively. This is in agreement with earlier data on the extraction of gold and palladium from hydrochloric acid with DOS in benzene. The results also show that palladium and platinum are extracted from an iodide medium as the disolvates. $PdI_2 \cdot 2DOS$ and $PtI_4 \cdot 2DOS$.

In DOS and other alkyl sulphides the bivalent sulphur atom has unoccupied *d*-orbitals. According to Pearson[11] they have the properties of a soft base. Such ligands form strong complexes with metal ions (or their complexes) which are soft acids, capable of donating *d*- or *p*-electrons with the formation of π-bonds. Hence dialkyl sulphides form stable complexes with Pd(II), Pt(II), Au(III), Cu(II), Ag(I), Au(I) and Hg(II), which are considered to be soft acids. Attempts to isolate alkyl sulphide complexes of platinum(IV), which exhibits intermediate hardness, failed.[12] There are no data available on the interaction of hydrogen ions with dialkyl sulphides. Hence it can be concluded that the extraction of protonated complexes of Au(III) and Pd(II) does not take place and that the extracted species are compounds containing metal–sulphur bonds.

As in halogen acid media AuX_4^- and PdX_4^{2-} occur, the distribution coefficients should diminish with increasing acid concentration when $AuX_3 \cdot DOS$ and $PdX_2 \cdot 2DOS$ are extracted. This can be clearly observed only in the case of the extraction of gold from hydrobromic acid medium.

This is probably due to the high stability constant, $K_4 = 10^{8.5}$ of the gold bromide complex,[13] compared with the value of $K_{3,4} = 10^{5.56}$ of the palladium complex.[14] The extraction of gold from bromide solutions is, however, less efficient than that from chloride solutions.

The dependence of the distribution coefficients on the acid concentration (Figs. 1–3) indicates that in the extraction system hydrochloric acid–DOS in cyclohexane, the separation of gold from platinum is more effective than the separation of palladium from platinum. Separation of gold and palladium from platinum can be done more effectively from hydrobromic acid medium. Platinum cannot be separated from palladium by extraction with DOS from iodide media.

REFERENCES

1. A. V. Nikolaev, V. G. Torgov, E. N. Gil'bert, V. A. Mikhailov, V. A. Pronin, L. G. Stadnikova and I. L. Kotlyarevskii, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1967, (6), 120.

2. V. G. Torgov, V. N. Andrievskii, E. N. Gil'bert, I. L. Kotlyarevskii, V. A. Mikhailov, A. V. Nikolaev, V. N. Pronin and D. D. Trotsenko, *ibid.*, 1969, (5), 148.
3. A. V. Nikolaev, V. G. Torgov, V. A. Mikhailov, V. N. Andrievskii, K. A. Bakovets, M. F. Bondarenko, E. N. Gil'bert, I. L. Kotlyarevskii, G. A. Mardezhova and S. S. Shatskaya, *ibid.*, 1970, (4), 54.
4. V. A. Mikhailov, S. S. Shatskaya, D. D. Bogdanova and V. G. Torgov, *ibid.*, 1976, (3), 34.
5. V. A. Mikhailov. N. A. Korol and D. D. Bogdanova, *ibid.*, 1975, (6), 29.
6. O. S. Shelovnikova, A. V. Nikolaev and R. J. Novoselov, *ibid.*, 1976, (3), 44.
7. M. F. Bondarenko, N. K. Lyapina, Yu. E. Nikitin, A. Kh. Sharipov, L. M. Zagryatskaya, V. S. Nikitina and M. A. Pais, *ibid.*, 1973, (3), 16.
8. D. M. Chizhikov, B. P. Kreingauz and G. M. Denisova, *ibid.*, 1970, (4), 120.
9. P. A. Lewis, D. F. C. Morris, E. L. Short and D. N. Waters, *J. Less-Common Metals*, 1976, **45**, 193.
10. Z. Marczenko, *Spectrophotometric Determination of Elements*, Horwood, Chichester, 1976.
11. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
12. S. E. Livingstone, *Quart. Rev.*, 1965, **19**, 386.
13. A. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, 1964
14. L. V. Companys, X. T. Morer and A. T. Carbonell, *Afinidad* 1974, **31**, 559.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH THIOBENZOYLACETONE (3-MERCAPTO-1-PHENYLBUT-2-EN-1-ONE)

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(*Received* 11 *March* 1977. *Revised* 4 *October* 1977. *Accepted* 20 *October* 1977)

Summary—The copper(II)-thiobenzoylacetone complex, extracted into benzene, is used for photometric determination of copper at 410 nm after excess of reagent has been removed by scrubbing with a buffer at pH12. The extraction is quantitative over a broad pH range (3.5–9.5). The method is highly sensitive for the determination of copper.

The spectrophotometric determination of copper with 1,1,1-trifluoro-3-(2-thenoylacetone) has been recently reported by Akaiwa *et al.*[1] They claim advantages of this method over previous methods for solvent extraction of copper with various β-diketones.[2–4] It is now shown that the solvent extraction of copper with thiobenzoylacetone (HSBA) followed by removal of the excess of reagent by scrubbing with a buffer solution of pH 12.0, without decomposing the $Cu(SBA)_2$ complex in benzene as a diluent, provides a more selective and fairly sensitive method.

EXPERIMENTAL

A stock solution of copper sulphate was prepared by dissolving 3.935 g of the analytical grade reagent in 500 ml of water containing 1% sulphuric acid, and standardized complexometrically with EDTA, PAN being used as indicator. Solutions of lower concentration were prepared by appropriate dilution. Acetate buffer of pH 6.0 was prepared by dissolving 16 g of sodium acetate in 1 litre of distilled water and acidifying with acetic acid to pH 6.0. For scrubbing, buffer solution of pH 12.0 was prepared by mixing 10 ml of 0.05*M* borax with 12.6 ml of 0.1*M* sodium hydroxide.

Thiobenzoylacetone was prepared from benzoylacetone as described earlier.[5] A $10^{-3}M$ solution in benzene was used. The reagent is preferably preserved in the refrigerator.

General procedure

Transfer a sample solution containing 1–20 μg of copper to a separatory funnel. Add 10 ml of pH 6.0 buffer, dilute with distilled water to 25 ml and shake the mixture with 10 ml of $10^{-3}M$ thiobenzoylacetone in benzene for about 10 min. After settling, run off the aqueous phase, then shake the greenish yellow organic phase twice (for 2 min) with 10 ml of pH 12 buffer to remove excess of reagent. Measure the absorbance of the copper complex at 410 nm against a reagent blank prepared similarly. Compute the amount of copper from the calibration curve.

RESULTS AND DISCUSSION

Effect of organic solvent

Various organic solvents such as benzene, toluene, xylene, chloroform, carbon tetrachloride, n-butanol, amyl alcohol and amyl acetate were tried. The absorbance of the complex was highest when benzene was used as the solvent.

Absorption characteristics

Figure 1 shows the absorption spectrum of the copper–thiobenzoylacetone complex measured against the reagent blank obtained by the procedure described, showing almost complete removal of residual HSBA from the organic phase. The spectrum of the reagent blank measured against benzene is also shown. The complex has

2. V. G. Torgov, V. N. Andrievskii, E. N. Gil'bert, I. L. Kotlyarevskii, V. A. Mikhailov, A. V. Nikolaev, V. N. Pronin and D. D. Trotsenko, *ibid.*, 1969, (5), 148.
3. A. V. Nikolaev, V. G. Torgov, V. A. Mikhailov, V. N. Andrievskii, K. A. Bakovets, M. F. Bondarenko, E. N. Gil'bert, I. L. Kotlyarevskii, G. A. Mardezhova and S. S. Shatskaya, *ibid.*, 1970, (4), 54.
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Summary—The copper(II)-thiobenzoylacetone complex, extracted into benzene, is used for photometric determination of copper at 410 nm after excess of reagent has been removed by scrubbing with a buffer at pH12. The extraction is quantitative over a broad pH range (3.5–9.5). The method is highly sensitive for the determination of copper.

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Table 1. Tolerance for various ions in determination of 10 μg of Cu(II) by extraction at pH 6.0.

Tolerance limit, μg	Foreign ion
5×10^4	Rb^+, Cs^+
1×10^4	Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, cit^{3-}, acetate$^-$, Zn^{2+}*
5×10^3	Cd^{2+}*, Pt^{4+}, Be^{2+}, I^-, SO_3^{2-}, PO_4^{3-}, F^-, $tart^{3-}$, malonate^{2-}, ReO_4^-, CrO_4^{2-}
2×10^3	Tl^+, Sb^{3+}, Rh^{3+}, Fe^{3+}*, Th^{4+}, UO_2^{2+}, Ce^{4+}, Zr^{4+}, WO_4^{2-}, $Mo_7O_{24}^{6-}$, AsO_3^{3-}, VO_3^-
1×10^3	Co^{2+}, Ni^{2+}, thiourea$^-$, ClO_4^-
5×10^2	Bi^{3+}, Ir^{3+}, Al^{3+}, SCN^-
1×10^2	Os^{6+}, Ru^{3+}, Cr^{3+}, Pb^{2+}*
None	Ag^+, Hg^{2+}, Pd^{2+}, $S_2O_3^{2-}$, $EDTA^{4-}$, CN^-, ascorbate$^-$

* Cu(II) was extracted at pH 4.0, to avoid co-extraction of these ions.

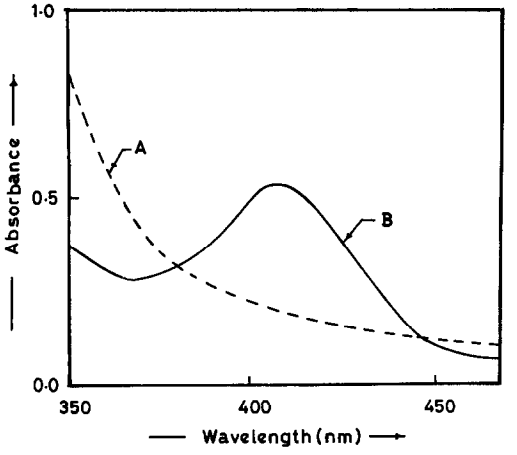


Fig. 1. Absorption spectra of (A) reagent blank *vs.* benzene (SBA $1 \times 10^{-3}M$; pH 6.0; scrubbed with pH-12 buffer) and (B) copper–SBA complex (Cu $1.56 \times 10^{-5}M$; SBA $1 \times 10^{-3}M$; pH 6.0; scrubbed with pH-12 buffer).

maximum absorbance at 410 nm. The molar absorptivity of the complex is 3.46×10^4 l.mole^{-1} cm^{-1}. The removal of the excess of reagent with buffer solution of pH 12 gave maximum difference in absorbance between the complex and the reagent blank. A similar technique was utilized by Uhlman *et al.*[4]

The calibration curve obtained at pH 6.0 is linear over the range 0.12–2.0 μg/ml at 410 nm. The sensitivity is comparable to that of earlier methods,[6] and in those methods a large excess of reagent was generally used, especially with dithizone[7] and cupral.[8] The absorbance remains constant for 48 hr, or even longer if the complex is stored in the dark or diffused light.

Reaction conditions

The extraction was found to be quantitative at pH 3.5–9.5. When copper was extracted with different volumes and concentrations of reagent it was found that a single extraction with 10 ml of $10^{-3}M$ reagent was quantitative. Varying the volume from 2.5 to 15 ml of $10^{-3}M$ reagent showed that 10 ml of reagent is adequate for complete extraction. The extraction is incomplete with a lower reagent concentration ($5 \times 10^{-4}M$). Use of a higher reagent concentration ($2 \times 10^{-3}M$) does not improve the results. Varying the shaking time showed that the extraction was complete if the equilibration time exceeded 4–5 min.

Interference

Various ions were tested for possible interference (Table 1). The tolerance limit was set as the amount of foreign ion needed to cause ± 2% error in the recovery of copper. Mercury(II), palladium(II), thiosulphate, cyanide, ascorbate and EDTA interfere seriously. The interference of bismuth and aluminium is eliminated by masking them with citric and malonic acids respectively.

The reagent provides a good method for separation of copper from nickel, cobalt(II), iron(III), cadmium and zinc, which are generally associated with it. Copper is selectively extracted with thiobenzoylacetone, followed by extraction and photometric determination of nickel with dimethylglyoxime, cobalt with 1-nitroso-2-napthol, iron with 1,10-phenanthroline, cadmium with 4-(2-pyridylazo)resorcinol and zinc with trioctylamine[6].

REFERENCES

1. H. Akaiwa, H. Kawamoto and F. Izumi, *Talanta*, 1976, **23**, 403.
2. S. M. Khopkar and A. K. De, *Z. Anal. Chem.*, 1959, **171**, 241.
3. V. M. Shinde and S. M. Khopkar, *Anal. Chem.*, 1969, **41**, 342.
4. E. Uhleman, B. Schuknecht, K. D. Busse, and V. Pohl, *Anal. Chim. Acta*, 1971, **56**, 185.
5. M. V. R. Murti and S. M. Khopkar, *Indian J. Chem.*, 1976, **14A**, 455.
6. A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand-Reinhold, London, 1970.
7. R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta*, 1953, **8**, 157.
8. G. Gottschalk, *Z. Anal. Chem.*, 1963, **194**, 321.

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SIMPLE METHOD FOR DETERMINATION OF SELENIUM IN BIOLOGICAL MATERIALS BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY USING A CARBON-TUBE ATOMIZER

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Summary—A method for determination of selenium in biological materials by flameless atomic-absorption spectrometry using a carbon-tube atomizer is described. The sample is burned by an oxygen-flask combustion procedure, the resulting solution is treated with a cation-exchange resin to eliminate interfering cations, the selenium is extracted with dithizone in carbon tetrachloride and the resulting selenium dithizonate is combined with nickel nitrate in the carbon tube to enhance the sensitivity for selenium and avoid volatilization losses. The method measures selenium concentrations as low as 0.01 μg/g with a relative standard deviation of 8%.

The most commonly used method for determination of selenium in biological materials is a fluorimetric procedure using 3,3'-diaminobenzidine[1,2] or 2,3-diaminonaphthalene.[3] The major difficulty with this method is that diaminobenzidine is a carcinogen and stringent regulations must be adhered to in order to ensure its safe use. In addition, the method is very time-consuming and there are some difficulties in the colour development. Recently flameless atomic-absorption spectrometric (AAS) methods using a carbon tube atomizer for the determination of selenium in water and waste water have been reported.[4,5] The use of such methods for determination of selenium in biological materials is impossible because of the suppression of the selenium absorbance by other species present (*e.g.*, Cu, Hg), and of severe scattering in the 180–220 nm region by inorganic salts which are highly concentrated in the digested solution of the sample. The use of ion-exchange resins for eliminating this problem in the determination of selenium in water has been reported,[6] but in the case of biological samples, the selenium in the sample is so diluted with digestion reagents and eluent that the sensitivity is lowered, and interference by inorganic anions cannot be eliminated. Mabuchi and Nakahara[7] have applied the selective extraction of selenium(IV) with dithizone in carbon tetrachloride to separate selenium from inorganic cations in 6*M* hydrochloric acid (except Cu, Ag, Te, Au, Hg and Bi). Martin *et al.*[5] attempted to prevent the volatilization loss of selenium in the carbon tube during the ashing stage by adding nickel nitrate to the digested solution.

The method described here utilizes flameless AAS, with pretreatment of the sample. The sample is burnt in an oxygen flask[8] and the resulting solution is treated with a cation-exchange resin to eliminate interference from cations. Selenium is extracted with dithizone in carbon tetrachloride to concentrate it and to eliminate interference from anions. The selenium dithizonate is combined with nickel nitrate in the carbon tube to enhance the sensitivity for selenium and to avoid volatilization losses of selenium during the ashing stage.

EXPERIMENTAL

Reagents

All solutions were prepared from distilled water and analytical grade reagents [except the standard selenium(IV) solution].

Standard selenium(IV) solution, 1000 *ppm*. Prepared and further diluted with 4*M* hydrochloric acid to give concentrations of 1.0, 0.5, 0.3, 0.1 and 0.05 ppm before use.

Standard selenium(VI) solution, 1000 *ppm*. Prepared by dissolving 1.835 g of selenic acid in water and diluting to 1000 ml. An aliquot of this solution is diluted with 4*M* hydrochloric acid to give concentrations of 1.0, 0.5, 0.3, 0.1 and 0.05 ppm before use.

Nickel solution, 5%. Prepared by dissolving 24.78 g of nickel nitrate hexahydrate in water and diluting to 100 ml. This solution is further diluted with water to give concentrations of 1.0, 0.8, 0.5, 0.1 and 0.05% nickel.

Dithizone solution, 0.01%. Prepared by dissolving 50 mg of refined dithizone in 500 ml of carbon tetrachloride.

Cation-exchange resin. Amberlite IR-120, converted into the hydrogen form by treatment with hydrochloric acid.

Hydroxylamine hydrochloride solution, 20%.

Apparatus

A Hitachi Model 308 atomic-absorption spectrometer, equipped with a Hitachi Model HFA heated-graphite atomizer and a deuterium background-corrector, was used. A Hitachi Model 056 recorder (10 mV range) was used to record peak-heights. A Jintan 50-μl microsyringe was used for injecting test solutions into the carbon tube. A Finnpipett 5–50-μl micropipette was used for injecting nickel nitrate solutions into the carbon tube.

Instrument settings. The 196.0 nm selenium resonance line was used. The line-source was a Hamamatsu selenium hollow-cathode lamp operated at 8 mA. Background correction was used for all measurements. Control settings on the HFA were experimentally optimized and provided the following drying, ashing and atomizing times and temperatures: dry at 100° for 30 sec, ash at 600° for 30 sec, atomize at 2500° for 10 sec. Argon was used as the furnace purge-gas at a flow-rate of 0.5 l./min.

Procedure

Drying and combustion of samples. Blood: 1 ml was added to 70 mg of absorbent cotton which was suspended by thread in a drying oven for 12 hr at 60°. Viscera and flesh: 1 g of the sample was taken on a piece of Japanese paper (5 cm^2) and dried for 12 hr at 60°.

Preparation of test solution. The dried sample was burnt in the oxygen flask containing 20 ml of 0.01*M* hydrochloric acid. The solution was then passed through a 1 × 10 cm cation-exchange resin column and the column was rinsed with 10 ml of water. To the combined solution were added

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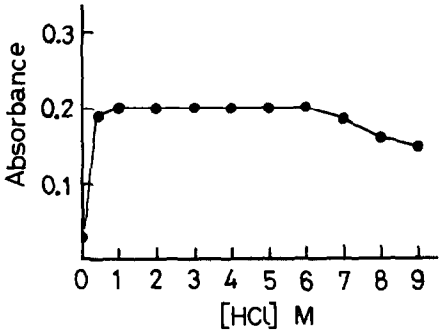


Fig. 1. Effect of acidity on the extraction of selenium with 0.01% dithizone solution in carbon tetrachloride; Se, 10 ng.

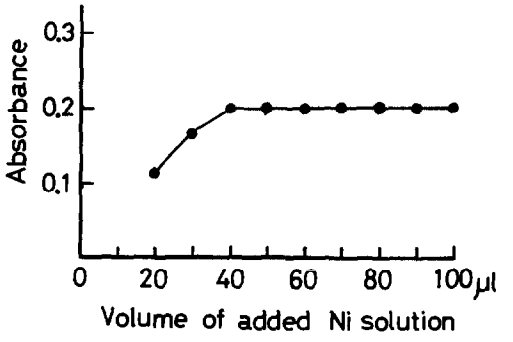


Fig. 3. Effect of volume of added 0.1% nickel solution on sensitivity; Se 10 ng.

2 ml of 20% hydroxylamine hydrochloride solution and 10 ml of conc. hydrochloric acid and the mixture was boiled for 5 min to reduce any selenate. The solution was cooled to room temperature, transferred to a separating funnel (the hydrochloric acid concentration of the resulting solution being *ca.* 3*M*), and the selenium extracted with 1 ml of 0.01% dithizone solution in carbon tetrachloride.

Analysis. Aliquots of the extract (20 µl) were injected into the carbon tube with a microsyringe. The carbon tetrachloride was evaporated by heating for 20 sec at 100°, 50 µl of 0.1% nickel solution were added to the residue and the selenium was determined.

RESULTS AND DISCUSSION

Extraction behaviour of selenium(IV)

Figure 1 shows the atomic absorption of selenium when the concentration of hydrochloric acid in the aqueous phase is varied before extraction of the selenium with dithizone in carbon tetrachloride. In the concentration range 1–6*M* hydrochloric acid the selenium absorbance remains constant so the hydrochloric acid concentration is not critical.

Effect of nickel on sensitivity

In order to prevent loss of selenium at the ashing stage it is necessary to add nickel.

Ashing conditions. Figure 2 shows the relationship between selenium absorbance and ashing temperature. In the absence of nickel, loss of selenium during the ashing stage begins at about 400° and the sensitivity drops very sharply from that point. With addition of nickel, loss of selenium does not occur until 900° and then the sensitivity falls gradually. Figure 3 shows the relationship between selenium absorbance and the volume of added 0.1% nickel solution. Satisfactory results were obtained for the effect of nickel on selenium absorbance when 40 µl of 0.1% nickel solution were added to 20 µl of the selenium dithizonate solution in carbon tetrachloride.

A nickel concentration in the range 0.1–0.5% gives a constant absorbance. When the concentration of nickel is 1.0%, incompletely ashed nickel nitrate or dithizone causes severe background absorption, exceeding the compensating capabilities of the deuterium background-corrector.

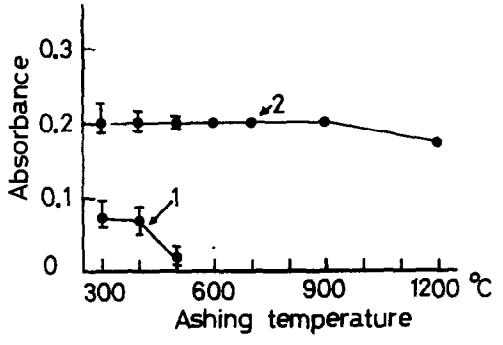


Fig. 2. Relationship between ashing temperature and absorbance of selenium. Curve 1: Se 10 ng. Curve 2: Se 10 ng + 50 µl of 0.1% Ni solution.

Interference study

Some cations (Cu, Ag, Te, Hg and Bi) show the same behaviour as selenium in the extraction stage. These cations suppress the selenium absorbance, so that separation of selenium with a cation-exchange resin is necessary. A column containing 10 ml of IR-120 cation-exchange resin in the hydrogen form was found to be satisfactory, the selenium being completely separated from the interfering cations without loss (see Table 1).

Reduction of Se(VI) to Se(IV)

It is probable that Se(VI) is present in the solution obtained from the oxygen-flask combustion. However, dithizone reacts only with Se(IV) so it is necessary to ensure that all the selenium is in the quadrivalent state. The selenium solution obtained after ion-exchange (in at least 3*M* hydrochloric acid) was treated with 2 ml of 20% hydroxylamine hydrochloride and boiled for approxi-

Table 1. Suppression effects on Se absorbance of diverse ions

Element	Added, µg	Suppression of Se absorbance, % A*	B†
Cu	5.0	0	0
	50.0	10	0
Bi	50.0	0	0
Hg	1.0	0	0
	5.0	10	0
	50.0	40	0
Ag	0.1	0	0
	1.0	10	0
	5.0	30	0
	50.0	70	0
Te	5.0	0	0
	50.0	20	0

* Determined without treatment of cation with ion exchange resin.

† Determined after treatment of cation with ion exchange resin.

Se, 0.1 µg.

Table 2. Analytical results of samples

Sample		Se added, μg	Found, μg	Mean, μg	Recovery, %	C.V, %
Human blood	1 ml	0	0.21, 0.20, 0.19 0.19, 0.20	0.20	96	4.2
	1 ml	0.5	0.67, 0.67, 0.69 0.69, 0.70	0.68		2.0
Tunny	1 g	0	0.23, 0.23, 0.25 0.28, 0.26	0.25	96	8.5
	1 g	0.5	0.71, 0.72, 0.78 0.71, 0.75	0.73		4.2
Pig liver	1 g	0	0.64, 0.60, 0.72 0.60, 0.68	0.65	93	8.0
	1 g	1.0	1.60, 1.56, 1.56 1.52, 1.64	1.58		2.8
Pig kidney	0.25 g	0	0.42, 0.39, 0.37 0.39, 0.37	0.39	97	5.2
	0.25 g	0.5	0.86, 0.88, 0.88 0.85, 0.90	0.87		2.2

mately 5 min to reduce Se(VI) to Se(IV). The calibration curve for standard Se(VI) solutions treated in this way was identical to that for standard Se(IV) solutions.

Application to sample analysis

Table 2 shows results obtained for various types of sample. The recovery values were 93–97% obtained for samples spiked with selenium and the relative standard deviation was 2–4%. According to the method proposed here, 0.01 μg/g levels of selenium can be accurately determined.

Acknowledgement—The author wishes to express his thanks to the Director of the Department of Chemistry, Mr. K. Katsumura, for permission to publish this paper.

REFERENCES

1. F. B. Cousins, *Australian J. Exp. Biol. Med. Sci.*, 1960, **38**, 11.
2. V. B. Dye, E. Brettauer, H. J. Seim and C. Blincoe, *Anal. Chem.*, 1963, **35**, 1687.
3. C. A. Parker and L. G. Harvey, *Analyst*, 1962, **87**, 558.
4. R. B. Baird, S. Pourian and S. M. Gabrielian, *Anal. Chem.*, 1972, **44**, 1887.
5. T. D. Martin and J. F. Kopp, *At. Absorption Newsletter*, 1975, **14**, 109.
6. E. L. Henn, *Anal. Chem.*, 1975, **47**, 428.
7. H. Mabuchi and H. Nakahara, *Bull. Chem. Soc. Japan*, 1963, **36**, 151.
8. K. Katsumura, M. Ishizaki, S. Ueno, T. Sasamoto, *J. Food Hyg. Soc. Japan*, 1973, **14**, 137.

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COULOMETRIC INVESTIGATION OF THE DRYING CONDITIONS OF HIGH-GRADE IRON ORES FOR CHEMICAL ANALYSIS*

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(*Received* 1 *June* 1977. *Accepted* 1 *September* 1977)

Summary—Drying conditions for several iron ores have been investigated by the coulometric microdetermination of water. Samples, which were heated in an atmosphere of dry argon at 110° for 3–4 hr and cooled, usually evolved less than 0.015% of water during a further 1 hr of heating. Therefore the difference in water content of the sample thus treated did not significantly influence the analytical results for total iron. Some magnetites and sintered pellet could be dried readily by heating for 2 hr in dry argon. Heating of samples of high water content for too long is not advisable as they may evolve some combined water.

Recently, Yoshimori and Tanaka[1] proposed a method for the determination of total iron in iron ores by precise coulometric titration. Although they obtained very high precision ($S_R \simeq 0.012\%$), the errors of the results were more than twice as large as those for the electrical measurement. They pointed out that one of the sources of error was the degree of dryness of the sample. For example, if there is 0.1% residual moisture in a "dried" sample, the result for total iron in the sample is 0.1% (relative) low. This corresponds to 0.06% Fe for an iron ore containing 60.00% total iron and exceeds the error of the precise coulometric titration.

* Presented, in part, at the International Conference for Analysis of Geological Materials, Prague, August 1976.

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REFERENCES

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2. V. B. Dye, E. Brettauer, H. J. Seim and C. Blincoe, *Anal. Chem.*, 1963, **35**, 1687.
3. C. A. Parker and L. G. Harvey, *Analyst*, 1962, **87**, 558.
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Summary—Drying conditions for several iron ores have been investigated by the coulometric microdetermination of water. Samples, which were heated in an atmosphere of dry argon at 110° for 3–4 hr and cooled, usually evolved less than 0.015% of water during a further 1 hr of heating. Therefore the difference in water content of the sample thus treated did not significantly influence the analytical results for total iron. Some magnetites and sintered pellet could be dried readily by heating for 2 hr in dry argon. Heating of samples of high water content for too long is not advisable as they may evolve some combined water.

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There are two types of water in iron ores. One is the water adsorbed on the surface of sample particles. The other is chemically combined water in the ore, and this may be removed by heating the sample at rather higher temperature. Both types are usually determined by heating the sample to constant weight at appropriate temperature.[2-4]

To evaluate the error due to the water content of a sample and also to find a means for distinguishing the two types of water, the method for the coulometric microdetermination of water proposed by Yoshimori *et al.*[5-8] was adopted.

According to Yoshimori,[9] the following factors are relevant to the efficiency of drying the sample: (1) the amount of sample, (2) the particle size, (3) the area and thickness of the sample layer, (4) the heat content of the container, (5) the atmosphere in the heating oven (mechanically circulated or not), (6) the temperature and length of heating, (7) the cooling of the heated sample (desiccant and desiccator) and (8) hygroscopic contamination of the dried sample during weighing. Conditions for (1)–(5) may be decided by internationally agreed procedures (for example, those of the International Standard Organization, ISO).

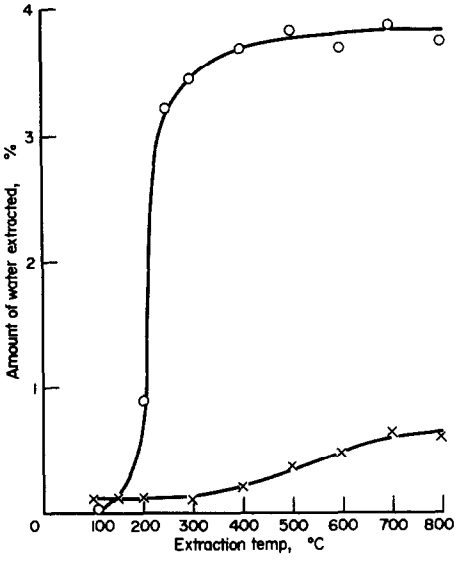


Fig. 1. The amounts of water extracted at various temperatures. Curve 1 ×——×: Texada magnetite. Curve 2 O——O: Rompin haematite (dried once at 110°C for 2 hr).

However, the handling of the small amounts of sample taken for the determination of iron should be identical in the collaborating laboratories so that the drying conditions are the same. Therefore, conditions (6) and (7) should be decided and investigated more precisely and minutely. Thus, the method for the determination of water, by which the drying conditions of standard reference materials for titrimetric analysis were investigated,[8] was applied here as described below.

EXPERIMENTAL

Apparatus and reagents

The apparatus and reagents used for the extraction and the coulometric determination of water were the same as those reported previously.[8]

Procedure

The procedure was also fundamentally the same as that already described.[8] Owing to the presence of combined water in the sample, however, the heating temperature for the extraction of residual water was changed as shown below. The sample (0.2 g) in a quartz boat was first heated at 110° for various periods of time in thoroughly dried argon (first heating). During this period and the second heating (described below), the argon by-passed the U-tube containing the desiccant. Then the sample was taken out of the furnace, and cooled for 60 min. During this cooling period, argon was allowed to flow through the U-tube containing the desiccant. The sample thus treated was in nearly the same condition as that of a sample which had been heated once and then cooled in a desiccator.[8] After that, the sample was again introduced into the furnace, and heated at the same temperature (second heating). The amount of water extracted by the second heating was determined by coulometry.[7,8]

The standard samples prepared by the Iron and Steel Institute of Japan were used throughout the investigation.

RESULTS AND DISCUSSION

In a preliminary experiment, the amounts of water extracted by the first heating of two samples (magnetite from Texada and haematite from Rompin) at various temperatures were determined and the results are shown in Fig. 1. The curves in the figure indicate that the hygroscopic moisture in this magnetite may be determined rather easily but that in the haematite can not. The haematite should therefore be dried under well-controlled conditions.

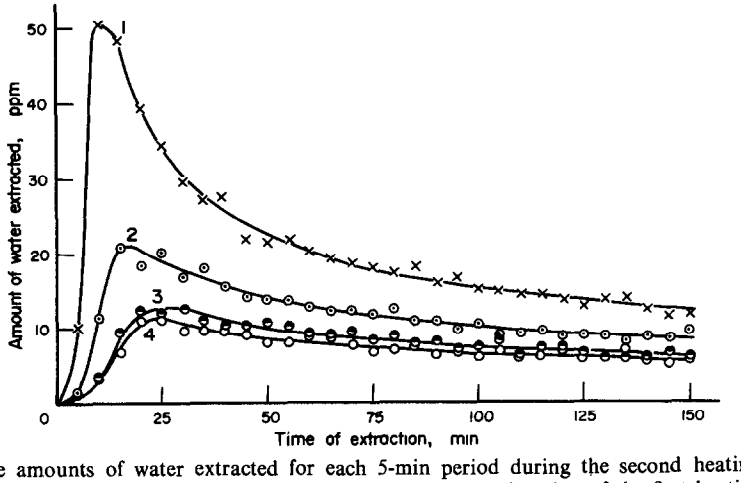


Fig. 2. The amounts of water extracted for each 5-min period during the second heating. Sample: Rompin haematite. The numbers of the curves indicate the duration of the first heating (hr).

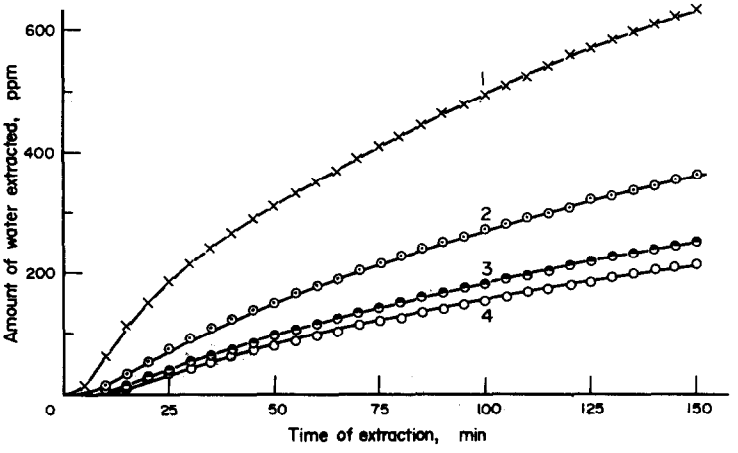


Fig. 3. The total amounts of water extracted by the second heating (calculated from the curves of Fig. 2) Sample: Rompin haematite. The numbers of the curves mean the same as in Fig. 2.

The other problem with such hygroscopic samples may arise during the cooling. The dried sample may absorb or release water in the atmosphere of the desiccator. Therefore, the procedure previously given was used here, and the amounts of water extracted by the second heating were determined.

Figure 2 shows the curves for extraction of water from a haematite sample (Rompin) by the second heating. The numbers on the curves indicate the length (hr) of the first heatings. They show the following. (1) The evolution of the water from the sample by the second heating began 5–10 min after the introduction of the cooled sample, and reached a maximum after 20 min. This indicates that the temperature of the cooled sample did not reach that of the furnace within the first 10 min. Therefore, if the sample is to be brought to constant weight by repeated heating, each heating time should be longer than about 40 min. Of course, this time interval may be affected by the heating conditions (the furnace, the sample container, the amount of sample *etc.*), and a small amount of sample is preferable. (2) The length of heating should not be longer than 1 hr in such a dry atmosphere,[9] otherwise the combined water is slowly extracted on further heating.

The cumulative amounts of water removed, calculated for the curves in Fig. 2, are shown in Fig. 3. The difference in the amounts of water extracted between 3 and 4 hr of heating was less than that between 2 and 3 hr. Therefore, the adsorbed water was nearly all removed from the sample by the first 3 hr of heating. Thus, if the sample was first heated for 3–4 hr and weighed, then heated a further 1 hr to attain constant weight, the decrease in the sample weight caused by the second heating was usually less than 0.015%, and decrease in weight when a 3-hr initial heating was used was less than 0.005% more than that for a 4-hr initial heating. Therefore, the difference in the sample weight does not significantly influence the results for the total iron content.

The relationships between the first heating time and the amounts of water extracted by the second heating are shown in Fig. 4, for two haematites. Constant weight is more easily attainable for this sample and the conclusion is the same as above. Similar results were obtained for sintered pellet (Marcona haematite) with desiccants of different power (Fig. 5). The curves indicate the following. (1) The sintered pellet is not hygroscopic, and 2 hr of heating suffices for constant weight to be attained; (2) there are differences in performance between desiccants of the same kind but obtained from different suppliers. When a powerful desiccant was used, however, the difference was only some tens of ppm, and probably would not influence the results for total iron content.

Results obtained with some local magnetite samples are shown in Figs. 6 and 7. They are similar to those shown in Figs. 3 and 4 respectively. The Dungun ore contained nearly the same amount of water as the Rompin haematite and the conditions for drying it must be carefully con-

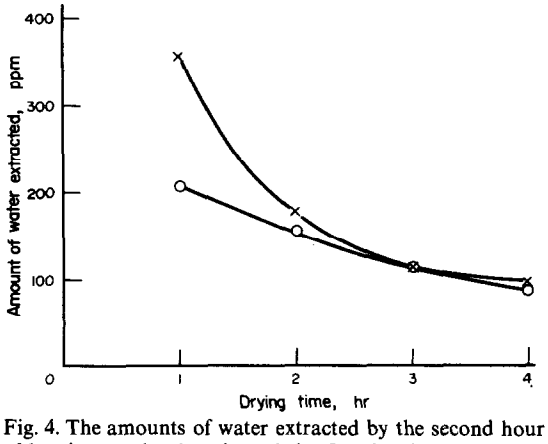


Fig. 4. The amounts of water extracted by the second hour of heating *vs.* the duration of the first heating. ×——×: Rompin haematite. O——O: Indian haematite.

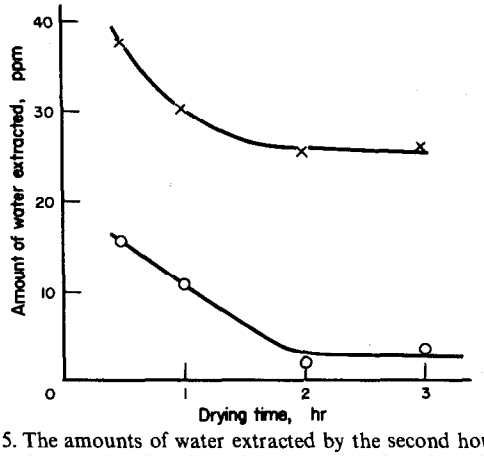


Fig. 5. The amounts of water extracted by the second hour of heating *vs.* the duration of the first heating. Sample: sintered pellet (Marcona). ×——×: $Mg(ClO_4)_2$ producer No. 1. O——O: $Mg(ClO_4)_2$ producer No. 2.

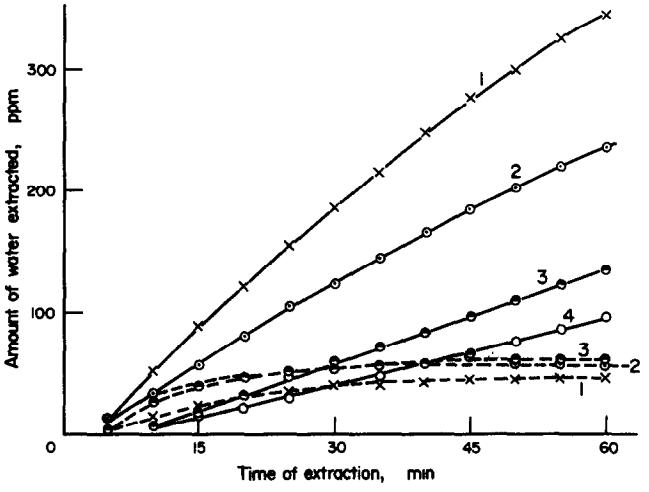


Fig. 6. The total amounts of water extracted by the second heating. The numbers of the curves mean the same as those of Fig. 2. Full line: Dungun magnetite. Broken line: Texada magnetite.

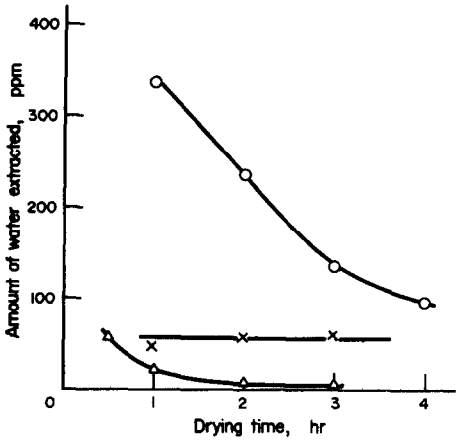


Fig. 7. The amounts of water extracted by the second hour of heating *vs.* the duration of the first heating. O——O: Dungun magnetite. ×——×: Texada magnetite. △——△: Iron sand (Philippine).

trolled. The magnetites from the Texada mine and the iron sand released water more easily. Heating for 2 hr in a dried atmosphere was enough for constant weight to be reached. As shown by curve 1 in Fig. 1, the combined water was not released from Texada magnetites at such a low temperature. Even for the Dungun ore, however, the difference between the amounts of water extracted from samples heated continuously for 3 and for 4 hr was less than 50 ppm, which does not significantly affect the results of total iron content in an iron ore.

Before conclusions are drawn, it should be emphasized that all the samples considered were heated in extremely dry argon and then cooled without exposure to atmospheric moisture. Therefore, the first heating should be prolonged if the sample is dried even in an ordinary fan-assisted convection oven. These problems have already been discussed elsewhere.[9,10]

Strictly speaking, hygroscopic iron ores such as many haematites and some types of magnetite should be dried under well-controlled, and individually established, conditions for the oven and atmosphere. For a very dry atmosphere and less than 0.5 g of sample, however, the results in this paper should give useful guidelines.

CONCLUSION

Samples of iron ores should be dried by heating less than 0.5 g for 3–4 hr in a very dry atmosphere, at a well-controlled temperature. The heating time of the second heating used to make sure of reaching constant weight should be at least 40 min. A powerful desiccant, *e.g.*, anhydrous magnesium perchlorate, should be used in the desiccator.

Some magnetites and iron sands may be dried very easily, and prolonged heating has no harmful influence. Very long heating of hygroscopic samples, however, may result in the evolution of combined water in appreciable amounts. Therefore, either prolonged or repetitive heating to reach constant weight is not advisable for hygroscopic samples.

In every case, the difference in the dryness of an iron ore does not influence the result for total iron content, if the sample is dried under well-controlled conditions.

REFERENCES

1. T. Yoshimori and T. Tanaka, *Talanta*, 1975, **22**, 33.
2. *International Standards* ISO 2596–1973(E) and ISO 3087–1974.
3. *ASTM Standards*, Part 12, E246–68, 1976.
4. G. E. F. Lundell, J. I. Hoffman and H. A. Bright, *Chemical Analysis of Iron and Steel*, Wiley, New York, 1931, p. 528.
5. T. Yoshimori and S. Ishiwari, *Bull. Chem. Soc. Japan*, 1969, **42**, 1282.
6. *Idem*, *Talanta*, 1970, **17**, 349.
7. T. Yoshimori, S. Ishiwari, Y. Watanabe, T. Harada and S. Yamada, *Trans. Japan Inst. Metals*, 1973, **14**, 396.
8. T. Yoshimori and N. Sakaguchi, *Talanta*, 1975, **22**, 233.
9. T. Yoshimori, *ibid.*, 1975, **22**, 827.
10. *Idem*, *Z. Chem.* (*Leipzig*), in the press.

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SOURCES OF COPPER AND CADMIUM CONTAMINATION IN SMALL BIOLOGICAL SAMPLES

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Summary—Copper and cadmium contamination is investigated in this work, with standard reference material No. 1571 (orchard leaf) from the National Bureau of Standards. Consideration is given to possible sources of contamination during the sampling and handling of small biological samples. Acid-washing techniques useful in removing potential contaminants are also discussed. Particular emphasis is placed on the contamination problems related to the analysis of micro-samples.

Studies of the biogeochemical behaviour of trace metals often require the analysis of small biological samples. This is particularly true of metal-uptake experiments involving phytoplankton and zooplankton. Experiments of this type rarely produce samples larger than a few milligrams dry weight. Since samples of this size may contain only a few nanograms of the metal of interest, contamination is a major concern, as is analytical sensitivity.

Heated graphite-furnace atomic-absorption or other similar flameless spectrophotometric techniques provide sensitivities not obtainable by flame techniques,[1,2] and can be used for direct analysis of solid samples.[3] However, sample homogeneity is necessary for the result to be reproducible. Since inhomogeneity in biological samples precludes this approach, a method for the destruction of organic matter that is dependable, fast and non-contaminating is needed. Low-temperature ashing systems have been used by a number of workers and may meet these requirements.[4–6]

This paper describes procedures employing low-temperature ashing followed by flameless atomic-absorption analysis that we have found to be successful in dealing with small biological samples resulting from metal-uptake studies on phytoplankton and zooplankton. During the evaluation of these procedures consideration was given to problems with experimental, sampling and analytical contamination of samples in relation to sample size and analytical sensitivity.

EXPERIMENTAL

Apparatus

An LFE model 505 low-temperature ashing system using quartz crucibles (3 cm in diameter, 1.5 cm high) was employed. Ultrapure water was made from distilled water by redistilling in a quartz sub-boiling still (model PB-5) available from Quartz Products Corporation. All atomic-absorption work was done with a Perkin–Elmer model 403 atomic-absorption system equipped with a deuterium background corrector and an HGA-2000 heated graphite furnace.

Reagents

The high-purity nitric and hydrochloric acids used and standard reference material No. 1571 (orchard leaves) were obtained from the National Bureau of Standards.

Procedure

In studies of the natural levels of metals in micro-organisms (phyto- and zooplankton) contamination must be taken into account at all stages from sample collection to final determination. Non-metallic sampling gear, non-metallic water-pumping systems, paint chips from ships' hulls, *etc.* become of major importance in collection of uncontaminated samples. Often, however, less obvious factors may develop into major contamination problems, but an exhaustive list of possible sources of contamination would be impractical here.

Containers used for culture growth must be made of a non-contaminating material. Teflon, which is ideal for trace metal work, is unsuitable because of its opacity. Plastic culture containers are suitable only if they can withstand treatment with dilute acids which remove metal deposits. Glass is therefore normally used but only after it has been soaked overnight in 0.05% hydrochloric acid and rinsed with distilled water. Some contamination is usually unavoidable, necessitating the use of as many control cultures as feasible in order to establish a range of ambient metal concentrations.

At the completion of the metal–culture experiment the organisms must be removed from the system. If these are handled improperly, erroneously high results may be obtained. Nylon mesh net may be used for gathering zooplankton from culture systems, but the net should be rinsed with dilute (0.05%) nitric acid before use. Phytoplankton may be concentrated by centrifugation or by filtration. Only acid-washed Teflon or polypropylene centrifuge tubes should be used. Filtration techniques are advisable only if the filters have been acid-washed and checked for contamination levels. After collection the samples are placed in acid-washed polyethylene vials and freeze-dried before analysis.

Acid-washing techniques

The acid-washing procedures described here closely follow those described by Patterson and Settle.[7] All Teflon ware is initially cleaned by soaking in hot concentrated reagent-grade nitric acid for three days. The Teflon is then rinsed with water obtained by sub-boiling distillation in quartz and placed in hot 0.05% NBS nitric acid for three days more. It is then removed from the dilute nitric acid, rinsed as before and stored in polyethylene bags. After the initial cleaning, a one-day soak in concentrated nitric acid followed by three days in dilute acid usually suffices. Polyethylene and polypropylene are cleaned in a similar manner except that hydrochloric acid is used instead of nitric.

Filter-washing techniques have been investigated by Wallace *et al.*[8] These workers examined acid-leaching procedures for reducing trace-metal levels in Whatman and Nucleopore filters. The filters were soaked for 24 hr in 1*M* NBS nitric acid and rinsed with the quartz-distilled (sub-boiling) water. Similar work in this laboratory indi-

cates that the copper remaining in the filter after cleaning approximates the value reported by Wallace (0.23 ± 0.07 ng/cm^2), but the cadmium was about an order of magnitude higher than the 0.012 ± 0.006 ng/cm^2 reported[8] earlier.

Sample preparation

Freeze-dried biological microsamples are weighed into clean quartz beakers. These beakers are cleaned as described above for Teflon, with the exception that they are stored in the dilute nitric acid. After weighing, the samples are ashed in a low-temperature asher for 16 hr (overnight) at 150 W. The resulting residue is dissolved in 5.0 ml of 10% NBS hydrochloric acid and placed in a clean polyethylene vial. The samples are then analysed by atomic-absorption spectrometry using a heated graphite furnace.

RESULTS AND DISCUSSION

The possible contamination of biological micro-samples during analysis was investigated by using NBS standard reference material No. 1571 (orchard leaves). Small portions (1–5 mg) were weighed accurately and carried through the procedure described above, as if they were cultured phytoplankton. Replicate analyses of the orchard leaf standard, with low-temperature ashing and wet-ashing with concentrated nitric acid were performed in order to establish a comparison of the two techniques. After destruction of organic matter by either technique the residue was dissolved with 10% hydrochloric acid and diluted to 5.0 ml in a Pyrex standard flask. These solutions were subsequently analysed for copper and cadmium by flameless atomic absorption. The copper concentrations found (12 ppm) agreed with the NBS certified value. However, as shown in Table 1, serious cadmium contamination (about an order of magnitude) existed. There were no significant differences between the results for low-temperature and wet-ashing. Most of the contamination thus appeared to have a common source. Investigation of the Pyrex flasks and the Pyrex boats used in the low-temperature asher indicated that this glassware was the source of the contamination. Table 2 shows the leachable cadmium found in the 5.0-ml Pyrex flasks before and after cleaning with concentrated nitric acid. This was established by washing the flasks with 5.0 ml of 10% hydrochloric acid and determining the amount of cadmium in the wash. Although these standard flasks had previously been cleaned, they were not used repeatedly as during the study shown in Table 1. This appeared to influence markedly the amount of leachable cadmium in the flask. However, from the data presented in Table 2 it appears that even after soaking in hot nitric acid for a week the flasks continued to be a major source of cadmium contamination. King *et al.*[9] and Struempler[10] have investigated the adsorption characteristics of cadmium on borosilicate glass and found that all of the cadmium adsorbed from dilute solutions is desorbed by lowering the pH. Their work, however, did not include acid-leaching studies at such levels as were used here.

Table 2. Leachable cadmium found in Pyrex standard flasks

Flask	Initial Cd found, *ng*	Final Cd found*, *ng*
A	82	1.5
B	38	0.96
C	26	1.3
D	49	0.30
E	50	2.1

* After soaking for 1 week in hot nitric acid.

To eliminate the use of the Pyrex flasks an Oxford macro-pipette was used to deliver the 10% hydrochloric acid used to dissolve the sample residues. Volume errors were insignificant in comparison to the contamination arising when Pyrex flasks were used. Other sources of contamination include the polypropylene tips used with the Oxford pipettes. Benjamin and Jenne also reported copper contamination from plastic tips.[11] The tips must therefore also be cleaned as described above, before use.

Additional analyses of standard reference material No. 1571 were made by the analytical procedure described above. These analyses included use of a low-temperature ashing system, wet-digestion with doubly distilled NBS and reagent-grade nitric acid for the decomposition of organic matter. The results shown in Table 3 indicate that the low-temperature ashing system or wet-ashing with NBS-quality nitric acid is imperative for reliable results to be obtained.

CONCLUSIONS

During the acid-leaching of the Pyrex flasks sodium ions may have been released. Culver and Surles have reported that sodium chloride causes a positive interference at the Cd 228.8-nm line when non-flame atomizers are used for atomic-absorption analysis.[12] These workers also reported that a continuum source may be used to compensate for non-atomic background absorption and they demonstrated

Table 1. Observed cadmium concentrations in NBS standard reference material No. 1571 (orchard leaf)

Sample weight, *mg*	Method	Total Cd found *ng*	*ppm*
5.24	LTA	6.18	1.18
6.60	LTA	17.2	2.68
5.60	LTA	5.10	0.91
6.43	LTA	8.68	1.35
5.27	LTA	10.0	1.90
6.42	WA	7.51	1.17
5.58	WA	6.92	1.24
5.07	WA	15	2.96
5.82	WA	11.90	2.06
5.21	WA	5.52	1.06
NBS certified value			0.11 ± 0.02

LTA = low-temperature ashing.
WA = wet-ashing.

Table 3. Cadmium concentrations found in NBS orchard leaf standard without the use of Pyrex standard flasks

Sample weight, *mg*	Method	Cd, *ppm*	Sample weight, *mg*	Method	Cd, *ppm*
5.57	1	0.08	4.51	2	0.11
8.55	1	0.10	5.42	2	0.15
4.78	1	0.12	5.96	2	0.13
5.74	1	0.10	7.43	2	0.11
5.44	1	0.13	7.21	2	0.10
5.60	1	0.14	7.13	3	1.88
11.19	1	0.13	5.00	3	2.72
5.52	1	0.14	5.77	3	1.70
6.55	1	0.12	5.00	3	2.56
4.56	1	0.12	6.00	3	2.53

[1] Low-temperature ashing.
[2] Wet-ashing with NBS nitric acid.
[3] Wet-ashing with reagent-grade nitric acid.

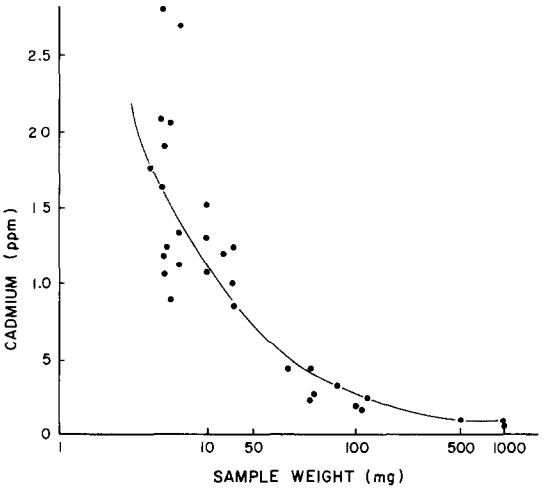


Fig. 1. The effect of Pyrex standard flasks on cadmium contamination in relation to sample weight of NBS orchard leaf standard.

this specifically for cadmium determination in 0.1% sodium chloride solution. The quantity of sodium released during the acid leaching of the Pyrex flasks in this work would certainly be less than enough to give a 0.1% solution and the use of a deuterium background corrector would therefore compensate for any non-atomic absorption due to sodium chloride. Hence, non-specific absorption at the Cd 228.8-nm line may be ruled out and since chemical interferences are not expected it may be concluded that the absorption was solely due to cadmium.

With increasingly larger samples the cadmium contamination becomes less significant as shown in Fig. 1. Orchard leaf standards weighing 500 mg or more gave results within the limits of error reported by NBS. The NBS certified value for SRM No. 1571 (orchard leaf) is based on at least a 250-mg sample. However, it is very unlikely that the cadmium concentrations in small samples such as those used for the results in Table 1 would vary by an order of magnitude from the bulk concentration, especially in view of the results reported in Table 3.

Although only copper and cadmium were investigated in this work, it was readily concluded that techniques suitable for one metal are not necessarily adequate for another.

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REFERENCES

1. F. J. Fernandez and D. C. Manning, *At. Absorption Newslett.*, 1971, **10**, 65.
2. I. W. F. Davidson and W. L. Secrest, *Anal. Chem.*, 1972, **44**, 1801.
3. J. D. Kerber, A. Koch and G. E. Patterson, *At. Absorption Newslett.*, 1973, **12**, 104.
4. C. E. Gleit and W. D. Holland, *Anal. Chem.*, 1961, **34**, 1454.
5. K. M. Hambridge, *ibid.*, 1971, **43**, 103.
6. T. R. Hauser, T. A. Hinners and J. L. Kent, *ibid.*, 1973, **44**, 1818.
7. C. C. Patterson and D. M. Settle, *Proc. 7th Materials Research Symposium*, Vol. 1, p. 321, P. Lafleur, ed., NBS Special Publication No. 4222, August 1976.
8. G. T. Wallace, Jr., I. S. Fletcher and R. A. Duce, *J. Environ. Sci. Health.*, 1977, **A12**, 493.
9. W. G. King, J. M. Rodriguez and C. M. Wai, *Anal. Chem.*, 1974, **46**, 771.
10. A. W. Struempler, *ibid.*, 1973, **45**, 2251.
11. M. M. Benjamin and E. A. Jenne, *At. Absorption Newslett.*, 1976, **15**, 53.
12. B. R. Culver and T. Surles, *Anal. Chem.*, 1975, **47**, 920.

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ANALYTICAL DATA

MIXED COMPLEXES OF Ni^{2+} OR Zn^{2+} AND CITRIC ACID WITH 2,2′-BIPYRIDYL IN AQUEOUS SOLUTION*

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Summary—The stability constants of ternary Ni^{2+} or Zn^{2+} complexes with 2,2′-bipyridyl and citric acid have been determined by means of pH-titrations at 25.0 ± 0.2° and an ionic strength of 0.1*M* (KNO_3). The stability constants of ternary complexes have been compared with those of similar ternary species.

In a previous paper[1] we described the formation of mixed complexes in aqueous solution containing Cu^{2+}, citric acid (H_3cit) and 2,2′-bipyridyl (bipy). The high stability of mixed complexes of the Cu(bipy)(cit)H and Cu(bipy)$(cit)^-$ types (in the acidic range of pH values) can be related to well-known stabilization effects observed when the Cu^{2+} ion interacts with 2,2′-bipyridyl and a secondary ligand containing charged oxygen atoms as donors.[2] For Ni^{2+} and Zn^{2+} few data have been published so far on the possible formation of mixed complexes with a heterocyclic compound such as 2,2′-bipyridyl and carboxylic ligands.[3–5]

We feel it is of some interest to study this subject further, and the present paper reports potentiometric data on the formation of mixed complexes in aqueous solution containing 2,2′-bipyridyl, citric acid and Ni^{2+} or Zn^{2+}.

EXPERIMENTAL

Apparatus and measurements

A Metrohm E388 potentiometer was used, equipped with glass and saturated calomel electrodes produced by the same firm. The glass electrodes were standardized both in the acidic and alkaline range of pH (pH = $-\log[H^+]$) by titrating standard solutions of nitric acid or potassium hydroxide and using the value of $pK_w = 13.75$.[6] The measurements were performed as previously reported,[1,6] at 25.0 ± 0.2°.

Reagents

The reagent solutions were made and standardized as reported previously[6,7]. All the solutions being titrated were made up to an ionic strength of 0.1*M* with potassium nitrate.

Procedure

The concentrations of the metal ions (C_M = Ni^{2+} or Zn^{2+}) ranged from 3 to 6m*M*, of 2,2′-bipyridyl (C_{bipy}) from 3 to 8m*M* and of citric acid (C_{cit}) from 3 to 9m*M*.

The study was done by taking potentiometric measurements of the hydrogen ion concentration in solutions containing reagent ratios (C_M:C_{bipy}:C_{cit}) of 1:1:1, 1:2:1, 1:1:2 and 1:1:3, during titration with alkali up to pH 9–9.5. With Zn^{2+} and a reagent ratio of 1:1:1, equilibrium in the potentiometric measurements was reached rather slowly (20–30 min) in the pH range 8–9.5.

Calculation

The stability constants were expressed as $\beta_{n,s,q,p}$ where the subscripts refer to M^{2+}, bipy, cit and H^+ respectively; thus the concentration of the *i*th species can be written as $C_i = [M]^{n_i}[bipy]^{s_i}[cit]^{q_i}[H]^{p_i}$. β_{n_i,s_i,q_i,p_i}. It was taken that $\beta_{n,s,q,p} = 1$ for the free components.

The stability constants were first evaluated graphically[8] and then refined by a least-squares calculation according to Wentworth's method.[9,10] The results of the refinement were considered reliable when the mean difference between calculated and experimental values of C_{OH} (corresponding to amount of base added at each point of the titration curves) was $\leqslant \pm 0.5\%$.

RESULTS AND DISCUSSION

The values of the protonation constants of the ligands and the stability constants of the binary complexes used in the calculation are shown in Table 1. For solutions containing the three reagents, we compared the experimental data of the titrations with those calculated (at the same values of C_M, C_{bipy}, C_{cit}) by assuming the presence in solution of only the free and binary species. The formation of the ternary complexes has been shown by the fact that at the same values of C_{OH} the experimental pH values were significantly lower than the calculated values.[3,11]

The most probable mixed complexes should be of the 1:1:1 type. By linear combination of the mass-balance equations the concentration of the complex M(bipy)(cit) can be eliminated and the values of [M], [bipy], [cit] (at known values of pH) can be calculated from the resulting three-equation system. Thus we evaluated the expression[8,12,13]

$$Y = \frac{C_{cit} - \sum_{i}^{I'} q_i[C_i]}{[M][bipy][cit]} \qquad (1)$$

formally corresponding to $\beta_{1,1,1,0}$, where I' is the number of species with known values of the stability constants. The values of Y are plotted against $X = 1/[H^+]$ in Fig. 1 for Ni^{2+}. The points pertaining to titrations for different ratios of C_M:C_{bipy}:C_{cit} fit the same curve well, and the

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Table 1. Protonation constants of 2,2'-bipyridyl and citric acid and formation constants of binary complexes with Ni^{2+} or Zn^{2+}, 25.0 ± 0.2°C, $I_c = 0.1M$ (KNO_3)

Metal ion	2,2'-bipyridyl			citric acid			
	$\log \beta_1^H = 4.41$ $\log \beta_2^H \simeq 5.5$ (12)			$\log \beta_1^H = 5.61$ $\log \beta_2^H = 9.91$ $\log \beta_3^H = 12.78$ (1)			
	$\log \beta_{MA}$	$\log \beta_{MA_2}$	$\log \beta_{MA_3}$	$\log \beta_{MAH}$	$\log \beta^M_{M(AH)}$	$\log \beta_{MA}$	$\log K^{M,cit,H_2O}_{M_2cit_2(OH)_2}$
Ni^{2+}	7.04 (8)	13.94 (8)	20.15 (8)	8.84 (15)	3.23 (16)	5.30 (15)	−4.71 (15)
Zn^{2+}	5.04 (6)	9.60 (6)	13.2 (6)	8.43 (16)	2.82 (17)	4.83 (16)	−2.94 (16)

Numbers in brackets are references.

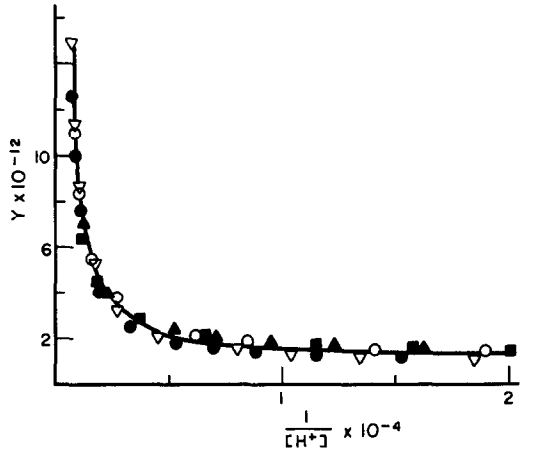


Fig. 1. Values of Y [see equation (1)] against $1/[H^+]$. ● $C_{Ni} = 4.00$; $C_{cit} = 3.94$; $C_{bipy} = 3.94$; $C_H = 19.60$. ○ $C_{Ni} = 5.00$; $C_{cit} = 5.06$; $C_{bipy} = 5.06$; $C_H = 25.20$. ▲ $C_{Ni} = 3.00$; $C_{cit} = 3.00$; $C_{bipy} = 3.00$; $C_H = 14.90$. × $C_{Ni} = 3.00$; $C_{cit} = 3.00$; $C_{bipy} = 6.00$; $C_H = 20.90$. □ $C_{Ni} = 3.50$; $C_{cit} = 3.50$; $C_{bipy} = 7.00$; $C_H = 24.35$. (concentrations in mM).

overall trend of the data is consistent with an equation of the type:

$$Y = \frac{\beta_{1,1,1,1}}{[H^+]} + \beta_{1,1,1,0}. \qquad (2)$$

Hence the plot suggests the presence in solutions both of Ni(bipy)(citH) and Ni(bipy)(cit) species, independently of the stoichiometric ratios of the reagents. Similar results have been obtained for Zn^{2+}.

The stability constants have been refined by a least-squares method, taking into account the experimental readings pertaining to each titration separately, to detect systematic errors. The mean values of $\log \beta_{n,s,q,p}$ are collected in Table 2, with their ranges.

In Table 3 we report the values [2,14] of

$$\Delta \log K_p = \log K^{Mbipy}_{Mbipy(citH_p)} - \log K^{M}_{M(citH_p)} \qquad (3)$$

This parameter allows us to evaluate the tendency of monoprotonated ($p = 1$) or unprotonated ($p = 0$) citrate to bond itself to M^{2+} or $Mbipy^{2+}$ ions.

Table 3. Values of $\Delta \log K_p$ for ternary systems

System	$\Delta \log K_1$	$\Delta \log K_0$
Ni–bipy–cit	+0.26	+0.02
Zn–bipy–cit	−0.03	−0.22
Ni–hm–cit[15]	—	−0.33
Zn–hm–cit[16]	—	−0.38
Cu–bipy–cit[1]	+0.24	—
Ni–bipy–pyr[14]	—	+0.36
Zn–bipy–pyr[14]	—	−0.01

In Table 3, values pertaining to other ternary systems containing citrate or 2,2'-bipyridyl are also shown. For the ligand system bipy–cit, the values of $\Delta \log K_p$ are higher for Ni^{2+} than for Zn^{2+}. The same trend (in $\Delta \log K_0$) has been observed with the ligand system bipy–pyrocatecholate[15] (pyr) whereas no significant difference was found in the ligand system cit–histamine (hm).[15,16] Comparison of the data in Table 3 suggests a specific effect of the 2,2'-bipyridyl towards Ni^{2+} ion. This effect for the mixed complexes of M(bipy)(citH) types is comparable with that given by Cu^{2+},[1] as the values of $\Delta \log K_1$ (Table 3) show.

Calculation of the species distribution shows that the values of α_M (% of metal ion present in each complex) at a fixed pH increase for the mixed complexes when the ratio of C_{cit} to C_M and C_{bipy} is increased. In Figs. 2 and

Table 2. Stability constants of mixed complexes of Ni^{2+} or Zn^{2+} with 2,2'-bipyridyl (bipy) and citric acid (cit); 25.0 ± 0.2°C, $I_c = 0.1M$ (KNO_3)

Metal ion	$\log \beta_{1,1,1,1}$	$\log K^{Mbipy}_{M(bipy)(citH)}$	$\log \beta_{1,1,1,0}$	$\log K^{Mbipy}_{M(bipy)(cit)}$
Ni^{2+}	16.14 ± 0.04	3.49	12.36 ± 0.03	5.32
Zn^{2+}	13.44 ± 0.06	2.79	9.61 ± 0.04	4.61

$$\beta_{1,1,1,0} = K^{M}_{M(bipy)(cit)} = \frac{[M(bipy)(cit)]}{[M][bipy][cit]}$$

$$\log K^{Mbipy}_{M(bipy)(citH)} = \log \beta_{1,1,1,1} - \log K^{M}_{Mbipy} - \log \beta^{1}_{H}$$

$$\log K^{Mbipy}_{M(bipy)(cit)} = \log \beta_{1,1,1,0} - \log K^{M}_{Mbipy}$$

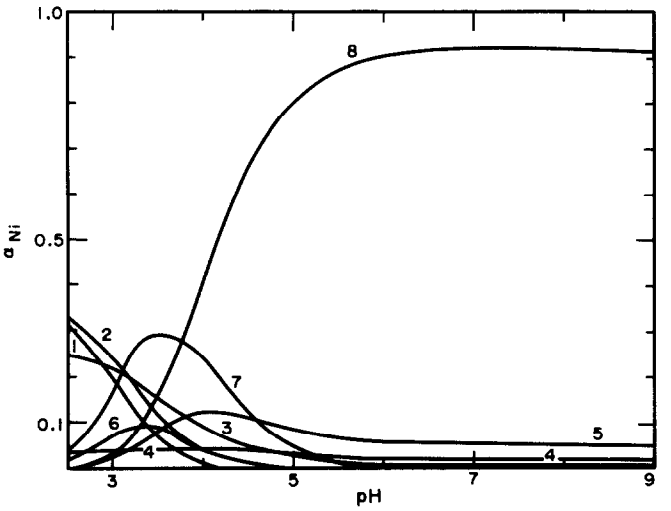


Fig. 2. Distribution of species as α_{Ni} *vs.* pH for the Ni^{2+}–2,2′-bipyridyl–citric acid system (C_{Ni} = 3.00m*M*; C_{bipy} = 3.00m*M*; C_{cit} = 9.05m*M*; C_H = 33.12m*M*) 1: Ni^{2+}; 2: $Nibipy^{2+}$; 3: $Nibipy_2^{2+}$; 4: $Nibipy_3^{2+}$; 5: $Nicit^-$; 6: NicitH; 7: Ni(bipy)(cit)H; 8: $Ni(bipy)(cit)^-$. C_H = concentration of free and dissociable hydrogen ion.

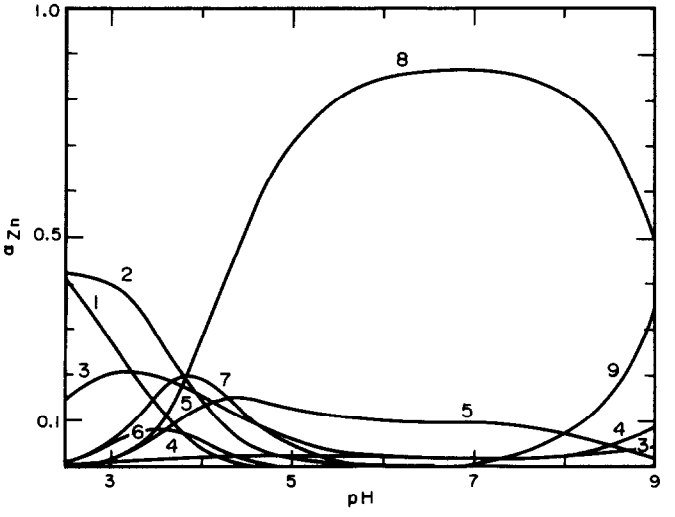


Fig. 3. Distribution of species as α_{Zn} *vs.* pH for the Zn^{2+}–2,2′-bipyridyl–citric acid system (C_{Zn} = 3.00m*M*; C_{bipy} = 3.02m*M*; C_{cit} = 9.00m*M*; C_H = 33.60m*M*). 1: Zn^{2+}; 2: $Znbipy^{2+}$; 3: $Znbipy_2^{2+}$; 4: $Znbipy_3^{2+}$; 5: $Zncit^-$ 6: ZncitH; 7: Zn(bipy)(cit)H; 8: $Zn(bipy)cit)^-$; 9: $Zn_2cit_2(OH)_2^{4-}$ C_H = concentration of free and dissociable hydrogen ion.

3, for example, we plot the values of α_M against pH, for $C_M:C_{bipy}:C_{cit} \simeq 1:1:3$, for Ni^{2+} and Zn^{2+}: the mixed complex of M(bipy)(cit) type is the predominant species in solution for both metal ions.

REFERENCES

1. P. G. Daniele, G. Ostacoli and A. Vanni, *Ann. Chim. (Rome)*, 1975, **65**, 465.
2. H. Sigel, *Angew. Chem. Intern. Ed.*, 1975, **14**, 394.
3. G. Ostacoli, P. G. Daniele and A. Vanni, *Atti Acc. Sci. Torino*, 1973–4, **108**, 539.
4. P. G. Daniele, G. Ostacoli and V. Zelano, *Ann. Chim. (Rome)*, 1975, **65**, 617.
5. H. Sigel, R. Griesser and D. B. McCormick, *Inorg. Chim. Acta*, 1972, **6**, 559.
6. P. G. Daniele, G. Ostacoli and V. Zelano, *Ann. Chim. (Rome)*, 1975, **65**, 455.
7. P. G. Daniele, G. Ostacoli and P. Amico, *ibid.*, 1976, **66**, 127.
8. G. Ostacoli, P. G. Daniele and A. Vanni, *ibid.*, 1975, **65**, 197.
9. W. E. Wentworth, *J. Chem. Educ.* 1965, **42**, 96.
10. P. G. Daniele, G. Ostacoli and A. Vanni, *Atti Acc. Sci. Torino*, 1974–5, **109**, 547.
11. A. Gergely, I. Nagypál and E. Farkas, *J. Inorg. Nucl. Chem.*, 1975, **37**, 551.
12. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 108. McGraw Hill, New York, 1962.
13. A. Vanni, M. C. Gennaro and G. Ostacoli, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1443.
14. R. Griesser and H. Sigel, *Inorg. Chem.*, 1971, **10**, 2229.
15. P. G. Daniele and G. Ostacoli, *Ann. Chim. (Rome)*, in the press.
16. *Idem, ibid.*, submitted for publication.

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ANNOTATIONS

THE DRYING OF SULPHIDE-BEARING MATERIALS IN A MICROWAVE OVEN: A CAVEAT*

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Summary—The drying of sulphide-bearing materials in a microwave oven should be undertaken with caution. Several sulphide minerals and sulphide-bearing materials have shown a susceptibility to oxidation (which may even be violent) during microwave drying and this could affect the results of subsequent work on these materials.

Because of convenience and speed, the microwave oven is widely supplanting the conventional oven for drying a variety of materials or determining their moisture content, *e.g.*, foodstuffs, clays. The application of microwave drying in process control of manufacture of inorganic chemicals (which are normally dried at below 150° in a conventional oven) has been recommended as an economy in analysis time.[1] Indeed, microwave drying may also seem attractive for powdered ores and concentrates, for example before chemical or mineralogical analysis, especially when the possibility exists of undesirable oxidation during drying in a conventional oven†. However, experience in this laboratory has revealed inherent dangers in the use of this technique, and it was considered worthwhile to issue this caveat. Some typical results obtained when drying various sulphide-bearing materials are presented.

EXPERIMENTAL

Apparatus

A Toshiba Deluxe microwave oven with a power output of 1.3 kW at 2450 MHz was used. Because of the variability of the radiation intensity throughout the chamber,[2] all samples were placed in a position marked on the chamber floor. The materials studied (0.5 g for the sulphide minerals and 0.5–5 g for mill tails concentrate) were placed in Vycor crucibles and irradiated for different time periods.

Materials

Lumps of high-purity pyrite, pyrrhotite, chalcopyrite, galena, sphalerite and chalcocite were crushed and the 65–100 mesh fraction was collected by dry screening. Non-sulphide impurities were removed by heavy liquid separation (s.g. 3.3). These minerals were therefore essentially dry.

The base-metals concentrate (200-mesh) contained approximately 12% moisture. The composition of the solids in it was 53% sphalerite, 35% pyrite, 4.5% galena, 3% chalcopyrite and ~1% pyrrhotite.[3]

Analysis

The leachable iron in samples of pyrite, pyrrhotite and chalcopyrite was determined by selective extraction with 10*M* phosphoric acid.[4] The leachable lead in galena, zinc in sphalerite and copper in chalcocite were determined by selective extraction with a 15% solution of ammonium acetate in 3% acetic acid.[5] This reagent was also used in the simultaneous determination of leachable lead and zinc in the base-metals concentrate (Table 1).

RESULTS

In the initial attempt in this laboratory to dry a sulphide-bearing material in a microwave oven, approximately 100 g of a pyrite–pyrrhotite ore were spread on a 20-cm watch glass and irradiated for 10 min. During this period, however, the evolution of sulphur dioxide was so great that the laboratory had to be evaluated. Inspection of the cooled material indicated that an appreciable amount of the originally grey sulphide had been oxidized to a reddish product, probably ferric oxide. As it seemed unreasonable that the heat required to evaporate ~0.3 g of water per 100 g of ore would be sufficient to promote the observed degree of oxidation, it was concluded that at least one other constituent must have absorbed the microwave radiation.

The effect of subjecting several of the more common sulphide minerals to microwave radiation was studied. Pyrite, chalcopyrite and sphalerite appeared to be unaffected for up to 40 min. The leachable metal content of the irradiated samples was the same as that of the unexposed minerals. Pyrrhotite and galena, however, underwent violent pyrotechnic oxidation even during a 1-min irradiation. The product formed from pyrrhotite was fused to the crucible and could be dissolved only with difficulty in hot concentrated acids. Chalcocite appeared to be unaffected unless exposed for more than 30–40 min. There were no readily observed signs of oxidation during the irradiation but both whitish and reddish products were present on removal of the chalcocite from the oven. X-Ray diffraction examination identified, in order of decreasing proportion, $CuO \sim Cu_2O > Cu_2O(SO_4) \sim Cu_2S$. The leachable metal content of the irradiated chalcocite also showed that the extent of oxidation was greater than that of the unexposed mineral. Visual examination after the leaching showed that the products had not dissolved completely. X-Ray diffraction identification found, in decreasing order, $Cu_2O > Cu_2S > CuO$.

An attempt was made to assess the feasibility of using microwave radiation to dry the base-metals concentrate, which was intended for subsequent metal recovery by chlorination. It had been hoped that a concentrate with less than 0.05% moisture and minimally oxidized could

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† Indeed, such oxidation, even at 70°, was a serious problem encountered in the study of a fine-grained base-metal concentrate from New Brunswick, Canada, being undertaken by the Mineral Sciences Laboratories.

Table 1. Leachable zinc and lead in base-metals concentrate

Drying period, *min*	Zn, *mg/g*	Pb, *mg/g*
Nil	3.87*	5.92*
Overnight at 75°	7.53	15.30
1 (microwave oven)	1.87	2.91
3 (microwave oven)	1.80	2.76
9 (microwave oven)	1.96	3.31

* Corrected for ~10% moisture content.

be obtained. The drying of the concentrate was efficient*; a 5-g sample (~10% moisture) appeared to require less than 1 min. However, even in this short time, the odour of sulphur dioxide was readily detectable. Table 1 shows the leachable lead and zinc content of samples of concentrate that were undried, dried overnight at 75° in a conventional oven, and dried in a microwave oven for various periods. The appreciable increase caused by overnight drying at 75° is obvious. The decrease for the three samples dried in the microwave oven, relative to the undried concentrate, is anomalous; therefore, it was concluded that irradiation affects the solubility of the oxidation products in 15% ammonium acetate solution in 3% acetic acid. A similar observation had been made for chalcocite.

* The drying time is, of course, related to sample size and moisture content when the radiation output is constant.

DISCUSSION

The examples given above illustrate that some sulphide-bearing materials are not amenable to drying in a microwave oven because they are susceptible to oxidation which could affect the results of subsequent work. Although alteration of principal constituents would be obvious and the material rejected, the occurrence of minor alteration might go undetected and cause some error in subsequent analysis, especially if the mineralogical composition were unknown. This error may vary from insignificance to minor importance for a bulk property, *e.g.*, the total metal content, but may be of considerable importance for other determinations such as the leachable metal content or the sulphide mineral content in materials such as soils. Indeed, as was found for chalcocite and the base-metals concentrate, incorrect values are obtained for those samples dried in a microwave oven. It is recommended that the susceptibility to microwave-induced oxidation of each sulphide-bearing material be ascertained before microwave drying procedures are used. Factors that affect this susceptibility include the nature of the sulphides present, their relative proportions in the material, particle size, sample size, moisture content and the time required for drying. Many of these criteria are being studied in this laboratory.

REFERENCES

1. J. A. Hesek and R. C. Wilson, *Anal. Chem.*, 1974, **46**, 1160.
2. Consumer Reports, *The 1977 Buyers' Guide*, 1976, p. 10.
3. W. Petruk and R. G. Pinard, *Mineral Sciences Lab. Rept.* MRP/MSL 76-141(IR), Department of Energy, Mines and Resources, Canada Centre for Mineral and Energy Technology, Ottawa, Canada.
4. H. F. Steger, *Talanta*, 1977, **24**, 251.
5. *Idem. ibid.*, 1977, **24**, 268.

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USE OF PRECISION COLORIMETRY FOR ELEMENTAL MICROANALYSIS*

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Summary—Spectrophotometric techniques are useful for microdeterminations of many elements in organic compounds and some inorganic compounds. It is possible to determine most metals and some non-metals (Al, Co, F, Fe, Mo, P, Pd, Pt, Si, Sn, Ti...) by applying spectrophotometric techniques described in the literature (most often for trace analysis) and using commercial reagents.

The increasing variety and number of elements found in organic compounds is leading microanalysts towards choosing techniques which they can work out rapidly, which require a single type of laboratory equipment for the determination of several elements, and make it possible to change rapidly from one element to another in the analysis. Precision colorimetry meets such requirements.

It is possible to determine most metals and some non-metals by applying spectrophotometric techniques described in the literature (most often for trace analysis) and using commercial classical reagents.

ADAPTING PRECISION COLORIMETRY TO ELEMENTAL ANALYSIS

For application of these techniques in elemental microanalysis, it is necessary that the accuracy, precision and other characteristics should be similar to those for other microanalytical techniques for determination of common elements in organic compounds, *viz.* the absolute error should be lower than 0.2–0.3%, interfering elements can be masked or corrected for, and the duration of an analysis should be not too long.

In order to achieve the desired accuracy and precision it is not only necessary to use appropriate balances for weighing samples and a precision spectrophotometer reading absorbances to 0.001, but also to conduct the analysis in a strictly reproducible manner. Thus "once for all" calibration curves should not be used. Instead, the standard solutions and sample solutions should be prepared by the same procedure at the same time, with identical quantities of identical reagents at the same temperature, the only difference being the presence of known volumes of standard solution in the former and of the solutions of the microanalytical samples in the latter.

The solutions should be left standing for the same period and undergo the same possible temperature changes before their absorbances are measured; air-conditioning, though advisable, is not absolutely necessary, but it should be pointed out that some colorimetric techniques, for instance tin or molybdenum determination, give erratic results when the ambient temperature reaches the 28–30° level.

The weight W mg of element contained in the unknown solution of absorbance A, is calculated from the average absorbance $\bar{a}$ of standard solutions containing w mg of this element:

$$W = wA/\bar{a}$$

There is a limiting value for the difference between w and W which should not be exceeded and which depends on the element being determined and on any divergence from the Lambert–Beer law found by testing the technique.

The preliminary destruction of an organic sample, generally achieved by the wet process (original or modified micro Lorenz technique) or by combustion in oxygen or with sodium peroxide, introduces reagents which may change the light-absorption properties of the final solution. A study must be made to find whether some reagents have to be rejected or one spectrophotometric technique changed for another.

However, it is often the case that though the effect of some reagents is not negligible it is reproducible when a definite and precise procedure is used; it is then convenient to prepare blank solutions in the same way as the sample solutions and to apply the whole procedure to them. This is not necessary when the blank effect is proved to be negligible, but this must be established by a careful study because the blank effect is not always manifested by an absorbance change which can be seen immediately. For instance, in determination of iron with tiron after a mineralization involving hydrogen peroxide, the colour of the complex is less stable than it is when the complex is prepared from a pure iron solution. It is therefore necessary to subject the blank to the decomposition procedure, and to make the measurements before the colour begins to fade. A similar effect occurs in determination of molybdenum and the analytical results are improved if the entire procedure is applied to the blank.

Most of the spectrophotometric techniques described in the literature have been developed for trace analysis or for determination of low contents of elements in rocks, alloys, waters, *etc.* Appropriate choice of capacities of the standard flasks utilized and the use of appropriate aliquots make it possible to adapt many of these techniques for the determination of major or minor elemental components of both organic and inorganic samples. The precision of the analytical results is not lowered by use of aliquots as much as might be expected, provided two or three replicates from the same solution are analysed and the mean is taken as the correct value.

As far as interfering elements are concerned the data found in the literature are generally of little or no use for application to microanalytical work. This is because organic compounds will contain relatively few elements, the nature of which will nearly always be known, and which are generally present in small atomic ratios, in contrast to the case with alloys, rocks or trace analysis. Moreover, the elements which interfere with a colorimetric determination usually belong to the same family as the one being determined, a situation seldom encountered in our case. For these reasons it is possible to use commercial reagents for elemental colorimetric determinations even when other elements interfere to some degree. It is then

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possible to correct the colorimetric results for the effect of interfering elements as a function of their concentration (as in phosphorus determination[1] in the presence of palladium, platinum or rhodium) or slightly to alter the procedure for the better (as in phosphorus determination[1] in presence of silicon or arsenic) or to mask interfering elements by means of complexation *etc.* In the determination of fluoride there are many interfering elements and it is necessary to eliminate them by distilling hexafluorosilicic acid by the Willard and Winter or other suitable method. This is of general use but very time-consuming; that is why for fluorine contents lower than 20% and in the presence of sulphur or phosphorus the direct alizarin complexone technique should be used instead of one of the bleaching methods such as decolouration of the ferric sulphosalicylate complex.

In comparison with the automatic analyser techniques for carbon, hydrogen, nitrogen and oxygen microdeterminations, the colorimetric techniques together with the necessary sample preparation at first sight appear to be much more time-consuming. However, they have compensating advantages, such as the possibility of determining various elements one after another without the need for separate specialized pieces of apparatus, most of which will not be in operation the whole time. In addition, there is no time-wasting conditioning of apparatus after a shutdown, and assistants already trained in one determination can quickly adapt to others. Furthermore, the use of flow-cells makes it possible to avoid the tedious handling of ordinary cells, but only if the reagents used do not dirty the walls of the cells and tubing, because flow-cells are much more difficult to clean; for instance they should not be used for colorimetric determination of tin with phenylfluorone as complexing agent. All things considered, the average time taken for an elemental determination by a colorimetric technique is very reasonable, and even more so if a large batch is dealt with at the same time.

Colorimetric techniques are used in our laboratory:

(*a*) together with prior combustion in an oxygen flask for fluorine determination;

(*b*) together with a wet decomposition process for determination of aluminium, cobalt, iron, molybdenum, phosphorus, palladium, platinum, tin and titanium;

(*c*) together with previous decomposition with sodium peroxide in a Würzschmitt bomb for silicon determination.

Techniques are also being developed for the microdetermination of elements such as boron, rhenium, tellurium, vanadium and zirconium.

Colorimetric methods have not been developed for metals such as nickel or copper, for which other techniques (atomic absorption, polarography, *etc.*) are already in use.

METHODS IN USE

The colorimetric determinations used in our laboratory are briefly outlined below.

Aluminium is determined at 490 nm by means of its red-orange complex with Alizarin Red S and calcium in buffered solution (pH 4.4–4.7).[2–4]

Cobalt is determined at 340 nm by means of its green-yellow complex with tiron in solution buffered at pH 9.6.[2,5]

Tin is determined at 520 nm by means of its orange complex with phenylfluorone in acidic aqueous methanolic medium in the presence of glycine and gelatine; under our conditions the presence of sulphate is necessary for obtaining correct results.[2,6,7]

Iron is determined at 480 nm by means of its red complex with tiron in buffered medium (pH 9.5); some interferences may be avoided by working at pH 3.5–4.5, though the sensitivity is then lower.[2,8,9]

Depending on the presence of interfering elements and its content in the sample, *fluoride* may be determined in two ways:

(*a*) in buffered medium (pH 2.8–2.9) by measurement of the decrease in absorbance of the ferric sulphosalycilate complex at 510 nm;[10–14]

(*b*) by means of its purplish-blue complex with alizarin complexone and Ce in aqueous acetone medium (buffered at pH 4.6), at 625 nm.[15,16]

Molybdenum is determined at 475 nm by means of the red complex obtained by reduction with potassium iodide in the presence of thiocyanate in 3 *M* hydrochloric acid medium.[1]

Palladium is determined at 408 nm by means of the brownish pink complex $[PdI_4]^{2-}$ obtained by the reaction of potassium iodide with Pd^{2+} in 0.25 *M* hydrochloric acid medium.[1]

Phosphorus is determined at 410 nm by means of the yellow phosphovanadomolybdate obtained in 0.26 *M* sulphuric acid medium.[1,11]

Platinum is determined at 406 nm by means of the yellow $[PtCl_4]^{2-}$ obtained by reduction of $[PtCl_6]^{2-}$ by stannous chloride in 1.8 *M* hydrochloric acid medium.[1]

Silicon is determined at 400 nm by means of yellow silicomolybdic acid; this determination is more time-consuming and more difficult than the others because the sample is decomposed with sodium peroxide in a Würzschmitt bomb and the large bulk of hydrogen peroxide generated in the process solution has to be destroyed so that it cannot interfere in the colorimetric measurements.[17]

Titanium is determined at 410 nm by means of its yellow complex formed with tiron in the presence of oxalic acid (in order to avoid the hydrolysis of Ti^{4+} salts) in buffered solution (pH 4.7).[1]

B, Re, Rh, Te, V and Zr are also determined,[18] but these techniques are still under development in order to solve problems related to extension of their field of application and the precision of the analytical results.

REFERENCES

1. E. Debal, R. Chassin and S. Peynot, *Talanta*, 1976, **23**, 35.
2. E. Debal, R. Chassin, S. Peynot and O. Poliakoff, *ibid.*, 1977, **24**, 491.
3. C. A. Parker and A. P. Goddard, *Anal. Chim. Acta*, 1950, **4**, 517.
4. J. A. Corbett and B. D. Guerin, *Analyst*, 1966, **91**, 490.
5. C. K. Bhaskare and S. K. Deshmukh, *Z. Anal. Chem.*, 1975, **277**, 127.
6. A. M. Leblond and R. Boulin, *Chim. Anal. (Paris)*, 1968, **50**, 171.
7. A. M. Dymov, I. G. Ivanov and T. I. Romantseva, *Zh. Analit. Khim.*, 1971, **26**, 2360.
8. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
9. G. V. Potter and C. E. Armstrong, *Anal. Chem.*, 1948, **20**, 1208.
10. R. Lévy and E. Debal, *Mikrochim. Acta*, 1962, 224.
11. E. Debal, *Chim. Anal. (Paris)*, 1963, **45**, 66.
12. E. Debal, S. Peynot and S. Raveau, *Bull. Soc. Chim. France*, 1969, 2919.
13. E. Debal, G. Nabias and S. Peynot, *ibid.*, 1971, 3373.
14. M. Poirier, *Talanta*, 1975, **22**, 607.
15. G. Charlot, Chimie Analytique Quantitative, Vol. I, *Méthodes Chimiques et Physicochimiques*, 6th Ed., p. 421. Masson, Paris, 1974.
16. E. Debal, G. Madelmont, S. Peynot and O. Poliakoff, unpublished.
17. E. Debal and M. Riocreux, *Talanta*, 1972, **19**, 15.
18. E. Debal, unpublished work.

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THE HIGH-TEMPERATURE ANALYTICAL USES OF VANADIUM(V) OXIDE*

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Summary—The review surveys the available representative information from several fields, on high-temperature analytical uses of vanadium(V) oxide during the last half-century. A brief historical background is included. The three main fields of use are organic microchemical analysis, macrocombustion determinations, and pyrohydrolysis, and the review covers apparatus and equipment, reagents, chemical considerations, characteristics of vanadium(V) oxide, procedural details, and evaluation of the results.

A number of elements or compounds of interest to the analyst are volatile at high temperatures after the destructive decomposition of the material and many methods for their isolation and determination exist. The relevant knowledge is usually classified according to the element determined or the techniques employed and it is often transferred from one field to another. However, there are instances where a more systematic evaluation of a particular aspect across several fields would be beneficial for its better understanding. Methodological details often escape the usual abstracting but they are crucial for an efficient development of new methods. This appears to be the case with the high-temperature analytical uses of vanadium(V) oxide which has been variously designated in the literature as flux, activator, catalyst, separation reagent, melting agent, additive and promoter.

The aim of this review is to survey the representative available information about these occasionally controversial uses, often from scattered sources in various fields and in foreign languages, thus providing the necessary background for the improvement of methods for the determination of various elements after their separation from matrices containing vanadium(V) oxide. The evaluation is structured according to the analytically more critical aspects of the practical applications of vanadium(V) oxide.

HISTORICAL

Historically, there are three distinctly different high-temperature analytical uses of vanadium(V) oxide: for microchemical analysis of organic compounds, combustion methods for organic and inorganic materials, and pyrohydrolysis.

The first use of vanadium(V) oxide in microchemical analysis can be traced to Schramm,[1] who half a century ago systematically investigated the properties of vanadyl-malonic acid and its salts. He used vanadium(V) oxide as the gravimetric weighing form. Also, he observed excellent freedom from complications caused by salts of alkali and alkaline earth metals, which can usually interfere by forming difficultly decomposable carbonates (or sulphates if sulphur is present). Therefore, an addition of a suitable catalyst is required. Also, carbon was completely ignited without entrapment or formation of carbides. Schramm had also devised the addition of vanadium(V) oxide to more difficultly combusted compounds of potassium, rubidium and caesium, and suggested its possible use as an efficient general catalyst. This idea was confirmed by Lorenz[2] who achieved complete combustion of difficultly combustible organic compounds by adding vanadium(V) oxide.

In a systematic investigation, Meyer and Tischbierek[3] proved the efficiency of vanadium(V) oxide as an oxygen-transfer catalyst for the oxidation. Combustions were more complete and about twice as fast as without it, but the catalyst needed to be in the molten state.

With these experiments vanadium(V) oxide was firmly established in organic microchemical analysis. Roth[4] used it in the analysis of organic boron compounds and stressed as its two outstanding properties the formation of a homogeneous liquid melt and the ability to function in the oxidation as a transfer catalyst. He substituted it for the customary potassium dichromate in all determinations of carbon and hydrogen in organic salts of alkali and alkaline earth metals.

For the microdetermination of sulphur in organic compounds, vanadium(V) oxide was independently introduced by Zinneke[5] and by Kirsten,[6] who had already used it for the analysis of inorganic compounds.

The use of vanadium(V) oxide as a catalyst and by far the best oxygen-donor in organic microanalysis continues.[7] Pickering[8] quotes its use in his review of heterogeneous oxidation processes, but according to Kirsten[9] it has been superseded by phosphoric acid for ultramicro elemental analysis of sulphur- and

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halogen-containing compounds. The standard ASTM method for combustion of petroleum products with the aid of vanadium(V) oxide in a resistance furnace has been reapproved.[10]

In 1954, Warf *et al.*[11] published the declassified results of the work on pyrohydrolysis for the determination of the fluorides, developed during the war for the Manhattan Project. Vanadium(V) oxide was a good accelerator, but it caused the results to be too high. The same difficulties were confirmed by Banks *et al.*,[12] and a standard reference work on fluorine by Nikolaev *et al.*[13] does not even mention its use in pyrohydrolysis. However, Newman[14] and Clements *et al.*[15] used vanadium(V) oxide or its mixtures in their pyrohydrolytic methods for the determination of fluorine in rocks and minerals. Doležal *et al.*[16] and Bock[17,18] cite very few details for use of vanadium(V) oxide, however.

After the publication of Kirsten's review,[6] a number of successful applications of vanadium(V) oxide to the determination of sulphur in inorganic materials followed. Hagerman and Faust[19] developed a macroanalytical combustion method for refractory materials. A thorough investigation by Burke[20] of the incompletely understood conditions of combustion has led in recent years to the development of commercially available instrumentation for carbon and sulphur determination in which vanadium(V) oxide is used routinely as a flux. These developments have been reviewed.[21,22]

The addition of vanadium(V) oxide is now used for the analysis of organic compounds;[4–7,18,23] inorganic materials;[11,12,24–27] iron, steel, nonferrous metals and their various alloys;[20,28–36] ores and intermediate products;[37–43] refractories, ceramics and glasses;[19,41,44] rocks and minerals;[14,15,45–48] soils;[23,49,50] and fuels.[10,37,42] Many of these methods are referred to in standard texts on decomposition of materials[16,17] or in chapters on sulphur and fluorine in reference works,[13,51–54] but without presentation of much methodological detail.

METHODOLOGY OF USE OF VANADIUM(V) OXIDE

Apparatus and equipment

Heating apparatus. To be effective in the sense discussed, vanadium(V) oxide must be heated. Various apparatus has been used for this, but a historical trend in step with the general development of the laboratory technology can also be discerned.

Burners. From the beginning until today burners have been used for heating,[5,14,15,19,24] and even when efficient electrical furnaces were available, burners have occasionally been preferred[14] or were used in combination with the electrical furnaces.[19,24] With a burner it may be easier to control the rate of reaction of the sample and the fusion of vanadium(V) oxide, and heating with a burner also allows faster cooling of the combustion tube between determinations.[14] However, the temperatures achieved are not sufficient for all requirements, and today, heating with a burner is little used.

Microchemical furnaces. This type of furnace is mainly used in laboratories associated with organic elemental analysis or similar problems.[6,7,9,55,56] It lends itself to slow progress of the fusion, similar to that obtained by heating with a burner. Generally, these furnaces are not built for temperatures much above 1000°, and their dimensions do not allow the use of the larger combustion boats which are necessary with the larger sample sizes in trace analysis, *e.g.*, for sulphur.

Resistance furnaces. These represent the largest class of apparatus used in connection with vanadium(V) oxide. They are the only kind employed in pyrohydrolysis, mainly for the determination of fluorine[11,12,16,17,26,27,57,58] and form the basis for many combustion methods on the macroscale.[25,31,32,37–44,47,59]

The maximum temperature attainable is about 1400–1550°. The dependence of the results, in the determination of sulphur, on thermodynamic equilibrium between the sulphur dioxide and trioxide, and the resulting difficulties, have somewhat slowed down the use of the resistance furnace in recent years. Burke's evaluation of vanadium(V) oxide for the determination of sulphur[20] did not include a study of the use of a resistance-type furnace. This problem was studied by Nebesar,[38,60,61] who developed a system suitable for the determination of several elements. In a recent method by Beesley and Chamberlain,[44] a resistance-type furnace is also used, but complex and expensive instrumentation, seldom available in an average laboratory, is required.

Induction furnaces. This type of furnace is not used in pyrohydrolysis or microchemical elemental analysis. The higher temperature attainable with the induction-type furnace and the minimal dust-carrying helped to resolve some of the earlier problems with the use of vanadium(V) oxide. A better understanding of the conditions and requirements for temperature control, in particular in the determination of sulphur, led to the development of a number of methods, all employing vanadium(V) oxide and an induction furnace.[20,28,29,33,34,36]

Sample-holders. The sample-holder, most often a combustion boat, is the only part of the apparatus to come in contact with the molten vanadium(V) oxide. The various devices generally used in combustion have been reviewed.[62] Many constructional materials have been tried for work with vanadium(V) oxide: unglazed porcelain;[3,7,44] glazed porcelain[19] which had to be covered with powdered silica to prevent its fusion with the flux; porous ceramics,[41] which were penetrated by the melt and fused to the combustion tube; fused silica,[14,15,47,49,55] so that the silica bed could be dispensed with;[24] platinum, in particular for pyrohydrolysis;[11,12,26,41] "Pyrolan",[37,42,43] a ceramic material of German origin; and special refractory ceramics for crucibles used in induction

furnaces,[20,28–30,33,34,36] to minimize slag penetration and thermal shock.

The fused silica, and particularly the platinum boats had to be cleaned for re-use because of their cost, thus increasing the complexity of the procedures. Further, carrier gas at high flow-rates tends to carry vanadium(V) oxide along the combustion tube. This causes considerable difficulty, which is accentuated with more reactive materials. To overcome these problems, special covers for use with vanadium(V) oxide and suitable for commercially available combustion boats were developed.[60]

Determinative step

The choice of the determinative step is closely linked with the interferences in the method and the volatility of the vanadium(V) oxide (to be discussed later).

In pyrohydrolysis with vanadium(V) oxide, results obtained for fluorine were too high[11,12] even in the analysis of individual compounds. This was later explained as the result of the presence of vanadium in the condensate[27] where it increases the consumption of the standard alkali solution used for the titration in the determinative step. In another pyrohydrolytic method, vanadium(V) oxide was found to be the most active accelerator,[26] but it was carried along the reaction tube and the titration with a solution of barium hydroxide led to erratic results. Further use had to be abandoned. However, when the alkali was replaced by thorium nitrate solution as titrant or an absorptiometric method was used, good results were obtained and vanadium(V) oxide was the preferred flux.[14] Clements *et al.*[15] also used, without complications, colorimetry or potentiometry with a fluoride ion-selective electrode after pyrohydrolytic separation of fluorine with the aid of a flux containing vanadium(V) oxide. Virtually any customary determinative steps can be used after decomposition of the sample with vanadium(V) oxide in the absence of water and under properly controlled conditions. Recently, highly acid-sensitive techniques, such as conductimetry in thallium(III) phosphate solution,[35] or in acidic hydrogen peroxide solution,[44] or alkalimetry with a sodium borate solution[33] have given reliable results, thus proving the non-interference of the molten vanadium(V) oxide. If acidic components are released, however, determinative steps sensitive to them can no longer be used.[33] In such cases selective instrumental methods, *e.g.*, non-dispersive infrared spectroscopy,[22] can be employed, or an interference-free titration method used, *e.g.*, iodometry.[33]

Chemical considerations

Preparation of vanadium(V) oxide. The early applications of vanadium(V) oxide in organic microchemical analysis usually dealt with fairly high amounts of elements of interest. Therefore, commonly available reagent grade preparations of vanadium(V) oxide were adequate. With the demand for increasingly lower limits of detection, in particular in combustion methods for carbon and sulphur, new methods of preparation had to be introduced because the commercially available reagent still contained appreciable amounts of sulphur and chlorine.[20,24,50]

Though Hagerman and Faust[19] used reagent grade powder as such, Larsen *et al.*[24] fused vanadium(V) oxide in a quartz dish overnight at 1000°, ground it, and then prepared individual 0.125-g portions, by fusion in and removal from quartz boats. Dokládalová[55] cleaned the reagent in the same way but did not prepare the melts separately. Lust and Van der Cook[25] also fused the reagent, but at 900° for 4 hr, then cooled and ground it and mixed it with 0.3 times its mass of infusorial earth.

Another group of workers relied on the thermal decomposition of reagent-grade ammonium metavanadate. Bloomfield[49] heated the reagent at 500–550° for 3–4 hr in an electric furnace. No grinding was necessary and the blank achieved for sulphur was < 5 ppm. It could have been even less if the flux had been fused. This method was also adopted by Newman[14] and by Sen Gupta[47] (who heated the reagent at 1000° for several hours). Sen Gupta stored the cooled melt in bulk in a desiccator to obviate the possible reaction of atmospheric sulphur dioxide with powdered reagent, and ground it in an agate mortar just before use. Beesley and Chamberlain[44] adopted Bloomfield's procedure. Harrison and Spikings[33] also heated ammonium metavanadate and preferred the resulting oxide to the commercially available "vanodiscs" (see below).

A third procedure was introduced by Burke.[20] He roasted reagent-grade vanadium(V) oxide for 16–20 hr at 670 ± 10° in a nickel–chromium alloy boat in a stream of air flowing at 1 l./min. He said higher temperatures should be avoided because of undesirable sintering. This procedure was also adopted by Shmelev and Glushko,[35] and led to the product commercially available from LECO, who in addition developed and marketed the "vanodisc" accelerator, a pressed tablet of iron and vanadium(V) oxide powders.[22,34]

Mixtures containing vanadium(V) oxide. Some methods use mixtures of vanadium(V) oxide with other substances. These can be prepared in bulk prior to the preparation of the analytical charge or mixed as required.

Hagerman and Faust[19] used silica not so much as a feature of the flux but for protection of the combustion boats. For samples containing molybdenum sulphide they had to add chromium sesquioxide and alumina. Bloomfield[49] introduced acid-washed kieselguhr in 1:5 w/w proportion to vanadium(V) oxide to prevent the formation of a liquid melt. This technique was also adopted by Sen Gupta,[47] but he also added "Celite" on top of the sample. Alundum is used in a similar manner.[10] Lust and Van der Cook[25] mixed the bulk reagent with 30% of its mass of analytical-grade infusorial earth, to improve the physical

characteristics of the fused mass, achieve better release of sulphur trioxide, and extend the life of the boats.

There are a few mixtures using other oxides in a prefused flux. Clements *et al.*[15] fused the vanadium(V) oxide with bismuth oxide and sodium tungstate, a mixture also reported by Bock.[17]

In the metallurgical field, Puzankova *et al.*[39] recently re-investigated a number of fluxes, some of which contained vanadium(V) oxide. Mixtures with copper or copper(II) oxide gave slightly higher recoveries of sulphur than the vanadium(V) oxide reagent alone, but lower than mixtures containing iron. This will be discussed later in the section on recovery.

Mixtures are also used in methods employing induction heating.[20,28,29,33,34,36] To achieve coupling of the induction current, a suitable metal must be present in the sample or added to it. This is most often iron, but nickel and particularly tungsten have been used recently. The mixture of vanadium(V) oxide and iron in the form of "vanodisc" tablets has already been mentioned.

Carrier gas and its flow-rate. The type and flow-rate of the carrier gas are more critical in the methods where the heating apparatus is not an induction furnace.

Since early times in organic elemental analysis, narrow tubes and moderate temperatures with oxygen flow-rate of some tens of millilitres per minute have been used.[5–7,56]

The small sample mass and the resulting easy combustion, the low gas flow, and only moderate temperatures, possibly achieved with movable burners or furnaces, have all contributed to the good handling characteristics and reputation of vanadium(V) oxide as a catalyst. However, with larger organic and metallic samples requiring macroscale combustions and an increased oxygen flow-rate for complete decomposition, difficulties appeared, most notably in the determination of sulphur. Various workers suggested oxygen flow-rates (in resistance furnaces) ranging from 30–35 ml/min[35] to 2 l./min,[59] and even 4 l./min.[42] Furthermore, a number of authors used nitrogen,[24,41,47,49,55] at flow-rates below 100 ml/min to reduce the formation of sulphur trioxide and moderate the rate of reaction. A few workers have used air for this purpose,[19,38] and also in pyrohydrolysis.[14,15] Other gases are not used to any great extent, but Puzankova *et al.*[39] recently compared oxygen, air, carbon dioxide, and helium, at flow-rates of 1.7–1.8 l./min. For iron and steel, oxygen was much better than air. For sulphate materials, neutral or weakly oxidising atmospheres were preferred, whereas for sulphides oxygen was preferred.

In methods using induction furnaces, an oxygen flow between 0.25[29] and 5 l./min[30] has been used, but 1–2 l./min appears to be usual.[20]

Characteristics of vanadium(V) oxide

Reactivity. There is no agreed definition of suitable characteristics of vanadium(V) oxide for high-temperature analytical applications. This is reflected in the various terms used and actions ascribed to it. Perhaps the most often used term is "reactivity", describing the fluxing reaction with the sample material. It may also involve the fluidity, another loosely used term.

Meyer and Tischbierek[3] established that vanadium(V) oxide was not reduced during the combustion of organic materials in a stream of oxygen and that it shortened the reaction time with carbon. Roth[4] obtained the best combustions of difficultly combustible compounds by using vanadium(V) oxide. Kirsten[6] had good results in expelling sulphur even from barium sulphate, provided a large quantity of the vanadium reagent was used at a high enough temperature and kept together on the bottom of the boat. Fraisse[7] confirmed the superiority of vanadium(V) oxide in achieving complete combustions of organic materials, but Kirsten[9] claims that in ultramicro analysis only orthophosphoric acid can adequately neutralize alkaline ash.

In pyrohydrolysis, particularly, vanadium(V) oxide has often been described as very active.[11,12] Matiašovský and Kubík[26] established that it was the most reactive activator among all tested, including the customary uranium and tungstic oxides, but did not use it further because of carry-over and erratic results. Two other studies[57,58] briefly mention the use of vanadium(V) oxide, and for Newman[14] it was the preferred flux for accelerating the rate of reaction.

In combustion methods, Hagerman and Faust[19] established the effectiveness of vanadium(V) oxide for the quantitative liberation of sulphur from materials of high thermal stability but they could not decompose molybdenum sulphide without the addition of some other oxides. Vanadium(V) oxide has been termed very effective (for sulphur liberation) in other discussions,[32,41] but according to Fulton and Fryxell[30] it does not improve the precision or recovery from ferrous alloys in spite of good burning characteristics.

Vorlíček and Dostál[42] established that vanadium(V) oxide was the best flux, and preferred it to copper and iron, for the decomposition of alkaline earth metal sulphates. They used it for the analysis of ores, coals and sinters. However, Puzankova *et al.*[39] recently studied the recovery of sulphur from the same sulphates and disagreed, but this might be because of a difference in opinion on what characteristics are considered to be the best. Their findings are discussed later, in the section on recovery.

Burke[20] obtained the best and fastest recoveries of sulphur with vanadium(V) oxide as the accelerator–flux. Harrison and Spikings[33] named it as one of the two best fluxes of all tested, and Beesley and Chamberlain[44] preferred it to iron because of the easier control of the reaction. However, according to Shelton,[40] attempts to decompose chromite in a resistance furnace at about 1300° with vanadium(V) oxide were unsuccessful because of incomplete decomposition.

Fluidity. Closely related to reactivity is fluidity, a property shown to be essential for the decomposition of sample materials. Meyer and Tischbierek[3] recognized that for proper action vanadium(V) oxide must be in the liquid state. Roth[4] pointed out the easy formation of homogeneous melts as one of its two outstanding properties. He (and Goto *et al.*[31]) stressed that it does not spatter or creep. Kirsten[6] remarked that the combustion boat must have a concave bottom to assemble all the fluid droplets of vanadium(V) oxide and achieve complete decomposition.

All these examples (except ref. 29) refer to the microchemical elemental analysis of organic compounds. When Bloomfield[49] used vanadium(V) oxide for soils, however, he observed that the formation of a liquid melt slowed down the evolution of sulphur oxides. To counteract this he introduced the addition of kieselguhr. Contrary to Bloomfield's experience, Beesley and Chamberlain[44] stress that having a thin layer of a melt with a low viscosity, helped by the addition of vanadium(V) oxide and high temperatures, facilitates the formation of bubbles and the escape of sulphur dioxide. Fischer *et al.*[29] report that the addition of vanadium(V) oxide helps in obtaining (in conjunction with iron) a well oxidized, bubble-free melt. Ray and Banerjee,[59] using temperatures of 1050–1100°, observed the formation of perfectly fluid melts if adequate quantities of vanadium(V) oxide were used, even for highly alloyed steels. Clements *et al.*,[15] using a mixed flux for pyrohydrolysis, noted the importance of a still more active (*i.e.*, fluid) flux. Recently, Harrison and Spikings[33] stressed, in the analysis of iron, steel and oxide materials, the importance of maintaining fluidity during the decomposition, achieved by high temperatures and by the addition of iron or vanadium(V) oxide as the best fluxes.

Volatility. In considering the volatility of vanadium(V) oxide, three aspects must be reviewed: its possible volatility from the molten state, the mechanical carry-over, and the volatility with water vapour. The first two may occasionally have appeared to be interrelated.

As already mentioned, the combustion of microquantities of organic materials in the presence of vanadium(V) oxide has not presented much difficulty. This may have been because of fortuitous coincidence of several factors related to the techniques used: small mass and therefore an easily achievable excess of the reagent, fluidity, relatively low temperatures, and the necessity for slow combustion because of the nature of the sample. Even with such a difficultly decomposable inorganic compound as barium sulphate, Kirsten[6] did not have difficulty. However, problems seem to have arisen with macrosamples and with the determination of sulphur under considerably different conditions.

Though Roth[4] experienced no complications from spattering of vanadium(V) oxide melts, Hagerman and Faust[19] had to introduce a metal shield made of thin gauge nickel to protect the quartz tube against spattering. When Green[32] assessed the possible use of vanadium(V) oxide for the determination of sulphur in cast iron, he noted considerable difficulties caused by its carry-over with iron oxide. A minimum quantity of vanadium(V) oxide and a preheat first without flow of oxygen were necessary for a trouble-free performance.

Other authors do not always mention the volatility of vanadium(V) oxide or possible near-explosive reactions with it but they often stress the importance of better control of the reaction. Their proposed methods include a number of techniques which help to slow down the rate of the reaction. These include moving burners;[5,19,24] moving electric furnaces;[7,23,35,55] the use of a less oxidizing gas, *i.e.* nitrogen[24,41,47,49,55] (usually at low flow-rates) or air;[14,15,19,38] and two-step heating at two temperatures.[42] Based on these experiences and considerations, a new approach for decomposition with vanadium(V) oxide has been developed,[38] the combustion boat being moved instead of the heating source. In spite of the continuously open analytical sytem, flushed with air at a high flow-rate, there is no carry-over and the reaction conditions are very reproducible without expensive instrumentation.

With the increased use of the vertical induction furnaces in conjunction with vanadium(V) oxide, many of the troubles experienced with the horizontal furnace have disappeared. Even at the highest attainable temperatures there is no discernible carry-over.

In pyrohydrolysis, a special kind of volatility of vanadium(V) oxide exists. It was mentioned earlier that the substance was found in the condensates from decompositions, but it was not understood why. The mechanism of transfer of vanadium(V) oxide at temperatures between 639 and 899° in the presence of water vapour was studied by Yannopoulos.[63] He determined the heat and entropy of reaction of steam with liquid and solid vanadium(V) oxide. From thermodynamic data, he indirectly deduced the presence of a volatile vanadium hydroxide, $VO(OH)_3$ (g), which has a vapour pressure that is twice the apparent vapour pressure of vanadium(V) oxide. Although the presence of vanadium in the condensates led a number of authors to stop using this accelerator in pyrohydrolysis,[11,12,26] it has been successfully applied in conjunction with a suitable determinative step.[14,15]

Catalytic action and oxidation power. From early in the use of vanadium(V) oxide in high-temperature analytical applications, its oxidation power has been recognized. Schramm[1] suggested that in organic elemental analysis vanadium(V) oxide might be preferable to chromate or silica mixtures because vanadium is an excellent catalyst. Meyer and Tischbierek[3] worked on the oxidation of carbon by combustion with oxygen in a vanadium(V) oxide melt. They established that a transfer catalysis probably takes place. During it, oxygen is transferred back to the vanadium

oxide, which is possibly only temporarily reduced in the oxidation reaction of carbon. Roth[4] had introduced vanadium(V) oxide as a standard catalyst instead of potassium dichromate for the prevention of carbonate formation, and since that time it has held a prominent place in organic microanalysis. Morris and Schnitzer[23] have chosen it as the best catalyst—in preference to cobaltic and tungstic oxides—for carbon determination in soil extracts, and Fraisse[7] considers it by far the best oxygen donor for carbon determination and superior to tungstic oxide.

After vanadium(V) oxide had been introduced into the determination of sulphur, another aspect of its catalytic action came into prominence and caused much discussion, namely its ability, under closely controlled conditions, to catalyse the conversion of sulphur dioxide into the trioxide, a property that has long been used in the production of sulphuric acid. Burke[20] summarized the thoughts of the two existing schools, one correctly maintaining that the product of the high-temperature combustion of sulphur from sulphur-bearing materials with vanadium(V) oxide is largely sulphur dioxide, and the other thinking it is sulphur trioxide. Interesting in this context is Zinneke's original work.[5] He used vanadium(V) oxide to liberate sulphur quantitatively, but oxidized the resulting products over a red-hot platinum contact, *i.e.* he did not rely on the catalytic properties of the vanadium(V) oxide itself to obtain sulphur trioxide prior to its isolation as silver sulphate. There still seems scope for research on this aspect.

In evaluating the oxidation power of vanadium(V) oxide, Green[32] reported that a minimum of about 3 g of it is required for the oxidation of 1 g of cast iron. But for iron, steel and associated materials Harrison and Spikings[33] obtained good results with only 1-g additions. The same quantity was also used by Svedung[36] who notes that vanadium(V) oxide is a convenient, strongly oxidizing fluxing agent.

Procedural details

Quantity of vanadium(V) oxide used and sample size. In organic elemental analysis it was easy to maintain suitable fusion conditions within the customary technical requirements. The few milligrams of sample material were easily combusted with virtually no residue and the ratio of vanadium(V) oxide to sample was always high. According to Roth[4] only two spatula tips of vanadium(V) oxide were needed. Even today, from 1 to 3 mg of the sample, or even less, is used with 3–4 times that quantity of vanadium(V) oxide.[7,23]

For macrocombustions and where trace elements are of particular interest, much more sample is needed, but quantities are seldom larger than 1 g, limitations usually being imposed by the volume of the sample-holder. For organic materials such as petroleum products, however, a maximum sample of 200 mg is suggested, with addition of 100 mg of vanadium(V) oxide.[10] In metallurgical analysis, an addition of about 1 g is customary,[20] and the ratio of vanadium(V) oxide to sample is generally greater than unity, to ensure proper fusion.[33,36,42,59]

For pyrohydrolysis, Banks *et al.*[12] suggest a ratio of sample to accelerator of at least 1:10, and Matiašovský and Kubík[26] for similar work use a ratio of 1:5.

It appears that fusion in a crucible with an induction furnace is easier to achieve. With conventional combustion boats and resistance furnaces, there is the tendency to use as little sample as practicable. This is evidenced by a number of workers using smaller samples, *e.g.*, Larsen *et al.*[24] limit the total quantity of sulphur to 2–8 μg, Newman[14] uses 10–100 mg of sample with 0.250 g of vanadium(V) oxide, Beesley and Chamberlain[44] 100 mg of sample with 50 mg of accelerator, and Shmelev and Glushko[35] 0.05–0.1 g of sample at a ratio of 5 (metal) to 3 (flux) for simple steels, and of 1:1 for alloy steels.

Preparation of the analytical charge. Great variations exist in the preparation of the analytical charge, depending to a large degree on the apparatus available. While in organic elemental microanalysis the sample is merely covered in the combustion boat with the required quantity of vanadium(V) oxide,[4,23] for organic macroanalysis the charge is also covered with alundum.[10]

Hagerman and Faust[19] spread the charge in several layers: first silica to protect the boat, then vanadium(V) oxide (first weighing), then sample (second weighing), again vanadium(V) oxide, and lastly silica on top. A similar procedure was adopted by Sen Gupta,[47] except that he did not use a bottom layer of silica and mixed in the sample with a spatula.

Larsen *et al.*[24] introduced the preparation of individual melts, each weighing 0.125 g, by fusion in a quartz boat and subsequent removal for later use. For the charge preparation, solid samples were weighed and spread between two melts, but solutions had first to be evaporated alone. Dokládalová[55] did not remove the melt, but proceeded with the determination in the same boat.

Matiašovský and Kubík[26] ground the fluoride sample together with the activator only after weighing it, and in a similar manner Newman[14] ground the weighed sample in an agate mortar with about one third of the required vanadium(V) oxide. After transferring the mix to a combustion boat, he "rinsed" out the mortar twice by grinding the remainder of the accelerator in it. A 30-min grinding of the weighed sample and flux mix in a mechanical agate mortar was recommended by Clements *et al.*,[15] with subsequent storage and then weighing into a boat.

The charge preparation in crucibles for the induction furnaces consists of simple loading with or without mixing. In a recent method,[36] cups made of thin aluminium foil (the sort used for cooking) were introduced to prevent the liquids from penetrating the ceramic material. To hold the blank level low and constant, these cups were used with all liquid and solid

samples. Crucibles containing 1 g of pure iron were ignited, cooled and stored in a desiccator in advance. Vanadium(V) oxide was added just before a determination.

Temperature of the decomposition. From the early beginnings when Meyer and Tischbierek[3] stressed that vanadium(V) oxide must be in liquid form to function properly and when even its melting point was incorrectly known—Roth[4] quotes the old value of 658 ± 5° (today 675°)—the steady increase in the temperature achievable has brought a parallel increase in the ease and success of the determinations.

Any attempt to classify the temperatures used will be arbitrary. Even so, we may consider three general ranges: moderate temperatures as produced by gas burners and resistance furnaces, up to 1000–1100°; temperatures up to about 1550°, achievable with the heavy-duty resistance furnaces; and temperatures which the induction furnaces can produce, up to 1800–2000°. There is a marked predominance of methods operating at the lowest level, very few at the intermediate one and increasingly more at the highest level of temperatures. The reasons are not only technological but probably also associated with the difficulties in controlling the reactive nature of vanadium(V) oxide. A classification of methods according to the heating source, *i.e.*, the general temperature level of operation, was given earlier in this paper. Here, only some more characteristic temperature data are presented.

The combustion temperature in a recent microchemical method by Fraisse[7] is about 950–1050°; Kirsten[6] raises the temperature to 1100° only for difficultly combustible compounds. The ASTM macromethod[10] specifies 1350°. Generally temperatures between 900° and 1100° are used.[19,24,47,55,59]

Unusually low temperatures are used for fluorine determinations by Clements *et al.*,[15] 700–750°, but Newman[14] says that the temperature is not critical; below 600° the reaction is slow but at around 850° vanadium(V) oxide starts to distil along the tube, and above 900° it is found in the condensate. Amongst those testing vanadium(V) oxide for use in determining fluorine but not introducing it into the final procedure, Banks *et al.*[12] used a temperature of 1000°, while Warf *et al.*[11] used 975°.

A few workers specify slightly higher temperatures: Shmelev and Glushko 1250°,[35] Green 1350°,[32] Vorlíček and Dostál 1350°.[42] Schoeffmann[64] stressed that even in the presence of vanadium(V) oxide a temperature of 1300° is not adequate to achieve a complete release of sulphur from highly alloyed and heat-resistant steels. Temperatures of 1400–1450° have also been used.[31,38,41,43,44] In the methods using vanadium(V) oxide in induction furnaces the temperatures are usually not specifically stated.

Fusion conditions. The fusion conditions perhaps show most clearly the developments and difficulty of progress during a half-century. In organic microchemical analysis, there have never been difficulties with the fusion with vanadium(V) oxide, but for the analysis of macrosamples the fusion became a complex operation. Hagerman and Faust[19] and Larsen *et al.*[24] gradually fused the analytical charge by slowly moving a burner along the combustion tube, protected by metal gauze and in which the boat was positioned just outside the furnace. Nearly constant attention was required. Bloomfield[49] controlled the fusion process by a battery of stationary burners, lighted at intervals. Moreover, the preparation of the analytical train was complex, requiring air, nitrogen and hydrogen to condition the copper and copper(II) oxide charges that were needed to ensure production of only sulphur dioxide. In a similar, improved method, Sen Gupta[47] later found that the copper turnings had to be replaced after five analyses.

In pyrohydrolysis, Newman[14] also used a group of burners, lighted in succession. A conditioning and intermediate handling and cooling of the analytical train was necessary as well. Clements *et al.*[15] dispensed with the intermediate cooling, but the fusion process still had to be controlled by successive lighting of a group of burners.

In an effort to save the time expended by the operator and control the fusion better, Dokládalová[55] introduced an automated prefusion of vanadium(V) oxide *in situ*, but cooling of the furnace prior to sample loading was still necessary. A further saving of time came from repeated use of the same melt, but this could be applied only to special materials. An interesting variant was introduced by Shmelev and Glushko,[35] who used an automatically moving furnace for the controlled gradual heating and fusion. In addition, four separate samples at a time were loaded in a long combustion tube, each being heated in succession.

Stepwise heating and fusion of the analytical charge at two temperatures was used by Vorlíček and Dostál[42] but they did not indicate whether the boat was moved into a hotter zone or the temperature was adjusted. Extending this approach, Nebesar[38,61] used fast and controlled movement of the boat, covered with a special cover. A reproducible fusion is achieved, yielding very fluid melts without creeping.

With induction furnaces the fusion is easier to control because of the geometry, automatic preheat, direction of carrier-gas flow, and temperature.

Duration of the decomposition. As with fusion conditions, the time required for the decomposition with vanadium(V) oxide depends on the technology available and is not always mentioned.

Typical times specified for the decomposition are: up to 3 min;[20,23,28,34] 3–10 min;[7,29,33,38] 10–25 min;[59] above 25 min.[3,14,15,19,24,42,47,49,55]

Evaluation of results

Reference materials and calibration. There are two approaches to calibration. Usually, the complete procedure is applied to reference samples or pure compounds, but sometimes the isolation of the elements

to be determined is assumed to be complete and only the measurement step is calibrated.

In the ASTM method for petroleum products[10] it is specifically stressed that vanadium(V) oxide must be included in all determinations, both of unknowns and calibration samples, because it has a definite effect on the values obtained.

Solutions of pure inorganic sulphur compounds (mostly potassium sulphate) are often used for the calibration of sulphur determinations. Larsen *et al.*[24] noted that low recoveries were obtained if the solutions were evaporated directly with vanadium(V) oxide and they therefore evaporated them separately. This effect was confirmed by Dokládalová[55] who observed that material deposited high on the walls of the boat escaped fusion with the reagent; if the solutions were evaporated in 0.1-ml portions directly onto the cooled vanadium(V) oxide melt, the effect was insignificant. Bloomfield[49] preferred to prepare the spectrophotometric calibration curve from a stock solution of sulphur dioxide in tetrachloromercurate solution, obtained by applying the complete combustion procedure to one aliquot of a standard solution of potassium sulphate. The same procedure was adopted by Sen Gupta,[47] who applied the complete combustion procedure to aliquots of a solution of potassium sulphate to obtain an exact empirical factor for the standard potassium iodate titration solution. For daily preparation of the spectrophotometric calibration curve he used one aliquot of a standard potassium sulphate solution, taken through the whole procedure, but divided into several fractions for the spectrophotometry.

A recent method, using an induction furnace, employed calibration with aliquots of a standard potassium sulphate solution, which were evaporated in aluminium cups within pre-ignited crucibles. This technique helped to reduce the blank and its variability considerably.

Standard metallurgical samples are used for the calibration of methods based on use of resistance-type furnaces[35,59] or induction-type.[20,29] The last-mentioned method used a spectrophotometric calibration curve for 300–400 measurements, all with the same batch of reagent. The time spent on calibration of instruments has been considerably reduced by the introduction of the single-point calibration.[22,34] This coincided with the commercial introduction of vanadium(V) oxide as a flux.

A unique calibration method is used by Beesley and Chamberlain[44] and, according to the latter author elsewhere, more by necessity than by choice. It employs gaseous sulphur dioxide and requires complex instrumentation and control to match the concentration, point of delivery, and rate of release from the sample. It is adaptable to virtually any material.

The smaller group of calibration methods relies almost solely on titration to measure the amount of the elements completely isolated from a matrix containing vanadium(V) oxide. Hagerman and Faust[19] used an alkalimetric titration, and their measurements gave good agreement for synthetically prepared samples. Green[32] employed standard alkalimetric and iodometric methods in his recovery studies on standard samples. Vorlíček and Dostál[42] used a standard hydroxide solution and compared the results with those by gravimetry. Vorlíček and Čejchan[43] switched to a standard iodine solution, basing their conclusions on known or theoretical values for the compounds investigated.

A recent report by Harrison and Spikings[33] completed nearly 15 years of work during which an alkalimetric stoichiometric method for sulphur in metallurgical materials was sought by many. A standard solution of sodium borate was used without employing samples for standardization purposes.

Newman[14] titrates fluoride, after a Willard and Winter distillation, with an empirically calibrated thorium nitrate solution, or uses spectrophotometry. Both methods give results in agreement with each other and with the results obtained by the standard Willard and Winter procedure. Clements *et al.*[15] also used two methods for measurements, *viz.* by ion-selective electrode or by colorimetry, each calibrated with prepared solutions. There was a small blank correction, obtained by completing the whole procedure without sample present.

Recovery of the elements determined. Several factors can influence the recovery and therefore the calibration by affecting any part of the analytical system. Because calibration requires much time and costly reference materials, there is a growing tendency either to reduce it, or to achieve 100% recovery (as in fluoride analysis[11,12]) and dispense with it altogether. Both approaches are used in vanadium(V) oxide methods.

Early work on the combustion of organic compounds established that vanadium(V) oxide helped to achieve a more complete recovery of carbon in the combustion to carbon dioxide.[1,3] Recoveries of sulphur in organic compounds were also generally improved by the use of vanadium(V) oxide.[5,6] With its introduction into macroanalysis, however, the great discussion on the problem of recovery of sulphur started.

Green[32] showed in an extensive study on vanadium(V) oxide that 100% recovery of sulphur from cast iron is impossible if only sulphur dioxide is finally measured. He obtained lower yields than by the usual combustion method and ascribed this to a probable catalytic action of the vanadium(V) oxide. It was otherwise regarded as a suitable flux. This led to the search for methods giving 100% recovery, which has ended with the method by Harrison and Spikings,[33] mentioned above.

Although complete recovery is attractive and feasible, most methods still prefer or must rely on the empirical calibration procedures, as already discussed, especially with less well known natural materials, for

which there are few reference materials. Even with the calibration procedures based on pure compounds, however, recoveries for a different type of material or a different concentration might not give reliable results.[46,48]

An important and unexplained anomaly was reported by Čejchan and Vorlíček[37] who could not decompose potassium sulphate to an extent greater than 89.5%, even by prolonged heating at 1300° with vanadium(V) oxide. This behaviour was unlike that of other sulphates tested, including calcium and barium. Potassium sulphate, however, has been used by many workers and often at much lower temperatures for calibration purposes. Moreover, according to Vorlíček and Čejchan,[43] up to 60 min at 1450° were needed for complete recovery of sulphur from chalcopyrite (~46% S).

Puzankova *et al.*[39] studied recovery of sulphur from magnesium, calcium and barium sulphates, using various fluxes; in no case was complete recovery achieved. For barium sulphate, it decreased from 85.5% for iron to 84.4% for copper/vanadium(V) oxide mixture, 84.2% for copper(II) oxide/vanadium(V) oxide mixture, and 82.6% for vanadium(V) oxide alone. In similar studies, a constant recovery of 86% was obtained by Shmelev and Glushko[35] for sulphur at the 0.01% level in various steels.

The high recoveries of fluorine by two of the methods[11,12] are associated more with the effect of interferences; the other two fluoride methods[14,15] are not based on recovery factors.

Interferences. The presence of interfering elements may affect the decomposition itself or the determination step. These elements can originate either in the sample material, *e.g.*, as alkaline ash in organic compounds, or be due to outside influence, *e.g.*, water in pyrohydrolysis. This problem has already been discussed in the section on volatility.

In the analysis of limestones, it was observed[46] that the residues from the combustion with vanadium(V) oxide[47] contained sulphur because of incomplete decomposition. Although the results were improved when the heating was prolonged, the time required was not practicable. In an earlier finding[43] it was reported that the combustion determination of sulphur at moderate temperatures (1000–1100°) is interfered with by the presence of calcium, barium, potassium and sodium carbonates, because the sulphates of these metals are formed and decompose very little or not at all at these temperatures. Magnesium carbonate does not interfere.

In addition to interfering elements that cause incomplete decomposition of the sample there are others that are characterized by their presence in the combustion products. The problem of trace impurities and their removal from the reagents used has already been mentioned. Much more serious and more difficult to deal with are the interfering elements that volatilize from the sample itself.

Hagerman and Faust[19] were confronted with this problem. When acidic components other than sulphur were expelled they had to determine them and use corrections. The presence of acidic components in natural materials, *e.g.* ores, is well known, and troublesome. Even the recent acid–base method of Harrison and Spikings[33] (with 100% recovery) must be changed in the presence of higher quantities of fluorine, chlorine and similar acidic components, the interference-free iodimetric determinative step then being used. A complicating factor is the inconsistency of the interference.

Another type of interference is the volatility of vanadium fluoride in a nitrogen atmosphere as reported by Larsen *et al.*[24] As a result of it, for isolation of sulphur from sodium zirconium fluoride they first had to use a preliminary fusion in air, according to the method of Hagerman and Faust,[19] which removed hydrogen fluoride and sulphur trioxide. These were trapped in a peroxide solution, which could easily be dealt with.

Precision and accuracy. It is impossible to collate meaningfully the multitude of results obtained throughout the years with the help of vanadium(V) oxide and present them in a statistical package. Data required for a rigorous comparison of methods, *e.g.*, according to IUPAC recommendations, are not always available. Nevertheless, authors often determine and quote the precision of new methods, which may range up to 10% at levels of 10^{-3}% or higher of the element determined.[20,35] At lower levels, the precision is usually,[28,36] but not necessarily,[24,55] poorer.

Accuracy is more difficult to establish, and several approaches are used. In organic analysis, where the element determined is most often a major constituent, the conventional rule of agreement within ± 0.2 or ± 0.3% absolute (depending on the element determined) between the calculated and experimental values is usually applied.[5,7,23]

Another approach is to analyse sample material or synthetic samples by the newly developed method and compare the results with those obtained by a previously recognized method. No rules for agreement exist in this case, and the accuracy achieved is usually judged by inspection and past experience. This approach might entail spiking of the sample with known amounts of the element determined.[14,15,19]

The last approach in evaluation of accuracy is based on comparison of the results obtained by the new method with the certified values of recognized standard reference materials, if available (*e.g.* refs. 29, 33, 36, 48). This is the most recent approach and lends itself well to statistical evaluation, *e.g.*, in interlaboratory tests.[36] For commercially available apparatus, an error of ± 0.0003 or ± 5% of the amount present, whichever is greater, is claimed.[34]

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REFERENCES

1. W. Schramm, *Z. Anorg. Allgem. Chem.*, 1927, **161**, 231.
2. L. Lorenz, *Dissertation*, Breslau, 1927, quoted in ref. 3.
3. J. Meyer and H. Tischbierek, *Z. Anal. Chem.*, 1930, **80**, 241.
4. H. Roth, *Z. Angew. Chem.*, 1937, **50**, 593.
5. F. Zinneke, *Z. Anal. Chem.*, 1951, **132**, 175.
6. W. Kirsten, *Anal. Chem.*, 1953, **25**, 74.
7. D. Fraisse, *Talanta*, 1971, **18**, 1011.
8. W. F. Pickering, *Crit. Rev. Anal. Chem.*, 1973, **3**, 271.
9. W. J. Kirsten, *Pure Appl. Chem.*, 1973, **34**, 63.
10. American Society for Testing and Materials, *ASTM Designation: D 1552-64* (Reapproved 1973), Philadelphia, Pa., 1973.
11. J. C. Warf, W. D. Cline and R. D. Tevebaugh, *Anal. Chem.*, 1954, **26**, 342.
12. C. V. Banks, K. E. Burke and J. W. O'Laughlin, *Anal. Chim. Acta*, 1958, **19**, 239.
13. N. S. Nikolaev, S. N. Suvorova, E. I. Gurovich, I. Peka and E. K. Korchemnaya, *Analytical Chemistry of the Elements; Fluorine*, A. P. Vinogradov, ed., Halsted Press, New York, 1972.
14. A. C. D. Newman, *Analyst*, 1968, **93**, 827.
15. R. L. Clements, G. A. Sergeant and P. J. Webb, *ibid.*, 1971, **96**, 51.
16. J. Doležál, P. Povondra and Z. Šulcek, *Decomposition Techniques in Inorganic Analysis*, Chap. 4. Iliffe, London, 1968.
17. R. Bock, *Aufschlußmethoden der anorganischen und organischen Chemie*, p. 72. Verlag Chemie, Weinheim/Bergstr., 1972.
18. *Idem, op. cit.* p. 201.
19. D. B. Hagerman and R. A. Faust, *Anal. Chem.*, 1955, **27**, 1970.
20. K. E. Burke, *ibid.*, 1967, **39**, 1727.
21. L. L. Kunin, E. V. Frolov and A. M. Vasserman, *Zh. Analit. Khim.*, 1972, **27**, 547.
22. B. Nebesar, *J. Chem. Educ.*, 1971, **48**, A751; 1972, **49**, A9, A63.
23. G. F. Morris and M. Schnitzer, *Can. J. Soil Sci.*, 1967, **47**, 143.
24. R. P. Larsen, L. E. Ross and N. M. Ingber, *Anal. Chem.*, 1959, **31**, 1596.
25. L. F. Lust and B. P. Van der Cook, *Sulfur Determination Supporting the Waste Solidification Program*, BNWL 265, July 1966.
26. K. Matiašovský and C. Kubík, *Chem. Zvesti*, 1962, **16**, 128.
27. Z. Řezáč and Z. Kubec, *Chem. Prumysl*, 1956, **6**, 195.
28. K. E. Burke, *Anal. Chem.*, 1974, **46**, 882.
29. W. Fischer, H. Bastius and R. Mehlhorn, *Neue Huette*, 1963, **8**, 35.
30. J. W. Fulton and R. E. Fryxell, *Anal. Chem.*, 1959, **31**, 401.
31. H. Goto, Y. Kakita and K. Makabe, *Bunseki Kagaku*, 1965, **14**, 244; *Chem. Abstr.*, 1965, **63**, 17142*b*.
32. H. Green, *Metallurgia*, 1959, **60**, 229.
33. T. S. Harrison and R. J. Spikings, *Anal. Chim. Acta*, 1973, **67**, 145.
34. LECO Corporation, Form No. 200-735, 1971, St. Joseph, Michigan 49085, U.S.A.
35. B. A. Shmelev and Yu. V. Glushko, *Zavodsk. Lab.*, 1970, **36**, 1188.
36. D. Swedung, *Scand. J. Metall.*, 1974, **3**, 75.
37. O. Čejchan and J. Vorlíček, *Sb. Prací Výzkum. Ústavu ŽDHE*, 1964, **5**, 155.
38. B. Nebesar, *Report MS-PP 72-5*, Department of Energy, Mines and Resources, Mines Branch, Ottawa, 8 February 1972; presented at the Pittsburgh Conference, Cleveland, 6–10 March 1972.
39. N. V. Puzankova, A. M. Dymov, V. V. Puzankov and V. K. Gruzinov, *Tr. Khim.-Met. Inst., Akad. Nauk Kaz. SSR*, 1973, **21**, 41.
40. B. J. Shelton, *Natl. Inst. Metall. Johannesburg Rept.*, No. 1681, 1975.
41. R. F. Statham, *BISRA, Proc. 19th Chemists' Conf. 1966, Scarborough*, MG/D/Conf./520/66, in discussion.
42. J. Vorlíček and J. Dostál, *Technický Zpravodaj VUŽDH*, 1962, **1**, 37.
43. J. Vorlíček and O. Čejchan, *ibid.*, 1963, **2**, 21.
44. W. J. Beesley and B. R. Chamberlain, *Talanta*, 1974, **21**, 318.
45. A. Filly, R. Letolle and M. Pusset, *Analusis*, 1975, **3**, 197.
46. L. M. Rundle, *Analyst*, 1974, **99**, 163.
47. J. G. Sen Gupta, *Anal. Chem.*, 1963, **35**, 1971.
48. *Idem, Anal. Chim. Acta*, 1970, **49**, 519.
49. C. Bloomfield, *Analyst*, 1962, **87**, 586.
50. P. L. Searle, *ibid.*, 1968, **93**, 540.
51. B. J. Heinrich, M. D. Grimes and J. E. Puckett, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, eds., Part II, Vol. 7, pp. 1–135. Interscience, New York, 1961.
52. C. A. Horton, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, eds., Part II, Vol. 7, pp. 207–334. Interscience, New York, 1961.
53. T. A. O'Donnell, in *Comprehensive Inorganic Chemistry: Fluorine*, Bailar, J. C., ed., 1st Ed., Vol. 2, p. 1009. Pergamon, Oxford, 1973.
54. C. J. Thompson and C. S. Allbright, in *The Analytical Chemistry of Sulfur and its Compounds*, J. H. Karchmer, ed., Part I, pp. 89–144. Wiley/Interscience, New York, 1970.
55. J. Dokládalová, *Z. Anal. Chem.*, 1965, **208**, 92.
56. R. C. Rittner and R. Culmo, *Microchem. J.*, 1966, **11**, 269.
57. M. J. Nardozzi and L. L. Lewis, *Anal. Chem.*, 1961, **33**, 1261.
58. H. P. Silverman and F. J. Bowen, *ibid.*, 1959, **31**, 1960.
59. H. N. Ray and S. Banerjee, *ibid.*, 1966, **38**, 777.
60. B. Nebesar, *New Single-Use Boat Covers for Dust Control in Combustion Sulphur Analysis*, Department of Energy, Mines and Resources, Mines Branch, Ottawa, 23 January 1969, unpublished report.
61. *Idem, Report MRP/MSL (CF) 75-3 (P)*, Department of Energy, Mines and Resources, Canada Centre for Mineral and Energy Technology, Ottawa, 12 March, 1975.
62. *Idem, Lab. Pract.*, 1969, **18**, 1290.
63. L. N. Yannopoulos, *J. Phys. Chem.*, 1968, **72**, 3293.
64. E. Schoeffman, *Stahl Eisen*, 1966, **86**, 1534.

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BESTIMMUNG VON STICKSTOFF IN REFRAKTÄRMETALLEN*—I
MOLYBDÄN UND WOLFRAM

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Zusammenfassung—Es wird über Ringversuche zur Stickstoffspurenbestimmung in Molybdän und Wolfram berichtet, welche im Rahmen des Arbeitsausschusses "Sonder- und Refraktärmetalle" des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute durchgeführt wurden. Folgende Stickstoffbestimmungsmethoden kamen zur Anwendung: klassische und modifizierte Kjeldahlverfahren, insbesondere ein neu entwickeltes Mikro-Kjeldahlverfahren; Inertgasschmelzextraktion; Vakuumschmelzextraktion; Ultrahochvakuumdiffusionsextraktion. Die Stickstoffwerte des ersten Ringversuchs streuten sehr stark. Daher wurden mögliche Fehlerquellen der Kjeldahlverfahren sowie die quantitative Stickstoffausbringung der Extraktionsverfahren näher untersucht. Im Rahmen eines zweiten Ringversuchs wurden folgende Ergebnisse erarbeitet: Der Stickstoffgehalt des untersuchten Molybdänblechs liegt bei 2 ppm, der des Wolframblechs bei 0,5 ppm. Klassische Kjeldahlverfahren sind zur Erfassung von Stickstoffgehalten unter 10 ppm in Metallen ungeeignet. Vielfach liegen die Nachweisgrenzen, vor allem bedingt durch Reagenzien- und Umweltkontamination, auch beträchtlich höher. Das Mikro-Kjeldahlverfahren und die Extraktionsverfahren sind in der Lage, Stickstoffgehalte in Metallen bestenfalls bis 1 ppm zu erfassen. Das einzige im sub-ppm-Bereich anwendbare Verfahren, welches zur Verfügung stand, war die Ultrahochvakuumdiffusionsextraktion. Die gute Übereinstimmung der für Molybdän erhaltenen Werte mit dem Mikro-Kjeldahlverfahren sowie mit den verschiedenen Extraktionsmethoden ist ein Beweis für die quantitative Stickstoffausbringung mit letzteren Verfahren.

Die physikalischen, insbesondere die mechanischen Eigenschaften von hochschmelzenden Metallen werden bereits durch ppm-Spurengehalte an Stickstoff entscheidend beeinflußt.[1] Vor allem die Sprödbruchübergangstemperatur und die Zugfestigkeit werden bei Molybdän und Wolfram durch ihren Stickstoffgehalt wesentlich mitbestimmt.

Die Löslichkeit von Stickstoff in Molybdän und Wolfram ist bei niedrigen Temperaturen extrem gering und erreicht erst über 1000° Werte im ppm-Bereich. Dabei ist die Stickstofflöslichkeit in Wolfram noch geringer als in Molybdän.[1–3] Aufgrund der geringen Löslichkeit bei Raumtemperatur werden bei der Abkühlung Nitride ausgeschieden. Die exakte analytische Erfassung von Stickstoffgehalten im unteren ppm-Bereich ist somit für die chemische Charakterisierung von Molybdän und Wolfram von ausschlaggebender Bedeutung.

Vergleichende Untersuchungen des Stickstoffgehaltes in Refraktärmetallen unter Anwendung verschiedener Bestimmungsverfahren wurden schon öfter vorgenommen, führten jedoch bisher nur bei Niob und Tantal zu einer befriedigenden Übereinstimmung der Meßergebnisse.[4–7] Bei Molybdän und Wolfram hingegen war durchwegs eine breite, methodenabhängige Streuung der Meßwerte zu beobachten.[8–10] Hier soll über Ergebnisse von Ringuntersuchungen berichtet werden, welche im Rahmen des Arbeitsausschusses "Sonder- und Refraktärmetalle" des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute durchgeführt wurden. Bei vorliegender Ringuntersuchung wurde zunächst eine bestürzende Streuung der Meßergebnisse festgestellt, jedoch konnte diese Streuung durch Optimierung der verwendeten Analysenverfahren bei einer weiteren Ringuntersuchung weitgehend abgebaut werden. Schließlich kam man zu einer eindeutigen Aussage

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sowohl was die Anwendbarkeit der eingesetzten Analysenverfahren betrifft als auch in bezug auf den Stickstoffgehalt der untersuchten Molybdän- und Wolframproben. Folgende Stickstoffbestimmungsmethoden kamen zur Anwendung: klassische und modifizierte Kjeldahlverfahren; Inertgasschmelzextraktion; Vakuumschmelzextraktion; Ultrahochvakuumdiffusionsextraktion.

EXPERIMENTELLER TEIL

Probenmaterial

Sintermetallurgisch vom Metallwerk Plansee hergestelltes Molybdän- und Wolframblech von 2,5 bzw. 2,7 mm Dicke wurde von Labor 6 mittels Vakuumschmelzextraktion auf Homogenität geprüft. Es wurde weder für das Molybdänblech noch für das Wolframblech eine auffallende Inhomogenität festgestellt.

Tabelle 1 gibt eine Übersicht der in den Blechen festgestellten Spurengehalte sowie über die durchschnittlich im verwendeten Sintermolybdän und -wolfram im Rahmen einer mehrjährigen laufenden Qualitätskontrolle festgestellten Spurenverunreinigungen. Mit Matrixgehalten von *ca.* 99,96% für Molybdän und *ca.* 99,98% für Wolfram zählen diese Metalle wohl mit zu den reinsten im technischen Maßstab hergestellten Metallen überhaupt.

Probenvorbereitung

Die Bleche wurden mit einer SiC-Trennscheibe in Stücke geschnitten. Folgende Beizvorschriften zur Oberflächenreinigung wurden eingehalten:[11]

Molybdän: Beizbad: 4 Volumenteile HF (40% ig) + 1 Volumenteil HNO_3 (65% ig); Beizdauer und -temperatur: 10 sec, Zimmertemperatur; Spülen: 20 sec mit HCl (36%ig), sodann dreimal mit Wasser und dreimal mit Methanol; Trocknen: mit Heißluft (*ca.* 60°, Fön); Residueller Oberflächenstickstoff nach dieser Behandlung: $<0{,}05\ \mu g/cm^2$.[11]

Wolfram: Beizbad: 1 Volumenteil HF (40% ig) + 4 Volumenteile HNO_3 (65% ig); Beizdauer und -temperatur: 2 min, Zimmertemperatur; Spülen: dreimal mit Wasser und dreimal mit Methanol; Trocknen: mit Heißluft (*ca.* 60°, Fön); Residueller Oberflächenstickstoff nach dieser Behandlung: $<0.05\ \mu g/cm^2$.[11]

Die Problen wurden bis zur Analyse im Exsikkator aufbewahrt. Ein Einfluß der Aufbewahrungsdauer auf die Stickstoffwerte wurde selbst bei mehrtägiger Lagerung nicht festgestellt.

Verwendete Analysenverfahren

In Tabelle 2 sind die wichtigsten Analysenparameter der in den einzelnen Laboratorien angewandten Verfahren zusammengefaßt.

Zum Mikro-Kjeldahlverfahren des Labors 5 ist zu erwähnen, daß dieses Verfahren eigens zur Verbesserung des Nachweisvermögens bei der Bestimmung des Stickstoffs in Reinstmetallen entwickelt wurde.[12] Nach dem Säuredruckaufschluß in einem geschlossenen System (stahlummanteltes PTFE-Gefäß)[13] trennt man das gebildete Ammonium nach Zusatz von Natronlauge in einer speziellen Mikro-Kreislaufdestillationsapparatur als Ammoniak mit Wasserdampf ab und absorbiert es in verdünnter Schwefelsäure. Seine Bestimmung erfolgt unmittelbar in der Vorlage der Apparatur in nur 2 ml Lösung durch Titration mit coulometrisch entwickeltem OBr^- und biamperometrischer Indizierung des Endpunktes. Mit Ausnahme des Aufschlusses läuft das Verfahren programmgesteuert ab. Die wesentlichen Vorteile dieser Methode gegenüber den klassischen Kjeldahldestillationsverfahren liegen in der Anwendung eines gegenüber der Laborluft völlig abgeschlossenen Systems, in der Verwendung kleiner Reagenzienmengen sowie im minimalen Totvolumen der Apparatur. Dadurch kann der Blindwert auf *ca.* 1 μg N gedrückt werden.

Zum Ultrahochvakuumdiffusionsextraktionsverfahren des Labors 5 ist ergänzend zu bemerken, daß die Eichung durch Einlassen definierter Stickstoffraten über ein Eichleck erfolgte. Eine quantitative Stickstoffextraktion ist aufgrund der vorliegenden thermodynamischen und kinetischen Daten zu erwarten.[1–3] Überdies besteht hier die Möglichkeit der direkten Beobachtung der Entgasungskinetik. Zur Kontrolle der Stickstoffausbringung wurden Niobproben mit definiertem Stickstoffgehalt analysiert.[7]

Tabelle 1. Chemische Charakterisierung des in der Ringanalyse eingesetzten Molybdän- und Wolframblechs sowie Durchschnittswerte des vom Metallwerk Plansee pulvermetallurgisch hergestellten Molybdäns und Wolframs aus der ständigen Qualitätskontrolle (QK). Mit Ausnahme der Matrixgehalte sind alle Werte Masse-ppm

Element	Molybdan		Wolfram	
	Blech für Ringversuch	Durchschnittsanalyse aus QK	Blech für Ringversuch	Durchschnittsanalyse aus QK
Mo bzw W	99,97%	99,96%	99,98%	99,98%
Ag, As, Co, H, Mn, N, Na, Nb, Pb, Ta, Ti, Zn, Zr	≤5	≤5	≤5	≤5
Al	12	10	<5	<5
Ba	<1	2	<1	3
C	20	15	16	15
Ca	16	5	<5	5
Cd	<1	<1	<1	<1
Cr	<10	<10	<10	<10
Cu	8	5	<5	5
Fe	31	50	12	20
K	7	<5	<5	<5
Mg	7	<5	<5	<5
Mo in W	—	—	90	40
Ni	<5	5	6	5
O	30	20	18	10
P	6	5	16	20
S	<2	5	<2	<2
Si	6	5	7	5
W in Mo	75	200	—	—

Tabelle 2. Übersicht der von den teilnehmenden Laboratorien angewandten Analysenverfahren sowie wichtigste Analysenparameter

Labor Nr	Angewandtes Analysen-verfahren	Einwaag. g	Aufschlußgefäße und Aufschluß- bzw Extraktions-bedingungen	Losungsmittel bzw. Bad/Flux	Verwendete Apparatur	Bestimmungs-verfahren	Blindwert, µg N $\bar{x}$	s
1	Makro-Kjeldahl	2	abgedeckte PTFE-Becher Mo: 3 hr bei 60–70° W· 3–4 hr bei 60–70°	40 ml HF x ml H_2O_2	Handelsubliche Apparatur	Spektrophotometrie mit Neßlers Reagenz [18]	Mo 88 W: 62	7(n = 4) 11(n = 4)
2	Makro-Kjeldahl	0,25	abgedeckte PTFE-Becher Mo: 3 hr bei gelindem Sieden W· 8 hr bei gelindem Sieden	Mo· 6 ml HF 2 ml H_2O_2 (30%) 3 ml H_2O W· 3 ml HF 10 ml H_2O_2 (30%)	Handelsubliche Apparatur	Spektrophotometrie, Indophenol-verfahren [17]	Mo: 17 W 20	1,5(n = 5) 2(n = 4)
3(*a*)	Makro-Kjeldahl	1	abgedeckte PE-Becher Mo 3 hr bei 60–70° W· 3–4 hr bei 60–70°	Mo· 3 ml HF 5 ml H_2O_2 W· 3 ml HF 6 ml H_2O_2	Apparatur von Ströhlein	Spektrophotometrie mit Neßlers Reagenz[18]	Mo: 45 W: 43	9(n = 3) 6(n = 3)
(*b*)	Inertgas-schmelz-extraktion	1	*ca* 2800° *ca* 1 5 min	Ni-Flux 0,4:1	Leco TN-15	Warmeleit-fahigkeits-messung	3	1(n = 6)
4	Halbmikro-Kjeldahl	0,5	abgedeckte PTFE-Becher Mo, W. 3 hr bei 70°	Mo, W 0,5 ml HF 2,5 ml H_2O_2 (30%)	Apparatur nach Zitat[14]	Spektrophotometrie mit Neßlers Reagenz	30	2(n = 24)
5(*a*)	Mikro-Kjeldahl	0,1 bzw 0,4	Druckaufschluß in PTFE-Gefaßen[13] 3 bis 5 hr bei 60° bzw. 80° und anschließend 3 hr bei 150°	Einwaage 0,1 g Mo, W 2 ml HF/H_2O_2 (30%) 1 5 Einwaage 0,4 g 0,4 ml HF 2 ml H_2O_2 (60%)	Kreislauf-Destillations-apparatur[12]	Coulometrische Titration mit biamperometrischer Indizierung des Endpunktes[12]	f Einwaage 0,1 g: 0,8 0,2(n = 9) f Einwaage 0,4 g 1,2 0,2(n = 4)	
(*b*)	Vakuum-schmelz-extraktion	0,4 bis 0,5	Extraktion 1 min bei 2500°	Pt-Flux 2 bis 3 1	Leybold Heraeus VH-9 mit Elektrodenofen	Gaschromato-graphie mit Warmeleit-fahigkeits-detektor	3–4 µg (vgl Text)	
(*c*)	Ultrahochvakuum-diffusions-extraktion	0,3 bis 0,4	Extraktionstem-peratur: Mo 2550° W· 2900°		Selbstgebautes Gerät[7] mit tie-gelfreier HF-Heizung	Quadrupol-Massenspek-trometer	N_2-Endpartial-druck $6{,}67 \cdot 10^{-8}$ Pa	
6	Vakuum-schmelz-extraktion	0,5 bis 0,7	Extraktion 1 min bei 2350°	Ni-Sn Bad 2·1·1	Balzers EAN 220	Warmeleit-fahigkeits-messung	3,8	0,3(n = 13)

ERGEBNISSE UND DISKUSSION

In einer ersten Ringuntersuchung wurden keine Absprachen bezüglich der Probenvorbereitung und Durchführung der Analysen getroffen. Jedes Laboratorium arbeitete nach den jeweils routinemäßig angewandten Bedingungen. Die Ergebnisse dieser Untersuchung sind in Abb. 1 für Molybdän (*a*) und Wolfram (*b*) dargestellt. Aus beiden Abbildungen ist ersichtlich, daß die Schmelzextraktionswerte im unteren ppm-Bereich liegen, während die Kjeldahlwerte über einen weiten Bereich streuen. Ferner sind beträchtliche Schwankungen in der Reproduzierbarkeit der Werte zu beobachten, die mit den einzelnen Kjeldahlverfahren erhalten wurden. Aufgrund dieser Ergebnisse wurden einerseits weitere Untersuchungen vorgenommen und andererseits für den zweiten Ringversuch folgende Absprachen getroffen.

Probenvorbereitung

Diese erfolgte für den zweiten Ringversuch einheitlich nach Vorschrift des Büro Eurisotop,[11] wodurch eine minimale und definierte Oberflächenbedeckung erzielt wird. Mechanische Oberflächenreinigungsverfahren wie Abschleifen oder Abfeilen der Oberfläche, wie sie in der Literatur empfohlen werden,[14] sind für Molybdän und Wolfram zur Analyse auf C, H, O, N ungeeignet.

Absprachen zur Durchführung der Kjeldahlmethode

Nachdem vor allem die Mittelwerte und die Reproduzierbarkeit der verschiedenen Kjeldahl-"Hausmethoden" sehr differierten, lag es nahe, daß hier besonders auf systematische Fehler zu achten sei und es wurden nach eingehender Diskussion folgende Richtlinien ausgearbeitet.

Vereinheitlichung des Aufschlußverfahrens. Da die in der Literatur angegebenen sehr niedrigen Blindwerte von 0,5 µg N für das Aufschlußverfahren mit K_2CrO_4–H_3PO_4–HF[10] trotz sorgfältiger Reagenzienreinigung nicht erreicht werden konnten und auch der Aufschluß mit H_2SO_4–K_2SO_4 zu beträchtlichen Blindwerten führte, wurde der Aufschluß mit HF–H_2O_2 vorgezogen. H_2O_2 und HF "Suprapur"

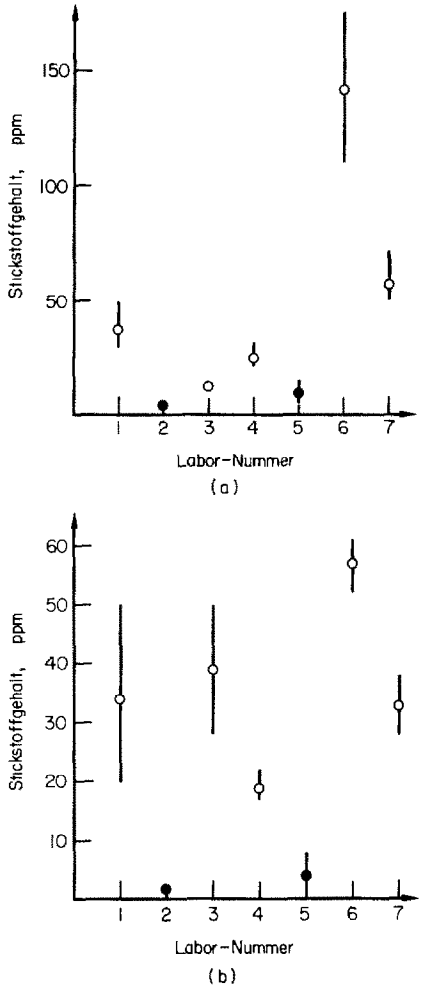


Abb. 1. Ergebnisse der 1. Ringuntersuchung zur Bestimmung von Stickstoff in Molybdän (*a*) und Wolfram (*b*) Labormittelwerte nach: ○ Kjeldahlverfahren und ● Vakuumschmelzextraktionsverfahren; die Streubreite wird durch den jeweils niedrigsten und höchsten von 4 bis 6 Einzelwerten gebildet.

erwiesen sich als genügend stickstoffarm und bedurften keiner weiteren Reinigung.

Ergänzende Untersuchungen zum Aufschlußverfahren. Um zu prüfen, ob bei der Verwendung von H_2O_2 keine Stickstoff-Verluste durch Oxidation zu elementarem N_2 auftreten, wie dies bei der Analyse von Nitriden des Ti, Zr, Nb und Ta schon beobachtet wurde,[15] hat man in Labor 5 nach dem Mikro-Kjeldahlverfahren Untersuchungen über die Stickstoffausbeute durchgeführt. In Tabelle 3 sind die Ergebnisse zusammengestellt. Die Werte, die an Proben des hochvakuumentgasten Mo-Drahtes (1 mm Durchmesser; 1900°; $1{,}3 \cdot 10^{-3}$ Pa) erhalten wurden, repräsentieren den Blindwert des Verfahrens, der aus den Stickstoffgehalten der Aufschlußsäure resultiert und unabhängig vom Probengewicht ist. Stickstoffmengen, die in Form von NH_4Cl-Lösung vor dem Aufschluß der Mo-Proben zugesetzt wurden, hat man quantitativ wiedergefunden. Weiterhin wurden N_2-begaste Mo-Drähte (1 mm Durchmesser; begast bei 1900° mit $6{,}5 \cdot 10^4$ Pa N_2) ebenfalls mit 2 ml HF/H_2O_2 (1:5) aufgeschlossen und der Stickstoffgehalt wurde bestimmt. Das Ergebnis stimmt mit 47 ppm ($s = 4$ ppm; $n = 7$) gut mit dem auf Grund der Begasungsbedingungen zu erwartenden Stickstoffgehalt von *ca.* 50 ppm überein. Mit der Vakuumheißextraktion (Diffusionsentgasung; 2 min/2300°) wurden an zwei Proben 47 bzw. 57 ppm Stickstoff ermittelt.

Um den relativ langsamen Angriff des HF–H_2O_2-Gemisches auf Molybdän und Wolfram zu beschleunigen, erwies sich die Verwendung von H_2O_2 (60% ig) als optimal. Dabei ließ man das HF–H_2O_2-Gemisch zunächst in der nur abgedeckten PTFE-Bombe bei 60° (Mo) bzw. 80° (W) bis zu 2 hr reagieren. Dann war die heftigste Gasentwicklung vorbei, man verschloß die Bombe und ließ zunächst noch eine Stunde bei 60° und dann 3 hr bei 150° ausreagieren. Die Dauer des Aufschlusses hängt wesentlich vom Reinheitsgrad der Proben ab. Durch Zonenschmelzen gereinigtes Material benötigt die längsten Aufschlußzeiten.

Kontamination aus der Laborluft. Wegen der Gefahr der Kontamination durch die meist ammoniakhaltige Laboratmosphäre,[10,17] vor allem bei langen Aufschlußzeiten, arbeiteten die meisten der an den hier diskutierten Ringversuchen beteiligten Laboratorien in speziellen Räumen abseits großer Laboratorien mit abgedeckten Aufschlußgefäßen. Wo dies nicht möglich war, konnten so niedrige Stickstoffgehalte, wie sie hier zu erfassen waren, nicht bestimmt werden. Am günstigsten erwies sich das Arbeiten in zumindest zeitweise fest verschlossenen PTFE-Bomben.

Tabelle 3. Untersuchungen zur Prüfung der Stickstoffausbeute beim Kjeldahlaufschluß mit HF/H_2O_2. Aufschlußbedingungen: 2 ml HF/H_2O_2(30% ig) (1:5), Druckgefäß, 3 bis 5 hr bei 50° und 5 bzw. 3 hr bei 150°

Probenmaterial	Einwaage, *mg*	ermittelter Stickstoff, *µg*	*ppm*†
Mo-Draht, entgast	116,8	0,77	
(1 hr, 1900°;	92,1	1,08	
$1{,}3\ 10^{-3}$ Pa)	112,0	0,76	
	91,1	1,30	
	88,0	0,86	
	61,7	0,83	
		$\bar{x} = 0{,}93$*	
		$s = 0{,}21$	
Mo-Draht entgast, mit	107,4	4,1	
3 µg N in Form von	95,4	4,05	
NH_4Cl aufgestockt	97,8	3,95	
		$\bar{x} = 4{,}03$	
		$s = 0{,}08$	
Mo-Draht,	109,4	5,85	45
N_2-begast bei	76,0	4,9	52
1900° und	77,2	4,5	46
$6{,}5 \cdot 10^{-4}$ Pa	75,4	4,0	41
	75,0	4,55	48
	86,1	5,4	52
	90,7	5,2	47
			$\bar{x} = 47{,}3$
			$s = 3{,}9$

* Blindwert resultiert aus Stickstoffgehalten der Aufschlußsäure und ist unabhängig von der Höhe der Molybdändrahteinwaage.

† Blindwert von 0,93 µg berücksichtigt.

Blindwertbestimmung mit Reinstmetallen. Wie schon Kallmann und Mitarbeiter feststellten,[10] werden in den Reagenzien enthaltene Nitratspuren bei der üblichen Blindwertbestimmung nicht miterfaßt. Andererseits werden jedoch beträchtliche Nitratmengen beim Löseprozeß eines Metalls reduziert. Dies führt zu einer unkontrollierbaren Ammoniumkontamination. Bestimmt man jedoch den Blindwert in Gegenwart von "stickstofffreien" Metallen, so läßt sich auch der durch den Nitratgehalt der Reagenzien eingeschleppte Stickstoff erfassen. Sämtliche in Tabelle 2 aufgelisteten Blindwerte wurden unter Verwendung von zonengeschmolzenem Wolfram bzw. von hochvakuumgeglühtem Molybdän (2,5 hr; 2000°; $1{,}3 \cdot 10^{-3}$ Pa) ermittelt.

Ausbeuteuntersuchungen für die Schmelz- und Diffusionsextraktionsverfahren

Die große Diskrepanz der meisten Kjeldahlwerte im Vergleich zu den Schmelzextraktionswerten im ersten Ringversuch (vgl. Abb. 1) warf die Frage auf, ob die Stickstoffausbringung bei den Heißextraktionsverfahren auch tatsächlich quantitativ ist. Wie schon früher erwähnt, ist eine quantitative Stickstoffausbringung selbst durch Diffusionsextraktion bei den angewandten Temperaturen (vgl. Tab. 2) aufgrund der thermodynamischen und kinetischen Daten zu erwarten.[1–3] Eventuell vorliegende Nitride sind leicht zersetzlich und die Stickstofflöslichkeit in Molybdän und Wolfram ist bei den während der Extraktion herrschenden Stickstoffpartialdrücken sehr gering. Auch bei Schmelzextraktionsverfahren sollte die Stickstoffausbringung bei Temperaturen über 2000° quantitativ sein.[2] Versuche, die Anwendbarkeit verschiedener Badmaterialien und Temperaturen betreffend, wurden vom Labor 6 durchgeführt und sind in Tabelle 4 zusammengefaßt. Ähnliche Versuche wurden auch an Wolfram und Molybdän mit etwas höherem Stickstoffgehalt (zwischen 5 und 10 ppm) durchgeführt. Die in Tabelle 4 aufgeführten Stickstoffwerte für Wolfram wurden für ein solches Blech mit höherem Stickstoffgehalt erhalten. Die Werte für das Blech des Ringversuchs lagen durchwegs an der Nachweisgrenze. Eine Temperatur von *ca.* 2350° ist sowohl für Molybdän als auch für Wolfram ausreichend. Höhere Extraktionstemperaturen brachten keine Erhöhung der Stickstoffwerte. Als Badmaterialien eignen sich für Molybdän und Wolfram in gleicher Weise: (*a*) Ni–Sn in einem Verhältnis Ni:Sn: Probe = 2:1:1; bei höherem Probenanteil treten Extraktionsverluste auf; dies beschränkt bei der Größe der Graphitkapseln des verwendeten Gerätes die Probeneinwaage für Molybdän auf etwa 0,7 g, für Wolfram auf 1 g; (*b*) Pt–Sn oder Pd–Sn mit der Probe in einem Verhältnis 4:1:2; (*c*) Ni/Ce (90:10)–Sn mit der Probe in einem Verhältnis 2:1:1.

Für Routineanalysen ist die Verwendung von Ni–Sn wohl am wirtschaftlichsten. Beste Ergebnisse werden auch mit der Pt-Flux-Technik des Labors 5 erhalten (Pt:Probe 2–3:1). Die Stickstoffausbringung durch Diffusion aus kompaktem Molybdän ist zwar möglich, sie verläuft jedoch nur bei dünnen Proben (≤ 1 mm) genügend schnell.[3] Bei dickeren Proben empfiehlt sich deshalb die Verwendung von Zuschlägen. Die Blindwerte sind für die Badmaterialien Ni–Sn, Ce/Ni–Sn, Pt–Sn und Pd–Sn durchwegs vergleichbar (*F*-Test, *t*-Test), ebenfalls für die angewandten Temperaturen. Den größten Einfluß auf den Blindwert ergaben unterschiedliche Öffnungszeiten des Systems zur Probeneingabe oder zur Badblindwertermittlung. Beide Zeiten müssen daher gleich sein und exakt eingehalten werden. Damit erscheint es zulässig, Gesamtmittelwerte für die unter Molybdän bzw. Wolfram tabellierten Blindwerte zu bilden (jeweils nach Tests für Ausreißer nach Dixon): Blindwerte bei der Mo-Analyse in μg N: $\bar{x} = 3{,}92$; $s = 0{,}28$; $n = 17$; Blindwerte bei der W-Analyse in μg N: $\bar{x} = 3{,}96$; $s = 0{,}38$; $n = 27$.

ERGEBNISSE DES ZWEITEN RINGVERSUCHS

Nach den beschriebenen Untersuchungen und unter Einhaltung der getroffenen Absprachen wurde ein zweite Ringversuch durchgeführt, dessen Ergebnisse in Tabelle 5 zusammengefaßt sind. Vor allem die Ergebnisse nach dem Kjeldahlverfahren haben sich gegenüber dem ersten Ringversuch wesentlich geändert. Mit Ausnahme des Labors 1 fanden alle Anwender des Makro- oder Halbmikro-Kjeldahlverfahrens Werte, die mit der jeweiligen Nachweisgrenze identisch sind. Für Wolfram trifft das auch für das Mikro-Kjeldahlverfahren zu, für Molybdän liegen die Werte mit letzterem Verfahren knapp über der Nachweisgrenze. Obwohl die Stickstoffwerte der Schmelzextraktionsverfahren für Molybdän hart an der Nachweisgrenze liegen, stimmen sie gut überein. Der wahre Stickstoffgehalt des untersuchten Molybdänblechs dürfte somit bei 2 ppm liegen. Für Wolfram reicht weder das kaum zu steigernde Nachweisvermögen des Mikro-Kjeldahlverfahrens noch das der Schmelzextraktionsverfahren aus, um den extrem niedrigen Stickstoffgehalt dieses Materials zu erfassen. Lediglich das nachweisstärkste der eingesetzten Verfahren, die Ultrahochvakuumdiffusionsextraktion, ergab reelle Werte um 0,5 ppm. Damit liegen die Stickstoffgehalte in den sintermetallurgisch hergestellten Refraktärmetallen Molybdän und Wolfram im unteren Einser-ppm Bereich, bei Wolfram sogar im Zehntel-ppm Bereich.

Bei den dritteljährlich durchgeführten chemischen Qualitätskontrollen für Fertigprodukte im Metallwerk Plansee ergaben sich seit Einsatz des Balzers EAN 220 durchwegs Werte < 5 ppm für alle untersuchten Molybdän- und Wolframformteile. Nur selten findet sich ein Wolframhalbzeug mit Stickstoffgehalten über 1 ppm, das Wolframblech, dessen Stickstoffwerte in Tabelle 4 angeführt sind. Für dieses Blech ergibt sich ein Mittelwert von 2,4 ppm N für alle Badmaterialien, Bad:Probe-Verhältnisse (mit

Tabelle 4. Untersuchungen zur Stickstoffausbringung bei der Vakuumschmelzextraktion für Molybdän und Wolfram

Bad-Materialien	Verhältnis Badmaterialien Mo,W	Temperatur, °C	Blindwerte, µg N	Einzelwerte ppm N	$\bar{x}$ der Gruppen	s der Gruppen
		1 *Molybdan* (Blech für Ringanalyse)				
ohne Bad	—	*ca.* 2580	1,5	1,2		
			1.8	1,0	1,1	0,1
			1,7	1,1		
Ni-Sn	2·1:2	*ca.* 2350	3.8	2,0		
			4,3	1,9	1.9	
			(1,8)	(1,7)		
	2 1 1	*ca.* 2350	3,4	2,4		
			3,5	1,9	2,2	$0{,}2_5$
			4,1	2,2		
		ca 2580	3,7	2,5		
			3.8	2.0	2,1	0,3
			4.0	2,1		
			4,2	1.8		
Ce/Ni-Sn	2 1 1	*ca* 2350	4,2	1.6	1.8	—
			4.3	2.0		
		ca 2580	3,8	2,7	2,4	—
			4,3	2,1		
Pt-Sn	4.1:2	*ca* 2350	4,0	2.3	2,1	—
			3,7	1.9		
Pd-Sn	4·1 2	*ca* 2350	3,7	2,5	2,0	—
			3,8	1,5		
		2. *Wolfram* (anderes Blech als das für die Ringanalyse verwendete)				
Ni-Sn	2:1 2	*ca* 2350	4,5	1		
			3,9	1.2	1,2₅	0,2
			4,4	1,5		
			3,5	1,3		
	2 1 1	*ca* 2350	3,5	2,7		
			3,8	1,5		
			3,8	1,5		
			4,3	3.4	2,7₁	1.0
			3,9	4.1		
			4.7	3,5		
			3,8	2,3		
		ca 2580°	4.6	1,8		
			4,4	3,1		
			3,4	1,9	2,4₅	0,6₅
			3,8	3,1		
			3,9	2,3		
Ce/Ni-Sn	2 1 1	*ca.* 2350°	3,6	3,0		
			3,6	1,8	2,5	0,7
			3,9	2.0		
			4,1	3,1		
Pt/Sn	4 1 2	*ca* 2350°	4,0	1,5		
			4,5	2,3	1,7	0,5₅
			3,7	1,3		
Pd-Sn	4 1.2	*ca* 2350°	3.6	2,7		
			3,9	3,2	2,5	0,8₅
		ca 2580°	3,5	1,3		
			4,3	2,8		

Analysenprogramm für alle Versuche mit dem Balzers Exhalograph EAN 220:
1. Analysenablauf (automatisch) mit Badmaterial: Aufschmelzen und Entgasen
2. Analysenablauf: Blindwertbestimmung
3. Analysenablauf nach Probenzugabe: Bruttowertbestimmung.
Analysenablaufdauer: je 3 min, davon *ca.* 1 min Heizdauer.
Nach jedem Analysenablauf muß 1 min gewartet werden, bis das Bad ausreichend abgekühlt ist. Darüberhinaus muß die Apparatur bei Blindwertbestimmungen genau so lange offen stehen wie beim Einführen der Probe zwischen 2. und 3. Analysenablauf (ca. 20 sec).

Ausnahme der Ni–Sn 2:1:2 -Werte) und Temperaturen mit $s = 0{,}8$ ppm N bei $n = 23$. Die gegenüber der Blindwertstandardabweichung höhere Probenstandardabweichung deutet hier wohl auch auf eine geringfügig inhomogene Stickstoffverteilung hin.

Das wohl bemerkenswerteste Resultat vorliegender Untersuchungen besteht in der guten Übereinstimmung der Mikro-Kjeldahl-Werte mit denen der Heißextraktionsverfahren. Dies ist der sicherste Beweis für die quantitative Stickstoffausbringung mit allen hier angewandten Extraktionsverfahren. Der Wert der verläßlichen Mikro-Kjeldahlmethode als Absolutmethode für Eichzwecke sollte dabei besonders hervorgehoben werden. Mit einer Analysenzeit von etwa 30 min (ohne Aufschluß) ist sie allerdings langsamer als die Heißextraktionsverfahren, die für Routinebestimmungen nach überprüften Extraktionstechniken vorzuziehen sind. Die Analysendauer bei den Heißextraktionsverfahren liegt bei etwa 10 bis 15 min.

Ein weiteres wichtiges, wenn auch nicht ganz neues Ergebnis[1,14] vorliegender Untersuchungen ist die Tatsache, daß Stickstoffgehalte unter 10 ppm mit den herkömmlichen Makro-Kjeldahldestillationsverfahren nicht bestimmbar sind. Der Blindwertpegel und die Standardabweichung der Blindwerte, die die Nach-

Tabelle 5. Ergebnisse des zweiten Ringversuchs zur Bestimmung von Stickstoffspuren in Molybdän und Wolfram

Labor Nr.	Analysenverfahren	Einzelwerte	Ergebnisse, *ppm N* $\bar{x}$	s
		1 *Molybdän*		
1.	Makro-Kjeldahl	79; 83; 82; 95; 124	93	9
2	Makro-Kjeldahl	≙ Nachweisgrenze	≤10	—
3	(*a*) Makro-Kjeldahl	≙ Nachweisgrenze	≤27	—
	(*b*) Inertgas-Schmelz-extraktion	≙ Nachweisgrenze	≤3	—
4	Halbmikro-Kjeldahl	≙ Nachweisgrenze	≤13	—
5	(*a*) Mikro-Kjeldahl	(*a*) Einwaage ca 0,1 g; 3,7; ≤1, 3,6; 2,9, ≤1, 2,5, ≤1; 3,7	≤3	—
		(*b*) Einwaage ca 0,4 g· 2,3; 3,6	3	—
	(*b*) Vakuum-Schmelz-extraktion	1,2; 5,7; 4,4; 5,6; 3,6	4	2
	(*c*) UHV-Diffusions-extraktion	(7,4); 2,9; 1,8; 0,8; 1,3	1,7	0,9
6	Vakuum-Schmelz-extraktion	vgl. Tabelle 4	2,1	0,34
		2. *Wolfram*		
1	Makro-Kjeldahl	38; 38; 40; 37; 41	39	
2	Makro-Kjeldahl	≙ Nachweisgrenze	≤10	
3	(*a*) Makro-Kjeldahl	≙ Nachweisgrenze	≤18	
	(*b*) Inertgas-Schmelzextraktion	≙ Nachweisgrenze	≤3	
4	Halbmikro-Kjeldahl	≙ Nachweisgrenze	≤13	
5	(*a*) Mikro-Kjeldahl	≙ Nachweisgrenze	≤1	
	(*b*) Vakuum-Schmelz-extraktion	≙ Nachweisgrenze	≤2	
	(*c*) UHV-Diffusions-extraktion	0,54; 0,37	0,46	
6	Vakuum-Schmelz-extraktion	≙ Nachweisgrenze	≤1,6	

Als Nachweisgrenze wurde wie üblich die dreifache Standardabweichung der Blindwerte angenommen.

weisgrenze bestimmen, sind zu erniedrigen durch: (*a*) Verkleinerung der Destillationsapparatur; je kleiner das Gesamtvolumen, desto nachweisstärker und störunanfälliger wird das Verfahren; (*b*) Verminderung des Volumens der verwendeten Reagenzlösungen, ermöglicht durch Halbmikro- bzw. Mikro-Techniken; (*c*) Verwendung von Reagenzien hoher Reinheit und die Vermeidung von Kontamination aus der Laborluft; je stärker geschützt gegen Umwelteinflüsse das Verfahren durchgeführt werden kann (Aufschluß im Druckgefäß, Destillation und Bestimmung in einer geschlossenen Apparatur), desto niedriger liegen die Blindwerte.

Der Blindwertbestimmung mit Reinstmetallen kommt ebenfalls eine maßgebliche Bedeutung zu. Blindwertbestimmungen ohne Verwendung stickstofffreier Metalle können zu groben positiven systematischen Fehlern führen. Wenn die zu analysierenden Metalle nicht in gasfreier Form verfügbar sind, kann Reinstaluminium herangezogen werden, das auf Grund seiner geringen Löslichkeit für Stickstoff Gehalte ≤ 1 ppm N erwarten läßt. Außerdem müssen Blindwertansätze genau so lange und derselben Laboratmosphäre ausgesetzt sein wie die zu messenden Proben. In Betrieben mit hoher Ammoniak-Kontaminationsgefahr können ohne besondere Vorkehrungen bereits Stickstoffmengen unter 100 μg nicht erfaßbar sein.

Die verschiedenen Endbestimmungsverfahren für das abgetrennte Ammonium sind alle vergleichbar (Spektrophotometrie mit Neßlers Reagenz bzw. nach dem Indophenolverfahren oder die Verwendung einer ammoniumsensitiven Elektrode). Die bestimmbaren Stickstoffmengen liegen durchwegs bei 1 μg. Bei Blindwerten von ≥ 10 μg N und zugehörigen Standardabweichungen von ≥ 2 μg kann das Nachweisvermögen dieser Endbestimmungsverfahren als ausreichend angesehen werden. Mit der coulometrischen Titration des Mikro-Kjeldahlverfahrens können noch 0,1 μg Stickstoff mit einem Variationskoeffizienten $\leq 15\%$ erfaßt werden.[12]

Für das klassische Kjeldahlverfahren zur Stickstoffspurenanalyse ist schließlich festzustellen, daß die Richtigkeit und Reproduzierbarkeit der Analysen keineswegs nur von der verwendeten Apparatur und vom Grad der Reagenzien- und Umweltkontamination abhängt. Gerade hier spielt auch die Sorgfalt, das Geschick und die Erfahrung des die Analysen durchführenden Laboranten eine entscheidende Rolle. Nicht selten werden an ein und derselben Apparatur unter identischen Bedingungen von zwei Laboranten durchaus verschiedene statistische Kennzahlen für dieses Verfahren erhalten. Was mit einer Halbmikro-Kjeldahlapparatur machbar ist, soll durch die statistischen Kennzahlen verdeutlicht werden, die im Rahmen einer Standardisierung nach Gottschalk[19] im Labor 4 erhalten wurden[20] und die in Tabelle 6 zusammengefaßt sind.

Niedrigere Nachweisgrenzen als die klassischen Kjeldahlverfahren weisen die üblichen Schmelzextraktionssysteme auf. Ist ihre Eichung wie im vorliegenden Fall mit Hilfe des Mikro-Kjeldahlverfahrens gewährleistet, so sind sie für die Routine wohl am zweckmäßigsten einzusetzen. Der Blindwertpegel liegt

Tabelle 6. Merkmalsmatrix für die standardisierte Stickstoffspurenbestimmung in Wolfram nach der Halbmikro-Kjeldahlmethode

ANWENDUNGSBEREICH			
Arbeitsbereich	5	bis	0,5 µmol N
	≙ 70	bis	7 µg N
Probemenge	500	±	10 mg
Gehaltsbereich	140	bis	14 ppm
VERFAHRENSKENNDATEN			
Standardabweichung	0 12 µmol N ≙ 1.64 µg N ≙ 3 28 ppm N		
Variationskoffizient:	2,3–23%		
Bestimmungsgrenze.	0,46 µmol N ≙ 6,5 µg N ≙ 13 ppm N		
Empfindlichkeit	2,011 ± 0,016 cm²/µmol		
Informationswertbereich	$E_x < 0{,}6$ und $E_B < 0{,}2$		
Arbeitsparameter	Meßkolbenvolumen 100 ml Meßwellenlänge 436 nm Schichtdicke: 4 cm Farbreagenz: Neßlers Reagenz Andere Parameter wie Art und Dimension der Kjeldahlapparatur, zugesetzte NaOH-Menge und Destillatvolumen vgl Zitat[16]		
Zeitbedarf	für Einzelbestimmung: 2 hr für Zehnerserie 10 hr		

beim Leco TN 15 des Labors 3 bei 3 µg N, beim Balzers EAN 220 des Labors 6 bei 4 µg N (vgl. auch Tab. 4) und beim Leybold-Heraeus VH 9 bei 3–4 µg N. Die Reproduzierbarkeit der Blindwerte ist beim Balzers Gerät am besten ($s = 0{,}3$ µg N) gegenüber $s = 1$ µg N beim Leco Gerät. Beim Leybold Heraeus-Gerät, das mit einem gaschromatographischen Detektor ausgerüstet ist, läßt sich der zu jedem Analysenwert gehörige N_2-Blindwert über den O_2-Peak mit Hilfe des apparatebedingten O_2/N_2-Verhältnisses mit einem Fehler $< 0{,}5$ µg N berechnen. Damit liegen die Nachweisgrenzen bei allen Geräten zwischen 1 und 3 µg N. Die von den verwendeten Wärmeleitfähigkeitsdetektoren noch erfaßbare kleinste Stickstoffmenge ist mit etwa 0,1 µg anzugeben.

Die einzige, im Arbeitskreis verfügbare Methode zur Erfassung von Stickstoffgehalten im Sub-ppm-Bereich ist die der Ultrahochvakuumdiffusionsextraktion. Obwohl ihr routinemäßiger industrieller Einsatz vor allem aufgrund der derzeitigen Irrelevanz der Erfassung so niedriger Stickstoffgehalte selbst in Refraktärmetallen nicht in Frage kommt, ist sie für richtungsweisende Untersuchungen an Reinstmetallen von größter Bedeutung. Auch die Möglichkeit der Verfolgung der Entgasungskinetik mit dieser Apparatur ist von grundlegendem Interesse.

Weitere Verfahren zur Stickstoffspurenbestimmung in Metallen wie die Funkenmassenspektrometrie oder aktivierungsanalytische Methoden standen dem Arbeitskreis nicht zur Verfügung und wurden bereits an anderer Stelle vergleichend diskutiert.[1]

LITERATUR

1. P. Albert, *Die Bestimmung des Stickstoffgehaltes hochschmelzender Metalle, ihre wirtschaftliche und technologische Bedeutung.* Kommission der Europäischen Gemeinschaften, Informationsheft Nr. 90, Brüssel, 1974.
2. G. W. Goward, *Anal. Chem.*, 1965, **37**, 117R.
3. E. Fromm und H. Jehn, *High Temp. High Press.*, 1971, **3**, 553.
4. W. F. Davis, J. W. Graab und E. J. Merkle, *Talanta*, 1971, **18**, 263.
5. G. Kraft, G. Paesold, C. G. Tombu und E. Lassner, *J. Less-Common Met.*, 1973, **30**, 311.
6. E. J. Merkle, J. W. Graab und W. F. Davis, *NASA* TM X-3067, Washington D.C., 1974.
7. M. Winterkorn, K. Schulze und G. Tölg, *Mikrochim. Acta*, 1977, Suppl. 7, 27.
8. D. L. Chase, *DMIC Rept.* 220, 1965.
9. K. Friedrich und E. Lassner, *J. Less-Common Met.*, 1967, **13**, 156.
10. S. Kallmann, E. W. Hobart, H. K. Oberthin and W. C. Brienza, Jr., *Anal. Chem.*, 1968, **40**, 332.
11. L. Quaglia, G. Weber, D. David, J. van Audenhove und J. Pauwels: *Traitements de surface des métaux non ferreux dans l'analyse des gaz.* Kommission der Europäischen Gemeinschaften, ITE-Bericht Nr. 90, Brüssel, 1976.
12. W. Werner und G. Tölg, *Z. Anal. Chem.*, 1975, **276**, 103.
13. L. Kotz, G. Kaiser, P. Tschöpel und G. Tölg, *ibid.*, 1972, **260**, 207.
14. S. Kallmann, R. Liu und H. Oberthin, *Air Force Materials Lab. Rep.*, AFML-TR-65-194, 1965.
15. H. Schneider und W. Hein, *6.* Plansee-Seminar, Mai 1969, Herausgeber: F. Benesovsky, S. 1028. Metallwerk Plansee, Reutte.
16. R. Stahlberg und W. Förster, *Neue Hütte*, 1970, **15**, 501.
17. *Handbuch für das Eisenhüttenlaboratorium*, Band 2, Verlag Stahleisen m.b.H., Düsseldorf, 1966.
18. *Analyse der Metalle, Band Schiedsanalyse*, 3. Aufl., S. 133. Springer Verlag, Berlin, 1966.
19. G. Gottschalk, *Z. Anal. Chem.*, 1975, 275, 1; 1975, **276**, 81, 257.
20. V. Scherer, Osram Forschung, München, persönliche Mitteilung.

Summary—This is a report on round-robin tests concerning the determination of nitrogen traces in molybdenum and tungsten, which were carried out by the refractory metals group of the chemistry section of the Gesellschaft Deutscher Metallhütten- und Bergleute. The following methods were used: classical and modified Kieldahl methods (in particular, a newly developed micro-Kjeldahl method), inert-gas fusion, vacuum fusion and ultrahigh-vacuum diffusion extraction. As the nitrogen values obtained by the first round-robin test exhibited considerable scatter, possible shortcomings of the various Kjeldahl methods, as well as the quantitative nitrogen recovery by the extraction methods, were carefully examined. The second round-robin test then gave the following results: the nitrogen content of the investigated molybdenum sheet was 2 ppm, the content of the tungsten sheet 0.5 ppm. Classical Kjeldahl methods are not applicable to the determination of nitrogen contents below 10 ppm. Frequently, detection limits of Kjeldahl methods range considerably above 10 ppm, mainly because of contamination by reagents and/or the laboratory atmosphere. The micro-Kjeldahl method and the hot-extraction and fusion-extraction methods are capable of determining nitrogen contents down to 1 ppm at best. The only method available for nitrogen determinations in metals at sub-ppm levels is by ultrahigh-vacuum diffusion extraction. The good agreement between the nitrogen values obtained for molybdenum by the micro-Kjeldahl method and by the various extraction methods is the most reliable proof of the quantitative nitrogen recovery by the extraction methods.

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GRAVIMETRIC DETERMINATION OF BERYLLIUM WITH SODIUM OXINATE*

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Summary—Sodium oxinate is found to precipitate Be(II) quantitatively in the pH range 7.5–8.2. The complex has the composition $Be_2O(C_9H_6NO)_2.2H_2O$, is stable and can be weighed directly after drying at 105–110°. A method for the estimation of Be(II) and its separation from interfering elements is described. The monohydrate has been prepared from the dihydrate and characterized. The results show the presence of hydroxyl bridges in the monohydrate. Methods using various organic reagents for the direct estimation of beryllium in ores and alloys have been examined and it is found that 4-chloro-2,5-dimethoxyacetoacetanilide gives the best results. A method for the determination of Be(II) in beryl without prior separation of Fe(III) and Al(III) is described.

There is a general lack of specific organic precipitants for the direct gravimetric determination and separation of beryllium(II). Although a few chelating agents, such as β-diketones,[1–6] Schiff's bases,[7] 8-quinolinol and its derivatives,[8–10] have been proposed for gravimetric determination of beryllium, on closer scrutiny they have been found to be neither specific nor precise. Selectivity has been attained in some instances by masking the interfering elements with EDTA. However, the application of these reagents to the analysis of beryl (which contains fair amounts of aluminium) and to the analysis of alloys is complicated and involves prior separation of interfering elements. Recently 4-chloro-2,5-dimethoxyacetoacetanilide has been used for the quantitative precipitation of beryllium from solutions containing Fe(III) and Al(III), in presence of EDTA,[11] and is now found suitable for the direct determination of beryllium in beryl.

Sodium oxinate has also been examined as a reagent for the determination of beryllium. It precipitates beryllium quantitatively in the pH range 7.5–8.2, forming a basic hydroxyquinolinate $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$ which can serve as the weighing form. Various other reagents have also been tested.

EXPERIMENTAL

Reagents

Beryllium stock solution was prepared by dissolving beryllium nitrate trihydrate, beryllium hydroxide or beryllium sulphate tetrahydrate in the appropriate acid and diluting with water, and was standardized gravimetrically.[12,13]

Sodium oxinate was prepared according to the reported methods[14,15] and used as a 1% solution in water.

All other reagents were analytical grade.

* N.C.L. communication number 2129.

Procedure

A 25-ml portion of standard solution containing approximately 10 mg of beryllium was diluted to about 125 ml with water in a 250-ml beaker. Then 60–70 ml of 1% sodium oxinate solution were added, with stirring. The pH of the resulting clear solution was adjusted to 7.5–8.0 by dropwise addition of 4*M* ammonia, with stirring. The bulky yellow crystalline precipitate was digested on a hot water-bath for 1 hr, collected on a weighed sintered-glass crucible (porosity No. 4), and washed with hot water till the washings were colourless (~200 ml), then dried at 105–110° for 2 hr, cooled in a desiccator and weighed as $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$. The maximum error in determination of 3.8–10.5 mg of beryllium was 0.3%.

Procedure when Al^{3+}, Fe^{3+}, Cu^{2+} and Zn^{2+} are present

Masking of these ions with EDTA was found unsatisfactory. Aluminium was therefore separated by precipitation as the oxinate at pH 4–5 in acetate buffer or with tannin in presence of ammonium nitrate, ammonium acetate and acetic acid.[16–19] Iron was removed as the oxinate or the tannin complex. Copper was removed by electrolysis[20,21] or precipitation as the oxinate at pH 4–5 in acetate buffer. Zinc was separated as the quinaldinate[22] or the oxinate. The results were satisfactory, the maximum error being 0.7% in the determination of 10 mg of beryllium in presence of 25–50 mg of aluminium, and 1% in presence of 10–25 mg of iron(III).

The effect of pH and amount of reagent was studied. The optimum pH range is 7.5–8.0 and 150% excess of reagent is required.

Composition of the precipitate

The dried complex (m.p. 295–300°, decomp.) was analysed. Found: C, 59.9%; H, 4.8%; N, 7.5%; Be, 4.95%. $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$ requires: C, 60.34%; H, 4.49%; N, 7.82%; Be, 5.03%. The dihydrate was dehydrated by heating at 80° under reduced pressure (~3 mmHg) for 16 hr. A quantitative yield of the monohydrate (m.p. 306–8°, decomp.) was obtained. Found: C, 63.4%, H, 4.6%; N, 8.0%; Be, 5.21%. $Be_2O(C_9H_6NO)_2 \cdot H_2O$ requires: C, 63.53%; H, 4.12%; N, 8.24%; Be, 5.30%. The results are slightly out with the accepted limits of error for elemental analysis, but seem conclusive when considered along with the other evidence.

Table 1. Gravimetric determination of beryllium in pure Be(II) solutions with organic reagents

Reagent	Be found,* *mg*	Be, %†	Be, *mg*‡
Hydroxide	9.76	4.91	3.99
Pyrophosphate	9.77	—	3.94
Tannin[18,19]	9.76	8.11	3.96
Cupferron[6]	9.93	6.03	3.47
Acetoacetanilide[1]	9.27	6.77	3.47
bis-Salicyladehyde-ethylenediamine[7]	9.76	5.62	4.78
2-Methyl-8-quinolinol[10]	9.72	7.29	3.91
8-Hydroxyquinoline[9]	9.48	—	3.74
4-Chloro-2,5-dimethoxy-acetoacetanilide[11]	9.76	4.91‖	3.92
Sodium oxinate	9.77	4.92§	3.94, 4.04

* Be taken, 9.76 mg.
† In beryl.
‡ In Be–Cu alloy, 3.98 mg of Be taken.
‖ With 2 g of EDTA added as masking agent.
§ After removal of interfering elements.

Various other organic reagents, including 4-chloro-2,5-dimethoxyacetoacetanilide, were used for analysis of pure beryllium solutions by the procedures described in the literature. The results are presented in Table 1.

Determination of beryllium in beryl

Finely powdered beryl (0.5 g) was fused with 15 g of sodium carbonate in a platinum crucible for about 15 min. The melt was cooled and taken up with hydrochloric acid (1:1). The solution was evaporated to dryness, the residue treated with 2 ml of perchloric acid and 5 ml of concentrated sulphuric acid, and the solution evaporated to dryness. The residue was dissolved in hot water and silica was filtered off, washed, ignited, and treated with hydrofluoric and sulphuric acids. The residue was fused with potassium bisulphate, the cooled melt was dissolved in water and the solution added to the main filtrate, which was then made up to 500 ml. The beryllium content was determined on 50-ml aliquots with various reagents. The results are presented in Table 1.

Determination of beryllium in Be–Cu alloy

The alloy (2 g) was dissolved in 50 ml of nitric acid (1:1) by gentle heating. The solution was boiled for 5–10 min, cooled and diluted to 500 ml. The beryllium content was determined on 50-ml aliquots. As copper(II) is quantitatively precipitated by 4-chloro-2,5-dimethoxyacetoacetanilide at pH 6.0–7.3,[11] the copper was separated electrolytically before precipitation of the beryllium. The results are shown in Table 1.

RESULTS AND DISCUSSION

Although 8-quinolinol has been proposed by earlier workers[8,9] as a gravimetric reagent for the determination of beryllium, there is considerable controversy concerning the nature of the precipitate. Rao *et al.*[8] reported quantitative precipitation in the pH range 7.16–8.12 and said that the beryllium oxinate was $Be(C_9H_6NO)_2$. Motojima, however, proposed the formula $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$.[9] In both procedures the complex may be weighed as such, but Rao *et al.*[8] apparently preferred to ignite it to BeO. Magee and Gordon[23] reported that because of its small ionic radius (0.31 Å) beryllium might be expected not to form a complex with 8-quinolinol. The procedures using 8-quinolinol were therefore examined and rather variable results (±3% error) were obtained. Further, acetic acid was found to interfere with the estimation, necessitating the use of undue excess of the reagent. During washing of the beryllium complex with dilute ammonia (1:100) to remove excess of the reagent, losses of the complex itself, due to dissolution, are observed (Table 2).

It was for these reasons that the water-soluble sodium salt of 8-quinolinol was considered, and it was found to give consistently satisfactory results. However, prior separation of Al(III), Fe(III), Zn(II), Cu(II), *etc.* is necessary. Acetate, sulphate, chloride *etc.* do not interfere.

Elemental analysis, infrared spectroscopy, thermogravimetry and differential thermal analysis clearly show that the precipitated beryllium complex has the composition $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$. Thermogravimetric and DTA curves for the complexes, $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$ and $Be_2O(C_9H_6NO)_2 \cdot H_2O$ are shown in Figs. 1 and 2. The dihydrate was also found to be formed when beryllium oxinate was prepared by precipitation from homogeneous solution,[24] and it was postulated that on loss of water during pyrolysis of the compound, an unstable intermediate was formed which immediately decomposed to form

Table 2. The effect of washing with dilute ammonia solution (1:100) in estimation of beryllium with 8-quinolinol (0.3528 g of complex used)

Wash solution used, *ml*	Wt. of complex after washing and drying, *g*	Loss, *g*
50	0.3402	0.0126
100	0.3305	0.0223
150	0.3278	0.0250
200	0.3221	0.0307

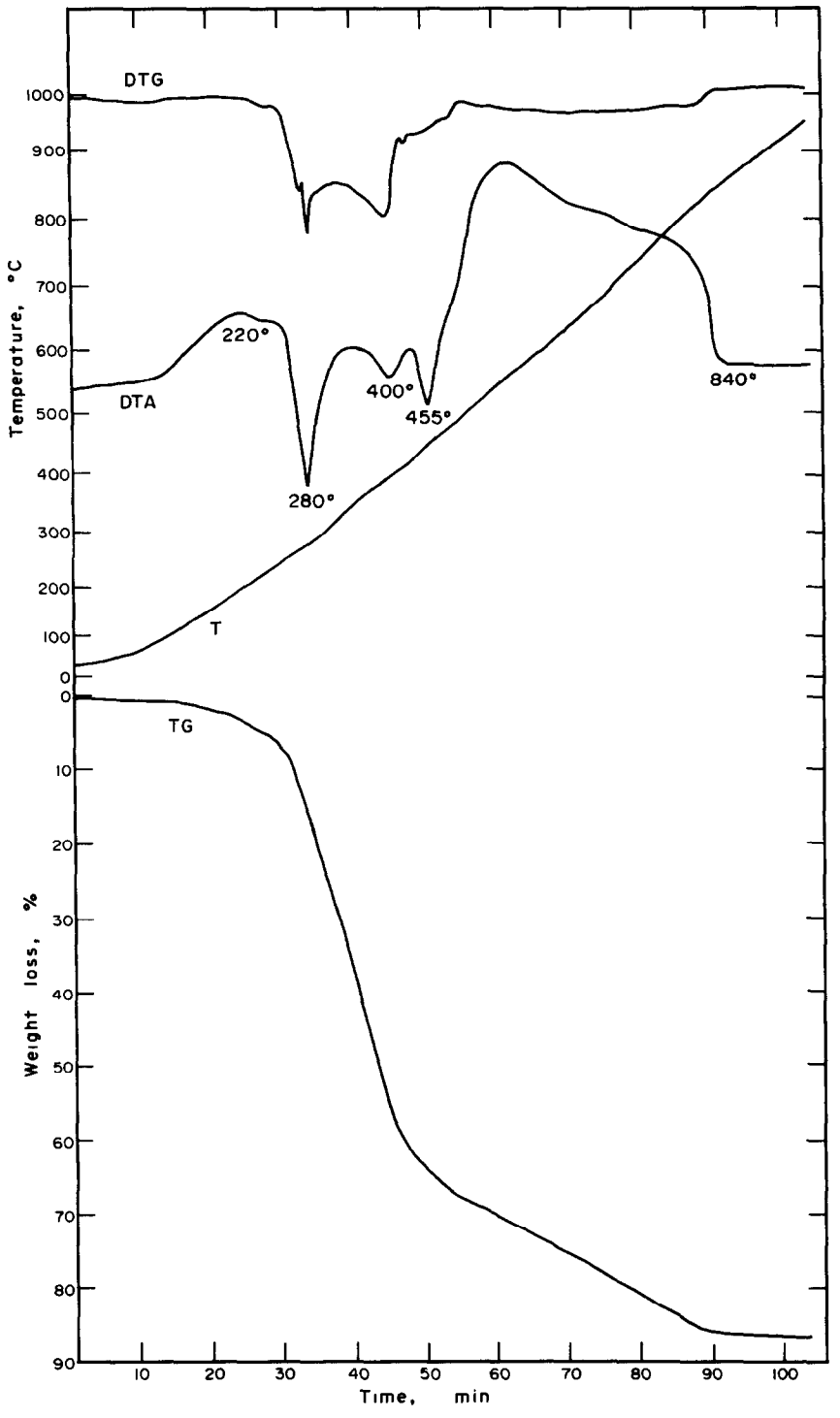


Fig. 1. TG, DTG and DTA curves for 200 mg of $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$. DTA sensitivity 1/10; no units for DTA and DTG.

beryllium oxide. Our results confirm that the dihydrate does not pass through a monohydrate stage on heating on the thermobalance, but also show that a thermally stable monohydrate can be formed by moderate heating under reduced pressure but decomposes on heating at about 240° and atmospheric pressure. This monohydrate was characterized from its elemental analysis, infrared spectrum and TG and DTA data. The OH band at 3315 cm^{-1} was observed but other OH modes could not be assigned unequivocally because of the absorption bands of the ligand. On heating, the compound shows a loss corresponding to removal of water of hydration, accompanied by decomposition of the complex, suggesting that the water is co-ordinatively attached, probably in the form of hydroxyl bridges. Beryllium compounds and

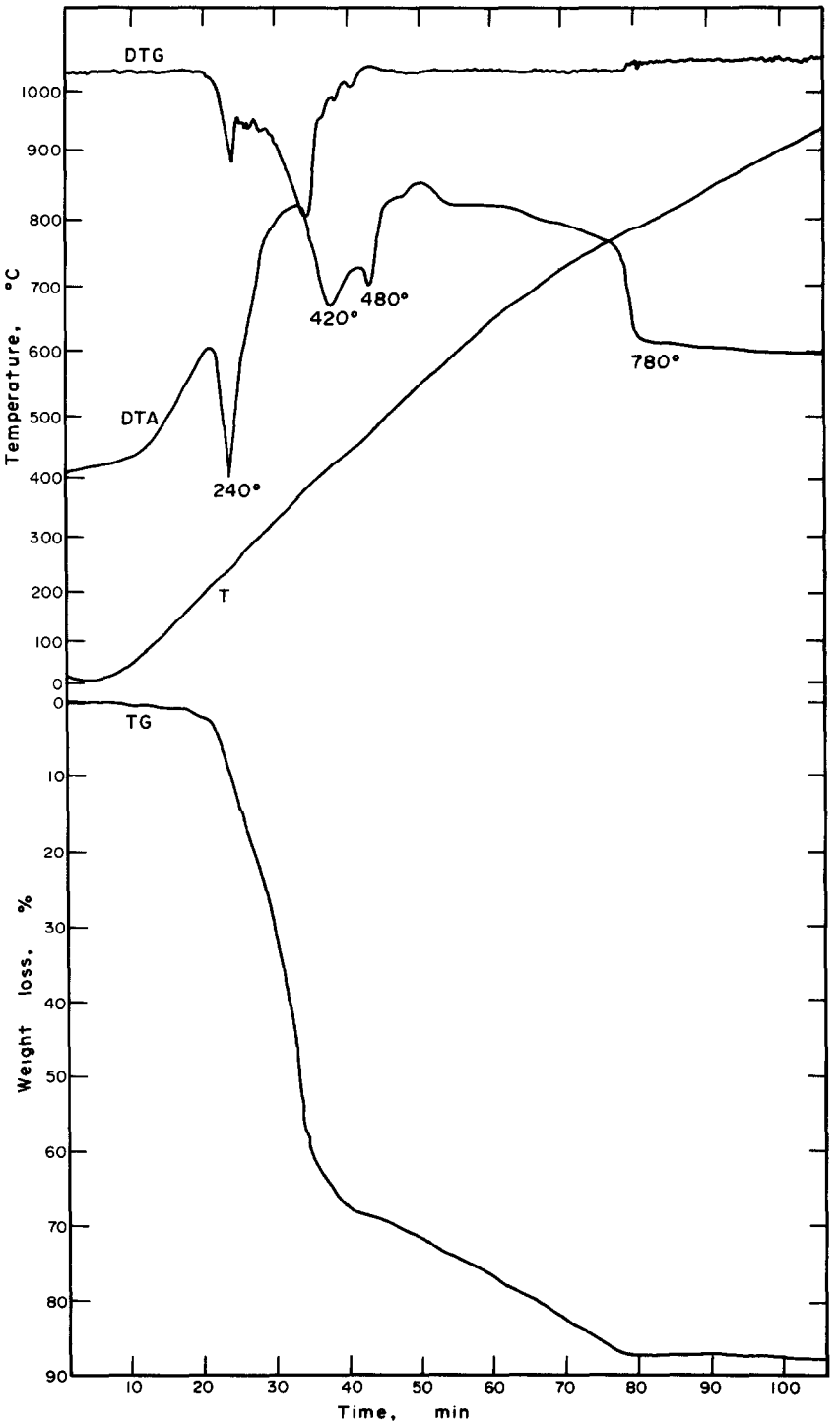


Fig. 2. TG, DTG and DTA curves for 200 mg of $Be_2O(C_9H_6NO)_2 \cdot H_2O$. DTA sensitivity 1/10; no units for DTA and DTG.

chelates containing such hydroxyl bridges have been reported.[25–28] Their presence in the monohydrate is confirmed by p.m.r. studies. The p.m.r. spectrum of the compound in trifluoroacetic acid (Fig. 3) shows a broad absorption centred at -3.47τ arising from hydroxyl protons [aromatic protons are observed at 1.0τ (2H and 4H) and at 2.17τ (3, 5, 6, and 7H)] and furthermore, there is no change in the spectrum after 48 hr (no exchange of the hydroxyl protons with protons of the acid group), indicating the probable presence of bridged hydroxyl groups. The hydroxyl-proton absorption disappears on addition of small amounts of D_2O to the sample, indicating that the monohydrate reverts to the dihydrate complex (which presumably contains no hydroxyl bridges) so the structure is (A) rather than (B). This is in agreement

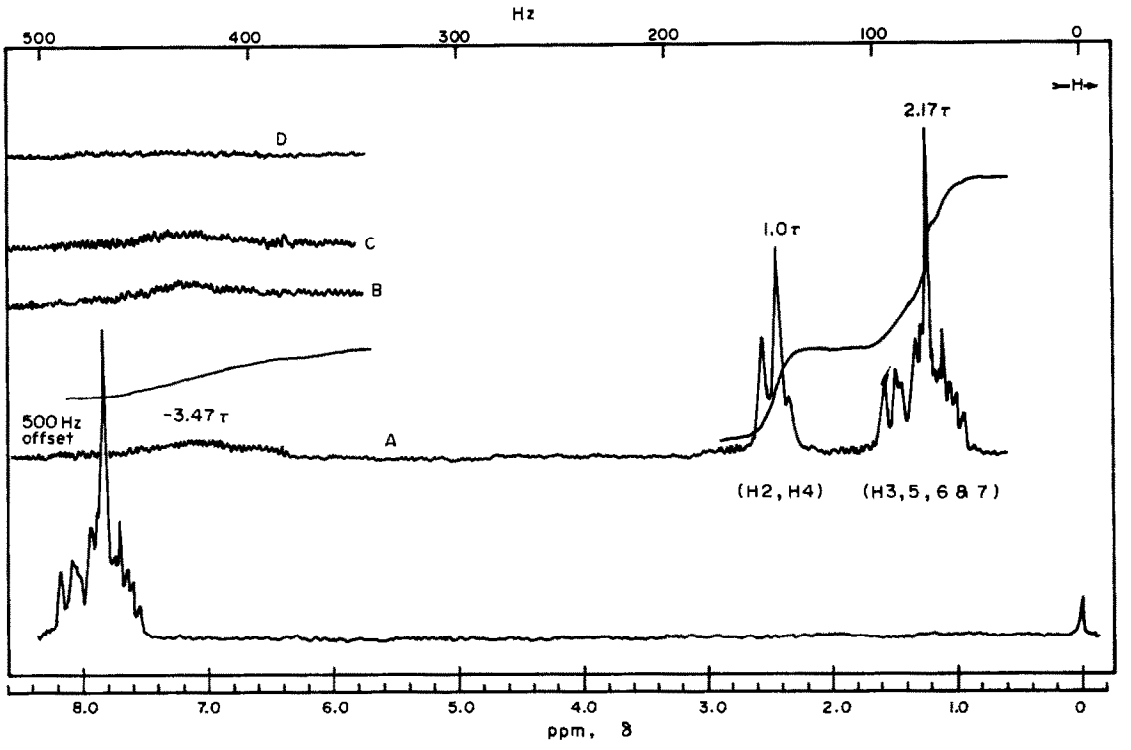
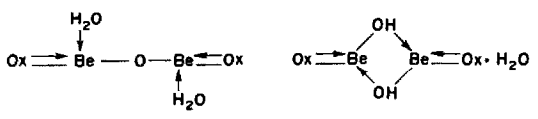
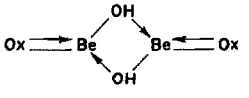


Fig. 3. Proton magnetic resonance spectra of $Be_2O(C_9H_6NO)_2 \cdot H_2O$ in trifluoroacetic acid (A) immediately after preparation, (B) after 24 hr, (C) after 48 hr, (D) after deuteration.

with the opinion expressed by Sastri and Prasad.[24]



These studies indicate that the monohydrate may have the structure:



The TG and DTA data show that the dihydrate is thermally stable up to 150–160°; accelerated weight loss occurs at 250–500°. Formation of BeO is complete at 840°. The weight loss at 200–220° suggests volatilization of one mole of water per mole of complex. Further loss of water on continued heating results in decomposition of the complex. The decomposition pattern for the monohydrate is similar to that for the dihydrate and shows that the compound, once it has been prepared as described, is stable up to about 240°.

The results for analysis of beryl (Table 1) clearly show that of the reagents examined only 4-chloro-2,5-dimethoxyacetoacetanilide gives consistently satisfactory results. Prior removal of Al(III) and Fe(III) is not required. However, in the analysis of Be–Cu alloy, since the reagent precipitates copper(II) at pH 6.0–7.3, prior separation of copper is necessary.

Cupferron, salicylaldehyde-ethylenediamine, tannin, 2-methyl-8-quinolinol and sodium oxinate give quite satisfactory results in the determination of beryllium from pure Be(II) solution (Table 1), but unfortunately these reagents are not selective. Masking with EDTA gives a certain degree of selectivity but prior separation of some elements is still necessary. We found tannin, acetoacetanilide and cupferron to give rather unsatisfactory results for analysis of beryl and Be–Cu alloy. Beryllium acetoacetanilide, although crystalline and thermally stable, is markedly soluble in hot water; the reported[29] experimental error is 3%. Beryllium cupferronate is soluble on heating, the reagent is sensitive to light, heat and atmospheric oxygen, and ignition to BeO is necessary.

REFERENCES

1. J. Das and S. Banerjee, *Z. Anal. Chem.*, 1961, **184**, 110.
2. E. S. Przheval'skii and L. M. Moiseeva, *Zh. Analit. Khim.*, 1960, **15**, 117.
3. Liu Shao-Ling and Yin T'an-Cheng, *Acta. Chem. Sinica*, 1962, **28**, 20; *Ref. Zh. Khim.*, 1963, 22G39.
4. E. Uhlemann and R. Fritzsche, *Z. Anorg. Allgem. Chem.*, 1964, **327**, 79.
5. E. S. Przheval'skii and L. Moiseeva, *Vestn., Mosk. Gos. Univ., Ser. Mat. Mekh., Astron., Fiz., Khim.*, 1959, No. 1, 203.
6. J. Das and S. Banerjee, *Z. Anal. Chem.*, 1962, **189**, 183.
7. B. R. Singh and S. Kumar, *Indian J. Chem.*, 1972, **10**, 663.
8. C. L. Sastri, G. Sriramulu and B. S. V. R. Rao, *J. Sci. Ind. Res. India*, 1955, **14B**, 171.
9. K. Motojima, *Nippon Kagaku Zasshi*, 1956, **77**, 95; *Chem. Abstr.*, 1957, **51**, 14474.
10. *Idem, Bull. Chem. Soc. Japan*, 1956, **29**, 29.

11. A. M. Hundekar, P. Umapathy and D. N. Sen, *J. Indian Chem. Soc.*, 1975, **52,** 71.
12. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., p. 517. Longmans, London, 1962.
13. J. Hure, M. Kremer and F. Le Berquier, *Anal. Chim. Acta*, 1952, 7, 37.
14. R. G. W. Hollingshead, *Oxine and its Derivatives*, Vol. II, p. 548. Butterworths, London, 1954.
15. W. O. Foye and J. R. Marshall, *J. Pharm. Sci.*, 1964, **53,** 1338.
16. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, p. 122 and references therein. Wiley, New York, 1953.
17. N. H. Furman (ed.) *Standard Methods of Chemical Analysis*, 6th Ed., p. 160. Van Nostrand, New York, 1962.
18. W. R. Schoeller and A. R. Powell, *The Analysis of Minerals and Ores of the Rarer Elements*, 3rd Ed. pp. 55–60 and references therein; Griffin, London, 1955.
19. L. Erdey, *Gravimetric Analysis*, Part II, p. 614. Pergamon, New York, 1965.
20. E. Halls, *Ind. Chem.*, 1941, **17,** 120.
21. V. G. Goryushina, *Zavodsk. Lab.*, 1955, **21,** 148.
22. P. Ray and A. K. Mojumdar, *Z. Anal. Chem.*, 1935, **100,** 324.
23. R. J. Magee and L. Gordon, *Talanta*, 1963, **10,** 851.
24. M. N. Sastry and T. P. Prasad, *ibid.*, 1967, **14,** 481.
25. A. Kakihana and L. G. Sillén, *Acta Chem. Scand.*, 1956, **10,** 985.
26. B. Carell and A. Olin, *ibid*, 1961, **15,** 1875.
27. A. W. Thomas and S. H. Miller, *J. Am. Chem. Soc.*, 1936, **58,** 2526.
28. R. M. Klein and J. C. Bailar, Jr., *Inorg. Chem.*, 1963, **2,** 1187.
29. A. V. Novoselova and L. R. Batsanova, *The Analytical Chemistry of Beryllium*, Israel Program for Scientific Translation, Jerusalem, 1968.

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0039-9140/78/0401-0209$02.00/0

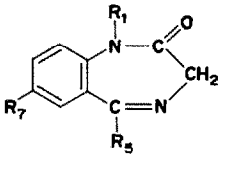
A SPECTROPHOTOMETRIC AND POLAROGRAPHIC INVESTIGATION OF THREE NEW CYCLOHEXENE-SUBSTITUTED BENZODIAZEPINES

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Summary—Three recently introduced benzodiazepine derivatives, tetrazepam (**I**), nortetrazepam (**II**) and menitrazepam (**III**) have been subjected to spectral and polarographic investigation. From the ultraviolet spectral data their pK_a-values have been determined: 4.28 (**I**), 4.3 (**II**) and 3.5 (**III**). From the polarographic measurements it can be concluded that in **I** and **II** the 4,5 C=N double bond is reduced with 2 electrons. For the first time for the benzodiazepine series it has been observed that in slightly alkaline solutions this process takes place in two separate 1-electron steps. In **III**, first the aromatic nitro group is reduced to a hydroxylamine group, then at more negative potentials the C=N double bond is also reduced; its reduction wave mostly coalesces with that for the 6-electron reduction of the nitro group to an amino group. A differential pulse polarographic method is presented, for the determination of **I**, **II**, **III** at concentrations as low as $10^{-7}M$.

Tetrazepam (**I**), 7-chloro-5-(1-cyclohexenyl)-2,3-dihydro-1-methyl-1H-1,4-benzodiazepine-2-one, nortetrazepam (**II**), 7-chloro-5-(1-cyclohexenyl)-2,3-dihydro-1H-1,4-benzodiazepine-2-one and menitrazepam (**III**), 5-(1-cyclohexenyl)-1,3-dihydro-1-methyl-7-nitro-2H-1,4-benzodiazepine-2-one are three recent muscle-relaxants and psychopharmaceutics produced by Laboratories Clin-Comar, Paris. Their spectrophotometric and polarographic behaviour does not seem to have been published although it will evidently play an important role in their analytical determination.



Tetrazepam (I)	R_1:	CH_3	R_5		R_7:	Cl
Nortetrazepam (II)	R_1:	H	R_5		R_7:	Cl
Menitrazepam (III)	R_1:	CH_3	R_5		R_7:	NO_2

In this paper we present a study of their spectral and polarographic behaviour, together with possibilities of analytical application, particularly at extremely low concentrations.

EXPERIMENTAL

Spectrophotometry

A Unicam SP 800 spectrophotometer was used for spectral measurements. Solutions were prepared by diluting the appropriate amount of stock benzodiazepine solution in dimethylformamide with an aqueous Britton–Robinson buffer of the desired pH value to give a concentration of $5 \times 10^{-5}M$ (or $4 \times 10^{-5}M$) of the benzodiazepine derivative and 10% dimethylformamide. The pK_a values were evaluated by making use of the equation:[1]

$$pK_a = pH + \log \frac{(A_{min} - A)}{(A - A_{max})} \qquad (1)$$

where A is absorbance at a given pH value, A_{max} is the maximum absorbance, *i.e.*, that corresponding to absorbance of the cation; A_{min} is the minimum absorbance, corresponding to the absorbance of the free base; all values are measured at the same wavelength. A fast scan-speed was used, and the instrument reference beam passed through a blank containing the buffer solution with the same concentration of dimethylformamide as in the samples.

Polarography

Direct current polarographic curves were recorded with a Radelkis OH-102 polarograph, equipped with a pen-recorder. A modified cell, similar to that according to Kalousek, with a saturated calomel electrode, was used in the polarographic measurements.

In a typical experiment, *e.g.*, when studying the influence of pH on the polarographic behaviour, a $5 \times 10^{-4}M$ solution of the benzodiazepine in a Britton–Robinson buffer containing either 10% or 50% dimethylformamide was deaerated by a stream of nitrogen (saturated with water and dimethylformamide in the same proportion) for 3 min and the i–E curve recorded at a rate of 250 mV/min, unless otherwise stated. The hanging mercury drop electrode used in some of the experiments was the AG CH-9100 type produced by Metrohm AG, Herisau. Differential-pulse polarographic curves were recorded with a PAR Model 174 A Polarographic Analyser (Princeton Applied Research Corp., Inc.) equipped with a PAR Model 172 Drop Timer Assembly. A cell was used containing a dropping mercury electrode as indicator, a saturated calomel electrode as reference and a platinum sheet as a working electrode. The measurements were performed in the differential-pulse mode with a 100-mV pulse applied with a 5-sec drop-time. The scans were started from a suitable potential according to the nature of the different reduction potentials of the compounds to be studied; the scan-rate was

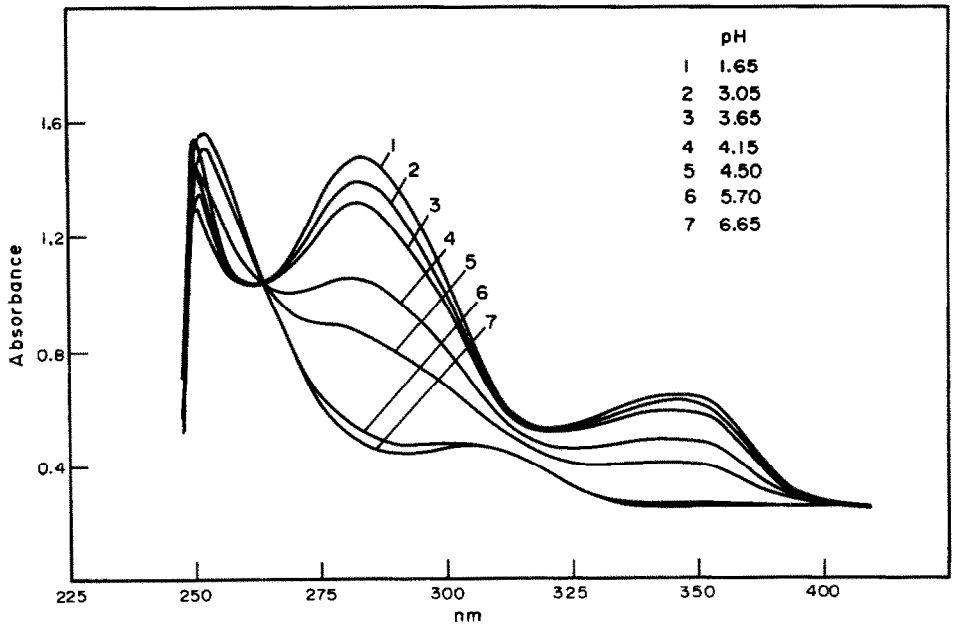


Fig. 1. The ultraviolet spectra of nortetrazepam as a function of pH.

1 mV/sec with a full-scale range of 1.5 V. The sensitivity was either 2 or 10 μA for full-scale deflection.

The samples of the three compounds were obtained from the producer, Laboratories Clin-Comar, through the courtesy of Professor G. Cauquis, Grenoble.

RESULTS AND DISCUSSION

Spectra and pK_a determination

Tetrazepam (**I**) and nortetrazepam (**II**) have similar ultraviolet spectra. **II** exhibits two absorption maxima in acid media, one at 283 nm and a less pronounced one at 347 nm. With increasing pH both maxima decrease up to about pH 6.6 (*cf.* Fig. 1). At higher pH-values a pH-independent spectrum with a diffuse peak at 305–310 nm is always obtained. The compound shows an isosbestic point at 265 nm. The molar absorptivities are 1.48×10^4 (λ = 283 nm, pH = 1.65, 10% DMF) and 6.4×10^3 l. mole^{-1}.cm^{-1} (λ = 347 nm, pH = 1.65, 10% DMF). The pK_a value of II, calculated according to equation (1), for absorbances measured at either 283 or 347 nm is 4.3.

Tetrazepam also shows a clear-cut band at 284 nm and another at 345 nm; the absorptions at these two wavelengths decrease with increasing pH-values up to pH 6.4. A pH-independent spectrum results at still higher pH-values: it is also characterized by a diffuse band at 305–310 nm. This compound shows an isosbestic point at 267 nm. A pK_a value of 4.28 has been obtained for (**I**). The molar absorptivities are 1.54×10^4 (λ = 284 nm, pH = 1.65, 10% DMF) and 6.2×10^3 l. mol^{-1}.cm^{-1} (λ = 345 nm, pH = 1.65, 10% DMF).

In contrast, menitrazepam (**III**) has a single major band at 281 nm which decreases in intensity with increasing pH; this band is followed by an indistinct shoulder at longer wavelengths. At pH > 6.4 a single

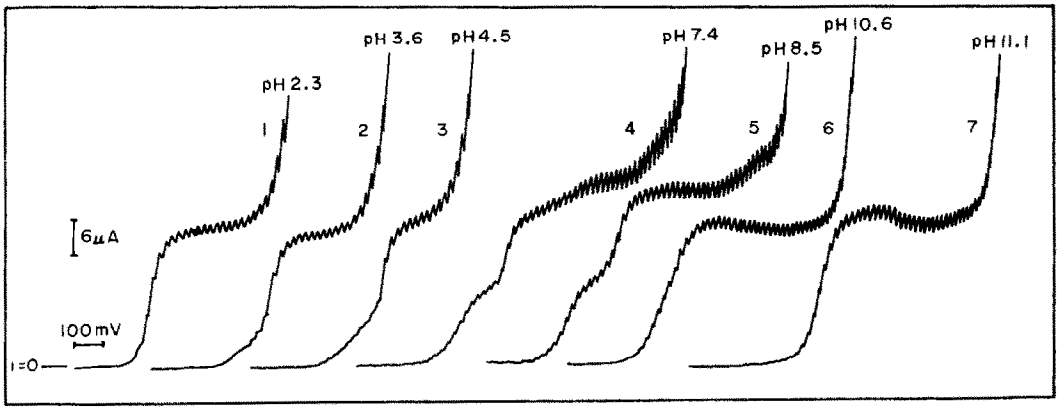


Fig. 2. The d.c. polarographic reduction of tetrazepam as a function of pH.

diffuse band appears at 310–315 nm. No isosbestic point has been found and the pK_a value is 3.5. The molar absorptivity is 2.45×10^4 l. $mol^{-1}.cm^{-1}$ (λ = 281 nm, pH = 1.65, 10% DMF).

With all three compounds Beer's law holds at any wavelength and pH over the concentration range from 10^{-5}–$5 \times 10^{-4}M$.

Polarographic behaviour

Both tetrazepam and nortetrazepam show a single, well-developed cathodic wave in acid solutions containing 10% dimethylformamide, *i.e.* either in 0.1*N* sulphuric acid or in Britton–Robinson buffers of pH 1–2. Above pH 2.3 a deformation appears on the wave (Fig. 2); still later, between pH 7.5 and 9.0 the original single wave splits into two waves of equal height; these waves merge into a single one again at higher pH-values. The adsorption of the electroactive species affects the shape of the wave at pH > 10.5. A similar behaviour was observed in solutions with 50% dimethylformamide; the two waves appear here between pH 5.0 and 9.0. The wave-heights are not significantly pH-dependent and the sum of the heights of the two waves corresponds approximately to the height of the single wave in acid media.

Diazepam (1-methyl-2,3-dihydro-5-phenyl-7-chloro-1H-1,4-benzodiazepine-2-one) which is closely related to tetrazepam—the difference being the benzene ring instead of the cyclohexene nucleus in position 5—gives a 2-electron polarographic reduction wave over the whole pH-range, the height of the wave being the same as that of the single wave or of the sum of the two waves of (I).

The half-wave potentials of (I) and (II) are a linear function of pH with $\Delta E_{1/2}/\Delta$pH equal to −0.075 V/pH. The half-wave potentials (V) in 0.1*N* sulphuric acid supporting electrolyte are as follows: −0.72 (I); −0.73 (II); −0.09, −0.40, −0.69 (III). Within the pH-region where two waves are formed, the $E_{1/2}$–pH plot represents the shift of the half-wave potential of the first wave with pH. The slopes of the log plots of the polarographic waves correspond to an irreversible process.

The polarograms of menitrazepam (III) exhibit a 4-electron wave, corresponding to the reduction of the nitro group to a substituted phenylhydroxylamine; this is followed by a more negative wave in which, for more acidic solutions, the 2-electron reduction wave of the 4,5 C=N double bond in the seven-membered ring coalesces with the further 2-electron reduction wave of the protonated form of the phenylhydroxylamine intermediate. As with nitrazepam,[4] with increasing pH-values the rate of the antecedent protonation decreases until the phenylhydroxylamine grouping becomes irreducible. Thus in neutral and alkaline media only the 4-electron wave can be seen, followed by a 2-electron wave. The half-wave potentials of both reduction waves are a linear function of pH with $\Delta E_{1/2}/\Delta$pH between −0.070 and −0.075 V/pH. The second wave, corresponding to the C=N reduction, also splits into two 1-electron waves in the pH-region between 7.5 and 9.0; this phenomenon becomes even more pronounced if a slower scan-rate is used, such as 0.55 mV/sec.

The heights of the reduction waves of tetrazepam (I) and nortetrazepam (II) are a linear function of the depolarizer concentration in the region from 5×10^{-5} to $10^{-3}M$ at different dimethylformamide concentrations and different pH-values. This holds true also for the region pH 7.5–8.5, in which two waves appear. Solutions of higher concentrations could not be investigated because of the poor solubility of both substances. The heights of the first and second waves of menitrazepam (III) are also a linear function of its concentration over the range from 5×10^{-5} to $2 \times 10^{-3}M$ at all pH-values.

With the Kalousek commutator, neither with I nor with II has reversible behaviour been found, regardless of the potential in the generation period and of the pH-value. This is in accordance with the slopes of the waves as obtained from their log plots. On the other hand, menitrazepam (III) gives an anodic wave on commutating in acid media (0.1*N* sulphuric acid or pH 2.3); its half-wave potentials are +0.23 and +0.20 V, respectively, regardless of whether the auxiliary potential chosen corresponded to the limiting current of the first or the beginning of the second cathodic wave. At pH 8.9 an anodic wave at −0.3 V results in a similar manner. Cyclic voltammetry with a hanging mercury drop also confirmed the irreversibility of the reduction of I and II. In a solution buffered at pH 7.8 where I and II give two peaks, the second peak decreases in height on repeated recording without renewal of the electrode surface. Finally only the main wave remains. With III ($10^{-3}M$ III, pH 7.8, 10% DMF) a sharp peak, characteristic of a nitro group reduction appears at −0.68 V and is followed by a second peak at −1.25 V. In the anodic branch an anodic peak results at −0.18 V. In the second cycle this peak forms a reversible couple with a cathodic peak which is followed by a much lower peak at −0.75 V and by a more negative one at −1.28 V. The two original cathodic peaks decrease on repetition of the cycles without renewal of the electrode surface, whereas both positive peaks representing the reversible couple remain almost constant (both with scan-rates of 50 and 100 mV/sec). As with nitrazepam it is evident that the reversible redox system is R.NHOH (intermediate from the first reduction step) and R.NO.

In contradistinction to the reduction mechanisms of the 4,5 C=N double bonds in most 1,4-benzodiazepines, *e.g.*, in diazepam[2,3] where this functional group takes up two electrons in a single polarographic wave, in I and II (and as a matter of fact in III, too) a relatively stable radical intermediate stabilized by conjugation with the double bond in the cyclohexene nucleus is formed between pH 5 and 9. (in III between pH 7.5 and 9.0). Here the reduction of the unpro-

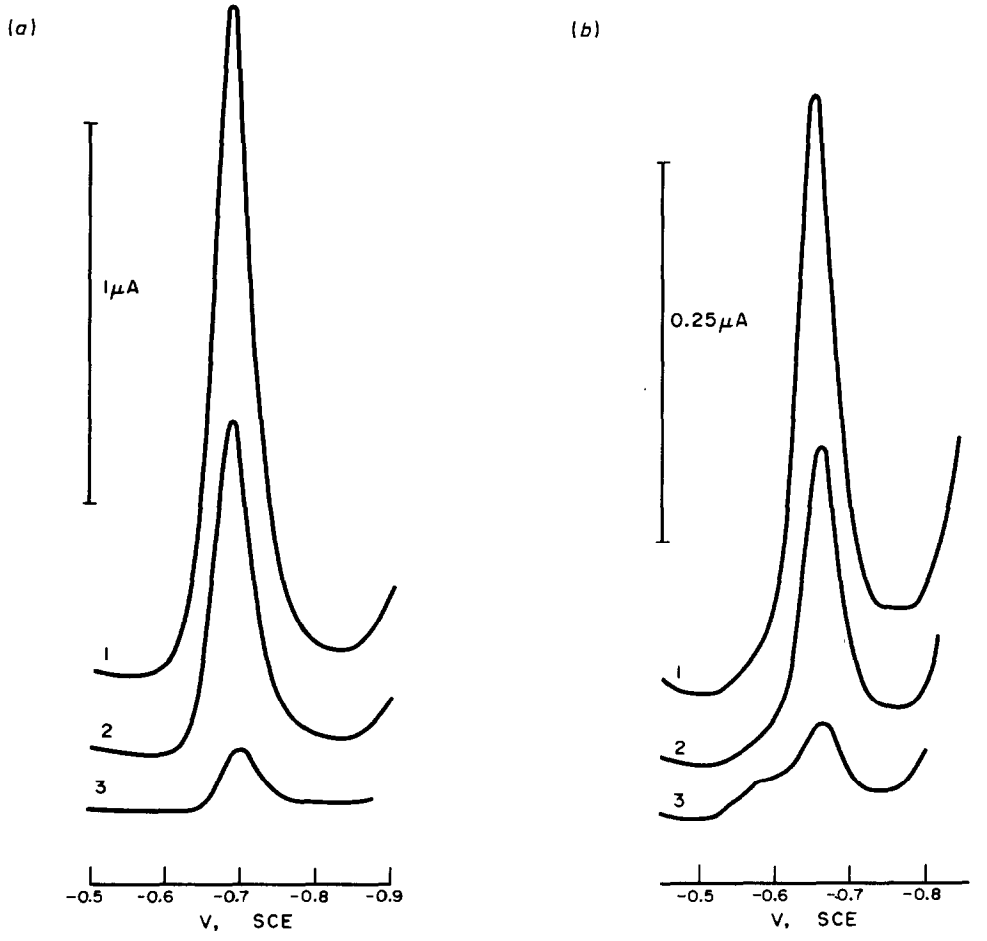
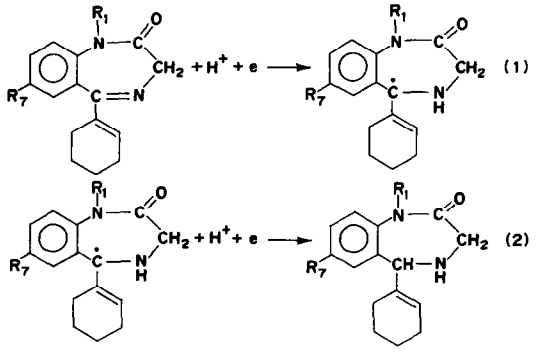


Fig. 3. Differential-pulse polarographic curves of tetrazepam (I) as a function of concentration. 0.1*M* H_2SO_4, drop-time = 5 sec, pulse 50 mV, scan-rate 1 mV/sec. (*a*) 1% dimethylacetamide, concentrations of I: *1*—5 × 10^{-6}*M*, *2*—2.5 × 10^{-6}*M*, *3*—5 × 10^{-7}*M*. (*b*) 0.1% dimethylacetamide, concentrations of I: *1*—5 × 10^{-7}*M*, *2*—2.5 × 10^{-7}*M*, *3*—5 × 10^{-8}*M*.

tonated molecule proceeds. The two one-electron waves can be interpreted as follows (in accord with the $E_{1/2}$–pH plots):



This would be the first case of a two-step reduction of this group in 1,4-benzodiazepines so far observed in polar media. In more acid media this two-electron process takes place in a single step. In **III** virtually the same reaction is preceded by the four-electron reduction of the nitro group. Although there is a good linear relationship between the wave-height of **I**, **II** and **III** and their concentration over the range from 5 × 10^{-5} to 2 × 10^{-3}*M* it is obvious that d.c. polarography can only be utilized in determining the three substances in pharmaceuticals where the quantity or the concentration is relatively high. This is why fundamental parameters and detection limits for the differential-pulse polarography of the three diazepines were investigated. The application of the results should lead to straightforward determinations in biological materials. The differential-pulse measurements were carried out with two different aqueous supporting electrolytes containing 0.01% dimethylacetamide, *viz.* 0.1*N* sulphuric acid and 0.1*M* acetate buffer of pH 4.2. The DPP peaks are somewhat deformed when the latter supporting electrolyte is used. The reduction potentials, E_p (in V), for the 0.1*N* sulphuric acid solutions are -0.71_5 (**I**); -0.72_5 (**II**); -0.08, -0.39_5, -0.69 (**III**). Over the concentration range from 2 × 10^{-7} to 10^{-6}*M* the function $i_{max} = f(c)$ is a straight line (*cf.* Fig. 3) for all three substances. This characteristic can be utilized for their determination at low concentrations in urine.

REFERENCES

1. A. Albert in *Physical Methods in Heterocyclic Chemistry*, A. R. Katritzky, ed., Vol. 1, p. 1, Academic Press, New York, 1963.
2. H. Oelschläger, J. Volke and H. Hoffmann, *Collection Czech. Chem. Commun*, 1966, **31**, 1264.
3. H. Oelschläger and E. Kurek, *Arch. Pharm.*, 1964, **297**, 431.
4. H. Oelschläger, J. Volke, G. T. Lim and U. Frank, *Arzneimittelforschung*, 1966, **16**, 82.

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POTENTIOMETRIC STUDIES OF COMPLEX FORMATION BETWEEN METHYLMERCURY(II) AND EDTA

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Summary—The protonation of EDTA (ethylenediaminetetra-acetic acid) and its complex formation with methylmercury(II) ions was studied by a potentiometric method at 25° in 1.0*M* $NaNO_3$. The protonation constants of EDTA and the equilibrium constants for the complexation reactions between methylmercuric ions and EDTA were evaluated by analysing the experimental data with the ETITR version of the general error-minimizing program LETAGROP. The results were used to develop an analytical method, based on complexometric titration and ion-exchange separation, for the determination of inorganic and organic mercury in the presence of one another.

A great deal of information about the various chemical aspects of organic mercury compounds as sources of environmental pollution,[1] their biodegradation and metabolism,[2,3] their formation by methylation of inorganic mercury in river and lake sediments,[4,5] in sewage sludges[6] and by animals and micro-organisms,[7] *etc.*, has been pouring into the chemical literature for the last few years, especially after the Minamata and Niigata episodes in Japan.[8,9] A thorough study of this literature leads to two rather important conclusions. First, it has been confirmed experimentally that inorganic and metallic mercury can be converted into methylmercury and dimethylmercury,[4,5] although the rate of conversion is slow and the amount of mercury methylated is quite small. Secondly, in most cases the cause of mercury poisoning has been identified as the organic mercury, frequently the methylmercury compounds, because it is in this form that mercury can be easily absorbed and accumulated in animal and human bodies.

At this institute, formation of complexes between methylmercuric ions and certain ligands commonly present in natural waters,[10–12] and also those which may have some biochemical and analytical significance,[13] has been studied. The results make it possible to establish a correlation between the complexed form in which methylmercury(II) is distributed in nature and its availability in a form which may or may not facilitate its uptake by living organisms.

Since these studies often necessitate accurate determination of organic as well as inorganic mercury, the former usually present in trace amounts, the present work aimed to devise an analytical method based on complexation of these substances with a suitable complexing agent. For this purpose EDTA (ethylenediaminetetra-acetic acid) was chosen. The formation of the methylmercury(II) complex of EDTA has previously been studied by Simpson[14] by a polarographic method, the formation of the species MeHgL, MeHgHL and $(MeHg)_2L$ being reported.

The methods currently available for determination of traces of mercury are atomic-absorption spectrophotometry, neutron-activation analysis and gas chromatography. None of these methods, however, distinguishes between organic and inorganic mercury.

EXPERIMENTAL

Reagents

Sodium nitrate (Merck, analytical grade) was dried at 110° and used without further purification. Methylmercury hydroxide (Ventron Alfa, Denmark) was assayed as described earlier.[12] Carbonate-free sodium hydroxide solution[15] was standardized against hydrochloric acid. Nitric acid ("Titrisol") was standardized against sodium hydroxide solution. Hydrochloric acid ("Titrisol") was assayed gravimetrically as silver chloride. A solution of the disodium salt of EDTA was made from the free acid by neutralizing half the available protons with standard sodium hydroxide solution and was then standardized against lead nitrate solution. Mercuric nitrate solution was standardized against EDTA after adjustment to pH 4 with hexamine, Xylenol Orange being used as indicator.

Dowex 2 × 4 (20–50 mesh) resin in the chloride form was converted into the nitrate form by treatment with 5*M* nitric acid, then washed free from acid. The exchange capacity of the resin[16] was found to be 3.4 meq/g of dry resin.

Doubly distilled, freshly boiled water was used to prepare all the solutions.

Apparatus

The titration vessel was a Metrohm 200-ml glass beaker with a cover (EA 880) with five inlets for electrodes, burette, degassing tubes, *etc.*

The electrodes used were a micro combination glass and silver–silver chloride electrode (HA-401 M5, Ingold, Zürich, Switzerland). The cell will be described elsewhere.[13] The e.m.f. values were read to 0.1 mV with a digital voltmeter (S 1016H, Systemteknik, Lidingö, Sweden). Titrant was added from a pneumatically-operated reagent pipette (AGA, Lidingö, Sweden), which could be adjusted to deliver any volume between about 0.5 ml and 5 ml, and which had a very high degree of repeatability.

An oil-bath was used to maintain the temperature of the

titration vessel at 25 ±0.05°. All the measurements were made in a room maintained at a controlled temperature of approximately 25°. For the ion-exchange separation a small column containing about 1.5 g (dry wt) of the resin was used.

Procedure

E'_0-*titration*. The pH-values were calculated from the expression

$$E = E'_0 + Q\log(H^+) + E'_j$$

where E'_0 is the standard potential, including the reference potential, and the contribution of the activity coefficients and junction potential that is independent of acidity; $Q = RT\ln 10/nF = 59.16$ mV at 25°; $E'_j = j_H[H] + j_{OH}[OH]$ accounts for the acidity-dependent contribution from the activity coefficients and the junction potential. The constants j_H and j_{OH} are characteristic of the ionic medium and were determined in separate experiments as described by Pehrsson *et al.*[17] E'_0 was determined by titrating 0.01*M* hydrochloric acid with 0.05*M* sodium hydroxide at constant ionic strength. Several values of E'_0 were then calculated from the equation above, and their mean was used in the subsequent calculations.

In the first series of titrations for evaluating the protonation constants an appropriate volume of EDTA solution was transferred to the titration vessel and sodium nitrate solution was added to keep the ionic strength at 1.0*M*. After the equilibrium was established between the electrodes and the solution, the titration, with sodium hydroxide in 1.0*M* sodium nitrate, was started. Sufficient time was allowed for equilibrium to be attained before more titrant was added. When all the protonation constants of EDTA were to be evaluated, the titration was carried out in presence of a known excess of nitric acid.

In the second series, the same procedure was adopted with a solution containing methylmercury(II), such that the molar ratio of methylmercury to ligand was about 1:2.

Several such series of titrations with varying concentrations of EDTA and methylmercury(II) were performed to collect enough data for subsequent treatment.

The solutions were kept free from atmospheric carbon dioxide by maintaining a nitrogen atmosphere over them. The nitrogen was taken from a cylinder, freed from carbon dioxide by passage through "Ascarite" and then saturated with water by bubbling through 1*M* sodium nitrate.

CALCULATIONS AND RESULTS

The following equilibrium reactions that can take place in a solution containing methylmercuric ion, MeHg, protons and complexing agent L, where L denotes the fully dissociated anion of EDTA, were considered. (Charges are omitted for simplicity.)

I Protonation of EDTA.

II Hydrolysis of methylmercuric ion.

III Reactions involving the formation of methylmercury(II) complexes with EDTA. For the present experimental conditions the most probable reactions that may be considered are

$$\begin{aligned} MeHg + L &\rightleftharpoons MeHgL \\ MeHg + H + L &\rightleftharpoons MeHgHL \\ MeHg + 2H + L &\rightleftharpoons MeHgH_2L \\ MeHg + OH + L &\rightleftharpoons MeHg(OH)L \\ 2MeHg + L &\rightleftharpoons (MeHg)_2L \end{aligned}$$

The hydrolysis of methylmercuric ions had already been studied[13] and the values for the equilibrium constants were used in subsequent calculations. The experimental data were analysed by the ETITR[18] version of the general error-minimizing computer program, LETAGROP. In the program, it is necessary to assume that a particular set of complexes is formed, which may here be represented by $(H)_p(MeHg)_q(HL)_r$, with equilibrium constants

$$K_{pqr} = [(H)_p(MeHg)_q(HL)_r][H]^{-p}[MeHg]^{-q}[HL]^{-r} \quad (1)$$

Starting from the initial estimates supplied, the program seeks the "best" values of the set of equilibrium constants K_{pqr}, minimizing the error-square sum

$$U = \sum_1^N (Y_{calc} - Y_{exp})^2 \quad (2)$$

where N is the number of available experimental points and Y is a parameter which is a function of the set of equilibrium constants K_{pqr} and the known experimental quantities such as C_{MeHg}, C_L and $\log[H^+]$.

In the present case the error-square sum

$$U = \sum_1^N (H_{calc} - H_{exp})^2 \quad (3)$$

is minimized. In the program H_{calc} and H_{tot} are calculated from the mass-balance expressions

$$C_{MeHg} = [MeHg] + \Sigma q K_{pqr}[H]^p[MeHg]^q[HL]^r \quad (4)$$

$$C_L = [HL] + \Sigma r K_{pqr}[H]^p[MeHg]^q[HL]^r \quad (5)$$

$$C_H = [H] + \Sigma p K_{pqr}[H]^p[MeHg]^q[HL]^r \quad (6)$$

Given the values of C_{MeHg}, C_L, $\log[H^+]$ and a set of equilibrium constants for the formation of the complex designated by (pqr), we can calculate for each point the values of [MeHg] and [HL] from (4) and (5) and H_{calc} from (6).

In ETITR this is done by the procedure BDTV.[19] In potentiometric titration, the proton excess is given by

$$C_{H(exp)} = (\overset{*}{C}_H \cdot V_0 - \overset{*}{C}_{OH} \cdot v)/(V_0 + v) \quad (7)$$

where $\overset{*}{C}_H$ = total initial concentration of ionized and potentially ionizable hydrogen, $\overset{*}{C}_{OH}$ = molar concentration of sodium hydroxide, V_0 = initial volume of the solution, and v = volume of titrant added.

In practice, the computer is used to test a series of different models, in which the sets of constants include those for several MeHg–EDTA complexes, and for hydrolysis of methylmercuric ions. In each case, the error-square sum,

$$U = \sum_1^{150} (H_{calc} - H_{tot})^2 \quad (8)$$

was minimized. The model which gives the minimum error-square sum, and which explains the experimental data satisfactorily, was accepted.

From Table 1 it is evident that model IV, in which the formation of the species MeHgL, MeHgHL and $MeHgH_2L$, in addition to hydrolysed species, was considered, gives the best description of the experimental data and a minimum value of the error-square

Table 1

Model No.	Equilibrium reactions assumed	log K*	U_{min}	σ(H)
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−4.157 ±0.100	263.13	1.361
II	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$	−4.686 ±0.045† −1.725 ±0.090 8.835 ±0.145	35.58	0.489
III	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$ $MeHg^+ + H^+ + L^{4-} \rightleftharpoons MeHgHL^{2-}$	−4.686 ±0.045† −1.725 ±0.090 9.141 ±0.046 14.239 ±0.016	11.26	0.276
IV	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$ $MeHg^+ + H^+ + L^{4-} \rightleftharpoons MeHgHL^{2-}$ $MeHg^+ + 2H^+ + L^{4-} \rightleftharpoons MeHgH_2L^-$	−4.686 ±0.045† −1.725 ±0.090 9.263 ±0.073 14.348 ±0.090 17.975 ±0.149	5.39	0.191
V	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$ $MeHg^+ + OH^- + L^{4-} \rightleftharpoons MeHg(OH)L^{3-}$	−4.686 ±0.045† −1.725 ±0.090 9.433 ±0.154 $K < 0$	85.88	0.667
VI	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$ $MeHg^+ + H^+ + L^{4-} \rightleftharpoons MeHgHL^{2-}$ $2MeHg^+ + L^{4-} \rightleftharpoons (MeHg)_2L^{2-}$	−4.686 ±0.045† −1.725 ±0.090 9.944 ±0.108 14.850 ±0.175 max 4.461‡	11.35	0.251

† The equilibrium constants for the hydrolysis of MeHg(II) were kept constant in all the models except model I. The equilibrium constants for hydrolysis were taken from reference 13.

* The limits given correspond approximately to log (K ± 3σ).

‡ When σ(K) > 0.2 K, the maximum value = log (K + 3σ(K)) is given.

sum. All the other models tested give larger errors and therefore cannot be accepted. In Tables 2 and 3, the equilibrium constants for various reactions, including those for the protonation of EDTA, are summarized. Some literature values are also given for comparison.

Table 2. Protonation constants of EDTA in 1.0M (Na, H)NO_3

Equilibrium reaction	log K†	log K*
$H^+ + L^{4-} \rightleftharpoons HL^{3-}$	9.987 ±0.021	10.34
$2H^+ + L^{4-} \rightleftharpoons H_2L^{2-}$	16.045 ±0.022	16.58
$3H^+ + L^{4-} \rightleftharpoons H_3L^-$	18.520 ±0.035	19.13
$4H^+ + L^{4-} \rightleftharpoons H_4L$	20.415 ±0.060	21.40

† The limits given correspond approximately to log(K ± 3σ).

* At μ = 0.1, from reference 21.

One set of experimental data is shown in Fig. 1. Curve I represents a theoretical titration curve for titration of EDTA alone with sodium hydroxide. This was calculated with HALTAFALL,[20] using the protonation constants for EDTA determined here (*cf.* Table 2). Curve II (full line) is also a theoretical curve, for the same titration in the presence of methylmercuric ions. This curve was also calculated with HALTAFALL, using the equilibrium constants given in Table 2.

The evident shift in pH and the fact that almost all

Table 3. Equilibrium constants for the complex formation of MeHg(II) with EDTA in 1.0M (Na, H)(NO_3, L)

Equilibrium reaction	log K(± 3σ)†	log K
$MeHg^+ + L^{4-} \rightleftharpoons MeHgL^{3-}$	9.263 ±0.073	
$MeHg^+ + H^+ + L^{4-} \rightleftharpoons MeHgHL^{2-}$	14.348 ±0.090	16.54‡
$MeHg^+ + 2H^+ + L^{4-} \rightleftharpoons MeHgH_2L^-$	17.945 ±0.149	
$Hg^{2+} + L^{4-} \rightleftharpoons HgL^{2-}$		21.8*
$Hg^{2+} + H^+ + L^{4-} \rightleftharpoons HgHL^-$		24.9*
$Hg^{2+} + OH^- + L^{4-} \rightleftharpoons HgOHL^{3-}$		26.7*
$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.686 ±0.045§	
$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−1.725 ±0.090§	

† The limits given correspond approximately to log(K ± 3σ).

* From reference 21.

‡ Value based on Simpson's data.[14]

§ From reference 13.

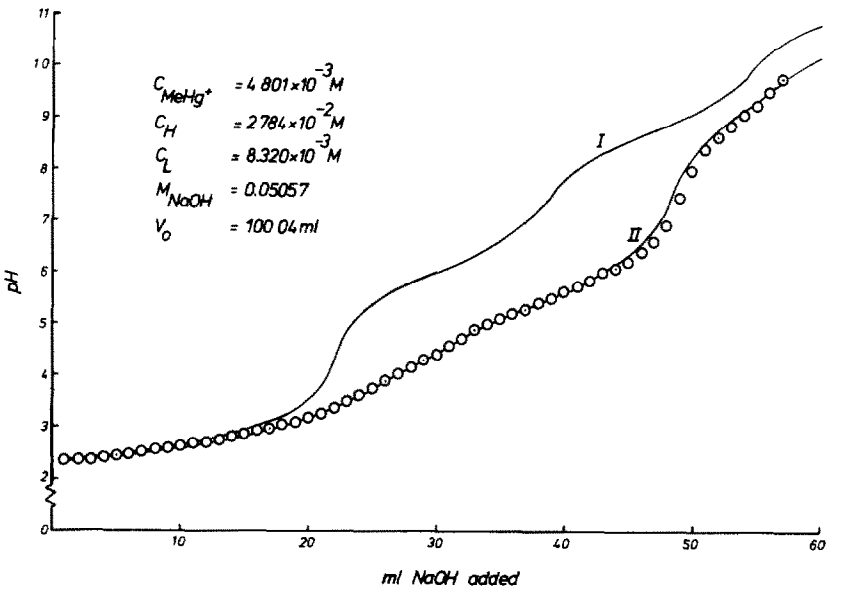


Fig. 1

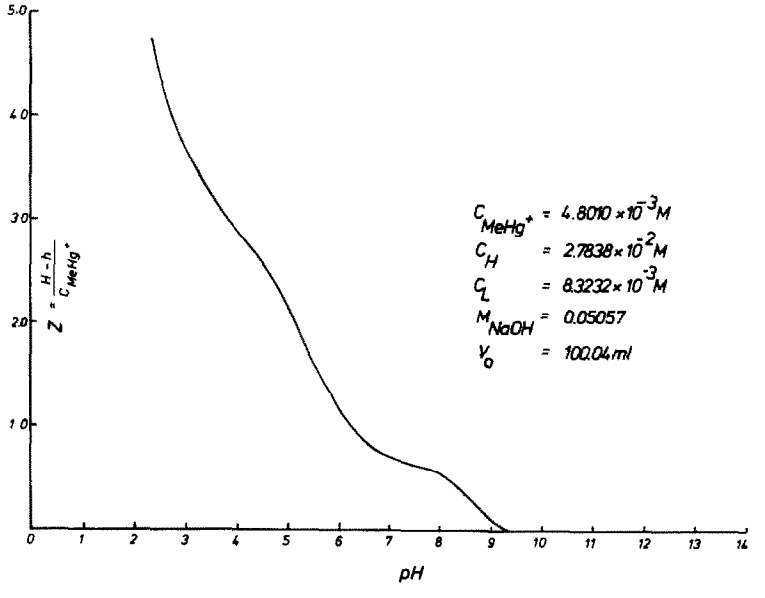


Fig. 2

the experimental points from the actual titration fall on the theoretical curve II is a clear indication of the formation of methylmercury(II) complex(es) with EDTA.

Figure 2 is a typical formation curve, in which $(H-h)/C_{MeHg}$ is plotted as a function of pH, for one set of experimental data; Fig. 3 shows the distribution of the error function, $(H_{calc}-H_{tot})$, also as a function of pH. The error is small and fairly uniformly distributed throughout the whole range of pH studied. In Fig. 4, the equilibrium distribution of various species is shown.

DISCUSSION

The equilibrium constants for the hydrolysis of methylmercury(II) and the stability constants of the methylmercury(II) and Hg(II) complexes with EDTA[21] are given in Table 3. It is evident that EDTA forms much weaker complexes with MeHg(II) than with Hg(II). The difference between the stability constants seems promising from an analytical point of view, and can be exploited to devise a procedure whereby MeHg(II) and Hg(II) can be determined in the presence of one another. This requires knowledge of the conditional stability constants of the

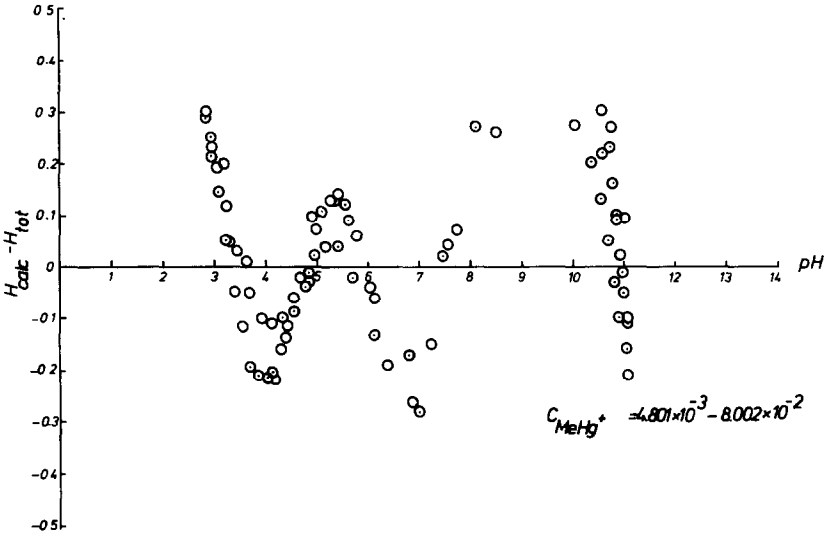


Fig. 3

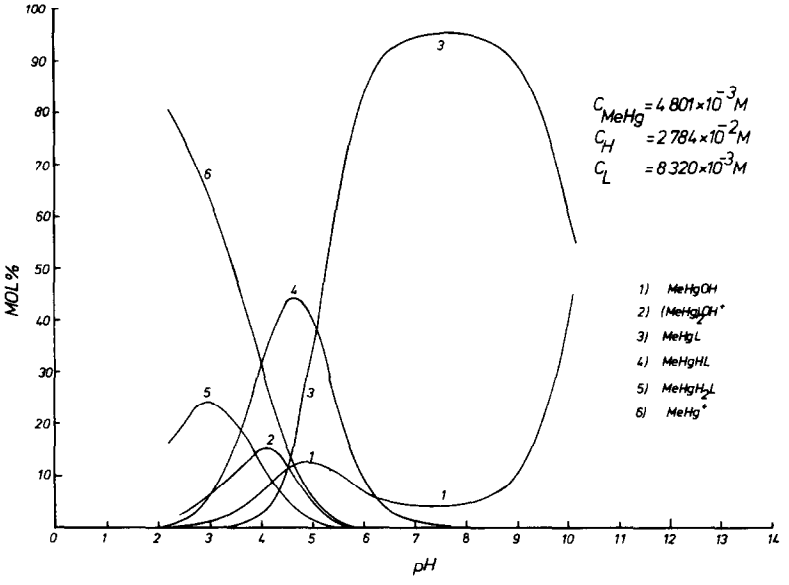


Fig. 4

metal–EDTA complexes. The conditional stability constant is given by the expression

$$K'_{ML} = K_{ML} \cdot \alpha_{ML}/\alpha_M \cdot \alpha_L$$

where the symbols have their usual significance (for details the reader is referred to the monograph by Ringbom[22]).

The conditional stability constant of the MeHg(II)–EDTA complex can be calculated, as a function of pH, from the equilibrium constants given in Table 3. Such calculations lead to the result that the maximum value of the conditional stability constant, K'_{MeHgL}, is about $10^{3.5}$ at pH 8. This would mean that it is not possible to titrate MeHg(II) with EDTA at any pH. K'_{MeHgL} attains a value less than 1 at pH 3 or less. At pH 4, the conditional stability constant of the Hg–EDTA complex, K'_{HgL}, is about $10^{11.3}$—a value sufficiently high to allow complexometric titration of Hg(II) with EDTA, with little or no interference from any MeHg(II) present in the solution. To verify this, attempts were made to titrate Hg(II) with EDTA in presence of various amounts of methylmercury(II). The titrations were performed at pH 4 (hexamine–nitric acid buffer) with Xylenol Orange as indicator. The results are given in Table 4.

To determine the MeHg(II), however, it is necessary to separate it from Hg(II) either by solvent extraction or by ion-exchange. Our ion-exchange experiments show that MeHg(II) can be quantitatively separated from Hg(II) by sorbing the latter on an anion-exchange resin [(Dowex 2 × 4 (20–50 mesh) in nitrate form)] in the presence of a slight excess of EDTA. The

Table 4. Determination of Hg^{2+} by complexometric titration with EDTA in presence of methylmercuric ions

$MeHg^+$ present in soln. *mg*	Hg^{2+} taken, *mg*	Hg^{2+} found, *mg*
—	42.45	42.45
—	42.45	42.45
25.12	42.45	42.37
25.12	42.45	42.47
50.25	42.45	42.42
50.25	42.45	42.45

distribution coefficient D, for both species between the resin phase and the aqueous phase, in the presence of an excess ($\approx 10^{-3}M$) of EDTA was determined as a function of pH. The results are given in Table 5. If we

Table 5. Distribution coefficient, D, of $MeHg^+$ and Hg^{2+} on Dowex 2×4 (20–50 mesh) in nitrate-form, in presence of $\approx 0.001M$ EDTA, as a function of pH

pH	$MeHg^+$	Hg^{2+}
2.0	0.695	41.75
3.0	0.777	615
4.0	0.812	>1000

D = amount of metal per g of resin (dry weight)/amount of metal per ml of aqueous phase.

choose to work at pH 4, a very small column containing about 1–1.5 g (dry weight) of the resin is required. A bigger column with more resin will result in excessive elution volumes. The filtrate can conveniently be analysed for MeHg(II) by atomic-absorption spectrophotometry. Our experiments with a PE 300 atomic-absorption spectrophotometer, set for the determination of mercury, gave quantitative results. No addition of methanol to standard solutions of Hg(II), to compensate for the methyl group in methylmercury, was found necessary.

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REFERENCES

1. K. Borg, H. Wanntorp, K. Erne and E. Hanko, *J. Appl. Ecol.*, 1966, **3**, 171.
2. G. Westöö and M. Rydälv, *Report on Mercury in Foods*, Joint FAO/WHO Expert Committee on Food Additives. Vår Föda, 1971, **7–8**, 1.
3. *FAO Fisheries Rept.*, No. 99, Rome 1971.
4. J. M. Wood, F. S. Kennedy and C. G. Rosen, *Nature*, 1968, **220**, 173.
5. S. Jensen and A. Jernelöv, *ibid.*, 1969, **223**, 753.
6. W. Mueller, *Vom Wasser*, 1972, **39**, 257.
7. N. Imura, *Taisha*, 1975, **12**, 195; *Chem. Abstr.*, 1976, **84**, 39362d.
8. T. Takeuchi, *Minamata Disease—A Study on the Toxic Symptoms by Organic Mercury*, Univ. of Kumamoto, Report of Department of Medical Sciences, 1966.
9. K. Irukayama, *Adv. Water Pollut. Res.*, 1967, **3**, 153.
10. O. Budevsky, F. Ingman and D. H. Liem, *Acta Chem. Scand.*, 1973, **27**, 1277.
11. F. Ingman and D. H. Liem, *ibid.*, 1974, **28**, 947.
12. M. Jawaid, F. Ingman, D. H. Liem and T. Wallin, *Proc. Conf. Effects Toxic Metals on Man and Environment*, Luleå, Sweden, 1976. *Acta Chem. Scand.*, 1978, **32**, 7
13. M. Jawaid, F. Ingman and D. H. Liem, *Acta Chem. Scand.*, in press.
14. R. B. Simpson, *J. Am. Chem. Soc.*, 1961, **83**, 4711.
15. *Some Laboratory Methods in Current Use at the Department of Inorganic Chemistry*, The Royal Institute of Technology, Stockholm, Sweden (available on request).
16. K. Bunzl and B. Sansoni, *Anal. Chem.*, 1976, **48**, 2279.
17. L. Pehrsson, F. Ingman and A. Johansson, *Talanta*, 1976, **23**, 769.
18. P. Brauner, L. G. Sillén and R. Whiteker, *Arkiv Kemi*, 1969, **31**, 365.
19. R. Arnek, L. G. Sillén and O. Wahlberg, *ibid.*, 1969, **31**, 353.
20. N. Ingri, W. Kakolowicz, L. G. Sillén and B. Warnqvist, *Talanta*, 1967, **14**, 1261.
21. J. Bjerrum, G. Schwarzenbach and L. G. Sillén, *Stability Constants*, Chem. Soc. (London) Spec. Publ. No. 7, 1958.
22. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963.

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SHORT COMMUNICATIONS

DETERMINATION OF THEOPHYLLINE IN PLASMA BY OXIDATION AT THE STATIONARY CARBON-PASTE ELECTRODE

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Summary—A method for the determination of the concentration of theophylline in plasma at therapeutic levels is described. The method is based on the oxidation of theophylline at the stationary carbon-paste electrode and involves a simple extraction procedure and differential pulse voltammetry. Possible interferences are discussed and typical calibration curves are presented.

Theophylline is a widely-used bronchodilator drug employed in the management of various asthmatic conditions. It is generally recognized that a plasma level falling in the range 10–20 μg/ml is necessary for effective bronchodilation in adults. Levels below this range are usually non-therapeutic, while higher levels may cause toxicity. The interest in monitoring the levels of theophylline in plasma has led to the development of a variety of methods. Early methods[1] were based on spectrophotometry of the extracted drug but were criticized for non-specificity. Subsequently, spectrophotometric methods were developed that allowed for the determination of theophylline in the presence of barbiturates.[2,3] A differential spectrophotometric method has also been reported.[4] Gas chromatography has been employed to increase both the specificity and selectivity of the measurement.[5,6] Various workers have employed high-performance liquid chromatography for the measurement of plasma theophylline. Gas-chromatography/mass-spectrometry has been used for the determination of theophylline in whole blood.[10]

This paper describes a method for the determination of plasma theophylline, based on the electrochemical oxidation of theophylline at a stationary carbon-paste electrode.

EXPERIMENTAL

Reagents

The water used in this study was distilled twice, the second distillation being in an all-glass system. Inorganic chemicals were analytical-reagent grade and used without purification. Commercially obtained theophylline, caffeine, uric acid, theobromine, xanthine, hypoxanthine, 3-methylxanthine, chloroform and 2-propanol were all used without prior purification.

Apparatus

A polarographic analyser system (Princeton Applied Research, Model 174) equipped with a drop-timer was used for all measurements. A three-electrode system was employed with a carbon-paste working electrode,[11] an Ag/AgCl reference electrode and a platinum-wire auxiliary electrode. The surface area of the circular carbon-paste electrode was 33 cm^2. All scans were taken at a rate of 10 mV/sec and the usual current sensitivity was 0.05 mA full scale. The modulation amplitude was 50 mV with a "drop time" of 0.5 sec. All measurements were made in the differential pulse mode. An X–Y recorder was used to record the voltamograms. All potential scans were performed at room temperature (21–24°).

Procedure

All solutions were prepared and allowed to stand for 5 min to attain static conditions prior to voltammetric analysis. Exactly 2.0 ml of spiked plasma sample were mixed with 1.0 ml of 0.5*M* Na_2HPO_4 buffer (pH 10) and extracted with 30 ml of a chloroform/2-propanol mixture (95:5). The organic layer was separated by rapid filtration through a phase-separating hydrophobic filter paper (Schleicher and Schuell 595HY). The organic layer was extracted with 7.0 ml of 0.1*M* sodium hydroxide. Exactly 5.0 ml of this aqueous extract was buffered to 7.4 by the addition of 3.0 ml of 0.5*M* NaH_2PO_4 buffer (pH 6.5). The differential pulse voltamogram was determined between +0.5 and +1.2 V (*vs.* Ag/AgCl reference electrode). The difference in the current measured at 0.8 and 1.15 V was plotted as a function of concentration.

RESULTS AND DISCUSSION

A typical differential pulse voltamogram of theophylline and 3-methylxanthine (which appears in blood as a metabolite of theophylline) is shown in Fig. 1, for 2 μg/ml of each in a phosphate buffer at pH 7.4. Under these conditions, the peaks overlap slightly and 3-methylxanthine appears to give a greater response. Even though 3-methylxanthine only accumulates to levels of about 4 μg/ml after prolonged administration of theophylline,[12] it represents a possible interference in a method designed to measure theophylline alone.

Other xanthine derivatives were examined as possible interferents and the results are shown in Table 1.

Of the compounds tested, only 3-methylxanthine interferes after extraction. In order to eliminate this possible interference, the extraction efficiency for theophylline and 3-methylxanthine was studied as a function of pH. At pH 8.5, 100% of the theophylline is extracted and at pH 9.5, 79% is extracted. In the case of 3-methylxanthine, 35% is extracted at pH 8.5 and only 18% at pH 9.5. From

* On sabbatical leave from the University of Alexandria, Alexandria, Egypt.

Table. 1. Study of possible interferences

Compound	Before extraction*	After extraction†
Uric acid	−§	−§
Theobromine	−	−
Xanthine	−	−
Hypoxanthine	−	−
3-Methylxanthine	+	+
Caffeine	+	−

* 20 μg/ml in phosphate buffer (pH 7.4).

† After extraction by procedure outlined for theophylline (see *Experimental*).

§ A negative sign represents no interfering peak in the potential region where the theophylline peak occurs. A positive sign indicates that an overlapping peak is obtained.

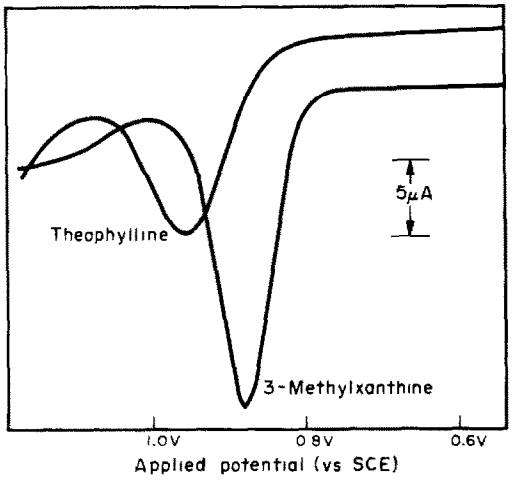


Fig. 1. Differential pulse voltamograms of theophylline and 3-methylxanthine in phosphate buffer (pH 7.4). Concentration of each compound 2 μg/ml.

these findings, a compromise pH of 9.0 was chosen to minimize the extraction of 3-methylxanthine while maximizing that of theophylline. When the theophylline concentration is 10 μg/ml, a 4-μg/ml concentration of 3-methylxanthine would create an error of about 10–15% in the measurement of the theophylline. Consequently this method may not be applicable to patients undergoing long term theophylline therapy.

If the sum of the metabolite, 3-methylxanthine, and theophylline is to be measured the extraction should be carried out at pH 7.5, at which both compounds are extracted quantitatively. However, since the voltamograms of the compounds overlap significantly, determination of each compound would be difficult.

A typical calibration curve for the recovery of theophylline in spiked plasma samples was linear, and could be described by the equation current (μA) = 0.614 × concentration (μg/ml) − 0.150, with a correlation coefficient of 0.998 and a standard error of the estimate ($S_{y,x}$) of 0.213 μA (two determinations for each of 4 points). The curve was also linear for the normal therapeutic range for theophylline when spiked plasma samples were mixed with pH-7.5 phosphate buffer and voltamograms of this mixture were taken directly. The correlation coefficient was 0.999 and there was a positive intercept which was probably due to naturally occurring substances which are oxidized under these conditions. This latter method of analysis represents a very rapid method for the determination of plasma theophylline, as very little sample preparation is needed. The main drawback is the large positive intercept. The cause of the intercept is being examined, and tests are being made to find whether it varies from plasma to plasma. As a determination requires only 1 ml of plasma, a 5-ml sample would suffice to establish a calibration curve for each subject.

Though this technique is not as sensitive and selective as chromatography, the instrumentation is simple, portable and requires a minimum of start-up time. The short time required for obtaining the voltamogram and the simple sample preparation make it a rapid method. The direct method may find utility in the rapid estimation of theophylline concentrations in plasma in emergency cases of toxicity.

REFERENCES

1. J. A. Schack and S. H. Waxler, *J. Pharmacol. Exp. Therap.*, 1949, **97**, 283.
2. P. Jatlow, *Clin. Chem.*, 1975, **21**, 1518.
3. J. Vasiliades and T. Turner, *Clin. Chim. Acta*, 1976, **69**, 491.
4. R. C. Gupta and G. D. Lundberg, *Anal. Chem.*, 1973, **45**, 2403.
5. G. F. Johnson, W. A. Dechtiaruk and H. M. Solomon, *Clin. Chem.*, 1975, **21**, 144.
6. D. Perrier and E. Lear, *ibid.*, 1976, **22**, 898.
7. M. A. Evenson and B. L. Warren, *ibid.*, 1976, **22**, 851.
8. R. F. Adams, F. L. Vandemark and G. J. Schmidt, *ibid.*, 1976, **22**, 1903.
9. G. W. Reng, V. Smith, A. Reng and W. L. Chiou, *Res. Commun. Chem. Pathol. Pharmacol.*, 1976, **15**, 341.
10. M. Sheehan, R. H. Hertel and C. T. Kelly, *Clin. Chem.*, 1977, **23**, 64.
11. P. T. Kissinger, C. Refshauge, R. Dreiling and R. N. Adams, *Anal. Lett.*, 1973, **6**, 465.
12. R. D. Thompson, H. T. Nagasawa and J. W. Jenne, *J. Lab. Clin. Med.*, 1974, **84**, 584.

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APPLICATIONS OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—V USE OF COMMERCIAL HOLLOW-CATHODE LAMPS

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Summary—The feasibility of using radiofrequency-excited commercial hollow-cathode lamps as Zeeman-modulated sources is examined. A supply frequency of 2.5 MHz is found to be generally suitable. At this frequency the d.c. and RF zero magnetic field lamp characteristics remain similar, and satisfactory magnetic stability is obtained. Suitable choice of magnetic field strength is found to give partial discrimination between analyte atomic-absorption and self-absorption within the lamp for emission lines showing an anomolous multiplet.

Zeeman-modulated (ZM) spectrometers for atomic-absorption measurements are of two types: instruments in which the magnetic field is applied across the source,[1–5] and those in which it is applied across the atomizer.[6,7] For reasons which will be considered in a subsequent paper[8] the first arrangement is felt to be preferable.

So far spectrometers of the first type have used magnetically stable sources such as electrodeless discharge lamps (EDLs) or d.c. discharge lamps of special design.[9] Recent work suggests, however, that conventional hollow-cathode lamps (HCLs) could be used provided they were driven from radiofrequency rather than d.c. power supplies.[10] As pointed out elsewhere,[6] such a development must be considered to be potentially advantageous, since the powerful ZM background-correction technique can then be used with routinely available sources. The present work was therefore done to examine the feasibility of operating RF-driven commercial HCLs within magnetic fields of sufficient strength for Zeeman modulation to be effective.

EXPERIMENTAL

The spectrometer used and the operating procedure are described in detail elsewhere.[8] The electromagnet and HCL power supply are described below.

The electromagnet was designed and supplied by the Hammond Transformer Co. It generated an average field of 10 kG in a 4-cm gap over a pole-face area of 8 × 8 cm at a power dissipation of 1 kW. The (fixed) gap was large enough to admit HCLs such as those supplied for example by Varian Techtron. The magnet was mounted with the field axis vertical. This permitted the HCL to be optically aligned horizontally by lateral displacement within the magnet gap. Vertical optical alignment was carried out by suitable adjustment of lens heights along the optical rail.

Lamps were driven from a variable radiofrequency power-supply covering the range 2–15 MHz. The supply used a single 6L6G as an anode-tuned oscillator, with low-frequency modulation applied by means of the screen grid bias to modulate the HCL output. The supply gave a maximum output of about 500 V (peak to peak) at 18 mA. The RF output was connected to the HCL cathode through a 30-pf variable capacitor for current control. The HCL anode was grounded through a current meter, in a similar manner to that used for the capacitively coupled sources described previously.[10]

Among currently available HCLs, those supplied by Perkin-Elmer are too large to fit within a 4-cm magnet gap. Corning lamps were investigated, but were found to be unsatisfactory because RF excitation failed to generate a plasma within the cathode cavity (although a weak plasma could be formed around its periphery). This effect is apparently due to the narrow cathode bore of these lamps, which causes their d.c. striking and running voltages to be unusually high, and is also thought to attenuate RF field strength within the cavity. Lamps supplied by Varian Techtron behaved satisfactorily and were used exclusively for this and for all subsequent work. One failure was encountered: a boron lamp, in which the plasma was abruptly extinguished within the cathode and reformed outside the cathode insulator. The failure occurred after half an hour of operation at 15 mA within a 6-kG field, and was attributed to an insulation breakdown since the discharge had the same appearance even on return to d.c. conditions.

RESULTS AND DISCUSSION

Appearance of the plasma

At zero magnetic field the RF cathode plasma appears little different from its d.c. counterpart. However, the diffuse anode plasma is considerably more dense, and may extend to fill the body of the lamp at high current levels. As the magnetic field strength is increased from zero, two lines of increasing intensity, lying in a plane perpendicular to the magnetic axis and parallel to the cathode axis, are formed along the cathode walls. These lines are presumably caused by the magnetic focusing of ions driven in an oscillatory manner along the cathode cavity by the applied RF field. The lines appear almost as (separate) point sources when viewed along the spectrometer axis, and are invariably the sources of greatest emission intensity within the cathode. Their position off the optical axis necessitates horizontal re-alignment of the lamp for each change in magnetic field strength. The lines also appear to represent regions of abnormally high sputtering, since after a few hours of operation in fields of 5–10 kG longitudinal grooves about 1 mm wide become etched into the cathode surface unless the lamp is rotated periodically.

A number of lamps have been driven successfully with the apparatus. Data are presented here for Cu, Fe, and Zn as elements showing a range of different sputtering, excitation and magnetic properties. Surprisingly, the Fe lamp behaved in a fairly similar manner to the others examined, except for its inability to form a cathode plasma at the higher RF frequencies used (Fig. 2). Equally surpris-

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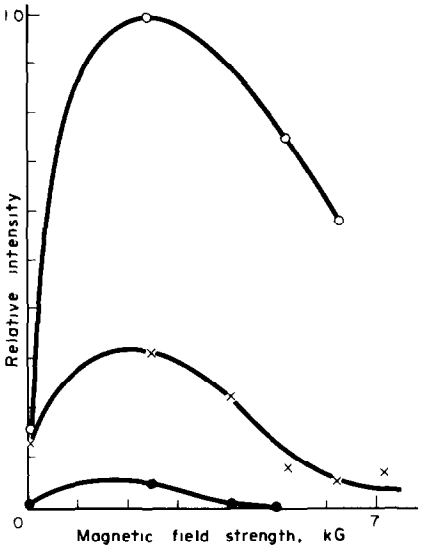


Fig. 1. Relative intensity *vs.* field strength for the Cu 3248-Å line at maximum supply output. × = 2.5 MHz; ○ = 5 MHz; ● = 15 MHz.

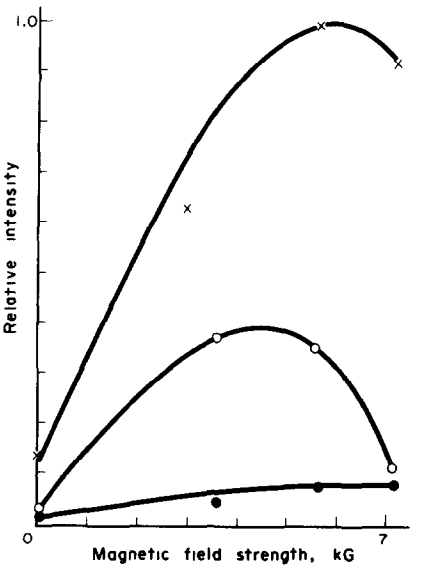


Fig. 3. Relative intensity *vs.* field strength for the Zn 2139-Å line. × = 2.5 MHz; ○ = 5 MHz; ● = 15 MHz.

ingly, it remained physically intact even after repeated cycling to 10 kG.

Lamp performance

Figures 1–3 show the dependence of the relative intensity on magnetic field strength and power-supply frequency for the three lamps examined. Figure 4 shows the relative intensity dependence on current for the Cu lamp at 2.5 MHz and zero field, with conventional modulated d.c. operation. The data are representative of the performance of the other lamps under these conditions, and illustrate the similarity of the excitation characteristics of HCL discharges driven by low RF and by d.c. power supplies. This similarity has been noted earlier.[10] The curves drawn illustrate the general trends and are not meant to be definitive.

As might be expected, variations in intensity with magnetic field strength tend to be slightly more pronounced at lower frequencies, as oscillation amplitudes within the lamp increase. In each case the intensity falls off markedly as the supply frequency is increased, which accords with the reported inability of high-frequency plasmas to cause sputtering.[11] From the data in Figs. 1–3, 2.5 MHz was chosen as a suitable general operating frequency: it was also found to be a suitable frequency for all the lamps subsequently examined.

At 2.5 MHz it was found that lamp spectra, zero-field stability plots, and the degree of self-absorption (as indicated by the dependence of absorption sensitivity on lamp current) were very similar to those obtained with d.c. excitation. Lamp stability also showed little change at low

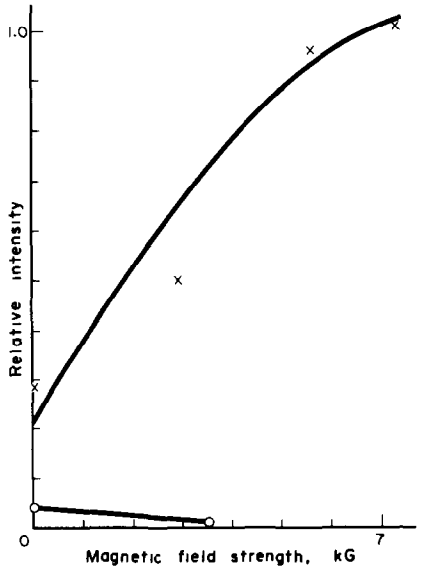


Fig. 2. Relative intensity *vs.* field strength for the Fe 2483-Å line. Data terminate at the upper field-strength/frequency limit for generation of a plasma within the cathode. × = 2.5 MHz; ○ = 5 MHz.

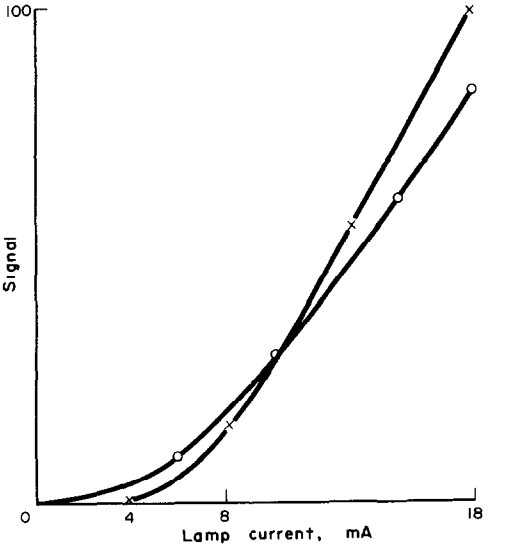


Fig. 4. Intensity *vs.* current for the Cu HCL. × ; RF response at 2.5 MHz, zero magnetic field. ○; modulated d.c. response. All results are normalized with respect to the maximum RF signal.

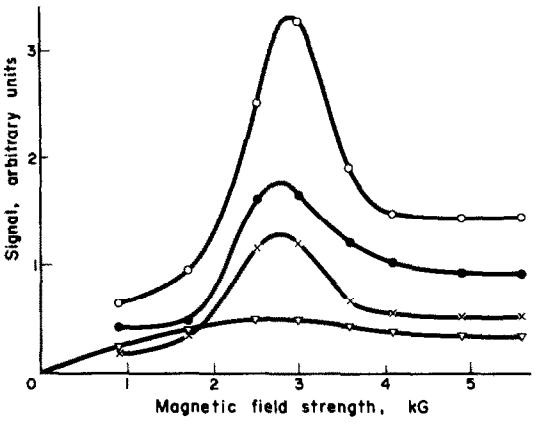


Fig. 5. Analyte to self-absorption signal ratio *vs.* field strength. Lamp current: × = 7 mA; ● = 12 mA; ○ = 18 mA. The bottom curve (▽) is the relative analyte absorption signal curve for 7-mA lamp current and a 0.030-ppm Cu^{2+} solution.

field-strengths, although small intensity fluctuations did become apparent at fields above about 5–6 kG. This instability reduced spectrometer performance only marginally,[8] and in any case could probably be reduced by improved stabilization of the power supply. In view of these similarities, further details will not be reported here.

An effect of interest that has no counterpart in the d.c. systems was the behaviour of the ratio, measured at fixed magnetic field strength, of the signal produced by atomization of a solution of given analyte concentration to the signal produced as a result of self-absorption within the HCL. When values of this ratio are measured at increasing values of the magnetic field strength, a maximum is obtained for those lines giving an anomolous multiplet. The data shown in Fig. 5 illustrates this effect for the Cu 3248-Å line, for which the maximum is particularly marked. Experimentally the data in Fig. 5 were obtained by setting up the spectrometer for normal ZM operation, and setting the instrument to zero output at zero field strength. As the field strength was increased the resulting departures of the spectrometer output from zero gave a direct measure of the self-absorption signal at any particular field strength. The corresponding analyte signal at that field strength was measured by aspirating an analyte solution of fixed concentration (0.1 ppm was used here) and observing the new signal thereby generated.

The reason for this behaviour is considered to lie in the narrowness of the self-absorption line profile relative to the absorption profile within the flame atomizer used here. As the magnetic field is strengthened, and the separation between the π-components of an anomolous multiplet thus increased, the π-absorption coefficient of a narrow absorption line falls faster than that of a broad line as an increasing fraction of the π-emission becomes frequency-shifted towards the wings of the absorption profiles. Both the behaviour observed and the explanation above probably refer to self-absorption which takes place in the main body of the lamp, well in front of the cathode, since absorbing atoms in the neighbourhood of the cathode would show Zeeman splitting of the absorption profile and the π and σ emission lines would be equally affected; a situation to which a source-modulated ZM spectrometer will not respond.

In practice the effect is of considerable use in the optimization of ZM spectrometry, since the maximum value of the ratio approximately indicates the magnetic field strength giving an optimum output signal to noise ratio. Thus plots similar to Fig. 5 were made for each line showing an anomolous multiplet, before experimental results were obtained by use of that line.[8]

CONCLUSIONS

The present work has shown commercial HCLs to be suitable as ZM sources, provided RF excitation is used and a suitably large magnet is available. A power supply frequency of 2.5 MHz is considered likely to be generally suitable for HCLs of the type supplied by Varian Techtron, although small changes from this frequency may give minor improvements in individual cases. The technical advantages of good intensity and stability that characterize the d.c. operation of HCLs are maintained under ZM conditions. The stability of a ZM HCL represents a particular advantage for reducing the background noise of ZM spectrometers: this aspect will be considered at more length later.[8] The advantage can be enhanced by selective discrimination against self-absorption signals through a suitable choice of magnetic field strength in the case of those lines showing an anomolous multiplet.

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REFERENCES

1. T. J. Hadeishi and R. D. McLaughlin, *Science*, 1971, **174**, 404.
2. T. J. Hadeishi, *Appl. Phys. Lett.*, 1972, **21**, 438.
3. R. Stephens and D. E. Ryan, *Talanta*, 1975, **22**, 659.
4. H. Koizumi and K. Yasuda, *Anal. Chem.*, 1975, **47**, 1679.
5. *Idem, ibid.*, 1976, **48**, 1178.
6. J. B. Dawson, E. Grassan, D. J. Ellis and M. J. Keir, *Analyst*, 1976, **101**, 315.
7. H. Koizumi and K. Yasuda, *Spectrochim. Acta*, 1976, **31B**, 523.
8. References in Part VI, R. Stephens, *Talanta*, 1978, **25**, in the press.
9. R. Stephens and D. E. Ryan, *ibid.*, 1975, **22**, 655.
10. R. Stephens, *ibid.*, 1977, **24**, 233.
11. H. Koizumi and K. Yasuda, *Spectrochim. Acta*, 1976, **31B**, 237.

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ASSESSMENT OF A NEW METHOD FOR THE DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF SILICON IN STEEL

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Summary—A procedure is described by which silicon in steel may be determined by differential pulse polarography after removal of iron. Silicomolybdic acid is formed within 20 min by reaction of the silicon with molybdate in the presence of methyl ethyl ketone: subsequent addition of citrate buffer prevents interference from phosphate and excess of molybdate. At the levels present in high-purity iron (~ 0.002%) the precision for silicon is better than that usually quoted for the molybdenum blue method. The steel is dissolved by standard procedures but iron must be removed before the silicon is determined. The lower limit imposed by the polarography is about 10^{-5}% silicon, but the practical lower limit is probably set by the difficulty of removing the last traces of iron.

The growing complexity of steel making has produced a need for analytical procedures capable of determining increasingly small amounts of elements in standard steel samples. Silicon in steel can be determined by several methods but the current British Standards Institution methods[1] are gravimetric (> 0.05% Si) and photometric (0.002–0.05% Si) techniques based on dehydration of silicic acid and on chemical reduction of silicomolybdic acid, respectively.

A procedure by which nanogram amounts of silicon can be determined by differential pulse polarography has been reported previously by the present authors.[2] This procedure, based on the polarographic reduction of β-silicomolybdic acid, was developed to give the highest sensitivity, and small concentrations of reagents were used to facilitate obtaining low blanks. At these low concentrations of silicon and reagents, 18 hr were required for complete formation of the β-silicomolybdic acid and solutions were conveniently left overnight for the reaction to reach completion.

In the present paper a procedure is described for determining higher concentrations of silicon more conveniently and this procedure has been applied to the determination of silicon in steel. At the concentrations of silicon and reagents used, formation of β-silicomolybdic acid is complete in 20 min. Dilution of the samples then allows complete masking of excess of molybdate, and phosphate in up to a 100:1 ratio to silicon, with citrate buffer. Iron interferes and is removed by mercury cathode electrolysis after dissolution of the steel by a standard procedure.[1]

EXPERIMENTAL

Apparatus

A Princeton Applied Research Corporation Model 174 Polarographic Analyzer and an Advance HR2000 recorder were used. A forced drop-time of 2 sec was imposed on the dropping mercury electrode and a platinum foil anode and a saturated calomel reference electrode were used. A pulse height of 50 mV was usually used, with a scan-rate of 2 mV/sec. The polarographic cell had a capacity of 50 ml. A pH-meter was used in the pH adjustment.

Mercury cathode electrolysis was done in a 100-ml cell fitted with a water jacket. A platinum foil anode was used. Current for the electrolysis was provided by a power unit capable of providing 10 A d.c.

Reagents

Use analytical-reagent grade chemicals throughout.

Sulphuric acid solution, 10% *v/v*.

Potassium permanganate solution, 2%, prepared and stored in polyethylene containers.

Ammonium molybdate solution, 1%. Prepared and stored in polyethylene containers.

Sodium hydroxide solution, 2*M*. Prepared and stored in polyethylene containers.

Hydrochloric acid solution, 1*M and* 0.1 *M*.

Citrate buffer. Dissolve 21 g of citric acid in 100 ml of 2*M* sodium hydroxide, dilute to 1 litre with water and adjust the pH to 2.5 with 1*M* hydrochloric acid. Prepare and store in polyethylene containers.

Triton X-100 solution, 0.2%.

Standard silicon solutions, 100, 10 *and* 1 μg/ml. Fuse 0.1000 g of silicon powder (99.99% pure) with 2 g of anhydrous sodium carbonate in a platinum crucible. Dissolve the cooled melt in water and dilute to 1 litre with water in a standard flask. If a glass flask is used, transfer the solution as soon as possible to a polyethylene container for storage. Dilute this 100-μg/ml solution as required, to obtain 10 and 1 μg/ml standards (also prepared and/or stored in plastic-ware).

Preparation of calibration graphs

Pipette 5 ml of ammonium molybdate solution into a 100-ml polyethylene beaker. Add 0–25 ml of the appropriate standard silicon solution (to cover one of the ranges 0–25, 0–250 or 0–2500 μg of silicon) and dilute to about 30 ml with water. Adjust the pH to 1.6 with 1*M* hydrochloric acid (stir with a magnetic stirrer). Let the solution stand for 20 min at room temperature. Transfer the solution completely to a 100-ml standard flask, washing the pH electrodes and beaker with 0.1*M* hydrochloric acid solution and dilute to 100 ml with 0.1*M* hydrochloric acid solution.

Pipette 10 ml of this solution into a 50-ml standard flask, add 2 ml of 1*M* hydrochloric acid and 10 ml of methyl ethyl ketone, dilute to volume with water and mix. Transfer 5 ml of this solution to a 25-ml standard flask, dilute to volume with citrate buffer, and mix. Transfer the solution to a polarographic cell, add 0.3 ml of Triton X-100 solution and deoxygenate the solution by passing nitrogen through it for 15 min. Record the differential pulse polarogram between −0.2 and −0.7 V, using a pulse height of 50 mV, a scan-rate of 2 mV/sec and a drop-time of 2 sec. On the same chart paper, without altering the zero-current position, record the differential pulse polarogram of a blank solution containing all the reagents but no silicon. Measure the height of the first peak at −0.37 V on the standard polarogram relative to the blank polarogram.

Procedure

Add 40 ml of 10% sulphuric acid to 1 g of the steel sample in a "Teflon" beaker and heat gently until the sample is dissolved. Oxidize the hot solution by dropwise addition of 2% potassium permanganate solution until a permanent precipitate of manganese dioxide is just obtained. Add two or three drops of 100-volume hydrogen peroxide until the precipitate of manganese dioxide is just discharged. Boil the solution to destroy excess of hydrogen peroxide. Cool, filter if necessary and dilute the solution to 50 ml in a standard flask with distilled water and mix. Transfer most of the solution to the mercury cathode electrolysis cell and electrolyse for about 1 hr at a current density of about 0.2 A/cm^2. Pass cold water through the jacket of the cell to keep the temperature of the solution below 40°. Continue the electrolysis until a spot test with potassium ferrocyanide shows that the concentration of iron remaining is negligible. Continue the electrolysis while pipetting 25 ml of the electrolysed solution into a polyethylene beaker. Adjust the pH of this solution to 1.6 with 2*M* sodium hydroxide solution. Add 5 ml of 1% ammonium molybdate solution and stir the solution with a magnetic stirrer. Continue the analysis according to the procedure for the preparation of the calibration graph starting at "Allow the solution to stand at room temperature for 20 minutes. . . ."

Note. When using the calibration graphs prepared as indicated above, note that only half of the steel sample is being taken here. For steel samples containing >0.5% of silicon, use a smaller aliquot of solution, or take a smaller sample weight, so that less than 2500 μg of silicon is taken after electrolysis. For all steel samples the amount of silicon taken may be adjusted by this means to give a more favourable placing on a calibration curve. In the present work from 0.3 to 1.4 g of steel was taken in order to obtain greater precision.

RESULTS AND DISCUSSION

The calibration graph obtained by using the first wave at −0.37 V is rectilinear whereas that from the second wave at −0.5 V is not. Typical polarograms of standard silicon solutions to which an iron(III) salt has been added and then removed by mercury cathode electrolysis are shown in Fig. 1. The effectiveness of the removal of iron can be seen if these polarograms are compared with those in Fig. 2 for which mercury cathode electrolysis was not applied, these polarograms clearly showing the suppression of the wave at −0.37 V by iron. The nature of the interference is not known and has not been investigated in the present work.

Results obtained with British Chemical Standard samples of high-purity iron and of steels are shown in Table 1. The coefficients of variation are satisfactory and the agreement with the certificate values is close. When the British Standard procedure[1] was used, a high-purity iron containing 0.002% of silicon gave an absorbance of about 0.04. The polarographic method described here gave a peak-height of about 0.05 μA at this level, measurable to about 1 nA, and indeed the procedure could be used to determine even lower silicon contents precisely. For some steel samples the second wave was distorted but this was immaterial as the results were based on the first peak.

The procedure has two main shortcomings. The first is the need to remove iron: other alloying metals that may

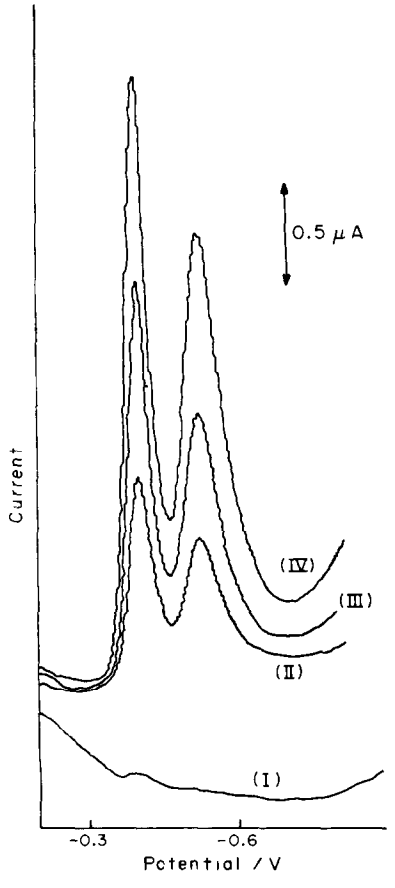


Fig. 1. Differential pulse polarograms of β-silicomolybdate in citrate buffer at pH 2.5 after removal of iron by mercury cathode electrolysis. Amount of iron(III) originally was equivalent to a concentration of 1 mg/ml in the measured solution. Silicon concentration of measured solutions: (*i*) 0, (*ii*) 0.08, (*iii*) 0.16, (*iv*) 0.24 μg/ml.

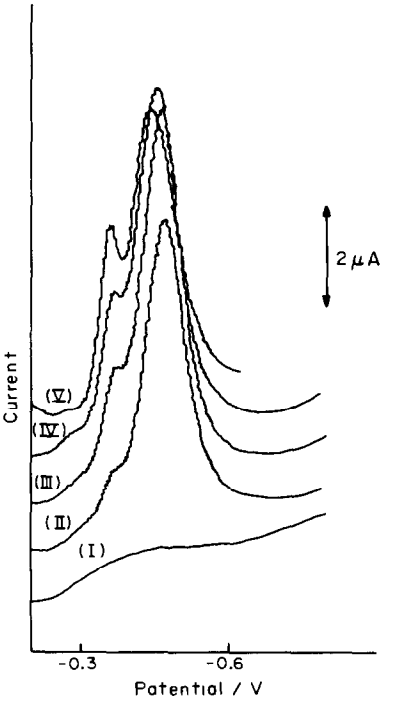


Fig. 2. Differential pulse polarograms of β-silicomolybdate in citrate buffer at pH 2.5 without removal of iron. Iron(III) concentration 1 mg/ml in the measured solution. Silicon concentration of measured solution: (*i*) 0, (*ii*) 1, (*iii*) 2, (*iv*) 3, (*v*) 4 μg/ml.

Table 1. Results obtained with British Chemical Standards iron and steel samples

	Silicon found, %	Mean %	Coefficient of variation, %*	Certificate value, %	Values given by individual analysts, %†
BCS 149/3 High-purity iron	0.00200 0.00210 0.00170 0.00165	0.0019	11.5	0.002	0.001; 0.002 0.002; 0.002 0.001; 0.002 0.002; 0.002
BCS 260/4 High-purity iron	0.00308 0.00293 0.00303 0.00300 0.00310	0.00303	2.4	0.003	0.003; 0.003 0.002; 0.002 0.003; 0.004 0.002
BCS 251 Low-alloy steel	0.0114 0.0110 0.0111 0.0113	0.0112	1.7	0.013	0.017; 0.012; 0.013 0.015; 0.016; 0.010 0.014; 0.010; 0.013 0.010; 0.016; 0.015
BCS 232/1 0.1% Sulphur carbon steel	0.074 0.071 0.076	0.073	4.0		0.07
BCS 237/1 0.1% Carbon steel	0.109 0.113 0.113 0.115	0.112	2.6	0.11_5	0.10_5; 0.11_5 0.11_0; 0.11_5 0.11_5; 0.10_5 0.12_5; 0.12_0
BCS 204/4 Ferro-chromium (high carbon)	0.223 0.237 0.210 0.222	0.223	5.9	0.22	0.22; 0.22; 0.20 0.24; 0.24; 0.22 0.23; 0.30
BCS 240/2 0.4% Carbon steel	0.245 0.246 0.236 0.242	0.242	2.0		0.25; 0.25 0.25
BCS 258/1 Low-alloy steel	0.963 0.950 0.987 0.973	0.968	1.9	0.96	0.96; 0.95 0.97; 0.97 0.96; 0.97 0.97; 0.96; 0.95

* By range method.
† From the certificate of analysis.

interfere are also removed by the mercury cathode analysis, however. The second is the need for extensive dilution after the rapid formation of silicomolybdate at high reagent concentrations, to permit masking of the excess of molybdate. This means that in making the polarographic measurements higher sensitivities are used than would normally be necessary.

At present there does not appear to be a need for determining silicon in steel at levels less than 0.002%, but should this eventually become necessary, the lower limit of detection by the present procedure could be reduced further by reducing the reagent concentrations and accepting a longer formation time for the heteropoly acid.[2] By these means the extensive dilution of sample could be avoided: in the present procedure only 0.5% of the sample is used for measurement. It would be necessary to investigate whether adequate removal of iron was possible.

Acknowledgements—The authors wish to thank the British Steel Corporation for financial support.

REFERENCES

1. British Standards Institution, *B.S. Handbook No. 19, Methods for the Sampling and Analysis of Iron, Steel and other Ferrous Metals*, London, 1970.
2. A. G. Fogg and A. A. Osakwe, *Anal. Letters*, 1976, **9**, 23.

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REACTION RATES BETWEEN WATER AND SOME MODIFIED RAPIDLY-REACTING KARL FISCHER REAGENTS

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Summary—Rate constants were determined for the reaction between water and various modified Karl Fischer reagents containing formamide, dimethylformamide or *N*-methylformamide. It was shown that the reaction rate can be increased by a factor of 100 by using a reagent containing 40% v/v formamide in pyridine compared to that obtained by use of the conventional methanolic reagent.

The original Karl Fischer reagent was prepared as a methanolic solution containing iodine, sulphur dioxide and pyridine.[1] Reaction rates between water and reagents based on these constituents have already been studied by the author,[2,3] who found the reaction to be first order with respect to iodine, to sulphur dioxide and to water. The reaction rate was not found to be significantly influenced by an excess of pyridine in the range 0.7–3*M*. The rate constant for a methanolic reagent that was 1*M* in pyridine was estimated to be $(1.2 \pm 0.2) \times 10^3$ $l^2.mole^{-2}.sec^{-1}$. In order to obtain a reasonably rapid reaction close to the end-point of a titration, where both the concentration of water and iodine must be low, it was found that the concentration of sulphur dioxide in the titration solution should be about 0.5*M*.

In some applications it has been found necessary to exclude methanol from the Karl Fischer reagent. The reason for this is that the presence of methanol in the system is a source of water in some samples because of esterification reactions when acids are present, or because of acetal and ketal formation accompanied by production of water when carbonyl compounds are present. Solubility can be another reason for the choice of a non-methanolic reagent. For example, formamide is able to replace methanol in the desired so-called second-step reaction with the pyridine–sulphur trioxide compound and also serves as an excellent solvent. In addition Bizot[4] suggested that the reaction rate between water and a reagent containing 20% v/v formamide is higher than that obtained with the conventional Karl Fischer reagent. However, no quantitative results for the kinetics of the reaction were reported. Archer and Jeater [5] proposed the use of *N*-ethylpiperidine to catalyse the Karl Fischer reaction, but Karlsson[6] found no observable improvements when this compound was used.

As is obvious from the literature there is a lack of basic systematic studies of the reaction rate between water and various modifications of the Karl Fischer reagent. Further improvement of the Karl Fischer method, especially with regard to trace determinations, is likely to be realized as a consequence of such studies. This paper essentially reports on evaluation of the reaction order and values of the rate constants for reactions in which formamide, dimethylformamide and *N*-methylformamide are involved. These solvents were chosen because they have large differences in their dielectric constants as well as in their pK_a values, which means that much information could be expected from these experiments.

In a recent series of papers Verhoeff *et al.*[7–9] reported on the mechanism and reaction rate of the Karl Fischer titration reaction. Good agreement was obtained[7] with the value of the rate constant reported by Cedergren[2] for a methanolic reagent 1*M* in pyridine and 0.2*M* in iodide. In addition, these authors concluded that the reaction rate could be increased by lowering the concentration of iodide. This was found to depend on the fact that two iodine species, tri-iodide and iodine (in equilibrium with iodide) were involved in the main reaction. The iodine reacts much faster and for very low iodide concentrations this species dominates and therefore determines the reaction rate. However, with respect to coulometric generation of iodine, for high current efficiency there must be a high concentration of iodide present, which means that the reaction rate cannot be increased by lowering the concentration of iodide in such procedures.

EXPERIMENTAL

The titration cell was set up with the base being investigated and standardized methanolic Karl Fischer (KF) reagent (1*M* pyridine, 0.6*M* sulphur dioxide and 0.1*M* iodine) added in excess. The current through the cell was indicated by a recorder (see Fig. 1) coupled to the amperometric cell. A true potentiometric end-point detection system described earlier[3] was used in some experiments. Water, slightly less than the amount equivalent to the KF reagent was then added and the changes in current with time were recorded. It was assumed that the current through the cell was proportional to the concentration of iodine complex.

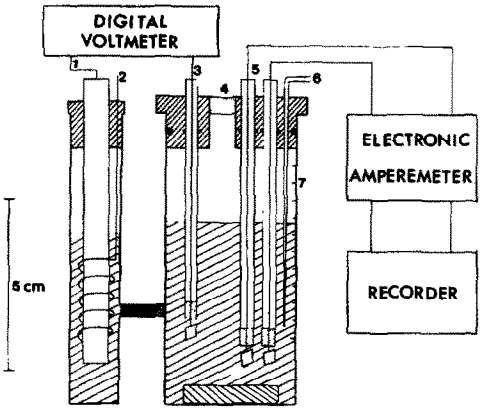


Fig. 1. Titration cell. (1) calomel reference electrode, (2) platinum wire reference electrode, (3) platinum foil indicating electrode, (4) silicone rubber septum, (5) platinum electrodes (amperometric system), (6) from burette, (7) volume markings.

Table 1. Reaction rate and rate constant for various combinations of reactants for a reagent containing 20% v/v formamide and 80% v/v pyridine

Time, *sec*	$[C_5H_5N\cdot I_2]$, $10^{-5}M$	$[C_5H_5N\cdot SO_2]$, M	$[H_2O]$, $10^{-5}M$	$-d[C_5H_5N\cdot I_2]/dt$, $10^{-6}mole\cdot l^{-1}\cdot sec^{-1}$	k, $10^4\ l^2\cdot mole^{-2}\cdot sec^{-1}$
7	1.25	0.69	0.54	1.1	2.4
12	0.91	0.69	0.20	0.33	2.6
14	0.90	0.69	0.19	0.24	2.0
9	1.08	0.69	0.37	0.59	2.1
10	1.33	0.37	0.87	0.92	2.1
12	1.15	0.37	0.71	0.71	2.4
13	0.98	0.37	0.54	0.92	2.1
16	1.07	0.37	0.63	0.58	2.3
				Mean value 2.3×10^4	
				Std. devn. 0.2×10^4	

Table 2. Reaction rate and rate constant for various combinations of reactants for a reagent containing 40% v/v formamide and 60% v/v of pyridine

Time, *sec*	$[C_5H_5N\cdot I_2]$, $10^{-5}M$	$[C_5H_5N\cdot SO_2]$, M	$[H_2O]$, $10^{-5}M$	$-d[C_5H_5N\cdot I_2]/dt$ $10^{-6}mole\cdot l^{-1}\cdot sec^{-1}$	k, $10^5\ l^2\cdot mole^{-2}\cdot sec^{-1}$
8	1.67	0.11	0.47	1.0	1.2
10	1.5	0.11	0.3	0.59	1.2
12	1.42	0.11	0.22	0.42	1.2
14	1.34	0.11	0.14	0.28	1.4
9	0.98	0.19	0.74	1.4	1.0
11	0.81	0.19	0.57	0.95	1.1
13	0.65	0.19	0.41	0.63	1.2
15	0.57	0.19	0.33	0.42	1.2
				Mean value 1.2×10^5	
				Std. devn. 0.1×10^5	

Table 3. Reaction rate and rate constant for various combinations of reactants for a reagent containing 20% v/v *N*-methylformamide and 80% v/v pyridine

Time, *sec*	$[C_5H_5N\cdot I_2]$, $10^{-5}M$	$[C_5H_5N\cdot SO_2]$, M	$[H_2O]$, $10^{-5}M$	$-d[C_5H_5N\cdot I_2]/dt$ $10^{-6}mole\cdot l^{-1}\cdot sec^{-1}$	k, $10^3\ l^2\cdot mole^{-2}\cdot sec^{-1}$
22	1.52	0.43	0.85	0.41	7.4
26	1.35	0.43	0.68	0.27	6.8
20	1.40	0.43	0.83	0.34	6.6
16	1.65	0.43	1.08	0.71	9.0
				Mean value 7.4×10^3	
				Std. devn. 1.1×10^3	

The following reagents were used: formamide (Merck p.a.), dimethylformamide (BDH, spectroscopic grade), *N*-methylformamide (Merck, for synthesis), *N*-ethylpiperidine (Merck p.a.), potassium iodide (Merck p.a.), sulphur dioxide (Fluka, >99.97%), pyridine (Mallinckrodt A.R.) and methanol (Merck p.a.). No chemical was dried or purified before use. The concentration of potassium iodide was 6 g/l. in each of the non-methanolic reagents. These reagents were prepared by mixing a solution of potassium iodide in the appropriate base with a solution of sulphur dioxide in pyridine. This mixture was then provided with an excess of iodine by means of a concentrated solution of iodine (Riedel de Haen, p.a.) in pyridine. All reagents were allowed to stand for one day before use. The actual concentration of sulphur dioxide in the titration solution was determined iodometrically in aqueous medium.

RESULTS

In his investigation of the kinetics, the author[2] measured the concentration of the iodine complex potentiometrically but in the present work amperometric measurement was used because of the simplicity with which the evaluation could be performed from the linear relationship between current and the concentration of the iodine complex. The response time of the amperometric system was less than 1 sec in the range 10^{-6}–$10^{-3}M$ iodine complex excess.

Tables 1–3 show the rate expression for a number of values of the concentrations. It was found that in every case the experiments satisfied the equation

$$-\frac{d[C_5H_5N\cdot I_2]}{dt} = k[C_5H_5N\cdot I_2] \times [C_5H_5N\cdot SO_2][H_2O], \quad (1)$$

Table 4. A summary of rate constants in various modified Karl Fischer reagents

Type of reagent	k, $l^2 \cdot mole^{-2} \cdot sec^{-1}$ (mean values)
20% dimethylformamide 80% pyridine	1.1×10^2
1*M* pyridine in methanol*	0.9×10^3
1*M* pyridine in methanol + *N*-ethylpiperidine†	0.9×10^3
10*M* pyridine in methanol	1.4×10^3
20% *N*-methylformamide 80% pyridine	7.4×10^3
20% formamide 80% pyridine	2.3×10^4
40% formamide 60%pyridine	1.2×10^5

* Previously determined[1] to be $(1.2 \pm 0.2) \times 10^3$.

† 1 ml of *N*-ethylpiperidine added directly to 40 ml of titration solution.

The rate constant, k, includes any possible contribution from the 20% v/v of formamide and 80% v/v of pyridine (Table 1) the 40% v/v of formamide and 60% v/v of pyridine (Table 2) and the 20% v/v of *N*-methylformamide and 80% v/v of pyridine (Table 3) in the media used. As can be seen from these tables the derived rate constants show good constancy for variations in $[C_5H_5N \cdot I_2]$, $[C_5H_5N \cdot SO_2]$ (not varied for the *N*-methylformamide system), $[H_2O]$ and $-d[C_5H_5N \cdot I_2]/dt$. Kinetic models other than that for equation (1) could not be made to fit the observations.

A summary of the results obtained for the rate constants for various modified Karl Fischer reagents is given in Table 4. For comparison the rate constants for methanolic reagents that are 1*M* and 10*M* in pyridine are included. The reaction rate in dimethylformamide medium is extremely slow. The value obtained with 1*M* pyridine in methanol, $(0.9 \pm 0.2) \times 10^3\ l^2 \cdot mole^{-2} \cdot sec^{-1}$, is somewhat less than that previously determined $(1.2 \pm 0.2) \times 10^3\ l^2 \cdot mole^{-2} \cdot sec^{-1}$. A tenfold increase in the concentration of pyridine only slightly increased the reaction rate. The addition of *N*-ethylpiperidine had no significant influence on the reaction rate under the conditions used (see Table 4). Formamide is more efficient than *N*-methylformamide in increasing the reaction rate. With use of 40% v/v formamide the reaction rate is 100 times that for the conventional methanolic Karl Fischer reagent, assuming both reagents to have the same concentration of sulphur dioxide. For each reagent tested the drift due to side-reactions was less than 0.04 ppm of H_2O per min. Higher concentrations of formamide than 40% v/v gave rise to larger drifts. For example with 60% formamide the drift due to side reactions was 0.2 ppm/min which made an adequate evaluation of the value of the rate constant impossible. The shapes of various concentration *vs.* time curves are illustrated in Fig. 2.

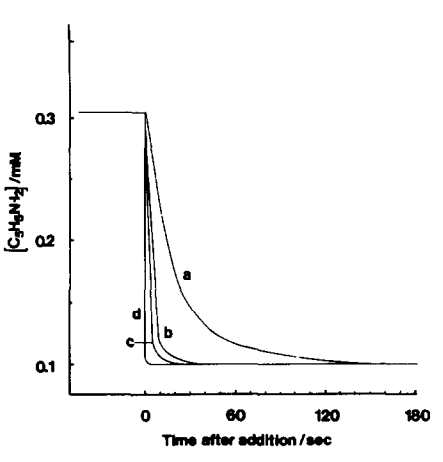


Fig. 2. Amperometrically measured concentration of iodine complex as a function of time for $2.1 \times 10^{-4}M$ of water (8.8 μmole) present at time zero. (*a*) 1*M* pyridine, 0.5*M* sulphur dioxide in methanol, (*b*) 0.4*M* sulphur dioxide in 20% v/v formamide and 80% v/v pyridine, (*c*) same as (*b*) except 0.7*M* sulphur dioxide, (*d*) 0.5*M* sulphur dioxide in 40% v/v formamide and 60% v/v pyridine.

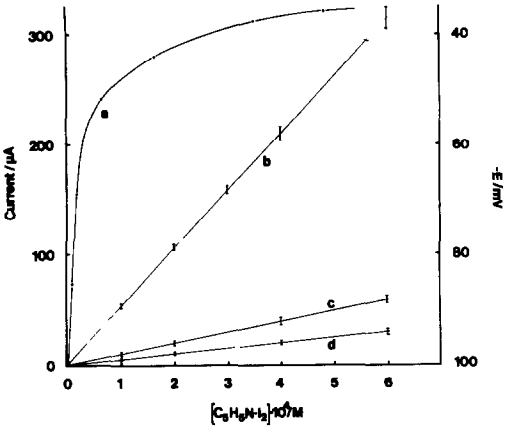


Fig. 3. Comparison between the amperometric sensitivity for various reagents: (*b*) 1*M* pyridine, 0.5*M* of sulphur dioxide in methanol, (*c*) 0.4*M* sulphur dioxide in a reagent containing 20% v/v formamide and 80% v/v pyridine, (*d*) 0.4*M* sulphur dioxide in 40% v/v formamide and 60% v/v pyridine. Curves *b*, *c*, and *d* are referred to the left-hand scale. Curve *a* represents the sensitivity in the potentiometric measurements and is referred to the right-hand scale. The bars denote the uncertainty in the current measurements.

DISCUSSION

As shown by the results given in this paper, formamide is a superior solvent for the Karl Fischer reagent with regard to the reaction rate. According to Table 4 there is no relationship between the dielectric constant of the solvent used and the calculated rate constant. On the other hand, the basicity of the reagent can, except for dimethylformamide, be directly related to the value of the rate constant. The reagents given in Table 4 are more basic (except dimethylformamide) as we go down the table. However, no simple relationship was found between pH and the size of the rate constant. A further investigation of this problem is in progress.

With a reagent containing 40% of formamide and 60% of pyridine, problems connected with slow reaction rates between water and the Karl Fischer reagent will be small, which is evident from the following example. Assume that we have 40 ml of spent reagent with an iodine-complex concentration of $10^{-5}M$ and that the working concentration of sulphur dioxide complex is 0.5*M*. In such a reagent the rate constant is $1.2 \times 10^5\ l^2 \cdot mole^{-2} \cdot sec^{-1}$ so the time required for 99.9% of a sample containing 0.36 μmole of water to react will be only 5 sec. In this example the iodine-complex concentration after reaction will be $10^{-6}M$. For comparison, at this low iodine-complex level

the time required with a methanolic reagent 0.5*M* in sulphur dioxide will be about 8 min.

Figure 3 shows a comparison between the amperometric sensitivity for various reagents. As can be seen, there is a loss in sensitivity for increasing concentrations of formamide. On the other hand, the sensitivity (potential *vs.* concentration of iodine-complex excess) in the potentiometric system is equal for all solvents. The potentiometric technique is recommended with respect to both accuracy and precision of the determination of the end-point. A plot of the potential of the potentiometric indicating system as a function of the iodine-complex concentration shows that the Nernst's equation is obeyed (slope 29.7 mV/decade) down to at least $10^{-5}M$. The practical consequence of the possibility of measuring such a low and stable iodine-complex excess will be an increased sensitivity of the previously described coulometric method,[10] as indicated by some preliminary results.

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REFERENCES

1. K. Fischer, *Angew. Chem.*, 1935, **48**, 394.
2. A. Cedergren, *Talanta*, 1974, **21**, 265.
3. *Idem, ibid.*, 1974, **21**, 553.
4. J. Bizot, *Bull. Soc. Chim. France*, 1967, 151.
5. E. E. Archer and H. W. Jeater, *Analyst*, 1965, **90**, 351.
6. R. Karlsson, *Talanta*, 1972, **19**, 1639.
7. J. C. Verhoef and E. Barendrecht, *J. Electroanal. Chem.*, 1976, **71**, 305.
8. *Idem, ibid.*, 1977, **75**, 705.
9. *Idem, Anal. Chim. Acta*, 1977, **94**, 395.
10. A. Cedergren, *ibid.*, 1974, **21**, 367.

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A SIMPLE METHOD FOR DISSOLUTION OF TANTALUM PENTOXIDE

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Summary—A simple and reproducible procedure has been developed for the dissolution of tantalum pentoxide. The oxide is fused with potassium nitrate and potassium carbonate in the ratio of 2:5:5. The cooled melt is dissolved in concentrated sulphuric acid. If a tartaric acid solution is desired, the sulphuric acid is evaporated and the residue dissolved in 20% tartaric acid solution.

Up to 500 mg of tantalum pentoxide of high purity can be dissolved in 40 ml of hot concentrated sulphuric acid containing 80 g of ammonium sulphate, but the method is time-consuming, continuous heating for 6 hr being required. Moreover the amount of tantalum pentoxide that can be dissolved is limited. The fusion of tantalum pentoxide with alkali metal hydrogen sulphate or pyrosulphate and the dissolution of the melt in concentrated sulphuric acid or tartaric acid solution[1] has been found to be difficult. In an attempt to develop a better method of dissolution, we fused tantalum pentoxide with KNO_3, $KCl + KNO_3$, $Na_2B_4O_7.10H_2O + Na_2CO_3$, $NaNO_3$, $Na_2S_2O_3$, $(NH_4)_6Mo_7O_{24}.4H_2O + (NH_4)_2SO_4$, Na_2SO_3, $Na_2MoO_4.2H_2O$, and $K_2CO_3 + KNO_3$, and tried dissolving the products in concentrated sulphuric acid and 20% tartaric acid solution. Only the melt obtained by the fusion of tantalum pentoxide with the potassium nitrate–potassium carbonate mixture gave a clear solution in hot concentrated sulphuric acid. The procedure is as follows. An intimate mixture of well-powdered Ta_2O_5(1 g) KNO_3(2.5 g) and K_2CO_3(2.5 g) in a 15-ml platinum crucible is heated in a furnace at 740–760° for 15 min. If the temperature is too high, *e.g.*, 840°, the cooled melt is insoluble in concentrated sulphuric acid; the temperature control is therefore important. The cold melt is transferred to a borosilicate glass beaker with not more than 25 ml of concentrated sulphuric acid and the contents of the beaker are heated on an electric heater for 30 min. During this treatment brown fumes are evolved, with vigorous effervescence. The cold melt is insoluble in 20% tartaric acid solution, so if a tartaric acid solution is desired then the sulphuric acid solution is evaporated to dryness and the residue dissolved in 20% tartaric acid solution. If the clear solution obtained in sulphuric acid is heated for 1 hr more, it becomes turbid. If the melt is left in the open air at room temperature for a day it becomes insoluble in hot concentrated sulphuric acid.

REFERENCE

1. F. Fairbrother, *The Chemistry of Niobium and Tantalum*, p. 224. Elsevier, Amsterdam, 1967.

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REFERENCES

1. K. Fischer, *Angew. Chem.*, 1935, **48**, 394.
2. A. Cedergren, *Talanta*, 1974, **21**, 265.
3. *Idem, ibid.*, 1974, **21**, 553.
4. J. Bizot, *Bull. Soc. Chim. France*, 1967, 151.
5. E. E. Archer and H. W. Jeater, *Analyst*, 1965, **90**, 351.
6. R. Karlsson, *Talanta*, 1972, **19**, 1639.
7. J. C. Verhoef and E. Barendrecht, *J. Electroanal. Chem.*, 1976, **71**, 305.
8. *Idem, ibid.*, 1977, **75**, 705.
9. *Idem, Anal. Chim. Acta*, 1977, **94**, 395.
10. A. Cedergren, *ibid.*, 1974, **21**, 367.

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REFERENCE

1. F. Fairbrother, *The Chemistry of Niobium and Tantalum*, p. 224. Elsevier, Amsterdam, 1967.

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DOSAGES THERMOMETRIQUES DE QUELQUES DIACIDES ORGANIQUES, EN MILIEU AQUEUX: MISE EN EVIDENCE DE LA NEUTRALISATION SUCCESSIVE DES DEUX GROUPES ACIDES DE FORCES VOISINES

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Résumé—Les acides maléique, fumarique, tartrique, glutarique et adipique sont titrés directement par une solution standard d'hydroxyde de sodium, à l'aide d'un appareillage automatique de titrage thermométrique. On obtient des diagrammes avec deux points d'inflexion correspondant à la neutralisation successive des deux groupes acides. Un étalonnage préalable permet de mesurer les chaleurs de neutralisation correspondantes et d'en déduire les enthalpies de dissociation dans l'eau de chacune des deux acidités. Des quantités de diacides de l'ordre de 3 à 10 × 10^{-4} mole sont titrées avec des déviations standard relatives de 3% environ.

De nombreux acides carboxyliques sont titrés, par thermométrie, par une solution d'hydroxyde de sodium étalon. Citons par exemple les travaux de Linde *et al.*,[1] Priestley *et al.*,[2] Jordan et Dumbaugh[3] portant sur la neutralisation de l'acide acétique, d'Harries,[4] Dumbaugh[5] Avedikian,[6] sur celle des dérivés halogénés des acides acétique et propionique. Harries[4] titre également un certain nombre de diacides carboxyliques. Le point le plus remarquable de ce dernier travail est que les deux stades d'ionisation des acides oxalique, malonique et succinique, peuvent être distingués alors que les différences de pK des deux acidités sont respectivement à 25° de 2,99,[7,8] 2,87,[9,10] et 1,43.[11,12]

Ces résultats expérimentaux sont le reflet des chaleurs de neutralisation différentes des deux acidités, que Harries détermine au cours de la même étude et dont les valeurs sont en accord avec les données de la littérature.[13] Les valeurs d'enthalpies d'ionisation des deux acidités d'un certain nombre de diacides[14] laissent prévoir un comportement semblable des acides glutarique, adipique, maléique, fumarique et tartrique lors de la neutralisation par de l'hydroxyde de sodium. Or pour des acides, Harries n'observe pas les points de demi-neutralisation intermédiaires. Ceci nous amène donc à reprendre l'étude du titrage thermométrique de ces diacides avec une solution d'hydroxyde de sodium.

PARTIE EXPERIMENTALE

Appareillage

L'appareillage est décrit par ailleurs.[15] Un mm de déviation sur le papier enregistreur correspond à environ 0,63 J.

Réactifs

Les acides tartrique, fumarique, maléique, adipique et glutarique sont des produits commerciaux. Leur pureté est vérifiée d'après leurs points de fusion. Ils sont mis en solution dans de l'eau distillée. Les solutions d'hydroxyde de sodium sont préparées par dilution de solutions étalon avec de l'eau distillée. Leur titre est vérifié systématiquement après chaque série de mesures et est environ 2M. Toutes les solutions titrées sont gardées en flacons bien bouchés.

Méthode

Pour chaque acide, les mesures sont effectuées pour 3 ou 4 concentrations différentes correspondant à un nombre de 3 à 12 × 10^{-4} mole dans 100 ml de solution. Pour chacune de ces concentrations, on effectue 9 essais en alternance avec le dosage de 100 ml d'une solution d'acide chlorhydrique 0,01M par la même solution d'hydroxyde de sodium. La neutralisation de l'acide chlorhydrique sert d'étalon calorimétrique interne et permet d'évaluer les chaleurs de neutralisation. Elle permet en outre de vérifier le débit de la burette automatique qui au cours de cette étude est fixée à 2 ml/mm. Il est également vérifié, en déterminant systématiquement avant et après chaque série de mesures, le volume versé en un temps déterminé. La vitesse de déroulement de papier enregistreur est de 30 mm/24 sec. La solution à doser (ou la solution d'acide chlorhydrique) est introduite à l'aide d'une pipette de 100 ml dans le vase réactionnel. L'agitation, le pont où sont incorporées les thermistances et l'enregistreur, sont branchés. Le pont est équilibré. Après 5 à 10 mn, le pont est rééquilibré et la burette est mise en marche. La courbe de titrage est alors enregistrée.

Les diagrammes obtenus ne s'écartant pas de la linéarité, les variations d'enthalpie sont mesurées par la méthode d'extrapolation de Jordan et Alleman,[16] plutôt que par la méthode de la tangente initiale. Pour l'évaluation des chaleurs de neutralisation, on détermine pour chaque concentration de l'acide à tester, la déviation moyenne sur l'enregistreur que l'on compare à la déviation moyenne due à la neutralisation de l'acide chlorhydrique. On fait ensuite la moyenne des chaleurs de neutralisation mesurées à diverses concentrations et ramenées à 1 mole. Pour l'évaluation des concentrations, on prend la moyenne des 9 mesures.

Tous les titrages sont effectués à température ambiante (23 ± 2°). L'enthalpie d'ionisation de l'eau est prise égale à 55740 J/mole.[17]

RESULTATS

Les diagrammes obenus pour les différents acides à différentes concentrations présentent en général deux points d'inflexion correspondant aux deux étapes d'ionisation: c'est-à-dire à la neutralisation des deux groupes acides. L'un des deux points correspond à la neutralisation totale de l'acide, l'autre à la demi-neutralisation (figure 1).

Comme pour les acides oxalique, malonique et succinique, les diagrammes présentent une pente plus accentuée après le premier point d'inflexion. La présence de celui-ci permet d'évaluer les enthalpies de neutralisation de cha-

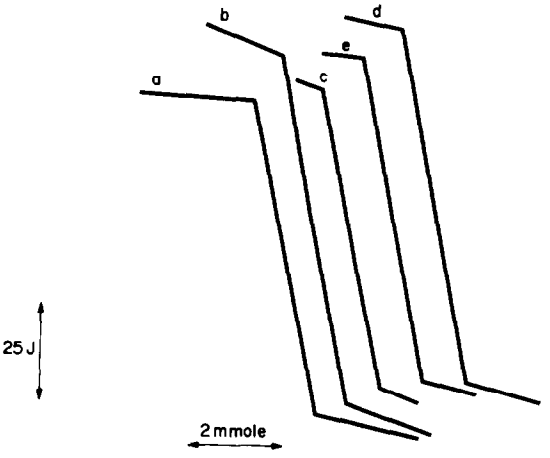


Fig. 1. Enthalpogrammes obtenus par dosage avec une solution aqueuse d'hydroxyde de sodium 2*N*. (a) acide fumarique $8{,}65 \cdot 10^{-4}M$. (b) acide maléique $8{,}99 \cdot 10^{-4}M$. (c) acide tartrique $8{,}02 \cdot 10^{-4}M$. (d) acide glutarique $8{,}97 \cdot 10^{-4}M$. (e) acide adipique $8{,}25 \cdot 10^{-4}M$.

cune des acidités. Les résultats analytiques et calorimétriques sont groupés dans les tableaux 1 et 2.

Les valeurs des enthalpies de neutralisation ΔH_n° d'un seul groupe carboxylique se situent dans l'intervalle de 54,34 à 63,12 kJ/mole. Elles permettent d'obtenir celles des enthalpies de dissociation acide ΔH_a° par la relation:

$$\Delta H_a^\circ = 55{,}74 + \Delta H_n^\circ \text{ kJ/mole}$$

où la constante est l'enthalpie d'ionisation de l'eau à 25°[17] (tableau 2). Les différences d'enthalpie de dissociations acides sont en accord avec les valuers publiées par Christensen, Izatt et Hansen.[14]

DISCUSSION

La plupart des méthodes de titrage conventionnelles, par exemple les titrages potentiométriques, sont fondamentalement des méthodes liées aux variations d'énergie libre par la constante d'acidité K_A. Par contre, les méthodes de titrage thermométrique, mettant en jeu la variation d'enthalpie $\Delta H = \Delta G + T\Delta S$, sont contrôlées à la fois par la variations d'énergie libre et par les variations d'entropie, qui par nature sone indépendantes l'une de l'autre. Par conséquent, un facteur "énergie libre" défavorable peut être compensé par le facteur entropique. Là réside un des intérêts de ce type de titrage (pour que ceux-ci puissent être mis en oeuvre, il faut que certaines conditions soient satisfaites; elles ont été définies par Tyrrell[18] pour le cas des réactions de neutralisation). Un bon exemple est le cas de l'acide borique[19] qui est titré directement, seul, par une solution d'hydroxyde de sodium, l'adjonction de mannitol n'étant plus nécessaire. La distinction des deux acidités des acides glutarique, adipique maléique, fumarique, tartrique (dont les différences de pK des deux acidités sont respectivement à 25° de 1,08[9], 0,99[9], 4,42[20] et 1,27) ainsi que celles des acides oxalique, malonique, et succinique[4] en fournit un autre exemple. En effet, des cinq acides étudiés dans ce travail, seul l'acide maléique présente une différence de pK (4,42)[20] entre ses deux acidités qui permet de les distinguer par des méthodes "classiques". Cette distinction provient du fait que les chaleurs de neutralisation des acidités de ces diacides sont différentes, la seconde étant supérieure à la première. Les valeurs des enthalpies de neutralisation des deux acidités se situent dans le domaine de −54,34 à −63,12 kJ/mol et ne sont donc pas grandement tributaires des constantes d'ionisation des groupes carboxyliques. Le facteur entropique compense donc le facteur énergie libre, ce qui explique nos résultats.

Tableau 1. Titrage des diacides par l'hydroxyde de sodium

Acide	Quantité, *mmole*	Rapport trouvé / mis	Nombre de mesures	Déviations standard relatives, %
Tartrique	0,802	1,00	9	3,0
	0,933	1,00	9	1,5
	1,073	1,00	9	2,4
	1,190	0,99	9	1,0
Adipique	0,825	0,99	9	3,3
	0,959	1,00	9	2,8
	1,090	1,00	9	1,2
Maléique	0,287	0,97	8	4,8
	0,689	1,01	9	4,8
	0,899	1,01	9	3,2
	0,997	1,03	9	4,0
	1,170	1,00	9	4,0
Fumarique	0,600	1,00	4	2,8
	0,686	1,03	8	3,6
	0,775	1,00	9	3,5
	0,865	1,00	8	2,3
Glutarique	0,750	1,00	9	2,9
	0,897	0,99	9	3,6
	1,070	1,01	9	1,3
	1,250	1,01	8	2,7

Tableau 2. Enthalpies de neutralisation*, *kJ/mole*

Acide	Enthalpie totale, ΔH_{nT}°	Enthalpie 1ère acidité, ΔH_{n1}°	Enthalpie 2ème acidite, ΔH_{n2}°	Enthalpie ionisation 1ère acidité, ΔH_{a1}°	Enthalpie ionisation 2ème acidité, ΔH_{a2}°	$\Delta(\Delta H_n^\circ)$
Adipique	−118,3	−58,5	−59,8	−2,8	−4,0	−1,2
				(−1,25)†	(−2,67)	(−1,42)
Tartrique	−110,4	−54,3	−56,0	1,5	−0,3	−1,8
				(3,09)	(−1,00)	(−2,09)
Glutarique	−120,4	−58,5	−61,9	−2,8	−6,1	−3,4
				(−0,50)	(−2,4)	(−1,92)
Fumarique	−120	−59,8	−63,1	−3,8	−7,4	−3,6
				(−0,46)	(−2,8)	(−3,30)
Maléique	−117,5	−56,4	−62,3	−0,6	−6,7	−6,1
				(0,33)	(−3,47)	(−3,80)

* ±0,8 kJ/mole

† Les valeurs entre parenthèses sont celles de Christensen, Izatt et Hansen.[14]

BIBLIOGRAPHIE

1. H. W. Linde, L. B. Rogers et D. N. Hume, *Anal. Chem.*, 1953, **25**, 404.
2. P. T. Priestley, W. S. Sebborn et R. F. W. Selman, *Analyst*, 1965, **90**, 589.
3. J. Jordan et W. H. Dumbaugh, Jr., *Anal. Chem.*, 1955, **31**, 210.
4. R. J. N. Harries, *Talanta*, 1968, **15**, 1345.
5. W. A. Dumbaugh, Jr., *Diss. Abstr.*, 1959, **20**, 1559.
6. L. Avedikian, *Bull. Soc. Chim. France*, 1966, 2570.
7. L. S. Darken, *J. Am. Chem. Soc.*, 1941, **63**, 1010.
8. G. D. Pinching et R. G. Bates, *J. Res. Natl. Bur. Stds.*, 1948, **40**, 412.
9. R. Gane et C. K. Ingold, *J. Chem. Soc.*, 1931, 2158.
10. W. J. Hamer, J. O. Burton et S. F. Acree, *J. Res. Natl. Bur. Std.*, 1940, **24**, 290.
11. G. D. Pinching et R. G. Bates, *ibid.*, 1948, **40**, 412.
12. *Idem, ibid.*, 1950, **45**, 327.
13. F. R. Bischowsky et F. D. Rossini, *Thermochemistry of Chemical Substances*, 1st Ed., Reinhold, New York, 1936.
14. J. J. Christensen, R. M. Izatt et L. D. Hansen, *J. Am. Chem. Soc.*, 1967, **89**, 213.
15. J. L. Burgot, *Talanta*, 1978, **25**, in press.
16. J. Jordan et T. G. Alleman, *Anal. Chem.*, 1957, **29**, 9.
17. J. D. Hale, R. M. Izatt et J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.
18. H. J. V. Tyrrell, *Talanta*, 1967, **14**, 843.
19. F. J. Miller et P. F. Thomason, *ibid.*, 1959, **2**, 109.
20. G. Dalgren et F. A. Long, *J. Am. Chem. Soc.*, 1960, **82**, 1306.

Summary—Maleic, fumaric, tartaric, glutaric and adipic acids are titrated directly with sodium hydroxide by means of an automatic thermometric titrimeter. The titration curves have two break-points, corresponding to the successive neutralization of the two acid groups. Previous standardization permits measurement of the heats of neutralization, from which the enthalpies of dissociation can be deduced. From 0.3 to 1 mmole of acid can be titrated with a relative standard deviation of about 3%.

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SELECTIVE DETECTION OF CARBOXYLIC ACIDS, UREAS AND PHENOLS AND SEMIQUANTITATIVE DETERMINATION OF CITRIC ACID BY CAPILLARY SOLID-STATE SPOT-TESTS

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Summary—Solid-state spot-tests for the selective detection of carboxylic acids, ureas and phenols have been developed. Mixtures of *p*-dimethylaminobenzaldehyde with *N*-methylurea and of *p*-dimethylaminobenzaldehyde with phthalic acid are used as reagents. Based on these tests a semiquantitative determination of citric acid is also developed. These tests utilize three properties of the coloured boundary: colour, length and direction of movement. Our work on capillary solid-state spot-tests,[1] has now been extended to some further organic compounds.

EXPERIMENTAL

Reagents

Analytical-grade reagents were used. Various mixtures of citric acid and starch were prepared. Reagent *A* was an equimolar mixture of *p*-dimethylaminobenzaldehyde (*p*-DAB) and *N*-methylurea, and reagent *B* an equimolar mixture of *p*-DAB and phthalic acid.

Procedures

General. A capillary was partly filled with *A* or *B* by continuous tapping and the solid test material was added to the open end. Both ends of the capillary were closed with cotton plugs with ("sealed") or without ("unsealed") a further seal of plasticine. Reagents and test materials were used either undried or after drying for 2 hr in an electrically heated oven at 60°. The unsealed or sealed capillaries were kept in the oven at 60°. Four combinations were tested: (*i*) undried materials in unsealed capillaries, (*ii*) undried materials in sealed capillaries, (*iii*) dried materials in unsealed capillaries and (*iv*) dried materials in sealed capillaries. The colour, length and direction of movement of the reagent/sample boundary after a definite interval of time were recorded.

Limit of identification of citric acid. Known volumes of a standard solution of citric acid were evaporated to dryness at 100°. The residues were then mixed intimately with *A*. The identification limit is 20 μg, which is much lower than the limit of 10 mg for detection with the same reagent in solution.

Spectra of solutions. Equal volumes of a 0.1*M* solution of the sample and a 1% solution of reagent *A*, both in 50% aqueous ethanol, were mixed and their absorbance recorded against 50% aqueous ethanol.

Semiquantitative determination. Capillaries containing reagent *A* and various concentrations of citric acid in starch (undried materials in unsealed capillaries) were kept at 60° for 2 hr. The length of the coloured boundary was recorded. A plot of citric acid concentration *vs.* length of boundary was linear over a certain range but did not pass through the origin; 10% citric acid gave a length of 1 mm and 75% gave 12 mm.

BIBLIOGRAPHIE

1. H. W. Linde, L. B. Rogers et D. N. Hume, *Anal. Chem.*, 1953, **25**, 404.
2. P. T. Priestley, W. S. Sebborn et R. F. W. Selman, *Analyst*, 1965, **90**, 589.
3. J. Jordan et W. H. Dumbaugh, Jr., *Anal. Chem.*, 1955, **31**, 210.
4. R. J. N. Harries, *Talanta*, 1968, **15**, 1345.
5. W. A. Dumbaugh, Jr., *Diss. Abstr.*, 1959, **20**, 1559.
6. L. Avedikian, *Bull. Soc. Chim. France*, 1966, 2570.
7. L. S. Darken, *J. Am. Chem. Soc.*, 1941, **63**, 1010.
8. G. D. Pinching et R. G. Bates, *J. Res. Natl. Bur. Stds.*, 1948, **40**, 412.
9. R. Gane et C. K. Ingold, *J. Chem. Soc.*, 1931, 2158.
10. W. J. Hamer, J. O. Burton et S. F. Acree, *J. Res. Natl. Bur. Std.*, 1940, **24**, 290.
11. G. D. Pinching et R. G. Bates, *ibid.*, 1948, **40**, 412.
12. *Idem, ibid.*, 1950, **45**, 327.
13. F. R. Bischowsky et F. D. Rossini, *Thermochemistry of Chemical Substances*, 1st Ed., Reinhold, New York, 1936.
14. J. J. Christensen, R. M. Izatt et L. D. Hansen, *J. Am. Chem. Soc.*, 1967, **89**, 213.
15. J. L. Burgot, *Talanta*, 1978, **25**, in press.
16. J. Jordan et T. G. Alleman, *Anal. Chem.*, 1957, **29**, 9.
17. J. D. Hale, R. M. Izatt et J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.
18. H. J. V. Tyrrell, *Talanta*, 1967, **14**, 843.
19. F. J. Miller et P. F. Thomason, *ibid.*, 1959, **2**, 109.
20. G. Dalgren et F. A. Long, *J. Am. Chem. Soc.*, 1960, **82**, 1306.

Summary—Maleic, fumaric, tartaric, glutaric and adipic acids are titrated directly with sodium hydroxide by means of an automatic thermometric titrimeter. The titration curves have two break-points, corresponding to the successive neutralization of the two acid groups. Previous standardization permits measurement of the heats of neutralization, from which the enthalpies of dissociation can be deduced. From 0.3 to 1 mmole of acid can be titrated with a relative standard deviation of about 3%.

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SELECTIVE DETECTION OF CARBOXYLIC ACIDS, UREAS AND PHENOLS AND SEMIQUANTITATIVE DETERMINATION OF CITRIC ACID BY CAPILLARY SOLID-STATE SPOT-TESTS

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Summary—Solid-state spot-tests for the selective detection of carboxylic acids, ureas and phenols have been developed. Mixtures of *p*-dimethylaminobenzaldehyde with *N*-methylurea and of *p*-dimethylaminobenzaldehyde with phthalic acid are used as reagents. Based on these tests a semiquantitative determination of citric acid is also developed. These tests utilize three properties of the coloured boundary: colour, length and direction of movement. Our work on capillary solid-state spot-tests,[1] has now been extended to some further organic compounds.

EXPERIMENTAL

Reagents

Analytical-grade reagents were used. Various mixtures of citric acid and starch were prepared. Reagent *A* was an equimolar mixture of *p*-dimethylaminobenzaldehyde (*p*-DAB) and *N*-methylurea, and reagent *B* an equimolar mixture of *p*-DAB and phthalic acid.

Procedures

General. A capillary was partly filled with *A* or *B* by continuous tapping and the solid test material was added to the open end. Both ends of the capillary were closed with cotton plugs with ("sealed") or without ("unsealed") a further seal of plasticine. Reagents and test materials were used either undried or after drying for 2 hr in an electrically heated oven at 60°. The unsealed or sealed capillaries were kept in the oven at 60°. Four combinations were tested: (*i*) undried materials in unsealed capillaries, (*ii*) undried materials in sealed capillaries, (*iii*) dried materials in unsealed capillaries and (*iv*) dried materials in sealed capillaries. The colour, length and direction of movement of the reagent/sample boundary after a definite interval of time were recorded.

Limit of identification of citric acid. Known volumes of a standard solution of citric acid were evaporated to dryness at 100°. The residues were then mixed intimately with *A*. The identification limit is 20 μg, which is much lower than the limit of 10 mg for detection with the same reagent in solution.

Spectra of solutions. Equal volumes of a 0.1*M* solution of the sample and a 1% solution of reagent *A*, both in 50% aqueous ethanol, were mixed and their absorbance recorded against 50% aqueous ethanol.

Semiquantitative determination. Capillaries containing reagent *A* and various concentrations of citric acid in starch (undried materials in unsealed capillaries) were kept at 60° for 2 hr. The length of the coloured boundary was recorded. A plot of citric acid concentration *vs.* length of boundary was linear over a certain range but did not pass through the origin; 10% citric acid gave a length of 1 mm and 75% gave 12 mm.

Table 1. Detection of carboxylic acids with reagent A at 60°

Acid	(*i*) Undried and unsealed					(*ii*) Undried and sealed					(*iii*) Dried and unsealed					(*iv*) Dried and sealed				
	CJ	CB	DM	l	State	CJ	CA	DM	l	State	CJ	CB	DM	l	State	CJ	CB	DM	l	State
Oxalic	Y	Y	→	12	—	Y	Y	←	8	M	Y	Y	←	3	—	Y	Y	←	5	—
Benzoic	LG	Y	→	8	gj	LY	LY	→	7	M	LG	Y	→	6	gj	Y	Y	→	12	—
Malic	LG	LG	→	5	—	G	LG	←	8	M	O	LG	→	2	—	Y	Y	→	6	—
Maleic	LG	Y	←	8	—	GY	GY	←	6	M	LG	LG	→	3	—	LG	—	—	—	—
Cinnamic	LY	—	—	—	—	LY	—	—	—	M	—	—	—	—	—	LY	—	—	—	—
Malonic	LG	LG	→	7	gj	G	G	→	2	M	GY	LG	→	2	gj	LG	LG	→	6	gj
Adipic	LY	LY	←	3	—	LY	—	—	—	M	LY	—	—	—	—	LY	—	—	—	—
Citric	O	OY	←	15	M	O	OY	←	16	M	O	LG	→	5	—	O	LG	→	15	—
Salicylic	G	LG	→ ←	15 6(G)	gj	G	G	←	17	M	G	LG	→	6	gj	G	Y	→	17	gj
Tartaric	O	LG	→ ←	5 4(LY)	—	O	LG	→	12	M	O	Y	→	2	—	O	LG	→	10	—
Succinic	—	—	—	—	—	—	—	—	—	M	—	—	—	—	—	—	—	—	—	—
Hippuric	LY	—	—	—	—	—	—	—	—	—	M	LY	—	—	—	LY	—	—	—	—
Ascorbic	LY	—	—	—	—	LY	—	—	—	—	LY	—	—	—	—	LY	—	—	—	—
Phthalic	G	LG	→	14	—	G	LG	→	12	M	G	G	→	2	—	G	G	→	13	—
Gallic	—	—	—	—	—	—	—	—	—	M	—	—	—	—	—	—	—	—	—	—
Fumaric	LG	—	—	—	—	LG	LG	←	4	M	LY	—	—	—	—	LY	—	—	—	—

CJ = colour at junction; CB = colour of boundary; DM = direction of movement; l = length of the boundary in mm (recorded after 2 hr); L = light; Y = yellow; G = green; O = orange; M = molten; gj = gap at junction; → = towards reagent; ← = towards test substance.

RESULTS AND DISCUSSION

p-DAB forms chromogens with ureas, phenols, amines, amino-acids *etc.* in the presence of acids, and these chromogens have been used for detection and determination in solution.[2,3] The concentration of the chromogens increases with acidity, and these reactions have been recommended[4] for detecting and determining free hydrochloric acid in gastric juice and mineral acids in adulterated wine. For solid-state detection of acids, a mixture of *p*-DAB with *N*-methylurea is used as the reagent. Of all the urea tried, *N*-methylurea produces the brightest colour at a very fast rate. The acids studied by us react with reagent *A* to form chromogens with a λ_{max} of 400–410 nm in solution. The reactions can be used for the detection and determination of acid in solutions, but are non-selective.

Table 1 shows that when combination (*i*) is used, the boundary sometimes moves in both directions. This may be due to surface moisture. With combination (*ii*) the coloured boundary melts. In this case the chromogen formed abstracts surface moisture and melts. A gap at the junction is formed under conditions (*i*), (*iii*) and (*iv*), owing to the compact nature of the chromogen. Under condition (*iv*) results are very reproducible whereas condition (*i*) is easier to use, the colours are brighter and the results reproducible, but the direction of movement of the coloured boundary depends on the amount of atmospheric moisture. It has also been observed[5] that the coloured boundary moves from the substance with the higher vapour pressure towards the substance with lower vapour pressure. Table 2 shows that the length of the boundary depends on the concentration of the diffusing molecules. This characteristic of solid-state reactions can be used for the semiquantitative determination of the diffusing species and this has been achieved for citric acid. Results given in Table 3 show that the length of the boundary and the intensity of its colour increase with time. Results for the solid-state spot-test detection of ureas and phenols are shown in Tables 4 and 5 respectively. Ureas and phenols were detected by using *p*-DAB in the presence of boric acid, potassium bisulphate, trichloroacetic acid or some other carboxylic acids listed in Table 1. The results obtained in the presence of a strong acid ($KHSO_4$) were less informative than those obtained in the presence of weak acids. Therefore phthalic acid–*p*-DAB mixture has been chosen as the reagent for ureas and phenols. The results obtained indicate that the colour, the length and the direction of movement of the boundary can be used for detection. This is an advantage of the solid-state spot-tests since only the nature and intensity of colour can be used for analytical purposes in solution-state tests.

Table 2. Colour and length of the boundary as a function of acid concentration at 60°*

Acid and concentration,%		CJ	CB	DM	1, *mm*
Citric,	100	O	LG	→	5
	50	O	LG	→	2
	25	O	—	—	—
Phthalic,	100	G	G	→	2
	50	G	G	→	1
	25	G	—	—	—
Salicylic,	100	G	LG	→	6
	50	G	LG	→	4
	25	G	LG	→	2
Malonic,	100	GY	LG	→	2
	50	GY	—	—	—
	25	LG	—	—	—

* After 2 hr, dried materials in unsealed capillary. Abbreviations same as in Table 1.

Table 3. Colour and length of the boundary at 60° as a function of time*

Acid	2 hr CJ	CB	DM	1	State	12 hr CJ	CB	DM	1	State
Tartaric	O	Y	→	2	—	O	LG	→	6	—
Citric	O	LG	→	5	—	O	G	→	>10	gj
Malic	O	LG	→	2	—	LG	LG	→	8	gj
Phthalic	G	G	→	2	—	G	G	→	8	—
Maleic	LG	LG	→	3	—	G	LY LG	→ ←	8 2	—
Salicylic	G	LG	→	6	gj	G	LG	→	>10	gj
Malonic	GY	LG	→	2	gj	LG	LG	→	9	gj

* Observations for dried materials in unsealed capillary, abbreviations as in Table 1.

Table 4. Detection of ureas with reagent B at 60°*

Urea	100% CJ	CB	DM	1	State	50% CJ	CB	DM	1	25% CJ	CB	DM	1
Urea	G	LG	←	2		G	—	—	—	G	—	—	—
Thiourea	GY	G	←	2		—	—	—	—	—	—	—	—
N-Methylurea	†BY	BY	→ ←	4 2		Y	Y	→ ←	2 1	LY	LY	→	1
1,3-Dibutyl-thiourea	Y	Y	←	6	(gj)	—	—	—	—	—	—	—	—
Allylthiourea	†RY	Y	→	6		O	O	→ ←	5 4	O	O	→ ←	4 1
Phenylthiourea	Y	Y	→	2		Y	—	—	—	Y	—	—	—
Phenylurea	GY	GY	→ ←	2 4		Y	—	—	—	Y	—	—	—

* Undried materials heated in unsealed capillary for 4 hr.
† B = bright; R = red; other abbreviations as in Table 1.

Table 5. Detection of phenols with reagent B at 60°*

Phenol	100% CJ	CB	DM	l		50% CJ	CB	DM	l	25% CJ	CB	DM	l
Catechol	GY	GY	→	11	(gj)	GY	GY	→	8	GY	GY	→	3
Resorcinol	GY	GY	→	5		GY	GY	→	4	GY	GY	→	2
Pyrogallol	V	V	→	4		LV	LV	→	2	LY	LV	→	2
			←	2				←	2			←	2
p-Nitrophenol	O	O	→	5		O	O	→	3	LO	LO	→	2
Phloroglucinol	LP	Y	←	2		LP	Y	←	1	LP	Y	←	1

* Undried materials heated in unsealed capillary for 4 hr; V = violet; P = pink; other abbreviations as in Table 1.

Thus in the homologous series of phenols, ureas and carboxylic acids tested, each member can be distinguished from the others on the basis of these properties. Of all the phenols tried, catechol gives the longest boundary, and the phloroglucinol boundary moves in the opposite direction to that for the other phenols. Although catechol cannot be differentiated from resorcinol on the basis of the colour (Table 3) it can be distinguished by considering the direction of movement of the boundary.

Similarly, amongst the ureas (Table 4) allylthiourea can be detected very selectively on the basis of the length of the boundary and its direction of movement. Table 1 shows that tartaric acid and citric acid cannot be distinguished on the basis of colour alone, but can be distinguished by the length of the boundary, especially when the reaction time is increased to 12 hr (Table 3). Table 1 shows that under condition (*iii*), the length of boundary cannot be used to distinguish salicyclic from citric acid, or malonic from phthalic, but dilution of the sample makes the distinction possible (Table 2).

It appears that the proposed method[6,7] is selective for the compounds studied and can be made more selective by keeping the capillary longer at a particular temperature and by diluting the test substance.

It is also clear that the rate of reaction in the capillary depends on (*a*) the melting point and (*b*) the length of the molecule of the diffusing species.[8] For example, the length of the boundary for phenols increases as the melting point increases. The phenol molecules are almost all the same in size and are all anhydrous. The melting points of allylthiourea and 1,3-dibutylthiourea are very close, but the 1,3-dibutylthiourea molecule is the longer. The boundary for allylthiourea does not move towards the reagent but that for 1,3-dibutylthiourea does.

REFERENCES

1. M. Qureshi, H. S. Rathore and A. Mohammad, *Talanta*, 1976, **23**, 874.
2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, New York, 1966.
3. C. A. Streuli and P. R. Averell, *The Analytical Chemistry of Nitrogen and its Compounds*, Parts 1 and 2. Wiley-Interscience, New York, 1970.
4. H. W. Van Urk, *Pharm. Weekblad*, 1929, **66**, 101.
5. M. Qureshi, S. Z. Qureshi, H. S. Rathore and A. Mohammad, *J. Phys. Chem.*, 1975, **79**, 116.
6. M. D. Cohen and B. S. Green, *Chem. in Britain*, 1973, **9**, 000.
7. P. I. Voskresenskil, *Talanta*, 1965, **12**, 11.
8. N. B. Singh, *Indian J. Chem.*, 1970, **8**, 916.

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ANNOTATIONS

THE STABILITY CONSTANT OF Pd–EDTA

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Summary—The literature value of the stability constant of the palladium-ethylenediaminetetra-acetate complex ($\log K_{Pd\text{–}EDTA} = 18.5$), is open to question. From replacement experiments with thorium a value $\log K_{Pd\text{–}EDTA} = 26.4$ has been found. This value is in better agreement with experimental facts from protonation studies at low pH and with the fact that excess of EDTA can be back-titrated in presence of Pd–EDTA at pH 1–2 with ions such as Bi^{3+}, Tl^{3+} and Th^{4+}. Some preliminary results are given for ternary complex formation between Pd^{2+}, EDTA and Cl^-.

From their electrochemical investigations MacNevin and Kriege[1] concluded that the logarithm of the stability constant of the Pd–EDTA complex is 18.5. This value, obtained by use of palladium electrodes, is the only one found in the literature.

Malik[2] determined the protonation constants of PdY (where Y is the fully dissociated EDTA anion) and found $\log K^{H}_{PdHY} = 3.1$ and $\log K^{H}_{PdH,Y} = 0.9$. The last value, following from measurements made at a pH near 0.9 and at a concentration level of $10^{-2}M$, raises some doubt about the value obtained by MacNevin and Kriege, as the existence of PdY at this pH is possible only if $\log K_{PdY}$ is some units larger than 18.5.

The possibility of back-titrating excess of EDTA in presence of PdY with Bi^{3+} at pH 1–2 (Pyrocatechol Violet as indicator) and the reported back-titrations[3,4] with Th^{4+} and Tl^{3+} at pH 3–5 are further indications that $\log K_{PdY} = 18.5$ is not correct.

Malik[2] found that bismuth cannot replace palladium from its EDTA complex at pH 0–1, from which he concluded that $\log K_{PdY}$ should exceed 23.7. This conclusion, however, is based on the stability constants for complexes of bismuth with EDTA and hydroxide, which were known rather inaccurately at that time and which need revision. The conditional constant of BiY is now better known, the value being $10^{8.0}$ for pH ≈ 0.[5] When bismuth is not able to replace palladium, the conditional constant for PdY should exceed this value for BiY by at least a factor of 10. With $\log \alpha_{Pd(OH)} = 0$, $\log \alpha_{Y(H)} = 21.4$ and $\log \alpha_{PdY(H)} = 4.0$—according to Malik's data[2]—a more accurate inequality can be derived for the stability constant of PdY:

$$\log K_{PdY} \geq 26.4 \qquad (1)$$

Malik also reports that zirconium can replace palladium from its EDTA complex at pH 0. Although the conditional constant of ZrY at this pH is not known very accurately, the value $\log K_{ZrY} = 9.6$ seems fairly reliable.[5] Assuming that the conditional constant of PdY has to be of the same magnitude for replacement, we estimate $\log K_{PdY} \sim 27.0$. Although this value is rather uncertain, we can conclude that the stability constant of PdY does not much exceed the lower limit set by equation (1).

In our laboratory palladium has frequently been determined at low pH and a concentration level of $10^{-4}M$ by complexometric titration with photometric end-point detection. As the reaction between palladium and EDTA is rather slow at room temperature and there is no suitable indicator for direct titration at a pH of about 2, back-titration with thorium was always used, with Semi-Xylenol Orange (SXO) as indicator.[6] The shift in equilibrium after the equivalence point within the few minutes after which the equivalence point has been reached and the final absorbances have been read can be neglected. At room temperature the displacement of palladium by thorium takes hours to reach completion, but the reaction proceeds rather quickly at temperatures above 80°. This phenomenon has been used to investigate the stability of the PdY complex.

Equal molar amounts of palladium, EDTA and thorium were heated at 90° to establish equilibrium and slowly cooled to room temperature. Then the consumption of thorium was determined by rapid titration with EDTA, SXO being used as indicator. From 20 determinations at pH 2.0 we found (charges are omitted for simplicity)

$$\frac{K'_{PdY}}{K'_{ThY}} = \frac{[PdY']}{[Pd']} \cdot \frac{[Th']}{[ThY']} = 50 \pm 5 \qquad (2)$$

Combining this with the conditional constant for Th–EDTA ($\log K' = 11.9$),[5] $\log \alpha_{Pd(OH)} = 0.2$,[5] $\log \alpha_{PdY(H)} = 1.1$,[2] and $\log \alpha_{Y(H)} = 13.7$, we find

$$\log K_{PdY} = 26.4 \qquad (3)$$

This value, for room temperature and ionic strength 0.1, is related to the conditional constant of Th–EDTA, so an accumulated uncertainty of about 0.5 is likely.

Ammonia and amines interfered strongly in the determination. Chloride was present from the dissolution of metallic palladium in concentrated nitric acid containing 5% of concentrated hydrochloric acid, but its final concentration was kept below $10^{-4}M$, which was sufficient to keep the palladium in solution but low enough to give no contribution to $\log \alpha_{Pd}$.[5] Surprisingly, it was found that the result given in equation (2) was hardly influenced by chloride concentrations up to $2 \times 10^{-3}M$. Up to this chloride level the average co-ordination number of the palladium with respect to chloride did not exceed 2 (for the palladium concentration used). It is known that PdY forms ternary complexes with chloride; PdYCl and $PdYCl_2$ are known.[2] In these compounds the EDTA acts as a bidentate ligand for palladium, leaving sufficient space around the palladium ion for two chloride ions. The ternary complex formation enhances the conditional constant of PdY. It can be supposed that the ratio of $\alpha_{PdY(Cl)}$ and $\alpha_{Pd(Cl)}$ does not change much up to a co-ordination number of 2. At chloride concentrations above $2 \times 10^{-3}M$ the conditional constant for PdY decreases sharply.

Nevertheless, because of the low reactivity of PdY, back-titration of excess of EDTA with thorium (SXO as indicator) remains possible up to $[Cl^-] = 0.03M$. From the displacement measurements tentative values of β_n could be deduced:

$$\beta_n = \frac{[PdYCl_n]}{[PdY][Cl]^n} : \log\beta_1 = 4.5, \log\beta_2 = 6.5$$

Further investigations will be undertaken to refine these values and will be reported in due course.

REFERENCES

1. W. M. MacNevin and O. H. Kriege, *J. Am. Chem. Soc.*, 1955, **77**, 6149.
2. S. C. Malik, *Thesis*, ETH, Zürich, 1970.
3. J. Kinnunen and B. Merikanto, *Chemist-Analyst*, 1955, **44**, 11.
4. *Idem, ibid.*, 1958, **47**, 11.
5. J. Kragten, *Atlas of Metal-Ligand Equilibria in Aqueous Solution*. Horwood, Chichester, 1977.
6. C. J. C. Pijpers, *Mikrochim. Acta*, 1976 I, 667.

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ON THE CONDENSATION OF SALICYLALDEHYDE WITH HYDRAZINE

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Summary—A simple procedure for preparing uncontaminated salicylaldehyde hydrazone is outlined. The condensation reaction of salicylaldehyde and hydrazine in 2:1 molar ratio usually gives initially a mixture of the three geometrical isomers of salicylaldazine: one isomer is bright yellow, another is cream, the third is light pink. The earlier reports of Feigl and of Terentev *et al.* on the use of salicylaldehyde in the detection of hydrazine have been found to be misleading and the later report of Jain *et al.* incomplete. A detailed account is now given and improved salicylaldehyde tests for hydrazine are recommended. The structure given by Jain *et al.* for the copper(II) complex of salicylaldehyde hydrazone is confirmed by means of infrared spectroscopy and microanalysis. Preliminary studies on the copper(II) complex of salicylaldazine are reported.

Some confusion appears to have arisen about the condensation reaction of salicylaldehyde with hydrazine which is the basis of the salicylaldehyde test for hydrazine as described by Feigl.[1] Jain *et al.*[2] attributed the earlier misleading and confused reports on hydrazones to the fact that it is difficult to prepare hydrazones from hydrazine, because they tend to react further, giving azines.[3]. They further reported that the condensation of salicylaldehyde with hydrazine gives two different compounds: salicylaldehyde hydrazone (SH), $HO{\cdot}C_6H_4CH = N{\cdot}NH_2$ (shiny white plates, m.p. 97.5°) and salicylaldazine (SA), $HO{\cdot}C_6H_4{\cdot}CH = N{\cdot}N = CH{\cdot}C_6H_4OH$ (shiny yellow plates, m.p. 210°, literature value[4] 208–210°, 213–214, 216°).

Our detailed studies reveal that it is not too difficult to prepare SH from hydrazine provided the following points are noted.

(*i*) Salicylaldehyde has to be added to hydrazine and the molar ratio of the reactants should be 1:1. Adding hydrazine to salicylaldehyde means that salicylaldehyde is initially in excess and some azine would be formed.

(*ii*) Fairly dilute ethanolic solutions of both reactants should be used.

(*iii*) The salicylaldehyde solution has to be added slowly and with stirring

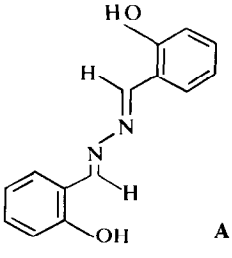
The reaction is exothermic and creamy white flakes crystallize from the reaction mixture on cooling (m.p. 93–95°). No heating is necessary.

When one mole of ethanolic solution of hydrazine hydrate is added to two moles of ethanolic salicylaldehyde solution at room temperature a mixture of the three geometrical isomers of salicylaldazine is usually obtained. The reaction is exothermic and no heating is required. In the course of our studies[5] we have isolated and identified the three geometrical isomers: Isomer A crystallizes as bright yellow needles from acetone (m.p. 222–223°); isomer B is light pink (m.p. 220°); isomer C is cream (m.p. 220°). Isomer B is not as stable as the other two. It transforms into the cream form at room temperature (~25°) after about 12 hr.

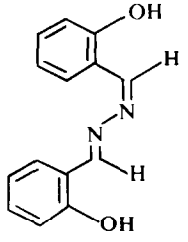
Feigl,[1] in describing a test for hydrazine with salicylaldehyde, claimed that "Benzaldehyde and other aromatic aldehydes condense with hydrazine and its salts to form water-insoluble colourless aldazines. Owing to its greater solubility in water salicylaldehyde is specially useful as a specific reagent." Jain *et al.*[2] have reported that he is mistaken, that the white compound formed is salicylaldehyde hydrazone, and that salicylaldazine is yellow. However, these authors have not realized that there are three possible geometrical isomers of salicylaldazine, which do in fact exist. Our detailed study reveals the following.

(1) The order of addition of reagents is extremely important. If ethanolic salicylaldehyde (2 mole) is added gradually with stirring to hydrazine hydrate (1 mole), some whitish product can be observed, owing to the formation of some hydrazone, but if the order is reversed as it should be, and ethanolic hydrazine is added to ethanolic salicylaldehyde, then at room temperature a mixture of the geometrical isomers is initially obtained; if the reaction mixture is heated on a water-bath for about 1 hr, the yellow isomer is obtained as the only product.

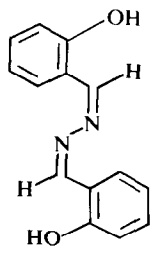
(2) Feigl's report[1] that aromatic aldehydes form colourless azines with hydrazine is not true. The most stable geometrical isomer, which is usually the most abundant, is generally yellow or cream in colour, as shown by the following azines prepared in our laboratories.



A



B



C

(*i*) Salicylaldazine (isomer A bright yellow, m.p. 222–223°); (isomer B light pink, m.p. 220°); (isomer C cream, m.p. 220°).

(*ii*) *p*-Anisalaldazine (isomer A yellow, m.p. 173°).

(*iii*) Cinnamaldehyde azine (isomer A orange, m.p. 176–178°).

(*iv*) *p*-Methylbenzaldazine (isomer A light yellow, m.p. 160–161°).

(*v*) Benzaldazine (isomer A yellow, m.p. 91–93°).

(*vi*) Acetophenone azine (isomer A yellow, m.p. 123–124°).

(*vii*) Benzophenone azine (creamy white, m.p. 166–168°).

Improved salicylaldehyde tests for hydrazine are given below

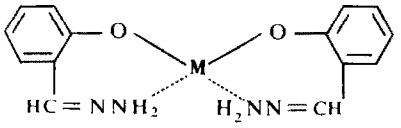
(*i*) Add test solution gradually with stirring to excess of ethanolic solution of salicylaldehyde in a small beaker and heat on a water-bath for at least 30 min. A bright yellow precipitate indicates that hydrazine is present.

Confirmatory tests are as follows.

(*ii*) With the test solution in a small beaker, add ethanolic salicylaldehyde solution drop by drop with stirring. If hydrazine is present, a whitish precipitate of salicylaldehyde hydrazone settles after the reaction mixture has cooled. Excess of salicylaldehyde leads to formation of the azine.

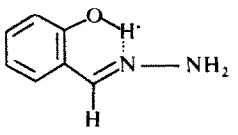
(*iii*) Chill both test solution and ethanolic salicylaldehyde solution in an ice–salt bath for at least 30 min and then add the test solution with stirring to the salicylaldehyde (still in the ice–salt bath). If hydrazine is present in the test solution, continued stirring produces a pink solid which is one geometrical isomer of salicylaldehyde azine. For this test to be successful, concentrated solutions of reactants should be used so as to obtain copious precipitates.

As to the Cu(II) chelates of salicylaldehyde hydrazone and salicylaldehyde azine, it is possible that the shiny crystalline leaves (m.p. 98°) prepared by Terentev *et al.*[6] were simply salicylaldehyde hydrazone crystals. The arguments of Jain *et al.*[2] appear valid, and their suggested structure



for the complex formed between Cu^{2+} and salicylaldehyde hydrazone is consistent with the following experimental evidence obtained in our laboratories.

(1) The infrared spectrum of salicylaldehyde hydrazone shows $\nu(C=N)$ at 1620 cm^{-1} and $\nu(NH_2)$ (two peaks) at 3283 and 3380 cm^{-1}. The OH-vibration frequency is absent, apparently because of very strong hydrogen-bonding leading to the formation of a heterocyclic six-membered ring:



The greyish-brown solid complex with m.p. > 300° has $\nu(C=N)$ at 1623 cm^{-1} but the $\nu(NH_2)$ peaks have shifted to 3140 and 3280 cm^{-1}, indicating that whereas the nitrogen atom of C = N is not involved in bonding, the *p*-orbital of the nitrogen atom in NH_2 is.

(2) The Cu(II) salicylaldehyde hydrazone complex, $C_{14}H_{14}O_2N_4Cu$, requires C 50.40%, H 4.23% and N 16.79%; the values found are C 50.3%, H 4.2% and N 16.6%.

The yellow isomer of salicylaldehyde azine, on the other hand, forms an orange-brown solid complex (m.p. 228°) with Cu(II). Preliminary infrared studies indicate that C = N is again not involved in the bonding. The only alternative donor sites left in the ligand are the hydroxyl groups, the vibrational frequencies of which are absent in the infrared spectrum. Further studies on this complex are in progress.

REFERENCES

1. F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Ed., p. 239. Elsevier, Amsterdam, 1968.
2. M. P. Jain and S. Kumar, *Talanta*, 1977, **24**, 149.
3. D. J. Cram and G. S. Hammond, *Organic Chemistry*, 2nd Ed., p. 378. McGraw-Hill, New York, 1964.
4. L. N. Ferguson and G. E. K. Branch, *J. Am. Chem. Soc.*, 1944, **66**, 1467.
5. E. C. Okafor, *J. Org. Chem.*, in the press.
6. A. P. Terentev, E. G. Ruchadze and Z. A. Fadeeva, *Zh. Analit. Khim.*, 1952, 7, 120.

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UNTERSUCHUNGEN ZUR ATOMSPEKTROSKOPISCHEN SPURENANALYSE IN $A^{III}B^{V}$-HALBLEITER-MIKROPROBEN—III

UNTERSUCHUNGEN ZUR SCHICHTABTRENNUNG UND ZUR SPURENANALYSE IN DÜNNEN GaAs SCHICHTEN

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Zusammenfassung—Es werden 3 Verfahren für die Abtrennung dünner Schichten vom GaAs hinsichtlich ihres Tiefenauflösungsvermögens und ihrer Reproduzierbarkeit miteinander verglichen: 1. Chemisches Ätzen mit methanolischer Bromlösung, 2. mechanische Abtrennung mit einem Hartschnittmikrotom und 3. chemisches Ätzen nach vorheriger anodischer Oxydation bei Verwendung der amperostatischen Arbeitsweise. Die Bedingungen wurden jeweils optimiert. Das Tiefenauflösungsvermögen liegt beim chemischen Ätzen bei 0,4 μm, beim mechanischen Abtrennen bei 1 μm und bei der anodischen Oxydation bei 0,02 μm. Somit ist die anodische Oxydation besonders für eine Profilanalyse, die mechanische Abtrennung für die Untersuchung dickerer Schichten geeignet. Das chemische Ätzen nimmt eine Zwischenstellung ein. Für die analytische Bestimmung der Spurenelemente in den sich ergebenen Mikroproben wurden die Atomemissionsspektrographie (AES) mit Gleichstrombogenanregung und die Atomabsorptionsspektrometrie mit elektrothermischer Atomisierung in einer Graphitrohrküvette (AAS) eingesetzt. Ein Vergleich der angegebenen Nachweisgrenzen zeigt, daß die absoluten Nachweisgrenzen der AAS und für die Mikroproben von 0,1 bis 0,2 mg auch die relativen Nachweisgrenzen durchschnittlich eine Zehnerpotenz besser als die der AES sind. Der Vorteil der AES liegt in der Möglichkeit der Simultanbestimmung mehrerer Elemente.

Für die Charakterisierung halbleitender Substanzen ist es erforderlich, neben Informationen über den Durchschnittsgehalt der Spuren-und Dotierungselemente auch Informationen über die Verteilung dieser Elemente in Substrat zu erhalten. Eine Grundlage für die Profilanalyse ist die Analyse dünner Schichten. Die Voraussetzungen, die für die erfolgreiche Lösung einer solchen Aufgabenstellung geschaffen werden müssen, sind: 1. es müssen zuverlässige Verfahren für die reproduzierbare Abtrennung dünner Schichten bestimmter Stärke und 2. nachweisstarke Verfahren für die Bestimmung der Spuren in diesen Mikroobjekten zur Verfügung stehen bzw. erarbeitet werden.

In der vorliegenden, gemeinsam von zwei Institutionen durchgeführten Arbeit werden 3 Varianten der Schichtabtrennung (chemisches Ätzen, mechanische Abtrennung und Ätzen nach vorheriger anodischer Oxydation) von GaAs-Substraten behandelt und die notwendigen Optimierungen atomspektroskopischer Methoden für die quantitative Erfassung der Spuren in den abgetrennten Materialien durchgeführt.

SCHICHTABTRENNUNG DURCH CHEMISCHES ÄTZEN

In der Literatur[1–4] sind einige Methoden für die Abtrennung dünner GaAs-Schichten (1–10 μm) beschrieben worden. Es wurden verschiedene Ätzmittel (HCl, HNO_3, Br_2–CH_3OH) eingesetzt. Das Ziel dieser Arbeit bestand vor allem in der Verbesserung des Tiefenauflösungsvermögens. Hierfür schien das Ätzmittel Br_2–CH_3OH am besten geeignet, denn dieses arbeitet beim einkristallinen GaAs sowohl für die 100—als auch für die 111—Orientierung im Diffusionsgebiet, wodurch die polierenden Eigenschaften bedingt sind und die Möglichkeiten für das nicht thermostatierte Arbeiten geschaffen werden.[2,5,6]

Darüberhinaus bietet dieses Ätzmittel folgende wünschenswerte Vorteile. 1. Die Komponenten lassen sich leicht reinigen. 2. Beide Komponenten lassen sich nach der Ätzung leicht entfernen. 3. Es lassen sich leicht Mikrovolumina (vgl. Cit. 7) für die Ätzung einsetzen, die die Auswahl einer bestimmten Oberfläche ermöglichen.

Experimentelles

Substanzen. GaAs-Einkristalle unterschiedlicher Leitfähigkeit. Methanolische Brom-Lösungen (Br_2-Konz. 0,1–0,4*M*).

Bedingungen. Ätzlösung 0,1 ml pro 1 cm^2 Substrat. Ätzzeit 1 min.

Messung der Schichtdicke. Interferenzmikroskop MII-4, UdSSR (Meßbereich bis 0,014 μm). Die Messung erfolgte an Stufen, die durch teilweise Bedeckung der Ätzfläche mit ätzfestem Lack erhalten wurden.

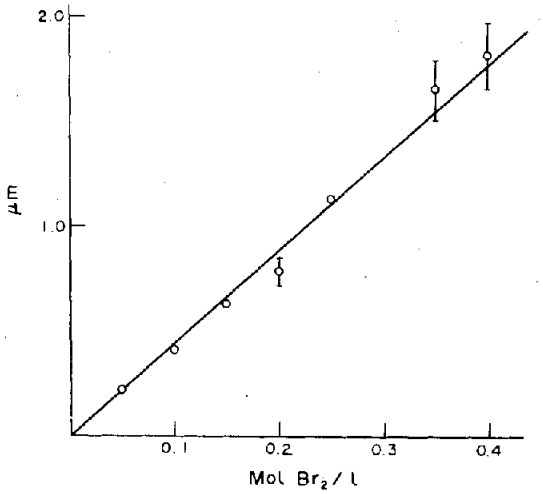


Abb. 1. Abhängigkeit der Schichtdicke des durch Br_2-CH_3OH abgeätzten GaAs von der Bromkonzentration der Lösung. Bedingungen: 0,1 ml Lösung/cm²; Atzzeit: 1 min.

Verfahrensweise. Das entsprechende Volumen der Ätzlösung wird mit einer Mikropipette auf die Oberfläche des Substrates gegeben. Nach 1 Minute wird die Ätzlösung mit einer Polyäthylenkapillare abgesaugt und kann dann zur analytischen Bestimmung der Spuren verwendet werden.

Optimierung und Ergebnisse des Verfahrens

In der Abbildung 1 ist die Abhängigkeit der Dicke der geätzten Schicht von der Bromkonzentration im Methanol dargestellt. Aus der Abbildung geht hervor, daß diese Beziehung für ein Konzentrationsgebiet von 0,1 bis 0,4*M* linear ist. Dabei ist zu beachten, daß die methanolischen Bromlösungen erst 2 Stunden nach ihrer Herstellung verwendet werden dürfen, da ihre Ätzaktivität in den ersten zwei Stunden größer, danach aber konstant ist. Der Grund für diese unterschiedliche Aktivität ist in einer Reaktion des Broms mit dem Methanol zu suchen, die jedoch noch nicht geklärt ist. Die relativen Standardabweichungen der Schichtdicken sind in Abhängigkeit von der Schichtdicke in der Abbildung 2 dargestellt worden. Es ist zu sehen, daß ab einer Schichtdicke von 0,7 μm die relative Standardabweichung bei 5% und für die angestrebten dünnen Schichten (0,2–0,4 μm) bei 6 bis 10% liegt. In der Tabelle 1 ist das Ergebnis der Ätzuntersuchungen in Abhängigkeit von den Eigenschaften des Materials (Leitfähigkeit, Orientierung und Dotierung) dargestellt. Die Tabelle 1 zeigt, daß bei den angewandten Bedingungen (0,1 *M* methanolische Bromlösung), keine Abhängigkeit der Dicke der geätzten Schicht und ihrer relativen Standardabweichung von den gewählten Parametern festzustellen ist. Es ist hinzuzufügen, daß sich auch die Oberflächenklasse (normalerweise 14) während der Ätzung nicht ändert.

MECHANISCHE ABTRENNUNG VON SCHICHTEN

Für einige Elemente, die leichtflüchtige Bromide bilden (z.B. Ge und Sn), ist die analytische Weiterver-

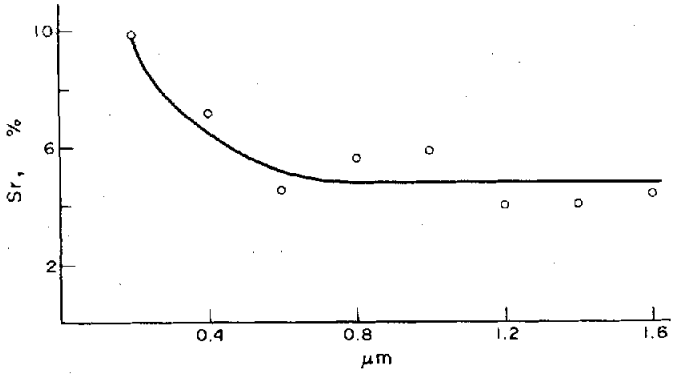


Abb. 2. Abhängigkeit der relativen Standardabweichung (S_r) der Schichtdicke von der Dicke der geätzten Schicht.

Tabelle 1. Abhängigkeit der Dicke der geätzten Schicht und der relativen Standardabweichungen von den Parametern von GaAs-Proben (Ätzbedingungen: 0,1*M* Br_2 in Methanol, 0,1 ml/cm², 1 min)

Probe	spezifischer Widerstand, Ω.cm	Orientierung	Schichtdicke, μm	relative Standardabweichung, %
GaAs	$6 \cdot 10^8$	100	0,4	7–12
GaAs	$6 \cdot 10^8$	111B	0,4	7–10
GaAs	10^5	100	0,4	5–8
GaAs/Te	10^{-2}	100	0,4	6–8
GaAs/Sn	10^{-2}	111B	0,41	5–7
Gesamtzahl der Messungen: 1000			0,4	8

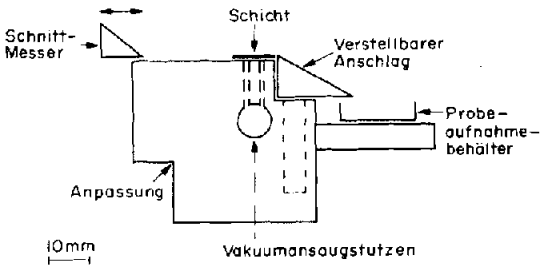


Abb. 3. Einrichtung zur Halterung von GaAs-Schichten am Hartschnittmikrotom.

arbeitung der durch Ätzung erhaltenen Lösungen nicht möglich. Es wurde aus diesem Grund der Versuch unternommen, über eine mechanische Abtrennung der Schichten vom Substrat lösungsmittelfreie Mikroproben zu gewinnen. Dieses Verfahren besitzt außerdem Vorteile, wenn dickere Schichten abgetrennt werden sollen.

Experimentelles

Substanzen. GaAs-Einkristalle.

Apparatur. Hartschnittmikrotom K, Fa. Jungk, BRD mit Diamantmesser. Ultramikrowaage 4431, Sartorius, BRD.

Optimierung und Ergebnisse des Verfahrens

In der Abbildung 3 ist die Halterung für die GaAs-Substrate dargestellt, die dem Hartschnittmikrotom angepaßt wurde. Es können bei diesem Verfahren nur planparallele Substrate eingesetzt werden, die gegebenenfalls auch mit Hilfe des Hartschnittmikrotoms dargestellt werden können. Die Substrate werden in vertikaler Richtung durch das angelegte Vakuum und in horizontaler Richtung durch den verstellbaren Anschlag fixiert. Mit dem Hartschnittmikrotom ist es prinzipiell möglich, durch einen Schnitt eine Schicht zwischen 1 und 30 μm abzutrennen. Im Fall des GaAs darf die Schnittstärke nicht größer als 1–2 μm gewählt werden, weil andernfalls die abgeschnittene, pulverförmige Substanz wegspritzt und auch das Substrat schnell zerspringt. Bei langsamer Schnittgeschwindigkeit und geringen Schnittstärken kann der größte Teil des Materials im Probeaufnahmebehälter gesammelt werden. Infolge des immer auftretenden Substanzverlustes ist eine Wägung der Mikroprobe vor der analytischen Weiterverarbeitung erforderlich. Ein Substrat von 6 × 6 mm liefert bei einer Schnittstärke von 1–2 μm eine Substanzmenge zwischen 0,1 und 0,3 mg GaAs in Pulverform, welche in etwa 0,1 ml HNO_3 gelöst und danach analysiert werden kann.

SCHICHTABTRENNUNG DURCH ÄTZUNG NACH ANODISCHER OXYDATION

Für ionenimplantierte und andere Materialien der Mikroelektronik ist eine Tiefenauflösung von etwa 0,01 μm erforderlich, die mit den bisher beschriebenen Verfahren nicht erreichbar ist. Gute Resultate erhielten wir für Si-Materialien durch chemisches Ätzen nach vorheriger anodischer Oxydation.[7]

Für die erfolgreiche Anwendung dieser Methode bei Verbindungshalbleitern sind folgende Bedingungen zu erfüllen.

1. Beide Komponenten des Substratmaterials müssen gleichmäßig oxydiert werden, wobei ebenfalls eine gleichmäßige Oxydation der eingesetzten Oberfläche erreicht werden muß.

2. Der verwendete Elektrolyt darf das oxydierte und nicht oxydierte Material nicht lösen und auch keine Zersetzungsprodukte auf der Oberfläche abscheiden.

3. Es soll eine bestimmte, reproduzierbare Beziehung zwischen den elektrischen Parametern der anodischen Oxydation und der Dicke der oxydierten Schicht bestehen.

In der Literatur sind einige Verfahren zur anodischen Oxydation beschrieben worden. Schwartz u.a.[8,9] verwendeten als Elektrolyt 30%iges H_2O_2 mit H_3PO_4-Zusatz und arbeiteten nach dem potentiostatischen Verfahren. Sie erhielten eine lineare Abhängigkeit der Schichtdicke (bis 0,2 μm) von der vorgegebenen Spannung. Butz u.a.[10] verwendeten 0,1 *M* Ammoniumzitrat- bzw. Ammoniumphosphat-Lösungen als Elektrolyte und erhielten bei potentiostatischer Arbeitsweise die gleiche lineare Abhängigkeit bis zu Schichtdicken von 0,35 μm. Dell'Oca u.a.[11] verwendeten Ammoniumpentaborat-Lösungen als Elektrolyt und arbeiteten bei konstanter Stromdichte (1 mA/cm^2). Müller u.a.[12] verwendeten speziell bei ionenimplantiertem GaAs *N*-Methylacetamid als Lösungsmittel.

Ausgehend von den Anforderungen kann man unter Berücksichtigung der Literatur folgende Schlüsse ziehen.

1. Die amperostatische Arbeitsweise ist der potentiostatischen vorzuziehen, denn im letzteren Fall sinkt die Oxydationsgeschwindigkeit mit der Zeit ab. Dadurch nimmt die niemals völlig vermeidbare Auflösung der oxydierten Schicht durch den Elektrolyten relativ zu.

2. Der Elektrolyt H_2O_2/H_3PO_4 ist unbeständig. Die Elektrolyte Ammoniumzitrat und -phosphat lösen das oxydierte Substrat mit zu hoher Geschwindigkeit (0,03–0,05 μm/min), so daß keine dünnen Schichten erhalten werden können. Vorteile in dieser Hinsicht besitzt der Elektrolyt Ammoniumpentaborat (Lösungsgeschwindigkeit 0,005 μm/min),[11] der von uns eingesetzt wurde.

Experimentelles

Substanzen. GaAs-Einkristalle, Zn-, Te- und P-dotiert (poliert).

Elektrolyt. Ammoniumpentaboratlösung, 0,2%ige.

Apparatur. Amperostat, Eigenbau, UdSSR.

Schichtdickenmessung. Ellipsometrisch und chemisch.

Verfahren. Die zu oxydierenden GaAs-Scheiben werden in eine vorher anodisch oxydierte Tantal-

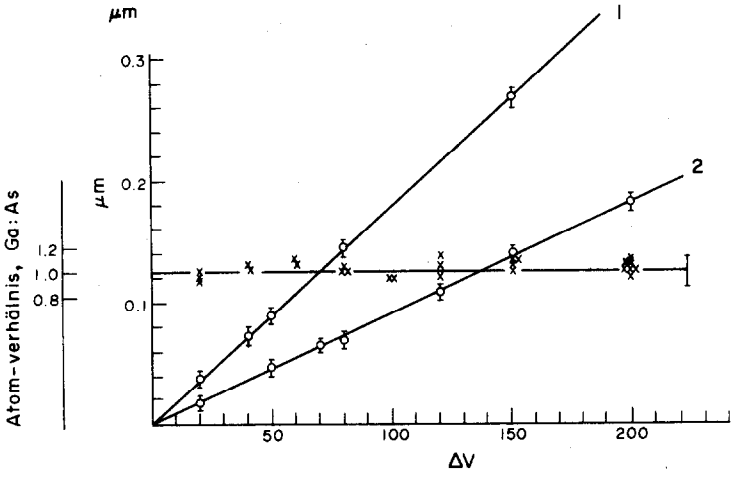


Abb. 4. Abhängigkeit der Dicke der oxydierten Schicht (1), der zu oxydierenden Schicht (2) und des Atomverhältnisses (Ga:As) × in der oxydierten Schicht von der sich bei anodischer Oxydation einstellenden Spannungsdifferenz

anode eingeklemmt die gegen eine Platinkathode geschaltet wird. Die nicht planare Seite wird mit Paraffin bedeckt. Die anodisch oxydierte Schicht wird abgespült und mit HF-Lösung (1:10 bis 1:20 verdünnt) abgeätzt. Diese Lösung wird mit einer Polyäthylenkapillare abgesaugt und kann analytisch weiter verarbeitet werden.

Optimierung und Ergebnisse des Verfahrens

Es wurde festgestellt, daß p-GaAs und n-GaAs mit einem Widerstand von $<10^{-2}$ bzw. $<10^{-3}$ Ω.cm gut oxydiert werden können. Bei größerem Widerstand war die oxydierte Schicht nicht gleichmäßig.

Die sich einstellende Anfangsspannung hängt von der angelegten Stromdichte und dem Widerstand des Materials ab. Es wurden Stromdichten zwischen 1 und 10 mA/cm² geprüft. Die besten Ergebnisse wurden bei Stromdichten zwischen 3 und 5 mA/cm² erhalten. In diesen Fällen war die Oxydationsgeschwindigkeit 10 bis 20 mal größer als die Lösegeschwindigkeit durch den Elektrolyten.

In der Abbildung 4 ist die Abhängigkeit der Dicke der oxydierten Schicht (Kurve 1), der zu oxydierenden Schicht (Kurve 2) und des Atomverhältnis (Ga:As) in der oxydierten Schicht von der sich während der Oxydation einstellenden Spannungsdifferenz ($\Delta U = U_{\text{Endspannung}} - U_{\text{Anfangsspannung}}$) bei amperostatischer Arbeitsweise dargestellt.

Es ist sichtbar, daß eine eindeutige lineare Abhängigkeit der Schichtdicken von der sich einstellenden Spannungsdifferenz (ΔU) vorliegt und daß sich das Atomverhältnis (Ga:As) in den oxydierten Schichten nicht ändert, d.h. beide Komponenten werden gleichmäßig oxydiert. Die Messung des Atomverhältnisses erfolgte nach Lösen der Schicht durch Flammen-AAS. Durch die Bestimmung der gelösten GaAs-Menge konnte auch die Richtigkeit der ellipsometrischen Schichtdickenmessung kontrolliert werden.

Es wurde weiterhin festgestellt, daß die Schichtdicke im optimalen Stromdichtegebiet nicht von der Stromdichte abhängt. Das Volumenverhältnis der oxydierten Schicht zur zu ozydierenden Schicht ist gleich 2 (vgl. Abb. 4, Kurve 1 und 2).

Die oxydierten Schichten zeigen bei einfacher Beleuchtung eine sehr klare Interferenz. Es ist möglich und vorteilhaft, durch Eichproben, die für Schichtdickenabstände von 0,005 bis 0,01 µm hergestellt wurden, die anodische Oxydation im Routinebetrieb zu kontrollieren.

In der Tabelle 2 sind die relativen Standardabweichungen der Schichtdicken sowohl für ein Substrat (15 verschiedene Stellen) und für 15 Substrate (mit

Tabelle 2. Reproduzierbarkeit der Schichtdicke bei anodisch oxydierten Schichten von GaAs

Verfahren	Schichtdicke, *nm*	relative Standard-abweichung, %
Messung an verschiedenen Stellen einer Schicht $n = 15$	24	5
	73	3
	460	0,8
Messung der Schichtdicke von 15 verschiedenen Scheiben	54	7
	260	2

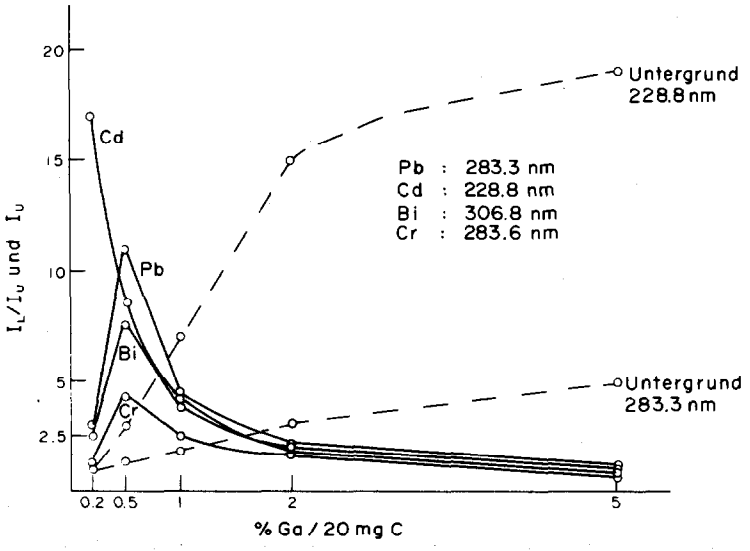


Abb. 5. Abhängigkeit des Linie-Untergrund-Verhältnisses (I_L/I_U) und des Untergrundes (I_U) von der Galliumkonzentration im Kohlepulver bei Anregung im 10 A Gleichstromdauerbogen.

je einer Messung) bei verschiedenen Schichtdicken dargestellt. Sie liegen zwischen 1 und 7%.

BESTIMMUNG DER SPUREN- UND DOTIERUNGSELEMENTE DURCH EMISSIONSSPEKTROGRAPHIE (AES) MIT GLEICHSTROMBOGENANREGUNG

Experimentelles

Apparatur. Spektrograph ISP-28, UdSSR.

Bedingungen. Gleichstromdauerbogen 10 A. Belichtungszeit: 8–10 sec.

Arbeitsweise. Die bei den 3 Schichtabtragungsverfahren erhaltenen Lösungen (methanolische Bromlösung, salpetersaure Lösung, HF-Lösung) werden auf 20 mg Spektralkohlepulver gegeben und unter einer IR-Lampe langsam eingedampft. Im Fall der methanolischen Bromlösung verflüchtigt sich dabei das Arsen als $AsBr_3$. Das Kohlepulver wird nach Homogenisierung in eine Graphitelektrode gegeben und im Gleichstromdauerbogen bei 10 A angeregt (vgl. Cit. 3). Dem Kohlepulver ist im allgemeinen zur Verbesserung des Nachweisvermögens ein leichtionisierbarer Stoff (z.B. 0,4% NaF, vgl. Cit. 13, 14) hinzuzufügen (vgl. nächsten Abschnitt).

Optimierung und Ergebnisse des Verfahrens

Da Gallium ein leicht ionisierbares Element ist, war zu erwarten, daß es einen Einfluß auf die Intensität der Spektrallinien ähnlich wie das Natrium ausübt (vgl. Cit. 14–17). Dieser Einfluß kann durch ein vorher aufgestelltes Nomogramm nach Karpel[1,17] korrigiert werden, aber die Nachweisgrenzen sind dann wegen der von Analyse zu Analyse nicht gleichen Konzentrationen des Galliums nicht optimal. Aus diesem Grund wurde der Einfluß der Galliumkonzentration auf die Intensität der Spektrallinien untersucht. Das Gallium wurde als $GaBr_3$ dem Kohlepulver hinzugefügt.

In der Abbildung 5 sind das Linie-Untergrund-Verhältnis ($I_L:I_U$) einiger ausgewählter Spurenelemente und die Intensität des Untergrundes (I_U) bei zwei ausgewählten Wellenlängen in Abhängigkeit von der Galliumkonzentration dargestellt worden. Das optimale I_L/I_U-Verhältnis ergibt sich für Pb, Cr und Bi (stellvertretend für die überwiegende Zahl der übrigen Elemente) bei einer Galliumkonzentration von 0,5% (0,1 mg Ga pro 20 mg Kohlepulver). Lediglich beim Cd liegt die optimale Galliumkonzentration niedriger. Das ist auf den in diesem Wellenlängengebiet mit der Galliumkonzentration stark ansteigenden Untergrund zurückzuführen. Im Sinne einer simultanen Multielementanalyse ist eine Galliumkonzentration von 0,5% anzuwenden.

Es ist vorteilhaft, das jeweilige Schichtabtrennungsverfahren so einzurichten, daß sich diese Galliumkonzentration direkt ergibt. Im Falle des chemischen Ätzens mit methanolischer Bromlösung ist folgendes Verfahren zu wählen: eine Schichtdicke von 0,38 μm liefert pro cm^2 0,1 mg Gallium, d.h. arbeitet man bei dieser Schichtdicke, dann kann die Regulierung durch Herstellung einer Relation zwischen gewählter Oberfläche und Kohlepulvermenge erfolgen. Vom homogenisierten Kohlepulver werden danach 20 mg für die Analyse eingesetzt. Im Falle der bei der anodischen Oxydation erhaltenen, geringen Schichtstärken ist die Konzentration des Galliums im allgemeinen zu niedrig (kleiner als 0,1% bezogen auf 20 mg Kohlepulver). In diesem Fall ist dem Kohlepulver eine Menge von 0,4% NaF hinzuzufügen (vgl. Cit. 13).

In der Tabelle 3 sind die Nachweisgrenzen für eine Reihe von Elementen dargestellt, die in Gegenwart von 0,5% Gallium erhalten wurden. Ein Vergleich mit Cit. 13 zeigt, daß die hier erhaltenen Nachweisgrenzen nicht schlechter als in Gegenwart von NaF sind.

Tabelle 3. Nachweisgrenzen von Spurenelementen in GaAs-Schichten (Fläche: 1 cm^2, Stärke: 0,4 μm) bei emissionsspektrographischer Bestimmung (Bedingungen entsprechen 0,5% Ga/20 mg Kohlepulver)

Spuren-element	Nachweisgrenzen absolut, *ng*	relativ, *At/cm³*	Spuren-element	Nachweisgrenzen absolut, *ng*	relativ, *At/cm³*
Ag	0,2	$3\cdot10^{16}$	In	0,3	$4\cdot10^{16}$
Al	0,3	$2\cdot10^{17}$	Mg	0,4	$3\cdot10^{17}$
Au	1 ·	$8\cdot10^{16}$	Mn	0,2	$6\cdot10^{16}$
B	0,8	$1\cdot10^{18}$	Ni	2	$5\cdot10^{17}$
Ba	2	$2\cdot10^{17}$	Pb	0,9	$7\cdot10^{16}$
Be	0,2	$4\cdot10^{17}$	Sb	4	$5\cdot10^{17}$
Bi	0,3	$2\cdot10^{16}$	Te	9	$1\cdot10^{18}$
Ca	2	$8\cdot10^{17}$	Zn	0,2	$5\cdot10^{16}$
Cd	0,2	$3\cdot10^{16}$	Fe	0,3	$8\cdot10^{16}$
Cu	0,2	$6\cdot10^{16}$	Co	0,8	$2\cdot10^{17}$
Cr	0,8	$2\cdot10^{17}$	Tl	1	$8\cdot10^{16}$

BESTIMMUNG DER SPUREN- UND DOTIERUNGSELEMENTE DURCH ATOMABSORPTION (AAS) MIT ELEKTROTHERMISCHER ATOMISIERUNG

Experimentelles

Apparatur. Atomabsorptionsspektrometer 811, Jarrell-Ash, USA. Graphitrohrküvette 1278, Beckman, USA.

Arbeitsweise. Die methanolische Bromlösung und die HF-Lösungen werden eingedampft und in 0,05 ml 1*N* HNO_3 aufgenommen. Die nach mechanischer Abtrennung erhaltene GaAs-Menge wird in 0,05 bis 0,1 ml HNO_3 gelöst. Es wird ebenfalls eingedampft und mit soviel 1*N* HNO_3 aufgenommen, daß die Konzentration des Gallium 0,05 mg/0,01 ml (ursprünglich 0,1 mg GaAs) nicht übersteigt. Das in die Graphitrohrküvette einzugebende Analysenvolumen liegt i.a. bei 0,01 ml. Die Trocknung, Veraschung und Atomisierung erfolgte bei jeweils optimierten Bedingungen (vgl. Cit. 18, 19).

Ergebnisse des Verfahrens

Die Ergebnisse des Verfahrens sind in der Tabelle 4 zusammengefaßt worden. Über die Optimierung und die Probleme, die bei den einzelnen Bestimmungen auftreten, wird in den folgenden Mitteilungen berichtet (vgl. Cit. 18, 19). Bei der Bewertung der Ergebnisse der Bestimmung des Zn und Mg muß berücksichtigt werden, daß bei den weniger empfindlichen Resonanzlinien bei 307,6 nm bzw. 202,5 nm gearbeitet wurde, weil die Allgegenwartskonzentration dieser Elemente ein Arbeiten bei den empfindlichen Resonanzlinien (213,8 bzw. 285,2 nm) unmöglich macht. Die theoretisch berechenbaren Nachweisgrenzen liegen somit für Zn etwa um den Faktor 1000 für Mg etwa um den Faktor 100 besser.

VERGLEICH UND SCHLUSSFOLGERUNGEN

1. Ein Vergleich der 3 behandelten Schichtabtrennungsverfahren ergibt, daß mit Hilfe des Ätzens nach anodischer Oxydation die dünnsten Schichten (Bereich 0,02–0,2 μm) in gut reproduzierbarer Weise abgetrennt werden können. Andererseits ist es mit dieser Technik nicht möglich, dickere Schichten abzutrennen. Die optimierte chemische Ätzung mit methanolischer Bromlösung gestattet es, Schichten zwischen 0,1 und 1 μm vom GaAs abzutrennen. Mit dem mechanischen Verfahren ist es möglich, pro Schnitt Schichten zwischen 1 und 2 μm und durch Wiederholung beliebig dicke Schichten in vertretbarer Zeit abzutrennen. Je nach dem analytischen Problem und den Eigenschaften des Materials ist die vorteilhafteste Technik einzusetzen, d.h. für eine einfache Schichtanalyse ist das mechanische Verfahren bzw.

Tabelle 4. Nachweisgrenzen von Spurenelementen in GaAs bei Bestimmung durch AAS mit elektrothermischer Atomisierung

Spuren-element	Wellen-länge, *nm*	Nachweisgrenzen absolut, *ng*	relativ, *At/cm³*	Spuren-element	Wellen-länge, *nm*	Nachweisgrenzen absolut, *ng*	relativ, *At/cm³*
Be	234,9	0,004	$2\cdot10^{16}$*	Pb	283,3	0,08	$1\cdot10^{16}$*
Cd	228,8	0,002	$6\cdot10^{14}$*	Sn	224,6	0,06	$2\cdot10^{16}$*
Ge	265,2	0,2	$9\cdot10^{16}$*	Te	214,3	0,17	$8\cdot10^{16}$†
In	303,9	0,05	$1{,}5\cdot10^{16}$*	Zn	307,6	6	$3\cdot10^{18}$*
Mg	202,2	0,02	$3\cdot10^{16}$*				

* Bezogen auf 0,1 mg GaAs.
† Bezogen auf 0,05 mg GaAs.

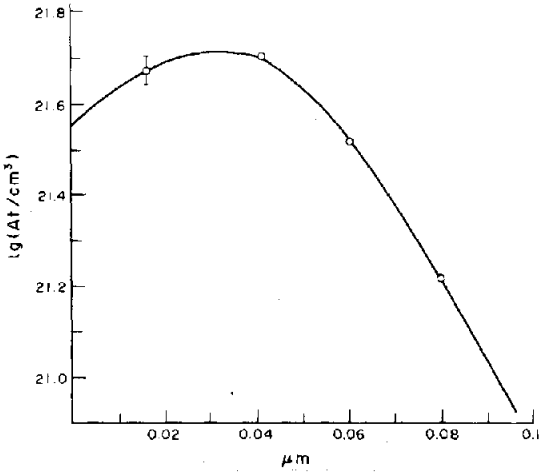


Abb. 6. Phosphor-Tiefenprofil von ionenimplantiertem GaAs. (Schichtabtrennung: Ätzung mit vorheriger anodischer Oxydation, Bestimmung: Emissionsspektrographie im Gleichstromdauerbogen).

die chemische Ätzung, für die Profilanalyse die chemische Ätzung mit und ohne anodische Oxydation vorteilhaft.

Ein Beispiel für das Ergebnis einer Profilanalyse für sehr kleine Abstände unter Anwendung der Ätzung mit vorheriger anodischer Oxydation ist in der Abbildung 6 dargestellt. Aus der Abbildung 6 geht hervor, daß ein einwandfreies Tiefenprofil für die P-Verteilung im ionenimplantierten GaAs durch wiederholte Abtrennung von 0,02-μm Schichten erhalten wurde.

2. Sowohl die AES mit Gleichstrombogenanregung als auch die AAS mit elektrothermischer Atomisierung in einer Graphitrohrküvette sind für die analytische Bestimmung von Spuren in Mikroproben nach jeweiliger Optimierung geeignet. Der Vorteil der AES ist ihr Multielementcharakter. Der Vorteil der AAS ist das bessere absolute und in den gegebenen Mikroproben auch relative Nachweisvermögen.

LITERATUR

1. N. G. Karpel, S. L. Kulyas, O. K. Fedorchuk und V. V. Stochik, *Zavodsk. Lab.*, 1971, **37**, 420.
2. N. M. Kuz'min, A. V. Emel'yanov, S. V. Meshchankina, V. L. Sabatovskaya, I. A. Kuzovlev and T. I. Zakharova, *Zh. Analit. Khim.*, 1971, **26**, 282.
3. I. A. Kuzovlev, O. A. Sverdlina und N. M. Kuz'min, *ibid.*, 1972, **27**, 199.
4. O. A. Sverdlina, I. A. Kuzovlev, V. S. Solomatin, V. Y. Yurkova, N. V. Kovykova, D. N. Nishanov und L. G. Shatalina, *Zavodsk. Lab.*, 1975, **41**, 172.
5. C. S. Fuller und H. W. Allison, *J. Electrochem. Soc.*, 1962, **109**, 880.
6. A. E. Emel'yanov und Yu. I. Pashintsev, *Thesen der 2. Forschungskonferenz über Galliumarsenid*, Tomsk, 1968.
7. I. R. Shelpakova, I. G. Yudelevich, T. A. Chanysheva, O. I. Shcherbakova und V. A. Usova, *Zh. Analit. Khim.*, 1975, **30**, 1310.
8. R. A. Logan, B. Schwartz und J. Sundburg, *J. Electrochem. Soc.*, 1973, **120**, 1385.
9. S. M. Spitzer, B. Schwartz und G. D. Weigle, *ibid.*, 1975, **122**, 397.
10. E. V. Butz und L. M. Vosmilova, *Elektronnaya Tekhnika, Serie 2, Poluprovodnikoviye pribory*, 1. Ausgabe, 1976, 109.
11. C. J. Dell'Oca, G. Yan und L. Young, *J. Electrochem. Soc.*, 1971, **118**, 89.
12. K. Müller, F. H. Eisen und J. W. Mayer, *ibid.*, 1975, **122**, 651.
13. I. G. Yudelevich, I. R. Shelpakova, L. M. Buyanova, L. S. Chuchalina, O. I. Shcherbakova, T. P. Serednyakova und L. V. Zelentsova, *Zh. Analit. Khim.*, 1974, **29**, 518.
14. I. G. Yudelevich, I. R. Shelpakova und S. M. Baturina, *Zh. Priklad. Spektrosk.*, 1971, **14**, 373.
15. M. A. Notkina, S. M. Solodovnik, L. A. Baranova, V. K. Lunina und T. I. Romantseva, *Zavodsk. Lab.*, 1962, **28**, 176.
16. N. G. Karpel', S. A. Kulyas und R. N. Rubinshtein, *ibid.*, 1967, **33**, 1086.
17. R. N. Rubinshtein und N. G. Karpel, *Nomograficheskiye rastshyoty v spektralnom analise*, Metallurgiya, Moskau, 1973.
18. K. Dittrich, *Talanta*, 1977, **24**, 725.
19. *Idem, ibid.*, 1977, **24**, 735.

Summary—Three methods for stripping thin layers of GaAs have been compared with regard to depth of layer and reproducibility. They are (1) chemical etching with methanolic bromine solution, (2) mechanical separation with a microtome, (3) chemical etching after a preliminary amperostatic anodic oxidation. Conditions were optimized. The depth of strip was 0.4 μm for chemical etching, 1 μm for the mechanical separation and 0.02 μm for the anodic oxidation method. Thus the anodic oxidation is specially suitable for profile analysis, and the mechanical method for investigation of thicker layers; chemical etching lies between them. The trace elements in the micro samples thus obtained were determined by d.c. arc atomic-emission spectrography (AES) and atomic-absorption spectrometry with electrothermal atomization in a graphite tube (AAS). The absolute and relative detection limits of AAS for the 0.1–0.2 mg micro samples were on average better by an order of magnitude than those of AES. The advantage of AES lies in the possibility of simultaneous determination of several elements.

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ATOMIC-ABSORPTION DETERMINATION OF BERYLLIUM IN GEOLOGICAL MATERIALS BY USE OF ELECTROTHERMAL ATOMIZATION

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Summary—A method is described for the atomic-absorption determination of beryllium in geological materials, that utilizes electrothermal atomization after a separation by solvent extraction. Samples are decomposed with hydrofluoric acid and nitric acid in Teflon-lined pressure decomposition vessels. Beryllium is isolated by its extraction as beryllium acetylacetonate at pH 8 into xylene and back-extraction in 3*M* hydrochloric acid. The method has been successfully applied to the determination of beryllium in 14 U.S. Geological Survey standard rocks. Four subsamples from four bottles of each standard sample were analysed in random order. The mean beryllium contents (ppm) are: AGV-1, 1.98; PCC-1, 0.024; MAG-1, 2.84; BHVO-1, 0.90; DTS-1, 0.026; SCo-1, 1.74; SDC-1, 2.52; BCR-1, 1.44; GSP-1, 1.22; SGR-1, 0.86; QLO-1, 1.83; RGM-1, 2.21; STM-1, 8.75; G-2, 2.29. An analysis of variance shows that all the samples may be considered homogeneous at $F_{0.95}$ except AGV-1 and DTS-1 which may be considered homogeneous at $F_{0.99}$.

Information on the concentration of beryllium in the ppm and sub-ppm ranges is required for various geochemical and environmental studies. Techniques based on atomic-absorption spectrometry,[1–8] emission spectroscopy,[9–12] fluorimetry,[13–15] and spectrophotometry[1,16–18] have been devised. Quantitative techniques for the isolation and concentration of beryllium are based on the extraction of beryllium acetylacetonate,[1,8,17] ion-exchange,[16] or co-precipitation.[16]

The high sensitivity of atomic-absorption spectroscopy in conjunction with electrothermal atomization was combined, in the work reported in the present paper, with a highly specific solvent-extraction separation. Beryllium acetylacetonate is extracted at pH 8 into xylene and back-extracted into 3*M* hydrochloric acid. Beryllium is then determined by atomic-absorption spectroscopy, with a heated graphite atomizer.

The beryllium content of geological materials is usually too low to allow the formation of independent minerals, and the beryllium is therefore contained in the structure of other minerals, most notably as a replacement for silicon within SiO_4 tetrahedra.[19] However, when independent minerals *are* formed, they are normally difficult to decompose (*e.g.*, beryl) by acid-digestion techniques. To insure against incomplete decomposition, a Teflon-lined pressure vessel[20] was used.

EXPERIMENTAL

Reagents

Ethylenediaminetetra-acetic acid, disodium salt (EDTA), 0.3*M*. Dissolve 111.7 g in water, adding sufficient ammonia to aid in the dissolution and yield a final solution of pH 8; dilute to 1 litre.

Bromophenol Blue solution, 0.05% in water. Add 0.1 g of sodium hydroxide per 250 ml to aid in dissolution.

Acetylacetone solution 10% (v/v) in xylene.

Standard Be solution, 1.00 mg/ml. Dissolve 1.965 g of $BeSO_4 \cdot 4H_2O$ in water, add 2 ml of conc. hydrochloric acid, dilute to 100.0 ml. Dilute appropriately to make working standards.

Apparatus and operation conditions

All extractions were performed in glass-stoppered test-tubes, with an automatic shaker.

A Perkin-Elmer 370 atomic-absorption spectrophotometer* equipped with a deuterium-arc background corrector, HGA-2100 graphite furnace, and model 56 recorder, was used. A beryllium hollow-cathode lamp was used at a wavelength of 234.9 nm and a spectral band-width of 0.7 nm. The conditions used for the HGA-2100 graphite atomizer were: drying at 110° for 20 sec; charring at 800° for 20 sec; atomizing at 2700° for 6 sec; gas—argon with gas-flow interrupted during atomization. The charring temperature is lower than the temperature recommended by the manufacturer (800° instead of 1200°) as discussed later.

Teflon-lined pressure decomposition vessels.

Procedure

Weigh 0.100–0.250 g of samples into the Teflon liner of the decomposition vessel. Add 2 ml of conc. nitric acid and 4 ml of conc. hydrofluoric acid. Close the pressure vessel and heat it on a hot-plate for 16 hr at 225°. Cool, then transfer the contents to a platinum dish and evaporate them to dryness. Add 2 ml of conc. sulphuric acid and heat until the SO_3 fumes appear. Cool. Add 4 ml of 3*M* hydrochloric acid and 7 ml of EDTA solution. Warm the solutions until clear. Cool. Add 1 ml of Bromophenol Blue solution and 12*M* ammonia dropwise until a permanent blue colour is obtained; add 2 drops in excess. Shake with 10 ml of 10% acetylacetone solution in xylene for 6 min. Strip Be by shaking the xylene extract with 4 ml of 3*M* hydrochloric acid for 10 min. Transfer the aqueous phase to a 5-ml standard flask and dilute to volume with 3*M* hydrochloric acid. Determine the absorbance of 10 μl of this solution with an atomic-absorption spectrometer, using background correction and a heated graphite atomizer, and calculate the amount of Be in the samples by

*Any trade names in this publication are used for descriptive purposes only and do not constitute endorsement by the U.S. Geological Survey.

Table 1. Effect of pH on the extraction of beryllium acetylacetonate into xylene

pH	Extracted, % 0.200 μg of Be	100 mg of BCR-1
2	40	0
4	96	10
6	94	49
8	>99	>99
9	98	>99

comparison with appropriate standards carried through the entire procedure.

Analysis of the USGS standard rocks

Four bottles of each of the following USGS (U.S. Geological Survey) standard samples were randomly selected: G-2, granite; GSP-1, granodiorite; AGV-1, andesite; PCC-1, peridotite; DTS-1, dunite; BCR-1, basalt; STM-1, nepheline syenite; RGM-1, rhyolite; QLO-1, quartz latite; SDC-1, mica schist; SCo-1, Cody shale; SGR-1, Green River shale; MAG-1, marine mud; BHVO-1, Hawaiian basalt. Four 100-mg subsamples from each bottle (*i.e.*, 14 standard samples, 4 bottles for each standard, 4 determinations for each bottle: 224 determinations total) were randomized and analysed for their beryllium content. Samples were analysed in groups of 18, plus standards.

Because of the lower beryllium contents of DTS-1 and PCC-1, it was necessary to analyse larger portions (250 mg), and these samples were analysed separately from the other 12 standards. Nevertheless, randomization was maintained throughout the experiment.

RESULTS AND DISCUSSION

Sample decomposition

The use of a Teflon-lined pressure vessel can be avoided if refractory minerals which contain Be (*e.g.*, beryl) are known to be absent. However, the mineralogy of most samples encountered by the analyst is unknown, and the pressure vessel is therefore strongly recommended. The decomposition procedure described above will produce a clear solution from a sample containing as much as 100 mg (maximum tested) of beryl.

Extraction of beryllium acetylacetonate

The xylene extraction of beryllium acetylacetonate in the presence of EDTA produces a solution that is free from matrix elements that interfere with the determination of Be. The effect of pH on the extraction of beryllium acetylacetonate was tested by extracting standard Be solutions and solutions of the USGS standard rock BCR-1. The results, given in Table 1, show that a pH of 8 is required to extract Be from a solution of a rock whereas the extraction of pure solutions is essentially complete at pH 4–9. Salts were evident at the aqueous-organic interface at pH 2 but not at higher pH values. The acetylacetone concentration in xylene was varied from 5 to 60% with negligible effect on the extraction at pH 8.

The length of time necessary for the extraction and back-extraction was also investigated. Extraction times less than 5 min lead to low results for rock solutions, but the extraction for pure Be solutions is complete within 1 min (minimum tested). The minimum times required for back-extraction are 5 and 8 min for pure Be solutions and rock solutions, respectively. The back-extraction is 94% complete for the rock solution after 5 min.

It was found that up to 1000 μg of fluoride (maximum tested) had no effect on the extraction of beryllium acetylacetonate.

Table 2. Effect of varying the charring temperature

Charring temperature, °C	Loss of Be, %
500	0
600	0
700	0
800	1.5
900	14.9
1000	61.2

Atomic-absorption spectroscopy

The instrumental settings used are outlined above. The drying and atomizing temperatures for the HGA-2100 graphite furnace are 110° and 2700°, respectively. Charring temperatures above 800° lead to losses when beryllium is atomized as the chloride: Table 2 shows the effect of varying the charring temperature.

Beryllium content of the USGS standard rocks

The beryllium contents determined in the present study are listed in Table 3 with the results of other investigators and with the results we obtained for some of the standard rocks by using the method of standard additions. Our results are in reasonable agreement with each other and with those reported by other authors.

Table 4 lists the individual results, the mean, the within-bottle standard deviation, and the F-ratio for each standard sample. One-way analysis of variance was applied to the data to determine if the variation between bottles was greater than the variation within bottles. For bottles of only two standard rocks (AGV-1 and DTS-1) was the mean sum of squares for bottles significantly greater than the variation within bottles at the 5% confidence level. Heterogeneity for beryllium in AGV-1 and DTS-1 was demonstrated at the 5% level but not at the 1% level. The overall relative analytical error calculated (12 degrees of freedom) ranged from 3.4 to 21%. If only samples having beryllium contents greater than 0.1 ppm Be are considered, the relative analytical error ranged from 3.4 to 14.2%.

Table 3. Comparison of Be contents, *ppm*, obtained in this study, with Be contents obtained by other techniques (AAS, atomic-absorption spectroscopy; HGA, heated graphite atomizer)

Sample	This work (AAS–HGA)	This work AAS–HGA (Method of standard additions)	Ref. 13 Spectrofluorimetry	Ref. 21 Emission spectroscopy	Ref. 15 Spectrofluorimetry	Ref. 22 Semiquantitative computerized emission spectroscopy	Ref. 23 Gas chromatography	Ref. 3 AAS–Flame
AGV-1	1.98 ± 0.08	1.95, 1.96	1.23	1.8	—	2.52	—	1.6
MAG-1	2.84 ± 0.18	—	—	—	2.7	2.97	—	—
PCC-1	0.024 ± 0.005	0.033	0.03	<0.5	—	<1.00	—	—
BHVO-1	0.90 ± 0.05	—	—	—	—	<1.00(3) 1.10(3)*	—	—
DTS-1	0.026 ± 0.003	0.035, 0.025	0.07	<0.5	—	<1.00	—	—
SCo-1	1.74 ± 0.06	—	—	—	1.6	1.90	—	—
SDC-1	2.52 ± 0.15	—	—	—	2.6	3.78	—	—
BCR-1	1.44 ± 0.07	1.58	1.59	3	—	1.66	1.53	2.3
RGM-1	2.21 ± 0.14	—	—	—	2.2	2.56	—	—
GSP-1	1.22 ± 0.05	1.43	1.76	1.0	—	1.30(5) <1.00(1)*	—	~1
STM-1	8.75 ± 0.34	—	—	—	9.0	11.85	—	—
SGR-1	0.86 ± 0.08	—	—	—	0.91	<1.00	—	—
G-2	2.29 ± 0.12	2.50, 2.60	3.20	2.3	—	2.52	2.07	2.3
QLO-1	1.83 ± 0.26	—	—	—	1.7	2.14	—	—

*Replicate determinations differ; numbers in parentheses indicate number of replicates.

Table 4. Concentration of beryllium in USGS standard rocks (S.D. is the within bottle standard deviation; NS means not significant at indicated confidence level)

Standard rock	Bottle (split/position)	Be, *ppm*	Mean, *ppm*	S.D., *ppm*		*F*-ratio
AGV-1	2/13	1.74, 1.87, 1.79, 1.94	1.98	0.08	5.72	$NS_{0.99}$
	52/21	2.04, 2.06, 2.06, 1.86				
	111/14	1.99, 2.12, 2.01, 2.02				
	14/18	2.06, 2.12, 2.09, 1.93				
PCC-1	39/26	0.031, 0.020, 0.021, 0.020	0.024	0.005	0.20	$NS_{0.95}$
	36/8	0.032, 0.022, 0.022, 0.022				
	39/16	0.033, 0.020, 0.024, 0.024				
	25/67	0.023, 0.023, 0.028, 0.027				
DTS-1	39/13	0.029, 0.029, 0.027, 0.027	0.026	0.003	4.07	$NS_{0.99}$
	40/16	0.031, 0.028, 0.028, 0.20				
	4/4	0.030, 0.028, 0.028, 0.027				
	4/27	0.020, 0.018, 0.025, 0.024				
SDC-1	119/4	2.51, 2.52, 2.80, 2.30	2.52	0.15	1.40	$NS_{0.95}$
	97/12	2.47, 2.24, 2.33, 2.58				
	61/24	2.52, 2.65, 2.40, 2.58				
	76/15	2.68, 2.57, 2.50, 2.70				
GSP-1	39/20	1.22, 1.19, 1.20, 1.25	1.22	0.05	1.36	$NS_{0.95}$
	65/11	1.28, 1.31, 1.12, 1.18				
	38/23	1.25, 1.29, 1.22, 1.26				
	55/5	1.22, 1.19, 1.18, 1.14				
BCR-1	80/7	1.54, 1.48, 1.56, 1.44	1.44	0.07	3.04	$NS_{0.95}$
	19/29	1.50, 1.33, 1.54, 1.51				
	67/32	1.48, 1.34, 1.34, 1.35				
	46/18	1.44, 1.40, 1.42, 1.34				
SGR-1	25/23	0.75, 0.95, 0.93, 0.76	0.86	0.08	0.47	$NS_{0.95}$
	28/3	0.84, 0.84, 0.97, 0.92				
	4/12	0.81, 0.90, 0.76, 0.85				
	33/19	0.95, 0.96, 0.85, 0.76				
QLO-1	9/24	2.04, 2.00, 1.82, 1.75	1.83	0.26	0.26	$NS_{0.95}$
	2/20	1.98, 1.85, 1.84, 1.71				
	17/23	2.00, 2.04, 1.89, 1.95				
	39/15	2.00, 1.76, 1.74, 1.80				
MAG-1	26/6	2.74, 2.98, 2.98, 2.75	2.84	0.18	0.069	$NS_{0.95}$
	38/3	2.65, 2.70, 2.78, 3.10				
	31/5	2.98, 2.96, 2.58, 2.88				
	12/27	2.98, 2.60, 2.80, 3.00				
BHVO-1	12/8	0.89, 0.98, 0.84, 0.89	0.90	0.05	0.30	$NS_{0.95}$
	4/1	0.89, 0.99, 0.81, 0.84				
	31/5	0.89, 0.93, 0.84, 0.90				
	50/14	0.89, 0.94, 0.95, 0.89				
SCo-1	26/3	1.76, 1.80, 1.81, 1.76	1.74	0.06	1.38	$NS_{0.95}$
	55/23	1.82, 1.74, 1.68, 1.78				
	40/15	1.86, 1.69, 1.67, 1.71				
	68/3	1.69, 1.62, 1.75, 1.73				
RGM-1	13/7	2.10, 2.15, 2.15, 2.21	2.21	0.14	0.49	$NS_{0.95}$
	55/4	2.13, 2.46, 2.25, 2.25				
	48/31	2.31, 2.40, 2.10, 2.03				
	54/5	2.47, 2.13, 2.19, 2.10				
STM-1	45/30	8.50, 9.10, 8.40, 8.30	8.75	0.34	0.87	$NS_{0.95}$
	21/26	8.75, 8.80, 9.10, 8.30				
	21/27	8.65, 9.40, 9.30, 8.50				
	41/10	8.95, 8.65, 8.65, 8.70				
G-2	56/4	2.47, 2.43, 2.40, 2.20	2.29	0.12	0.91	$NS_{0.95}$
	75/8	2.50, 2.18, 2.10, 2.18				
	16/23	2.35, 2.20, 2.23, 2.28				
	116/17	2.35, 2.40, 2.23, 2.18				

REFERENCES

1. J. Korkisch, A. Sorio and I. Steffan, *Talanta*, 1976, **23**, 289.
2. B. Fleet, K. V. Liberty and T. S. West, *ibid.*, 1970, **17**, 203.
3. W. Luecke, *Neues Jahrb. Mineralogie Monatsh.*, 1971, **6**, 263.
4. J. D. Taylor and T. W. Steele, *U.S. At. Energy Comm.*, NIM-173, 1967.
5. D. C. Manning, *At. Absorption Newsletter*, 1967, **6**, 35.
6. D. L. Bokowski, *Am. Indus. Hyg. Assoc. J.*, 1968, **29**, 474.
7. T. V. Ramakrishna, P. W. West and J. W. Robinson, *Anal. Chim. Acta*, 1967, **39**, 81.
8. S. L. Sachdev and P. W. West, *Environ. Sci. Technol.*, 1970, **4**, 745.
7. P. W. Kehres and W. J. Poehlman, *Appl. Spectry.*, 1954, **8**, 36.
10. J. F. Kopp and R. C. Kroner, *ibid.*, 1965, **19**, 155.
11. W. C. Tennant and J. R. Sewell, *Geochim. Cosmochim. Acta*, 1969, **33**, 640.
12. C. W. Ondrick and N. H. Suhr, *Chem. Geol.*, 1969, **4**, 429.
13. W. R. Meehan, *Earth Plan. Sci. Letters*, 1969, **7**, 1.
14. J. D. Coserove, J. Morgan and P. Pakalns, *Australian At. Energy Comm. Rept.*, AAEC/TM 87, 1961.
15. V. Machacek, I. Rubeska, V. Sixta and Z. Šulcek, *U.S. Geol. Survey Prof. Paper* 840, p. 73, 1976.
16. J. R. Merrill, M. Honda and J. R. Arnold, *Anal. Chem.*, 1960, **32**, 1420.
17. R. F. Abernethy and E. A. Hattman, *U.S. Clearinghouse Fed. Sci. Tech. Inform., P. B. Rep. No.*, 196606, 1970.
18. P. Pakalns and W. W. Flynn, *Analyst*, 1965, **90**, 300.
19. K. Rankama and Th. G. Sahama. *Geochemistry*, p. 444. University of Chicago Press, Chicago, 1950.
20. B. Bernas, *Anal. Chem.*, 1968, **40**, 1682.
21. N. H. Suhr, private communication quoted by F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.
22. F. G. Walthall, A. F. Dorrzapf, Jr. and F. J. Flanagan, *U.S. Geol. Survey Prof. Paper*, 840, p. 99, 1976.
23. K. J. Eisentraut, D. J. Griest and R. E. Sievers, *Anal. Chem.*, 1971, **43**, 203.

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SPECTROGRAPHIC DETERMINATION OF GOLD AND PLATINUM METALS IN GEOLOGICAL AND OTHER MATERIALS BY FIRE-ASSAY PRECONCENTRATION*

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Summary—A method is described for the determination of gold, platinum, palladium, rhodium and iridium at microgram levels in geological and other materials by a combination of fire-assay preconcentration and emission spectrography. The noble metals are collected into 4-mg silver or platinum prills by a normal fire-assay technique. These prills are arced between graphite electrodes at 12 A d.c. No buffer is required to prevent ejection of the prill. Gold, platinum and palladium are determined in the silver prills and gold, palladium, rhodium and iridium in the platinum prills. Low, but reproducible, results are found for iridium. At the 0.08 ppm level an overall coefficient of variation of 11% is found. This technique is simple and rapid for the determination of the precious metals.

This report describes the experimental work performed to establish suitable techniques and operating conditions for the analysis of precious metals by a fire-assay spectrographic technique. A proposed geochemical survey for precious metals, requiring the determination of gold and platinum down to a level of 50 ppM (parts per milliard) in a large number of small samples (< 10 g), initiated this investigation and the development of a simple, rapid and reliable analytical method for the determination of gold and platinum in small samples.

The average level of precious metals in crustal rocks ranges from 1 ppM for iridium to 10 ppM for platinum and palladium.[1] The determination of these elements often requires an extraction and concentration procedure. Fire-assay fusion executed properly and employing a suitable collector[2] usually provides an efficient and reliable means of separating and concentrating the precious metals from large proportions of base metals and gangue material.

There are two procedures available in this laboratory for the determination of the required elements once a fire-assay prill has been produced, *viz.* atomic-absorption spectrometry and emission spectrography. The atomic-absorption procedure requires dissolution of the prill in *aqua regia* and aspiration of the resulting solution directly into the flame. The small mass of sample to be used (< 10 g) and the low levels of precious metals present in the sample preclude the use of this technique for the present purpose, but the direct emission spectrographic analysis of the fire-assay prill appears to meet the necessary requirements. An additional advantage is that this method is faster than the corresponding atomic-absorption technique[3] for simultaneous multielement analysis.

Several spectrographic techniques have been described in the literature for the determination of precious metals.[4–12] Recent methods have favoured arcing the prill on a copper electrode or in a cupped graphite electrode,[9,12] with or without buffering[8,11] by a precious metal powder[9] or a precious metal compound.[10,12] The metal prill analysed is derived from gold,[10] silver[8,9,12] or platinum[11] employed as collectors. Spectral lines derived from the prill[8,9,11,12] or buffers[9,12] have been used for internal standardization.

Heady and his co-workers reported successful arcing of platinum prills in graphite electrodes without the presence of any buffers to prevent bead ejection[11] but found that silver prills required a buffer.[9] The present investigation simplified Heady's procedure and established a technique for arcing both silver and platinum prills in undercut graphite cup electrodes, without the use of an internal standard or the presence of a buffer to prevent bead ejection. A procedure was established for the routine determination of gold, platinum, palladium, rhodium and iridium in all samples. This method has been used for the determination of the precious metal content of plant-process intermediates and products derived from test-work performed on the retreatment of gold and uranium dumps. The fire-assay preconcentration technique[13] is based on the standard practice on the Witwatersrand with the addition of 4 mg of silver or platinum as collector.

EXPERIMENTAL

In addition to the standard fire-assay equipment,[13] the spectrographic apparatus listed in Table 2 was used. A Jarrell-Ash Console Microphotometer was employed for the visual matching of the spectral lines of samples with the standard lines.

Reagents

The chemicals used were of analytical-reagent grade unless otherwise stated. All water used was mixed-bed de-

* Part of this work was discussed at the Conference on Atomic Spectroscopy, held at the National Physical Research Laboratory, CSIR, Pretoria, 19 August 1975.

mineralized water. All standard metal solutions had a final acid concentration of 2*M* hydrochloric acid.

Lead foil. Assay grade; 150-mm diameter circles weighing approximately 25 g.

Primary standard gold solution. Gold wire (Table 1) was added to 30 ml of *aqua regia* and the mixture warmed gently. When the gold had dissolved, the solution was evaporated to incipient dryness and cooled; 5 ml of conc. hydrochloric acid were added, then the mixture was warmed to effect dissolution of solids and cooled. The solution was diluted to volume and mixed well.

Primary standard solutions of platinum and palladium. The appropriate mass of metal (Table 1) was dissolved in the same way as gold, but after the dissolution in hydrochloric acid the solution was evaporated to incipient dryness and cooled, and the residue was taken up in 10 ml of conc. hydrochloric acid by warming, then the solution was cooled, diluted to volume and mixed well.

Primary standard solutions of rhodium and iridium. The appropriate mass of compound (Table 1) was added to 40 ml of 6*M* hydrochloric acid and the mixture warmed gently. When the compound had dissolved, 10 ml of conc. nitric acid were added, the solution was evaporated to incipient dryness and cooled. Then 40 ml of 6*M* hydrochloric acid were added, the mixture was warmed to dissolve the solids and cooled. The solution was diluted to volume and mixed well.

Silver and platinum solutions for fire-assay prills. Silver nitrate crystals (1.260 g) were dissolved in water, diluted to 100 ml in a standard flask and mixed well. Platinum sponge or wire (0.4000 g) was dissolved in 120 ml of *aqua regia* as described above, and the final solution diluted to 100 ml in a standard flask.

Preparation of standard calibration solutions. The primary solutions were diluted to prepare secondary standards covering the range 0.1–100 μg/ml of gold, platinum, palladium, rhodium and iridium, care being taken that the final hydrochloric acid concentration was at least 2*M*.

Procedure

Preparation of standard silver prills. Standards were prepared for fire-assay fusion in dishes fashioned from lead foil circles. Hydrazine sulphate (0.5 g), 4 mg of silver (as silver nitrate solution) and the appropriate volumes of gold, platinum and palladium solutions to cover the range 0.01–600 μg of each element were added to the dishes, the smallest possible volumes of standards being used in order to avoid dissolution of the lead foil by the hydrochloric acid present. The solutions were carefully evaporated to dryness, then the lead dishes were folded to retain the residue and submitted for fire assay. Three standards were prepared, each containing 1000 μg of one of the three noble elements. The solution blank (to check for any contamination) was made by following the procedure described for the preparation of the primary platinum stock solution but without the platinum. A 2-ml aliquot of this solution was taken for the preparation of the "solution blank prill". A fire-assay blank was obtained by submitting a 25-g portion of lead foil and 4 mg of silver to fire assay.

Preparation of standard platinum prills. Standards and fire-assay blank prills were prepared as described for the silver prills except that 4 mg of platinum replaced the silver and the appropriate volumes of gold, palladium, rhodium and iridium solutions were added to cover the range 0.01–100 μg of each element. The solution blank was obtained by following the procedure described for the preparation of the primary rhodium stock solution but without the rhodium salt. A 2-ml aliquot of this solution was taken for the preparation of the "solution blank prill". Four standards were prepared, each containing 1000 μg of one of the four elements.

Preparation of samples

All samples were milled to give 70–80% of particles smaller than 74 microns. Samples containing large amounts of sulphides were roasted overnight, at a temperature starting at 350° and gradually rising to 650°.

Sample weights

For the determination of microgram levels of gold, palladium, platinum, rhodium and iridium a minimum total sample mass of 200 g is desirable for preconcentration by fire assay. Either 50-g duplicate subsamples (>0.5 ppm of one element) or a single 100-g subsample (<0.5 ppm of all elements) should be extracted by fire assay into silver prills for the determination of gold, platinum and palladium, and a 100-g subsample is extracted into a platinum prill for the determination of gold, palladium, rhodium and iridium. Normally 10-g samples of geological concentrates are extracted by fire assay and gold, platinum and palladium determined in silver prills. If there is sufficient sample, duplicate 10-g subsamples are extracted, whereas the whole sample mass is taken if this is less than 10 g.

Fire assay

The fire-assay techniques[13] employed are based on the standard practice on the Witwatersrand.

Spectrographic procedure

The prills are arced under the conditions listed in Table 2. Under these conditions the film is able to record 27 spectrograms. A 10%-transmission neutral filter is used to prevent overexposure of the film. Glow from both electrodes is screened out by focusing the arc onto a diaphragm. Standard films are prepared by arcing the range of standard prills. The spectral lines and concentration ranges used are given in Table 3. Sample spectral lines are visually matched with the standard spectral lines.

The elements that can be collected along with the precious metals under normal circumstances were found to cause no interference. The elements checked were lead, copper, nickel, iron and bismuth. For convenience in the visual matching of the lines, alternatives can be selected from Table 3.

RESULTS AND DISCUSSION

Preliminary investigation on silver prills

Initially, 10 mg of silver were employed as a collector for gold, platinum and palladium, as used by Whitehead and Heady.[9] The silver prills were arced at 12 A d.c. without a buffer, with graphite anodes 4.5 mm in diameter and having a 2.2-mm diameter cup 5 mm deep. Prills were frequently found to be ejected. By changing to National L3906 undercut electrodes, bead ejection was stopped completely and exposure times were materially decreased.

Some suppression of the gold intensity is observed in the presence of 100-fold or more of its mass of platinum or palladium. This occurs only with the standards, however, because platinum and palladium are usually present in relatively minor quantities.

First attempts to produce a series of standards incorporating gold, platinum and palladium in the range 0.01–2000 μg showed an unexpected problem. The standards were prepared as described above, but without the addition of hydrazine sulphate and with 10 mg of silver as collector. All the spectral lines showed good gradation except those of the lower gold standards (<1.0 μg) which were very poor in this

Table 1. Primary standard stock solutions

Element	Compound used (Johnson Matthey "Specpure")	Quantity added, *g*	Final volume, *ml*	Metal concentration, *μg/ml*
Au	Gold wire	0.1000	100	1000
Pt	Platinum sponge or wire	0.1000	100	1000
Pd	Palladium sponge	0.1000	100	1000
Rh	$(NH_4)_3RhCl_6 \cdot 1\frac{1}{2}H_2O$	0.3841	100	1000
Ir	$(NH_4)_3IrCl_6 \cdot H_2O$	0.2477	100	1000

Table 2. Spectrographic conditions

Spectrograph:	Jarrell-Ash 1.5 metre, Wadsworth mount. 1180-grooves/mm grating.
Electrodes:	anode: 3/16-in. diameter graphite with undercut cup, National Graphite L3906. cathode: 1/4-in. diameter graphite rod, technical grade, National Graphite L4309, cut into 5-mm lengths and with one end machined to a 90° point.
Excitation:	d.c. arc burning at 12 A.
Arc gap:	5 mm maintained during burn.
Exposure:	100 sec.
Wavelength range:	210.0–480.0 nm, first order.
Spectrographic slit:	30 μm wide, 0.9 mm long.
Attenuation:	10% neutral filter with diaphragm 1 mm wide.
Film:	Kodak Spectrum Analysis Film 5367 No. 1.
Processing:	AGFA-GEVAERT G150 developer (1 + 4), 5 min; wash, 20–30 sec; AGFA-GEVAERT AGEFIX (1 + 1), 4 min; wash, 5 min; dry in air.

Table 3. Spectral lines and concentration ranges

Element	Analytical line, *nm*	Concentration range, *μg*
Au	267.595	0.01–3
	274.826	2–300
	270.089	20–600
Pt	265.945	0.01–3
	264.689	1–30
	269.843	10–300
Pd	340.458	0.01–1
	342.124	0.1–3
	344.140	0.5–50
	292.249	5–300
Rh	346.204	0.1–10
	337.225	1–30
	292.409	5–60
Ir	322.078	0.1–5
	292.702	0.1–10
	298.112	3–60

respect. The blanks, in some cases, were found to contain more gold than the lower standards. After a thorough search for possible sources of contamination, it was concluded that, though there was a small amount of gold in the reagents used, a large part of the contamination probably derived from volatile gold(III) chloride emanating in the furnace from adjacent pots which contained the higher standards. This problem was effectively solved by reducing the gold(III) chloride to metallic gold by the addition of hydrazine sulphate to the standards, before the drying.

Minor variations in the blank level still occur, however, preventing maximum utilization of the available sensitivity—0.01 μg of gold is considered, at present, the lower practical limit and this is equivalent to a detection level of 0.001 ppm on a 10-g sample. Table 4 lists the practical lower limits of detection for the elements of interest.

Table 4. Practical lower limits of detection

Element	Lower limit, *μg*	Detection level for 100-g sample, *ppM*
Au	0.01	0.1
Pt	0.01	0.1
Pd	0.01	0.1
Rh	0.1	1
Ir	0.1	1

Techniques established

Determination of gold, platinum and palladium in silver prills. New standards were prepared, each element being restricted to the range 0.01–600 μg and the prill size reduced from 10 to 4 mg. Collection of gold, platinum and palladium was satisfactory in the smaller prill by the technique described. Silver was found to be a poor collector for rhodium and iridium when these elements were included in the analytical scheme.

The excitation conditions adopted ensure that the bulk of the silver is volatilized during the first 20 sec of arcing. Gold appears next in the arc, followed by palladium and platinum. After 90 sec the bead is completely consumed. However, because platinum seeps into the electrode, the film is exposed for an additional 10 sec.

Determination of gold, palladium, rhodium and iridium in platinum prills. Four mg of platinum were found to be satisfactory as collector for gold, palladium, rhodium and iridium. All the spectral lines showed a good gradation over the calibration range investigated. Exactly the same procedure as described above for the preparation and analysis of the silver prills was followed for the platinum prills.

Unfortunately there is confusion in the literature concerning the efficiency of the recovery of iridium by fire-assay fusion and cupellation of the lead button to give a silver or platinum prill. Broadhead *et al.*[11] showed that platinum is an efficient collector for iridium at the 20-μg level, but reported losses at the 1-μg and >50-μg levels. Other authors[2,14,15] who have reported losses of iridium did not employ platinum as a collector. Iridium alloys with platinum,[16] but is completely immiscible with lead and silver.[2] Despite these recorded losses, silver has been successfully used as a collector for precious metals, including iridium.[8,12] However, it would appear that provided there is no variation in the technique, reproducible results are obtained.

Sampling

Gold and the platinum-group metals occur as discrete particles in the matrix minerals. These particles may be elemental in composition, as in the case of gold, or constituted of specific minerals as in the case of the platinum-group metals. The consequence is that the statistical chance of obtaining representative analytical samples is reduced with decreasing sample size[17] and, therefore, the precision of the analysis improves with increase in the sample mass taken. Strong and Murray-Smith[18] have reported that satisfactory results are obtained for the determination of gold with a 20-g sample mass for ores containing up to 5 ppm of gold. This would suggest that for most samples 20 g is a practical minimum mass for the extraction of precious metals by fire assay.

The major problem encountered with the application of this method was the inhomogeneity of the samples, which came from metallurgical test-work and were submitted for fire assay and spectrographic evaluation. Originally the ground sample was split into three subsamples, two of 10 g and one of 100 g, for analysis. Palladium and platinum were usually determined in the duplicate 10-g subsamples extracted into silver prills. Rhodium and iridium were determined in the 100-g subsample concentrated into a platinum prill. A 100-g subsample was required in order to achieve the required limit of detection (1 ppM). Not unexpectedly, platinum and palladium showed inconsistent line intensities when the 10-g duplicate subsamples were used. These inconsistencies were found to be associated with either the platinum or palladium lines and sometimes both lines in the same sample. Furthermore the palladium values determined on the 100-g subsample extracted into the platinum prill showed a more consistent level within batches than the values obtained from the duplicate silver prills. It was concluded that the inconsistent line intensities observed could be attributed to inhomogeneity of the sample with respect to the precious metal content. It was decided, wherever possible, to extract duplicate 50-g subsamples into silver prills when one element was present at a level of >0.5 ppm. This was found to reduce the frequency of occurrence of the observed line inconsistencies. When all the elements were present at a level of <0.5 ppm a single 100-g subsample was taken.

Accuracy and precision

One reference sample of a precious metal ore (SARM-7), obtained from the South African Bureau of Standards, Pretoria,[19] and a synthetic sample have been used for statistical evaluation of the method. Accuracy and precision data are presented in Tables 5 and 6.

The synthetic sample was made by adding gold, platinum and palladium in solution to acid-washed sand, drying, and crushing as fine as possible. Twenty-two 10-g aliquots were extracted by fire assay by the same operator on the same day and the prills obtained were analysed spectrographically. From the results given in Table 5, an overall coefficient of variation of approximately 11% at the 0.08-ppm level was obtained. The method was found to work well if small calibration standard intervals were used.

The major problem with any natural solid powdered standard is the inhomogeneity of the sample with respect to its trace-element content. Precious metals are often found in separate discrete minerals and are particularly susceptible to sampling errors. The main reason for the high coefficients of variation reported in Table 6, for the analysis of SARM-7, is that relatively large calibration standard intervals are required to evaluate the intensities of the analyte lines. The elemental concentrations for gold, palladium and platinum are in excess of the normal working levels employed in the routine application of the method, and small sample masses have therefore been taken. The agreement found is very good. In the particular case of iridium, the low value appears to be at variance with the findings of Broadhead *et al.*[11] This laboratory employs a cupellation temperature of 930°, which is higher than that used by Broadhead, and is likely to lead to iridium losses through volatilization and possible adsorption of iridium by the cupel material.[14,15] In the early investigational work, gold was used as a collector for iridium. During the arcing process, the gold prills were found to eject globules in the form of a fine spray. This led to irreproducible losses of the precious metals and further work on gold collection was discontinued. From the data on the analysis of SARM-7, the iridium losses appear to be consistent, and therefore the iridium contents determined for plant-process intermediates and products are satisfactory for test-work control.

Table 5. Statistical data on the synthetic standard

Element	No. of detns.	Concentration added, *ppm*	Mean concentration found, *ppm*	Coefficient of variation, %
Au	21	0.08	0.076 ± 0.0073	9.6
Pt	21	0.08	0.080 ± 0.0065	8.2
Pd	21	0.08	0.077 ± 0.012	15.2

Table 6. Statistical data on the fire assay spectrographic analysis of SARM-7

Element	No. of detns.	Prill*	Average concentration found, *ppm*	Coefficient of variation, %	Certified values, 95% confidence level, *ppm*	Fire-assay atomic-absorption, this laboratory, *ppm*	Typical results, other laboratories,[19] *ppm*
Gold	26	Ag	0.34 ± 0.09	26	0.31 ± 0.015	0.30	0.305 ± 0.078
	19	Pt	0.29 ± 0.05	17			
Palladium	28	Ag	1.55 ± 0.39	25	1.53 ± 0.032	1.58	1.54 ± 0.17
	19	Pt	1.53 ± 0.35	23			
Platinum	18	Ag	3.78 ± 1.21	32	3.74 ± 0.045	3.72	3.72 ± 0.25
Rhodium	19	Pt	0.21 ± 0.033	16	0.24 ± 0.013		0.24 ± 0.06
Iridium	19	Pt	0.039 ± 0.010	26	0.074 ± 0.012		0.069 ± 0.032

*Ag prill: 1-g sample extracted into 4 mg of silver.
Pt prill: 10-g sample extracted into 4 mg of platinum.

Table 7. Comparative analytical data on a leached residue

Element	Chemical analysis, *ppm*	Spectrographic analysis, *ppm*	
		Ag prill	Pt prill
Au	39	41	33
Pt	45	49	—
Pd	147	150	>100

One further sample, a leached residue derived from metallurgical test-work, has been analysed by the spectrographic technique and by the nickel sulphide collection technique.[20] The results are presented in Table 7.

The agreement is good. For the spectrographic technique, ten 1-g aliquots were extracted into 4 mg of silver and nine 1-g aliquots were extracted into 4 mg of platinum, and the mean value was calculated.

To compare the efficiencies of silver and platinum for the collection of rhodium and iridium both the leach residue and SARM-7 have been extracted into silver and platinum prills by fire assay. The results of the analyses are given in Table 8.

From the differences in values observed, platinum is seen to be a superior collector to silver for rhodium and iridium. An additional feature noted is that the individual values determined on the platinum prills are more consistent than those determined on the silver prills. This is in agreement with the findings of Beamish[2] and Broadhead.[11] However, other authors[8,12] have obtained satisfactory results for silver as a collector.

Since this visual spectrographic method was introduced in 1973, over 20 000 samples have been analysed for their precious metal content. The accuracy and precision of the analysis by this method are governed by the distribution of the precious metals in the sample and by any deviations from the optimum standard intervals of the calibration.

Table 8. Comparison of silver and platinum employed as collectors for rhodium and iridium

Sample	No. of detns.	Prill	Sample mass taken, *g*	Rh *ppm*	Ir *ppm*	Range, *ppm*	
						Rh	Ir
Leach residue	10	Ag	1	1.7	1.1	0.1–4.0	<0.1–3.0
	9	Pt	1	6.9	3.3	5.0–9.0	2.0–4.0
SARM-7	5	Ag	10	<0.01	<0.01	—	—
	19	Pt	10	0.21	0.039	0.15–0.25	0.025–0.050

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REFERENCES

1. B. Mason, *Principles of Geochemistry*, 3rd Ed., Wiley, New York, 1966.
2. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon, London, 1966.
3. R. C. Mallett, D. C. G. Pearson, E. J. Ring and T. W. Steele, *J.S. Afr. Chem. Inst.*, 1972, **25**, 219; *Talanta*, 1972, **19**, 181.
4. H. de Laszlo, *Ind. Eng. Chem.*, 1927, **19**, 1366.
5. J. Seath and F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 535.
6. C. L. Lewis, *Can. Mining Met. Bull.*, 1957, **50**, 163.
7. J. Hafty and L. B. Riley, *Talanta*, 1968, **15**, 111.
8. P. G. Sim, *Appl. Spectry.*, 1974, **28**, 23.
9. A. B. Whitehead and H. H. Heady, *ibid.*, 1970, **24**, 225.
10. A. F. Dorrzapf, Jr. and F. W. Brown, *ibid.*, 1970, **24**, 415.
11. K. G. Broadhead, B. C. Piper and H. H. Heady, *ibid.*, 1972, **26**, 461.
12. E. F. Cooley, K. J. Curry and R. R. Carlson, *ibid.*, 1976, **30**, 52.
13. V. S. Dillon, *Assay Practice on the Witwatersrand*, Chamber of Mines, Johannesburg, South Africa, 1955.
14. J. I. W. Watterson, R. V. C. Robert, E. van Wyk and T. W. Steele, *Natl. Inst. Metall. Repub. S. Africa Rept*, No. 1048, 1970.
15. G. T. Georgiev and D. Apostolov, *J. Anal. Chem. U.S.S.R.*, 1972, **27**, 445.
16. J. Hafner and R. Volterra in T. Lyman, ed., *Metals Handbook*, 8th Ed., Vol. I, p. 1191. American Society for Metals, Metals Park, Ohio, 1973.
17. H. E. Clifton, R. E. Hunter, F. J. Swanson and R. L. Philips, *U.S. Geol. Survey Paper*, 625-C, 1969.
18. B. Strong and R. Murray-Smith, *Talanta*, 1974, **21**, 1253.
19. T. W. Steele, J. Levin and L. Copelowitz, *Natl. Inst. Metall. Repub. S. Africa, Rept*, No. 1696, 1975.
20. R. V. D. Robert, E. van Wyk, R. Palmer and T. W. Steele, *ibid.*, 1371, 1971; *J.S. Afr. Chem. Inst.*, 1972, **25**, 179.

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ELECTROCHEMICAL PROPERTIES OF METAL COMPLEXES OF DITHIO-ACID DERIVATIVES AND THEIR APPLICATION IN EXTRACTION POLAROGRAPHY

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Summary—Metal complexes with dithiocarbamic (dtc), xanthic (xan) and dithiophosphoric (dtp) acids give rise to one or more polarographic waves in dimethylformamide and in mixtures of extracting solvents and ethanol. The electrons are found to be transferred stepwise in the case of unfilled *d*-shell metal complexes. The shift of half-wave potential depends on the ligand, increasing in the order dtp < xan < dtc. In solvents with low solvation power the electrode processes are more reversible. The linear dependence of the limiting current on the chelate concentration has been used for determining the metal in the organic phase without re-extraction. Pb(II), Bi(III) and As(III) have been separated with dtp as extractant, and the concentrations of Co(II), Ni(II) and Zn(II) complexes (simultaneously extracted) have been determined polarographically.

Metal complexes formed with various substituted dithio-acids have recently found wide application in analytical chemistry. Dithio-acids and their simple salts are of great importance as reagents for extraction, separation and determination of metal ions by various methods, mainly photometric.[1–4] The use of dithio-acids in extraction polarography can be successfully applied for solving new analytical problems. The effective application of this method requires a systematic and detailed investigation of the electrochemical behaviour of the metal complexes in non-aqueous media.

This paper presents data on the electrochemical reduction of some metal complexes formed with the dithio-compounds given in Table 1. Cyclic chronovoltamperometry and d.c. and a.c. polarography were employed. Dimethylformamide (DMF), acetonitrile (AN), and 2:3 v/v mixtures of benzene, toluene, *m*-xylene, chloroform, ethylacetate or isoamyl alcohol with methanol were used as solvents.

EXPERIMENTAL

Apparatus

The polarographic measurements were performed with an LP-7 polarograph (Czechoslovakia), PO-5122 oscillographic polarograph model 03 (USSR) and a.c. polarograph PPT-1 (USSR). All voltammetric measurements were made with a three-electrode cell at 25 ± 0.2°. The dropping mercury electrode (d.m.e.) was used as the working electrode for recording the current–voltage curves. At 25 cm mercury pressure and zero applied voltage, the characteristics of the capillaries used were: $m = 2.96$ and 0.61 mg/sec and $t = 4.81$ and 7.50 sec respectively. The experiments were carried out with a drop-time of 0.5 sec (electromechanical device). The auxiliary electrode was a mercury pool. The reference electrode consisted of a mercury pool in a DMF solution of tetraethylammonium perchlorate, placed in a glass tube ending in a cracked glass-bead junction with the bulk solution.

Reagents

The dithio-acids and their salts and metal chelates were synthesized by methods reported in the literature.[5–8] Their purity was checked by determining the m.p. and by elemental analysis. The organic solvents were purified by a standard technique. The supporting electrolytes used were 0.1*M* tetraethylammonium perchlorate in DMF and 0.2*M* lithium perchlorate in ethanol. All solutions of the complexes were prepared in solvent previously deoxygenated with purified hydrogen.

RESULTS AND DISCUSSION

The electrochemical behaviour of the complexes is best seen from the data obtained for DMF media. It is possible to identify two different systems of electrode reactions, corresponding to two types of process on the d.m.e.

All the complexes formed by metals with filled *d*-electron shells are reduced in DMF to the metal amalgams in one step. Electroreduction of the transition metal chelates formed by xan or dtp and the bivalent metal ions proceeds in a similar way. The diffusion-controlled current, i_d, is proportional to the concentration of chelate in the range $1–5 \times 10^{-4} M$, and practically independent of the mercury pressure head corrected for the back-pressure. Plots of $\log i_p$ *vs.* $\log V$ (i_p is the limiting current on the cyclic voltamperograms, V is the scan-rate of potential) exhibit slopes of 0.5. These results also suggest that the limiting currents are diffusion-controlled. Plots of $\log i/(i_d - i)$ *vs.* E are straight lines with a slope of approximately $60/n$ mV (n is the oxidation state of the central atom in the chelate) (Table 1). The limiting currents and microcoulometric analysis indicate that the waves for the Pb(II), Tl(I), Bi(III), Cu(II) and Hg(II) chelates correspond to the transfer of n electrons per molecule. From these results the wave appears to be reversible. This interpretation is supported by the parameters of

Table 1. Polarographic data for reduction of ML_n complexes in DMF, concentration $2 \times 10^{-4} M$

Complexes		$-E_{1/2}$, V					i_d, μA				
		R					R				
L	M	Me	Et	Pr	Bu	Pip	Me	Et	Pr	Bu	Pip
dtc	Cr(III)	1.13	1.17	—	1.21	—	0.28	0.28	—	0.26	—
		1.57	1.69	—	1.75	—	0.54	0.51	—	0.48	—
	Mn(III)	0.55	0.56	0.56	0.58	0.58	0.27	0.30	0.28	0.25	0.36
		1.72	1.79	1.83	1.94	1.92	0.62	0.64	0.71	0.54	0.78
	Fe(III)	0.61	0.63	0.62	0.63	0.61	0.32	0.33	0.31	0.26	0.33
		1.59	1.64	1.65	—	1.60	0.28	0.31	0.33	—	0.31
		1.84	1.89	1.88	1.84	1.86	0.29	0.31	0.34	0.48	0.33
	Co(III)	0.94	0.96	0.95	0.97	0.94	0.30	0.29	0.29	0.33	0.34
		1.33	1.34	1.37	1.39	1.36	0.29	0.29	0.31	0.32	0.34
		1.86	1.87	1.86	1.88	1.81	0.33	0.32	0.33	0.35	0.36
	Ni(II)	1.34	1.36	1.39	1.38	1.34	0.33	0.31	0.30	0.32	0.28
		1.71	1.81	1.83	1.82	1.70	0.38	0.37	0.34	0.42	0.29
	Cu(II)	0.65	0.68	0.69	0.71	0.70	0.68	0.67	0.68	0.54	0.71
	Zn(II)	1.43	1.51	1.53	1.53	1.49	0.65	0.63	0.52	0.51	0.65
	Cd(II)	0.85	0.92	0.95	0.94	0.90	0.46	0.46	0.37	0.31	0.42
	Hg(II)	0.78	0.81	0.82	0.85	0.79	0.60	0.58	0.57	0.54	0.56
	Tl(I)	0.54	0.58	0.60	0.61	0.55	0.34	0.38	0.26	0.27	0.35
	Pb(II)	0.75	0.78	0.81	0.82	0.77	0.64	0.61	0.55	0.52	0.77
	Bi(III)	0.64	0.66	0.65	0.71	0.62	0.98	0.85	0.74	0.68	1.05
		Me	Et	Pr	Bu	Am	Me	Et	Pr	Bu	Am
xan	Fe(III)	0.53	0.55	0.55	0.57	0.64	0.42	0.44	0.41	0.39	0.36
		1.11	1.08	1.09	1.14	1.13	1.01	0.92	0.93	0.81	0.87
	Co(III)	0.85	0.89	0.92	1.14	1.21	0.35	0.34	0.32	0.29	0.31
		1.21	1.22	1.23	1.33	1.39	0.77	0.78	0.61	0.53	0.67
	Ni(II)	1.51	1.50	1.65	1.64	1.66	0.66	0.62	0.65	0.61	0.63
	Zn(II)	1.19	1.20	1.18	1.23	1.28	0.56	0.57	0.54	0.57	0.51
	Cd(II)	1.27	1.29	1.30	1.27	1.28	0.53	0.52	0.51	0.51	0.47
	Pb(II)	0.68	0.71	0.72	0.69	0.74	0.62	0.59	0.61	0.58	0.59
	Bi(III)	0.50	0.53	0.56	0.59	0.61	1.11	1.05	0.98	0.99	0.95
		Me	Et	Pr	Bu	i-Bu	Me	Et	Pr	Bu	i-Bu
dtp	Fe(III)	0.53	0.57	0.61	0.61	0.64	0.51	0.47	0.45	0.43	0.47
		1.02	1.09	1.12	1.15	1.21	0.94	1.06	0.98	0.98	0.94
	Co(II)	0.95	1.05	0.89	1.13	1.10	0.70	0.68	0.69	0.65	0.64
	Ni(II)	0.55	0.56	0.54	0.56	0.53	0.75	0.77	0.81	0.72	0.74
	Zn(II)	0.90	0.89	0.88	0.91	0.92	0.74	0.72	0.77	0.68	0.73
	Tl(I)	0.48	0.50	0.51	0.55	0.52	0.46	0.47	0.45	0.44	0.48

the cyclic chronovoltamperograms. With DMF medium symmetric anodic–cathodic peaks are observed on the $i = f(E)$ curves ($E_p = 58/n$ mV). The ratio between the heights of the anodic and cathodic peaks of these chelates is approximately 1.0 (in the range where V is less than 0.5 V/sec).

The shape of both the d.c. polarograms and the cyclic curves is essentially dependent on the depolarizer concentration, because of the adsorptivity of the complexes on the d.m.e. Increasing the depolarizer concentration up to $1 \times 10^{-3} M$ results in maxima appearing on the d.c. polarographic waves of the Bi(III), Cu(II), Pb(II) and Tl(I) complexes. The ratio of anodic to cathodic current is less than unity in this case and $\log i_p / \log V$ exceeds 0.5.

The nature of the ligand affects the discharge characteristics of the chelate. The cathodic shift in $E_{1/2}$ with increasing size of R in a homologous series (Table 1) is due to increase in the electron-donor properties of the ligand.

The second scheme involves a stepwise electron-transfer. Thus the first stages are reversible. Dithiocarbamate complexes of bivalent transition metal ions with unfilled *d*-shells and the complexes formed between tervalent metal ions and all the ligands investigated have the same reduction mechanism. Complexes with the central atom in a low oxidation state are formed as intermediate products. The polarographic curves of complexes of the $M^{n+}(R_2NCS_2)_n$ have n stages corresponding to the successive transfer of n electrons (M = Cr, Fe, Co, Ni). For the chelates FeL_3, CoL_3, CrL_3 and $Mn(R_2NCS_2)_3$, where $L = ROCS_2^-$ or $(RO)_2PS_2^-$, the discharge proceeds in two stages with the transfer first of one electron and then of two electrons (Fig. 1). The stepwise reduction of the chelates is complicated by dissociation of the in-

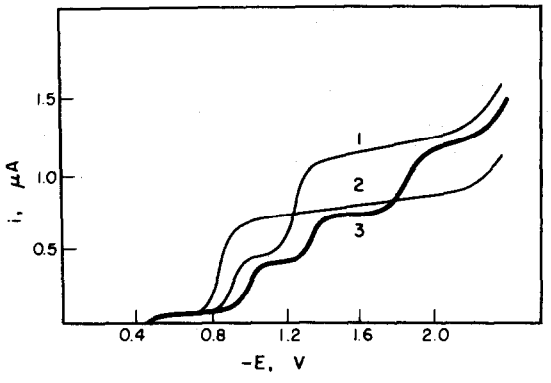


Fig. 1. Polarograms of $1 \times 10^{-4}M$ $Co(Etxan)_2$ (1), $Pb(Et_2dtc)_2$ (2) and $Co(Et_2dtc)_3$ (3) in DMF.

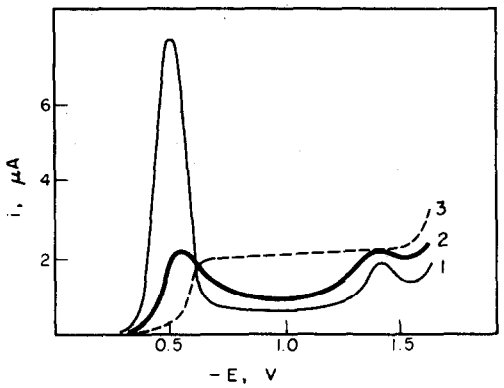


Fig. 2. A.c. (1, 2) and d.c. (3) polarograms of $5 \times 10^{-4}M$ $Fe(Me_2dtc)_2$ (1, 3) and $Fe(Mexan)_3$ (2) in benzene–ethanol mixture, $0.2M$ in $LiClO_4$.

termediates, with formation of the anion L^-, which may be detected by means of the anodic wave resulting from the interaction of this anion with mercury[9] under the conditions of cyclic voltamperometry.

The nature of the central atom has a considerable effect on this process. In general, the stability of the one-electron transfer products is correlated with the stability of the initial complexes. From the effect on the cyclic $i = f(E)$ curves of changing the polarization amplitude it is concluded that the products formed by the transfer of one electron to the Cr(III), Mn(III) and Fe(III) complexes then dissociate:

$$ML_3 + e \rightleftarrows [ML_3]^- \rightleftarrows [ML_{3-p}]^{(1-p)-} + pL^-$$

$$[ML_{3-p}]^{(1-p)-} + e \rightarrow [ML_{3-p}]^{(2-p)-} \xrightarrow{+e} [ML_{3-p}]^{(3-p)-} \rightarrow M(O) + (3-p)L^-$$

In the case of the Co(III) and Ni(II) complexes with dtc the splitting of the anion occurs at subsequent stages of the electrode process:

$$ML_n + e \rightleftarrows [ML_n]^-$$

$$[ML_{n-1}]^- + e \rightarrow [ML_n]^{2-} \rightarrow [ML_{n-1}]^- + L^-,$$

$$[ML_{n-1}]^- + e \rightarrow [ML_{n-1}]^{2-} \rightarrow M(O) + (n-1)L^-$$

The $E_{1/2}$ of the reversible one-electron process becomes more negative as the electron-donor properties of the substituent are increased in accordance with the increase in stability of the complexes in the same series (found potentiometrically).[10]

Though in some cases discharge of the chelates is complicated by adsorption effects, the ease of reduction of the investigated complexes formed between metals and dithio-acid derivatives depends on the nature of the central atom, and corresponds to the metallic characteristics of the metal–ligand bond.[11] If we compare the reduction potentials of the complexes formed by different dithio-compounds, we may notice a certain regularity in each case: a shift of $E_{1/2}$ towards negative potentials, effect increasing with the ligands in the order dtp < xan < dtc.

Data concerning the effect of the nature of the solvent on the polarographic characteristics of complexes of Fe(III) with different ligands are given in Table 2. The limiting currents decrease with increase in the solvent viscosity. Chelate solvation in a given solvent also plays a certain part. The change of i_d on transition from aromatic hydrocarbons to acetic esters reflects the growth of the degree of complex solvation leading to enlargement of the depolarizer molecule and, consequently, to decrease of the diffusion coefficient.

The adsorption of complexes and the character of the electrode process are of great importance in practical application of dithio-acids and their salts in extraction polarography. The adsorption activity of complexes with dithio-compounds is greater in mixed solvents (ionizing solvent—methanol). This may be used for concentrating complexes on the dropping mercury electrode and for improving the sensitivity of determination in the case of the pulse techniques. The high reversibility of the electrode process, depending on the nature of the solvent, makes it possible to improve the sensitivity of determination when a.c. polarography is used (Fig. 2). Complexes of metals with filled *d*-shells gives polarographic waves of more reversible nature in benzene–methanol solvents (Fig. 3). It is therefore advisable to use aromatic hydrocarbons as extraction solvents; polarographic measurements should be carried out in mixed solvents.

The choice of a ligand depends on the nature of the problem and the objective in question. Greater sensitivity of determination by the a.c. polarographic method may be achieved by using dialkyldithiocarbamates as extractants; the dialkyldithiocarbamate complexes are more reversibly reduced. The difference in the degree of reversibility of the polarographic waves of the dtc and xan complexes may be accounted for by their great ability to form solvates, characterized by a slow charge transfer at the electrochemical stage

Table 2. Effect of solvents on the reduction of $1 \times 10^{-3} M$ FeL_3

Solvent	$DN^*_{SbCl_5}$	Viscosity, $mN \cdot sec \cdot m^{-2}$	L (R = Et)	$-E_{1/2}$, V	i_d, μA
AN	14.1	0.34		0.61	2.25
			dtc	1.59	2.17
				1.89	2.21
			xan	0.55	2.32
				1.13	4.57
			dtp	0.53	2.40
				1.07	4.93
Acetone	17.0	0.30	xan	0.54	2.12
				1.22	4.35
			dtp	0.52	2.24
				1.10	4.65
DMF	26.6	0.80		0.63	1.42
			dtc	1.61	1.35
				1.87	1.36
			xan	0.55	1.87
				1.07	3.77
			dtp	0.57	2.10
				1.06	4.11
DMSO	29.8	1.96		0.62	1.38
			dtc	1.59	1.31
				1.91	1.37
			xan	0.53	1.62
				1.14	3.41
			dtp	0.54	1.92
				1.11	3.75

* Donor number relative to $SbCl_5$ (Gutmann).

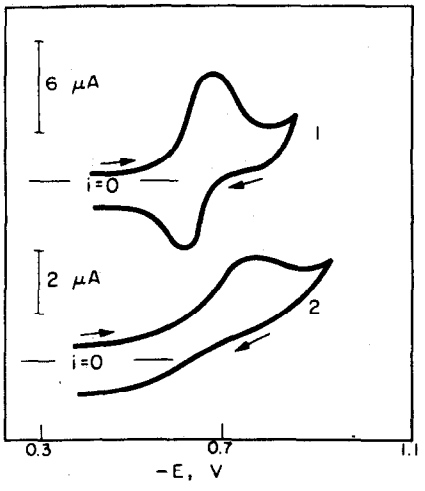


Fig. 3. Cyclic voltammagrams of $5 \times 10^{-4} M$ $Cd(Bu_2dtc)_2$ in ethanol–benzene mixture (1) and in DMF (2).

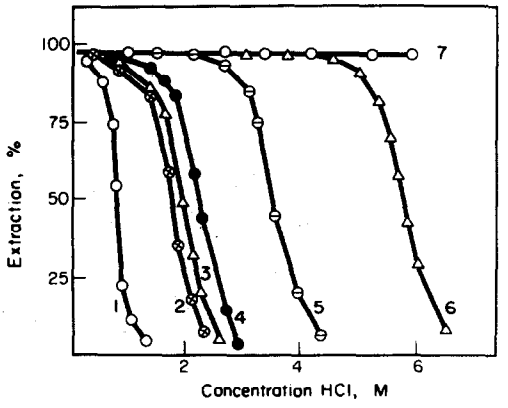


Fig. 4. Influence of pH on the extraction of metal complexes with Et_2dtp. 1—Cd, 2—Co, 3—Ni, 4—Zn, 5—Pb, 6—Bi, 7—As.

proper. Dtp compounds are of greatest significance for use in extraction from strong acid media, their complexes being stable under these conditions. This is important for determining such elements as bismuth, antimony and arsenic which form complexes with dithio-acids only at low pH.

The linear dependence of i_d on concentration, observed under certain conditions for all the complexes investigated, may be used for determining the elements directly in the organic phase without re-extraction.

Because of the lack of information on the extraction of dithiophosphates and xanthates by aromatic hydrocarbons we have studied conditions for the toluene-extraction of complexes formed between metals and these ligands. Hydrochloric acid solutions

Table 3. Determination of Ni(II) in presence of Co(II), reagent dtp (R = Et), solvent benzene

Taken, *mg/ml*		Found, *mg/ml*		Error, %	
Co	Ni	Co	Ni	Co	Ni
0.00230	0.00270	0.00231	0.00266	3.1	2.7
0.00620	0.00150	0.00641	0.00145	5.1	4.8
0.00250	0.00840	0.00247	0.00841	4.1	1.4

Table 4. Determination of As(III) in presence of Bi(III) and Pb(II), reagent dtp (R = Et), solvent toluene

Taken, *mg/ml*			Found, *mg/ml*			Error, %		
As	Bi	Pb	As	Bi	Pb	As	Bi	Pb
0.00350	0.00410	0.00360	0.00354	0.00399	0.00367	6.9	3.6	4.0
0.00520	0.00550	0.00600	0.00519	0.00557	0.00607	3.8	3.3	2.3
0.00730	0.00850	0.00350	0.00732	0.00861	0.00353	3.4	2.9	9.6
0.00250	0.00850	0.00600	0.00254	0.00862	0.00605	10.5	2.6	5.6

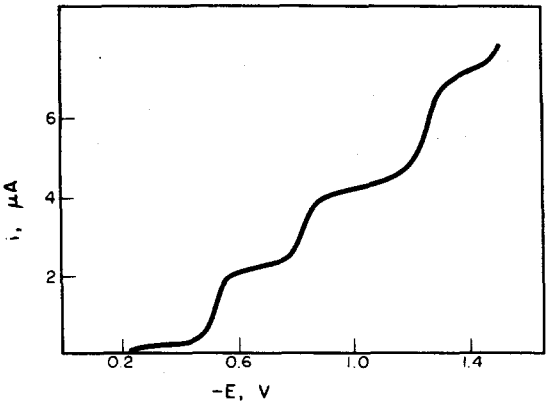


Fig. 5. Polarograms of $1 \times 10^{-3} M$ $M(Et_2dtp)_2$ (M = Ni, Zn, Co) in benzene–ethanol mixture 0.2*M* in $LiClO_4$.

with a fivefold reagent excess were used for the extraction. Figure 4 shows sufficiently good separation of Pb(II), Bi(III) and As(III). If dtp is used as extraction reagent, the Co(II), Ni(II) and Zn(II) complexes can be jointly extracted together and determined polarographically in the same solution (Fig. 5). Results are presented in Tables 3 and 4. The data obtained have been used to develop some methods of analysis of industrial and natural resources: the determination of lead in alloys, of zinc in the blood of animals,[12] and of fungicides.[13,14]

REFERENCES

1. A. Hulanicki, *Talanta*, 1967, **14**, 1371.
2. D. J. Halls, *Microchim. Acta*, 1969, 62.
3. Yu. A. Zolotov and N. M. Kuzmin, *Solvent Extraction*, p. 184. Khimiya, Moscow, 1971.
4. I. P. Alimarin and Yu. A. Zolotov, *Zh. Analit. Khim.*, 1975, **30**, 1253.
5. D. Coucouvanis, *Prog. Inorg. Chem.*, 1970, **11**, 233.
6. J. R. Wasson, I. M. Woltermann and H. J. Stoklosa, *Fortschr. Chem. Forschung*, 1973, **35**, 65.
7. M. I. Kabachnik and T. A. Mastryukova, *Izv. Akad. Nauk USSR*, 1953, 121.
8. T. A. Mastryukova, A. E. Shipov and M. I. Kabachnik, *Zh. Obshch. Khim.*, 1961, **31**, 507.
9. A. M. Bond, A. T. Casey and J. R. Thackeray, *J. Electrochem. Soc.*, 1973, **120**, 1502.
10. V. F. Toropova, G. K. Budnikov and N. A. Ulakhovich, *Zh. Neorgan. Khim.*, 1974, **19**, 1852.
11. R. Chant, A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Austral. J. Chem.*, 1973, **26**, 2533.
12. G. K. Budnikov, V. F. Toropova, N. A. Ulakhovich and I. P. Viter, *Zh. Analit. Khim.*, 1975, **30**, 2120.
13. *Idem, ibid.*, 1974, **29**, 1204.
14. G. K. Budnikov, G. S. Supin, N. A. Ulakhovich and N. K. Shakurova, *ibid.*, 1975, **30**, 2275.

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CHEMICAL PHASE-ANALYSIS FOR KYANITES

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Summary—A new method is presented for determining the kyanite present in a refractory aluminium silicate rock. The sample is digested with hydrofluoric acid for 2–3 hr, the excess of acid is removed or complexed and the residue is filtered off, dried and weighed. The residue is the undissolved kyanite and any topaz and tourmaline present. Corrections may be applied for the solubility of kyanite in hydrofluoric acid and for the topaz. Many non-refractory aluminium silicate minerals tested were found to be decomposed almost completely by this treatment. Corundum, tourmaline and certain garnet minerals, besides topaz, may be left undissolved, however, and interfere.

The grade and therefore the price of Lapso Buro Kyanite is at present mainly decided on the basis of the alumina content, on the assumption that nearly all the alumina is associated with the kyanite or a similar refractory phase and that aluminium has been accurately determined. The first of these assumptions is not generally correct because some of the alumina will be in non-refractory minerals likely to occur alongside the kyanite.

Chemical analysis alone, therefore, is not a sufficient criterion for deciding the refractory mineral (kyanite) content or the quality of the refractory, since it does not reveal the form in which other elements or deleterious impurities are present. For example, presence of iron in the crystal lattice of a refractory mineral is thought to be deleterious since it can cause cracking and parting in the final product.[1] The usual chemical analysis will not be able to differentiate between the two situations. A combination of chemical phase-analysis and elemental analysis might be more successful.

A survey by Varley[1] indicated that the main non-refractory or deleterious minerals associated with high-alumina refractory silicates may be quartz, micas (muscovite, biotite, vermiculite), feldspars, garnets, graphite, magnetite, limonite, pyrite and clay-minerals. The chief non-refractory minerals associated with the kyanite deposit studied here are mainly quartz and micas with very minor amounts (1–2% in low-grade rocks) of other minerals such as rutile, corundum, garnet, *etc.*

The method of attack used in the work reported here has been found (Table 5) to decompose the following minerals completely: quartz, micas (sericite, muscovite and biotite), feldspars, magnetite and other iron oxides, pyrophyllite and other simple silicates. Carbonaceous matter and pyrite, if present, can be eliminated by a variation of the procedure, the former by igniting the residue from the acid attack and the latter by using an oxidative attack (procedure *A*, below). Titanium-bearing oxides and garnets dissolve partially. A few garnet minerals such as andradite, almandite and spessartite have been reported to be decomposed by treatment with hydrofluoric acid.[2] Tourmaline was found in this study to be unattacked even by overnight treatment with hydrofluoric acid.

Topaz, a high-alumina refractory silicate, remains unattacked. Other high-alumina refractory silicate minerals not encountered in the Lapso Buro Kyanite deposits, and therefore not studied here, are sillimanite, dumortierite, mullite, and andalusite. They are all likely to behave similarly to kyanite, and as they are all convertible into mullite at high temperatures they are considered harmless (they are in fact, used as substitutes for kyanite in the refractory industry).

The method is very accurate when judged by the normal standards of chemical phase-analysis, where 5–10% error is not unusual.[3] It is very simple and rapid in comparison with other techniques of chemical analysis of silicate rocks, and platinum ware is not essential. It gives only the relevant information, *i.e.*, the actual refractory-mineral content and should therefore be useful for both buyers and sellers of the raw material. The relative insolubility of kyanite and topaz in hydrofluoric acid may have further potential for utilization.

EXPERIMENTAL

Procedure A

Weigh accurately a 1-g sample of 100-mesh material into a platinum dish or large crucible. Add 15 ml of concentrated hydrofluoric acid and cover the vessel (a polythene cover may be used). Digest on a boiling water-bath for 2–3 hr with occasional swirling. After the digestion add 10 ml of concentrated perchloric acid and evaporate to fumes. Rinse the sides of the dish with water and again heat to fumes. Add about 50 ml of hot boiling water, boil for a while and filter off on a tared Gooch crucible (with an asbestos pad). Dry at 120°, cool and weigh. The weight of the residue is taken as the kyanite content after correction for solubility (see below) and any topaz present. The topaz content can be calculated from a separate fluoride estimation, but it is rare for topaz to be associated with kyanite.

* Throughout the text the term solubility is used in the sense of the amount of mineral or minerals dissolved by a given acid combination under specified conditions, as found from the amount left undecomposed.

Procedure B

This procedure is shorter and does not need platinum ware. Weigh a 1-g sample of 100-mesh material into a 250-ml polythene beaker. Digest the sample as in procedure *A* after adding 15 ml of concentrated hydrofluoric acid.

After the digestion add carefully 30 ml of hot 20% boric acid solution, mix and filter as in procedure *A*. Use a policeman to transfer all the residue. Wash 4 or 5 times with hot water. Dry, cool, weigh and calculate as in procedure *A*.

RESULTS AND DISCUSSION

*Solubility (rate of decomposition) of kyanite**

In $HF-HClO_4$ and $HF-H_3BO_3$. The results for the solubility of kyanite in these acid mixtures are summarized in Tables 1–4. It may be seen that the raw kyanite of commerce sold as the best variety from Lapso Buro (locally called Elephant's Egg) is considerably soluble in these acid combinations, but that once leached with hydrofluoric acid, the Lapso Buro Kyanites show little further decomposition in the acid.

The important conclusions to be drawn are as follows.

(*a*) Even the purest kyanite from the Lapso Buro deposits contains varying amounts of silicate minerals or quartz which decompose easily with hydrofluoric acid, and after decomposition of these minerals the rate of dissolution of the pure kyanite left is low and fairly constant.

(*b*) The rate of further decomposition of leached samples varies slightly with the nature of the kyanite, crystalline kyanite decomposing at a slower rate than the fine-grained massive variety, and ranges from 11.6 to 16.5 mg for a 1-g sample in 15 ml of hydrofluoric acid in the usual time of 2–3 hr. This shows that a correction of 1–2% will be needed for a 1-g sample. A negative error of less than 2% will occur if no correction is applied, which is adequate for chemical phase analysis.

(*c*) There is essentially no difference between the results obtained by the two procedures (see Table 2).

(*d*) Kyanite, whether raw or leached with hydrofluoric acid, slowly continues to decompose in hydrofluoric acid (see Table 3).

(*e*) There is not much difference (see Table 4) in the total amount of kyanite decomposed in a given time, whether the amount of hydrofluoric acid is varied and the weight of sample kept constant or the amount of sample is varied and the volume of acid kept the same. This shows that the amount of sample dissolved in hydrofluoric acid in a given time does not represent the actual solubility since the acid is not saturated with respect to kyanite phase; it represents only the slow decomposition of the mineral grains by the acid, and is therefore dependent on the surface area exposed to attack and hence on the grain size and mass of the sample (Table 4). However, under the conditions described in this report the rate of attack of hydrofluoric acid on kyanite is so slow that only an insignificant part of the kyanite dissolves in 2–3 hr whereas the majority of silicates and quartz dissolve in about an hour. This gives sufficient accuracy for the

Table 1. Solubility of kyanite and topaz in $HF-H_3BO_3$ (procedure *B*, see text)

Expt.	Sample description and locality	Sample size taken, *g*	Sample found undecomposed, *g*	Decomposed* (dissolved), %
A	Massive kyanite (MK-1), locally called Elephant's Egg/Lapso Buro	1.0000	(a) 0.9261	7.39
			(b) 0.9277	7.23
			(c) 0.9250	7.50
			(d) 0.9240	7.60
			(e) 0.9280	7.20
B	Massive kyanite (MK-1), same as above, after treating with HF so as to leach all HF-soluble minerals	1.0000	(a) 0.9850	1.50
			(b) 0.9841	1.59
			(c) 0.9835	1.65
			(d) 0.9840	1.60
C	Bladed kyanite (BK-1) with bluish crystals; Lapso Buro	1.0000	(a) 0.9544	4.56
			(b) 0.9570	4.30
			(c) 0.9607	3.93
			(d) 0.9550	4.50
D	Bladed kyanite (BK-1), same as above, after treating with HF so as to leach all HF-soluble minerals	1.0000	(a) 0.9883	1.17
			(b) 0.9877	1.23
			(c) 0.9884	1.16
		10.2500	(d) 0.9854	1.46
E	Kyanite slab (bladed crystals) kept in 100 ml of HF for 3 days			
F	Topaz (TO-1); pure crystals taken from topaz vein; Topaz Hill, Lapso Buro	1.0000	(a) 0.9953	0.47
			(b) 0.9964	0.36
			(c) 0.9943	0.57
			(d) 0.9959	0.41
G	Kyanite (bulk sample No. 1) after leaching with HF so as to remove all HF-soluble minerals; Lapso Buro (See Table 2, Expt. E for HF-soluble minerals present in this sample)	1.0000	(a) 0.9858	1.42
			(b) 0.9863	1.37

* Calculated on whole sample basis.

Table 2. Comparison of data obtained by treatment with $HF-HClO_4$ (procedure *A*) and $HF-H_3BO_3$ (procedure *B*) (see text for details)

Expt.	Sample description and locality	Sample size, *g*	Found undecomposed			
			$HF-HClO_4$		$HF-H_3BO_3$	
			g	%	*g*	%
A	Massive kyanite (MK-1), same as for Expt. A, Table 1; Lapso Buro	1.0000	(a) 0.9280	7.20	Compare with data in Table 1,	
			(b) 0.9291	7.10		
			(c) 0.9307	6.93		
B	Topaz (TO-1), same as for Expt. F in Table 1; Lapso Buro	1.0000	(a) 0.9929	0.71	Compare with data in Table 1, Expt. F	
			(b) 0.9931	0.69		
C	Topaz bulk sample (TS-1); Lapso Buro	1.0000	(a) 0.6693	33.07	0.6688	33.12
			(b) 0.6671	33.29	0.6743	32.57
			(c) 0.6623	33.77	0.6650	33.50
D	Topaz bulk sample (TS-2); Lapso Buro	1.0000	(a) 0.6750	32.50	0.6781	32.19
E	Kyanite bulk sample No. 1; Lapso Buro	1.0000	(a) 0.3426	65.74	0.3386	66.14
			(b) 0.3407	65.93	0.3372	66.28
			(c) 0.3411	65.89	0.3323	66.77
F	Kyanite containing quartz (PC/1); Kanyaluka near Mosaboni	1.0000	(a) 0.6957	30.43	0.6944	30.56
			(b) 0.6948	30.52	0.6973	30.27

Table 3. Solubility of kyanite and topaz with time in $HF-H_3BO_3$ (procedure *B*), sample size 1.0000 g

Expt.	Sample	Time, *hr*	Sample found undecomposed, *g*	Dissolved, %
A	Massive kyanite (MK-1)	1	0.9369	6.31
		2	0.9267	7.33
		2.5	0.9261	7.39
		3	0.9258	7.42
		4	0.9210	7.90
		(*)24	0.8790	12.10
B	Massive kyanite (MK-1) as above, treated with HF so as to leach all soluble minerals	1	0.9894	1.06
		2	0.9850	1.50
		3	0.9845	1.55
		(*)96	0.9405	5.95
C	Bladed kyanite (BK-1) with bluish crystals	1	0.9720	2.77
		2	0.9637	3.63
		2.5	0.9607	3.93
		3	0.9540	4.60
		4	0.9510	4.90
D	Topaz (TO-1) pure crystals taken from topaz vein; Topaz Hill Lapso Buro	1	0.9984	0.16
		2	0.9966	0.34
		3	0.9973	0.27
		4	0.9954	0.46
		48	0.9933	0.67
		(*)120	0.9903	0.97

* More HF added as required. Alternate heating on water-bath (during daytime) and cooling (during nights).

Table 4. Solubility of kyanite with different weights of sample and varying volume of HF (procedure *B*), 2.5 hr digestion period

Sample	Sample size, *g*	HF, *ml*	Sample undecomposed, *g*	Sample dissolved, *mg*
Massive kyanite (MK-1) previously treated with HF to remove all soluble minerals	0.2500	15	0.2450	5.0
	0.2500	30	0.2442	6.8
	0.5000	15	0.4872	12.8
	0.5000	30	0.4864	13.6
	1.0000	15	0.9841	16.9
	1.0000	15	0.9850	15.0
	1.0000	30	0.9800	20.0

Table 5. Effect of $HF-H_3BO_3$ attack on certain other rocks and minerals

Rock or mineral	Sample size, g	Sample found undecomposed, g	Dissolved, %	Remarks
Quartz (pure)	0.5000	0.0014	99.86	—
Quartz (pure)	0.5000	0.0020	99.80	0.75 g each of Na_2CO_3 and K_2CO_3 added
Quartzite (black)	1.0000	0.0131	98.69	Undecomposed mass black. Partly volatilized on ignition (carbonaceous matter)
Sericite	1.0000	0.0164	98.36	—
Garnetiferous muscovite–sericite schist	1.0000	0.0186	98.14	Undecomposed mass black. Garnets (?)
Garnetiferous muscovite–mica	1.0000	0.0756	92.44	Undecomposed mass black. Garnets (?)
Carbonaceous state	1.0000	0.0690	93.10	Undecomposed mass black, mostly volatilized on ignition (carbonaceous matter)
Pyrophillite (pure)	0.5000	0.0023	99.54	—
Tailings from copper concentrator plant at Mosaboni	1.0000	0.0124	98.76	Complex silicates. Undecomposed mass black, did not volatilize on heating. May be garnets

Table 6. Solubility of kyanite and topaz in certain other acid combinations (sample size 1.0000 g)
(*a*) $HCl-HClO_4$ = HCl followed by $HClO_4$ and heating to fumes
(*b*) $HCl-H_2SO_4$ = HCl followed by H_2SO_4 and heating to fumes
(*c*) $HF-HClO_4$ = Procedure *A*.

Expt.	Sample	Acid combination	Undissolved, %	R_2O_3 in the filtrate, %	Remarks
A	Massive kyanite (MK-1)	(*a*)	97.97	2.01	Acid-soluble Fe and Al—may be from oxides or from partial decomposition of simple silicates
B	Massive kyanite (MK-1) after treating with HF to leach all soluble minerals	(*a*)	99.98	—	—
		(*b*)	99.97	—	—
C	Topaz (pure)	(*a*)	99.92	—	—
		(*b*)	99.90	—	—
D	Topaz bulk sample (TS-1)	(*a*)	98.98	0.98	R_2O_3 may be from oxides of Fe and Al, *etc.*
		(*b*)	66.71	11.55	R_2O_3 mainly derived from decomposition of silicates (micas, *etc.*)
E	Topaz bulk sample (TS-2)	(*a*)	97.33	—	
		(*b*)	67.50	13.38	Contained 1.10% CaO in dissolved portion
F	Kyanite bulk sample No. 1	(*a*)	94.90	—	
		(*b*)	94.95	5.0	R_2O_3 from Fe and Al oxides
		(*c*)	34.07	9.75	or partial decomposition of simple silicates
G	Kyanite containing quartz (PC/1)	(*a*)	99.34	0.70	
		(*b*)	69.57	0.82	Low R_2O_3 shows most of the impurity is due only to quartz

determination of kyanite in presence of other common impurities. A correction may be estimated for the variety of kyanite and applied if greater accuracy is required.

(*f*) Topaz, so far as can be concluded from the one pure topaz sample studied here, remains practically unattacked by hydrofluoric acid (see Tables 1–3). Hydrochloric or perchloric acid attack will cause a small loss from this sample (Table 6) and this may be due to surface coatings of oxides of iron and aluminium. Impure topaz samples treated with hydrofluoric acid to remove soluble minerals and then filtered off, show the same insolubility on further treatment with hydrofluoric acid.

In $HCl-HClO_4$ and other acid combinations. The solubility of kyanites and topaz in some other acid combinations has also been studied and the results are reported in Table 6. It is seen that the solubility of pure kyanite in other acid combinations is very low, as expected, since most silicates and quartz are insoluble

in mineral acids. However, a few impure samples showed a fair amount of attack and the soluble part was found to give rise to an "R_2O_3" precipitate. It appears that iron and aluminium oxides are mainly dissolved, with some contribution from weathered micas and other acid-soluble silicates. Massive kyanite showed about 2% Al and Fe dissolving in hydrochloric–perchloric acid mixture (Table 6). The same kyanite, after treatment with hydrofluoric acid to remove soluble minerals, showed no further solubility in hydrochloric–perchloric acid mixture.

Possible reasons for relative insolubility of kyanite and topaz in hydrofluoric acid

A survey of the literature indicated that nearly all silicates yield to attack by hydrofluoric acid and this is, of course, the basis of the Berzelius method for opening out rock samples.[4] However, andalusite, topaz and some varieties of tourmaline have been reported to be incompletely attacked.[5] In a modified procedure Koenig[6] decomposed feldspars with hydrofluoric acid alone. Feldspars and other simple silicates have been reported to dissolve in even much milder acids such as fluosilicic[7] or fluoboric which Line and Aradine[8] claim will dissolve a variety of silicates such as feldspars, micas, talc, andalusite, cordierite, *etc.* However, it appears to be doubtful whether such a complex silicate as andalusite dissolves completely in such a weak acid as fluoboric.

The relative insolubility of kyanite and topaz may possibly, therefore, be ascribed to the comparatively compact (and hence impenetrable) structure of these silicates, wherein the Al and Si atoms cannot be approached easily by the acid.

All the Al atoms occupying structural positions in these minerals are 6-co-ordinated and none of them replaces Si atoms.[1] The Al atoms are surrounded by 6 oxygen atoms, two of them being shared with adjacent Al atoms, giving the structure independent SiO_4 groups. The remaining Al atoms are supposed to lie between 6 oxygen atoms in kyanite, 5 in andalusite and 4 in sillimanite.[9] This may indicate that the kyanite structure is more stable than that of andalusite or sillimanite.

This atomic arrangement in refractory silicates is quite different from that in the other simple aluminosilicates such as feldspars, in which 4-co-ordinated Al atoms occupy structural positions similar to those of the Si atoms.[1]

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REFERENCES

1. E. R. Varley, *Sillimanite*, p. 165. Overseas Geological Surveys Mineral Resources Division, London, 1965.
2. E. Reichen and J. J. Fahey, *Bull. U.S. Geol. Surv.*, 1962, 1144-B, B-3.
3. H. F. Steger, *Talanta*, 1976, **23**, 81.
4. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, p. 1034. Wiley, New York, 1953.
5. *Idem, op. cit.*, p. 930.
6. E. W. Koenig, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 314.
7. S. L. Chapman, J. K. Syers and M. L. Jackson, *Soil. Sci.*, 1969, **107**, 348, quoted in ref. 3.
8. W. R. Line and P. W. Aradine, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 60.
9. E. S. Dana, *Mineralogy*, p. 612. Asia Publishing House, Bombay, 1962.

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SHORT COMMUNICATIONS

COMPOSITION OF PHOSPHORIC ACID SOLUTIONS OBTAINED WHEN ORTHOPHOSPHORIC ACID IS USED AS SOLVENT FOR IRON-CONTAINING SAMPLES BY HEATING: THE INFLUENCE OF NITRIC ACID, SULPHURIC ACID AND IRON(III)

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Summary—The dissolution of an iron-containing substance in orthophosphoric acid either alone or mixed with nitric acid or nitric acid–sulphuric acid mixture at 270–280° has been examined, to determine the composition of the solutions which are used for analytical determinations. The possibility of condensation of H_3PO_4 and formation of polyphosphoric acids during the dissolution has been proved. Solutions which may contain pyrophosphoric acid, tripolyphosphoric acid and tetrapolyphosphoric acid have been obtained. The exact composition of these solutions depends on the initial H_3PO_4 concentration, the heating time, and, in some cases, the presence of nitric acid and sulphuric acid. It is assumed that the nitric and sulphuric acid affect the loss of water and therefore the thermal dehydration of the orthophosphoric acid during the dissolution. No qualitative changes in the phosphoric acid composition have been observed in the presence of Fe(III). Formation of Fe(III) polyphosphates is assumed.

Orthophosphoric acid, alone or in an acid mixture, has limited use in analytical practice, for dissolving inorganic substances. The interference of phosphate in some chemical and physicochemical processes may be taken as the main reason for that. Orthophosphoric acid, is, however, an excellent solvent for substances difficult to dissolve.[1] The interference of phosphate may be eliminated by separation of the ions to be determined. The choice of an effective analytical method for separation and determination will be facilitated by knowledge of the state of these ions in the phosphoric acid solution, especially with regard to complex-formation.

In practice, samples of the type mentioned are usually dissolved by heating (for 10–120 min) at 200–400° (*e.g.*, on a sand-bath) with 5–25 ml of conc. orthophosphoric acid and up to 10 ml of sulphuric acid.[1] Cooling and dilution to a convenient volume gives a solution suitable for the analytical determination. The composition of this solution is of prime interest for the analyst. Three questions arise: (1) whether any condensation of the orthophosphoric acid takes place during the dissolution of the sample; (2) which polyphosphoric acids are to be expected in the resulting acidic solution; (3) what is the influence of other acids and the matrix components on the composition of the solutions obtained. They arise because of the dehydration and condensation of orthophosphoric acid heated at temperatures higher than 100°,[2,3] resulting in a complex mixture of polyphosphoric and metaphosphoric acids, which increase in tendency towards, and degree of, complex formation with increasing extent of condensation.

The published work on the mechanism of dehydration and condensation of orthophosphoric acid, on the composition of the resulting mixtures of phosphoric acids and on their hydrolysis, is useful only as a guide, because the experimental conditions used for these investigations are quite different from those used in an analytical determination.

The aim of the present work was to investigate the dissolution of an iron-containing sample in orthophosphoric acid alone and in mixtures with small amounts of nitric acid and sulphuric acid, and to determine the composition of the solutions obtained.

EXPERIMENTAL

Reagents

Phosphoric acid (s.g. = 1.69), nitric acid (s.g. = 1.38), sulphuric acid (s.g. = 1.84), citric acid, 50% w/v solution; sulphosalicylic acid, 10% w/v solution in 7*M* ammonia. Iron(III) solution (20 mg/ml) made by dissolving iron powder in nitric acid.

Acid chromatographic solvent: 25 ml of 20% trichloroacetic acid solution (50 g of trichloroacetic acid and 3.4 ml of 25% ammonia solution in 250 ml of water), 65 ml of acetone, 10 ml of distilled water.[4]

Colour-developing solution: 1 g of ammonium molybdate tetrahydrate, 5 ml of 70% perchloric acid and 1 ml of conc. hydrochloric acid, diluted with distilled water to 100 ml.[5]

All reagents used were analytical grade.

Procedure

Different amounts of 86% orthophosphoric acid, and also 50 ml of 1*M*, 4*M* and 8*M* orthophosphoric acid, alone or mixed with nitric acid (1.5–5 ml) or sulphuric acid (0.1–10 ml) were heated in 100-ml Erlenmeyer flasks on a sand-bath at 270–280° for various times from 10 to 120 min. When the heating was over, water was added to make the volume 50 ml and the solutions were cooled to room temperature.

The phosphoric acid composition was determined by paper chromatography and densitometry.[4,5] One ml of the solution was neutralized with chilled ammonia to the

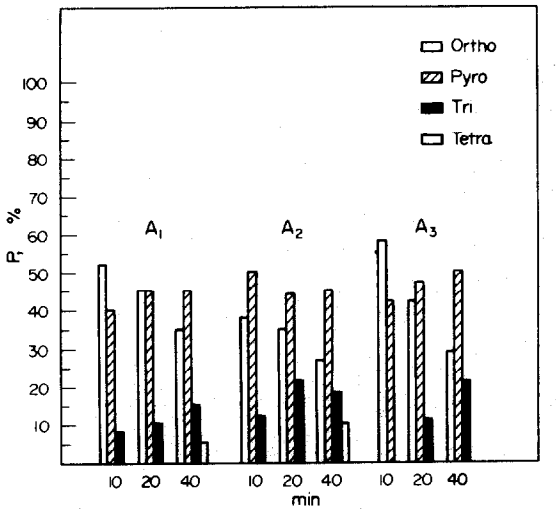


Fig. 1. The composition of the solutions obtained after heating 3.4 ml of 86% H_3PO_4: A_1—H_3PO_4; A_2—H_3PO_4 and 1.5 ml of HNO_3; A_3—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

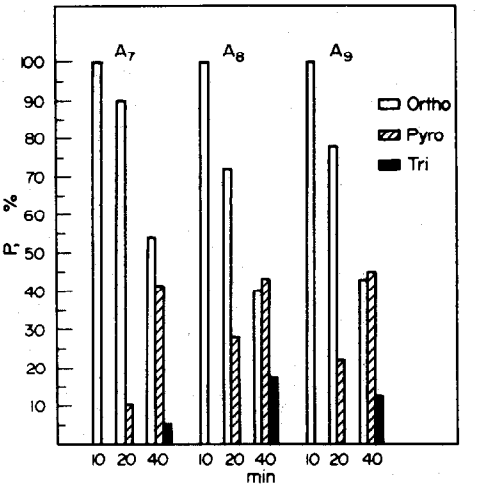


Fig. 3. The composition of the solutions obtained after heating of 37.1 ml of 86% H_3PO_4: A_7—H_3PO_4; A_8—H_3PO_4 and 1.5 ml of HNO_3; A_9—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

phenolphthalein end-point (in order to "fix" the phosphoric acid composition). After dilution (to give a total phosphoric content of 2 mg/ml), 15 μl of the solution were applied to the start-line on Whatman N3 paper, 300 × 40 mm, cut in the form shown in ref. 6, and were developed for 120–150 min at room temperature. Then the paper was dried at 80° for 30 min, sprayed on both sides with the colour-developing reagent and dried for another 5 min. When exposed to ultraviolet light the yellow phosphomolybdate complex was reduced to molybdenum blue. To avoid a blue background colour, the chromatogram was then sprayed with 7*M* ammonia. After drying at 50° for 10–20 min, the colour density of the blue spots was measured (standard deviation 2.3%, relative error 6%). The content of each phosphoric acid species was expressed as a relative percentage.

One g of iron powder was added to 1*M*, 4*M* and 8*M* orthophosphoric acid. The solutions were heated and analysed as described above. To prevent the precipitation of the iron as phosphate and/or hydroxide during neutralization and dilution, 2 ml of 50% w/v citric acid solution were added. It was found experimentally that the citrate ions change neither the phosphoric acid composition nor the positions of the zones on the chromatogram.

Since it was of interest to find the distribution of the iron among the phosphate components, some of the chromatograms were sprayed with a 10% w/v solution of sulphosalicylic acid in 7*M* ammonia. The red spots obtained showed the distribution of the iron.

RESULTS AND DISCUSSION

The results are plotted in Figs. 1–6 as functions of the heating time. As seen, the longer the heating time, the more complex is the composition of the solution. This is to be expected from the data reported for the dehydration of

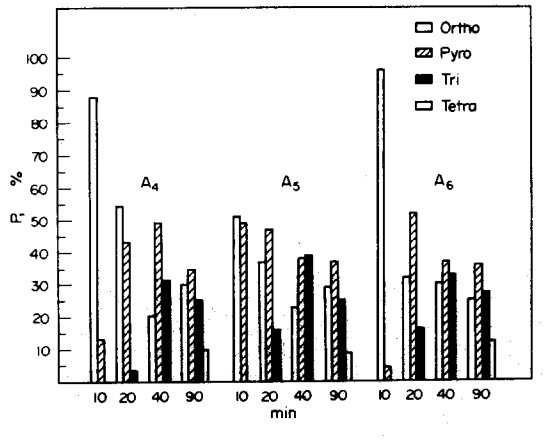


Fig. 2. The composition of the solutions obtained after heating of 13.5 ml of 86% H_3PO_4: A_4—H_3PO_4; A_5—H_3PO_4 and 1.5 ml of HNO_3; A_6—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

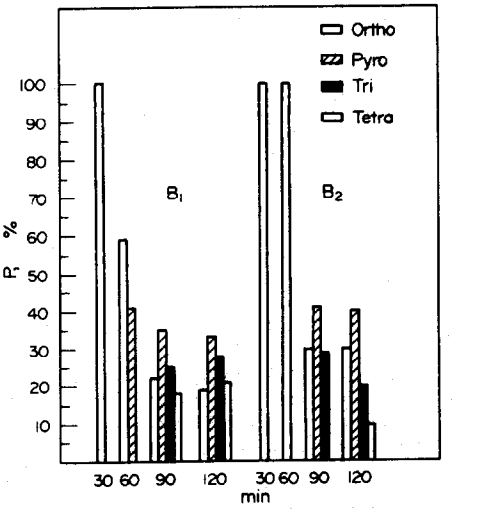


Fig. 4. The composition of the solutions obtained after heating of 50 ml of 1*M* H_3PO_4: B_1—H_3PO_4 and 1.5 ml of HNO_3; B_2—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

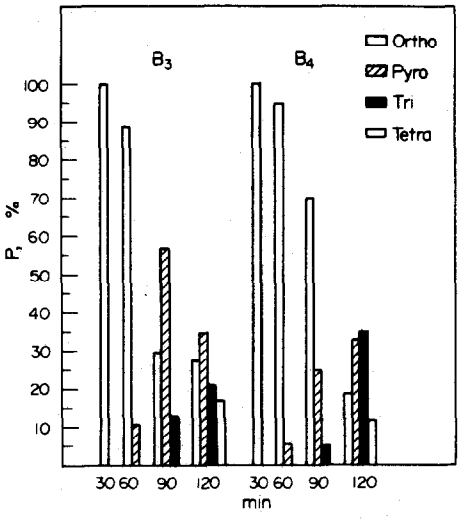


Fig. 5. The composition of the solutions obtained after heating of 50 ml of 4*M* H_3PO_4: B_3—H_3PO_4 and 1.5 ml of HNO_3; B_4—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

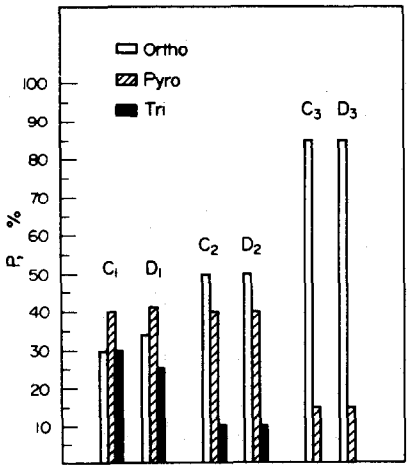


Fig. 7. The composition of the solutions obtained after 90 min heating of 10 ml of 8*M* H_3PO_4: *C*—a solution cooled after being diluted to 50 ml; *D*—a solution not cooled before being diluted to 50 ml. The compositions were determined: C_1 and D_1—60 min after the heating; C_2 and D_2—24 hr after the heating; C_3 and D_3—after storing for a week.

orthophosphoric acid.[2,3] The degree of condensation and the relative proportions of the polyphosphoric acids are dependent on the starting volume of solution, presumably because of the variation in the heating time necessary to reach 100% orthophosphoric acid, which is required for the condensation to begin.[2]

There is a slight increase in the quantity of pyrophosphoric acid when a mixture of orthophosphoric acid and nitric acid is heated, and the initial concentration of nitric acid is relatively high (Figs. 1–3). Easier loss of water and therefore easier concentration of the orthophosphoric acid to 100% during the heating may be assumed to be the reason. As a result, the condensation proceeds further than when nitric acid is not added.

The degree of condensation decreases when sulphuric acid is added to the orthophosphoric–nitric acid mixtures (solutions A_3, A_6 and A_9). The effect of sulphuric acid depends strongly on the heating time: when a solution containing this acid is heated longer, *e.g.*, for 90 min (Fig. 2), the phosphoric acid composition does not depend on the sulphuric acid added, although sulphate is present in the solutions after the heating is over. Practically no changes in the composition are observed when the quantity of sulphuric acid is increased from 0.1 to 1.6 ml and the solutions are heated for 40 min, and only orthophosphoric acid is obtained when the quantity of sulphuric acid is increased to 10 ml. In this last case the formation of pyrophosphoric acid begins after nearly 120 min of heating. We assume that the addition of sulphuric acid probably decreases the degree of condensation by slowing down the loss of water and hence the rate of concentration of the orthophosphoric acid. As a result, a longer heating time is necessary for the condensation to begin.

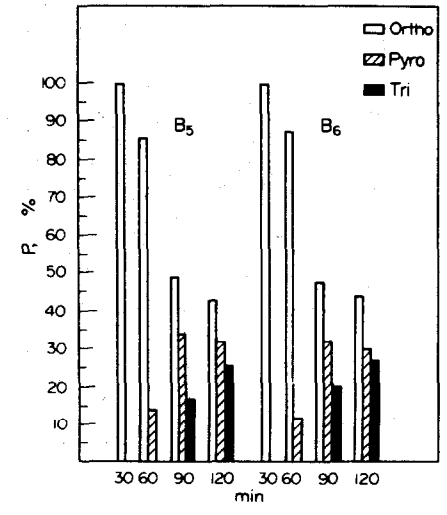


Fig. 6. The composition of the solutions obtained after heating of 50 ml of 8*M* H_3PO_4: B_5—H_3PO_4 and 1.5 ml of HNO_3; B_6—H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4.

From the data on hydrolysis of polyphosphoric acids[2] it is seen that on dissolution and dilution with water, the acids hydrolyse more or less rapidly. The dissolution and dilution result in a rise in the temperature, which in some cases can reach 120–140° (depending on the P_2O_5 content).[2] In that work the solutions obtained after heating were diluted to 50 ml and cooled with running water. We therefore examined the phosphoric acid composition of solutions which had not been thus cooled after the dilution. The results for "quenched" and "unquenched" solutions are compared in Fig. 7, and show that the effect of the post-dilution cooling is not very important; the addition of water and the rise in temperature during the dilution cause only a little hydrolysis of the polyphosphoric acids to orthophosphoric acid.

The general pattern is the same when mixtures of 50 ml of 1*M*, 4*M* and 8*M* orthophosphoric acid with nitric acid, or nitric–sulphuric acid mixture are heated. The longer heating time necessary is to be expected. The nitric acid appears to have no effect. The influence of sulphuric acid is the same as that described above. In general, pyrophosphoric acid is obtained after nearly an hour of heating, and tripolyphosphoric and tetrapolyphosphoric acid after 90–120 min.

The results of the experiments with 4*M* orthophosphoric acid with iron added are presented in Fig. 8. Although only qualitative, they show that in general the presence

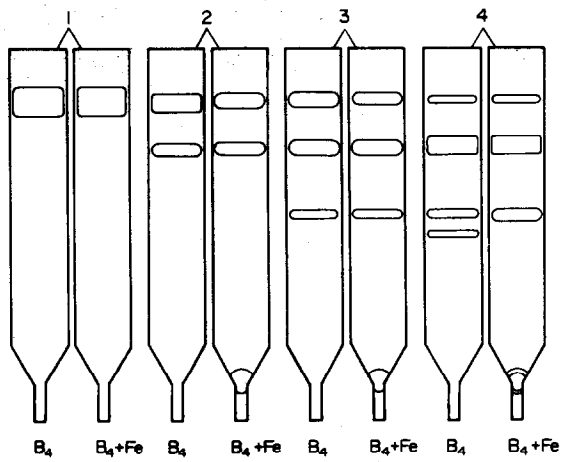


Fig. 8. Qualitative composition of solutions containing 50 ml of 4*M* H_3PO_4, 1.5 ml of HNO_3 and 0.1 ml of H_2SO_4 (B_4) and the same + 1 g of iron. The solutions were heated for: 1—30 min; 2—60 min; 3—90 min; 4—120 min.

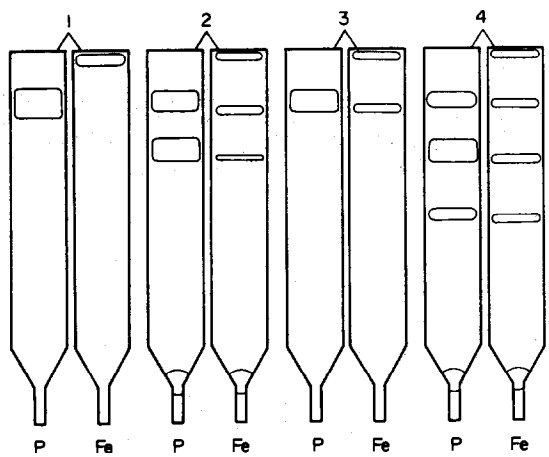


Fig. 9. The distribution of iron(III) between the phosphoric acid components: 1—50 ml of 4*M* KH_2PO_4 + Fe(III) (20 mg/ml); 2—50 ml of 2*M* KH_2PO_4 + 1*M* $K_4P_2O_7$ + Fe(III) (20 mg/ml); 3—50 ml of 8*M* H_3PO_4, 1.5 ml of HNO_3, 0.1 ml of H_2SO_4 + Fe(III) (20 mg/ml), heating time 30 min; 4—the same as 3, heating time 90 min.

of the iron does not affect the course of the condensation. A phosphorus-containing substance is formed which stays at the start, and this contains the bulk of the iron. This fact and the experimental results in Fig. 9 indicate that iron(III)–pyrophosphate and/or iron(III)–polyphosphate complexes are formed. The possibility of their formation and their position on the chromatogram was also assumed by other authors.[7]

CONCLUSION

The results obtained show that when orthophosphoric acid is used as a solvent for inorganic substances at temperatures higher than 100°, polyphosphoric acids can be formed during the heating. They do not hydrolyse fully during subsequent dilution, and are present in the solutions obtained. According to the mechanism of dehydration and condensation of orthophosphoric acid[2] the composition of these solutions depends on the concentration and quantity of the orthophosphoric acid, and also on the temperature and the heating time.[2,3] Under our experimental conditions, solutions are obtained which contain pyrophosphoric acid ($H_4P_2O_7$), tripolyphosphoric acid ($H_5P_3O_{10}$) and tetrapolyphosphoric acid ($H_6P_4O_{13}$) along with the orthophosphoric acid.

The addition of nitric acid may sometimes increase the amount of pyrophosphoric acid. We assume that up to at least 5 ml of nitric acid (in 50 ml of phosphoric acid) will not have any other effect. In the presence of sulphuric acid, the composition of the solutions may vary according to the relative concentration of this acid and the heating time. The higher the sulphuric acid concentration and shorter the heating time, the less is the likelihood of forming polyphosphoric acids. In the presence of iron, polyphosphate complexes are probably formed.

The polyphosphoric acids are good chelating agents for many metal ions.[2] When orthophosphoric acid is used as a medium for analytical separations and determinations, the presence or absence of these acids may introduce some interfering (or conversely some useful) masking effects. That is why the composition of the phosphoric acid solutions must be taken into account. By addition or omission of water or sulphuric acid it is possible to shift the composition of these solutions in the desired direction.

REFERENCES

1. R. Bock, *Aufschlussmethoden der anorganischen und organischen Chemie*, p. 63. Verlag Chemie, Weinheim, 1972.
2. *Gmelin's Handbuch der anorganischen Chemie*, 8 Auflage, Vol. 16, Teil C, Verlag Chemie, Weinheim, 1965.
3. L. N. Schegrov, V. V. Pechkovski and A. S. Eschenko, *Zh. Prikl. Khim.*, 1970, **43**, 990.
4. B. N. Bernhart and W. B. Chess, *Anal. Chem.*, 1959, **31**, 1026.
5. E. Karl-Kroupa, *ibid.*, 1956, **28**, 1091.
6. D. Chobanov and N. Kozev, *Chromatographia*, p. 159. Nauka i iskustvo, Sofia, 1971.
7. T. C. Woodis, *Anal. Chem.*, 1964, **36**, 1682.

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EXTRACTIONAL SPECTROPHOTOMETRIC DETERMINATION OF ANIONIC SURFACTANTS IN WATERS WITH REMACRYLBLAU B AND REMACRYLROT 2BL

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Summary—The cationic dyes Remacrylblau B and Remacrylrot 2BL have been investigated as analytical reagents for the determination of anionic surfactants in waters. Extractional spectrophotometric procedures are proposed. The lowest quantity of anionic surfactant determinable (expressed as lauryl sulphate) when a 1-cm cell is used is 14 μg/l., with a standard deviation of 1 μg/l.

Many cationic dyes have been proposed for the extractional spectrophotometric determination of anionic surfactants in waters: Methylene Blue,[1–4] Methilenegrune,[5] ferroin[6] and Azur A.[7] In the analysis of potable water there are many difficulties because of the strong interference of other anions (Cl^-, NO_3^-, HCO_3^-, PO_4^{3-}) which are present in much higher concentration than the surfactants. These interferences can be decreased by using suitable dyes added in small quantities. We have investigated 19 cationic dyes of the Remacryl, Maxilon, Astrazon, Basacryl and Diorlin types as analytical reagents. Remacrylblau B and Remacrylrot 2BL have been found to be the most suitable. In the present work we propose routine procedures for the extractional spectrophotometric determination of anionic surfactants in waters by use of these two cationic dyes.

EXPERIMENTAL

Preliminary studies were made with a model solution containing (in mg/l.): Cl^- 250, NO_3^- 50, SO_4^{2-} 210, HCO_3^- 500, Ca^{2+} 156, Mg^{2+} 55 and Na^+ 188. Sodium lauryl sulphate was used as a reference standard in terms of which the anionic surfactant concentrations could be expressed.

The solutions of the dyes were prepared by dissolving the compounds (recrystallized from ethanol) in 5 ml of 0.1*N* sulphuric acid and diluting to 100 ml with distilled water. The homogeneity of the dyes was checked by thin-layer chromatography on silica gel G with 11 mobile phases consisting of different combinations of chloroform, propanol, pyridine, acetic acid, ethyl methyl ketone, ethyl acetate, ethanol, methanol, dimethylformamide, n-butanol, benzene and water.[8] Only one spot was obtained for each dye with all the phases.

All the reagents used were *pro analysi* grade. The chloroform was doubly distilled. In all the cases the volume of the water phase was 50 ml and of the organic phase 10 ml.

RESULTS AND DISCUSSION

In acid medium anionic surfactants form blue (with Remacrylblau B) and red (with Remacrylrot 2BL) complexes which can be extracted with chloroform under conditions in which the dye remains in the water phase. The absorption spectra of the chloroform phases are shown in Fig. 1. The absorption maximum of the complex of lauryl sulphate (LS) with Remacrylblau B is at 623 nm and that of the complex with Remacrylrot 2BL at 538 nm. It is found that 0.25 ml of the Remacrylblau B solution (0.50 ml of Remacrylrot 2BL solution) is enough for complete bonding of 40 μg of LS when 0.04% solutions of the dyes are used. These quantities of the dyes were used for all the experimental work covered by Figs. 1 and 2 and Tables 1–6.

Kinetic studies

It was found (Tables 1 and 2) that only 5 min are necessary for extraction of the complexes, and a single extraction gives about 95% recovery. The reaction in the water phase occurs immediately and a delay of 20 min before extraction

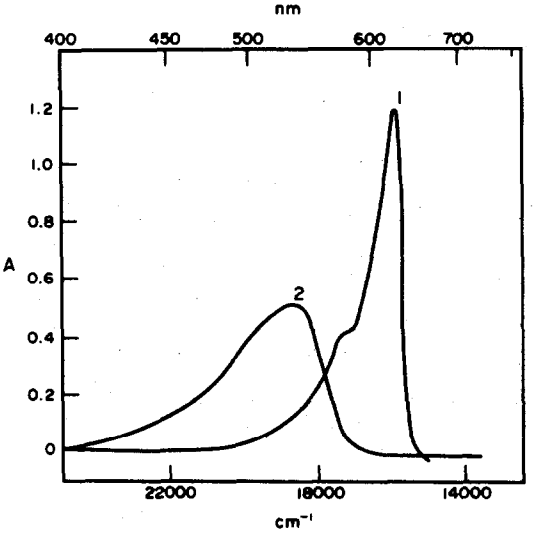


Fig. 1. Absorption spectra of the chloroform extracts of the complexes of lauryl sulphate with Remacrylblau B (1) and Remacrylrot 2BL (2), 30 μg of LS, 1-cm cell, blank–chloroform.

Table 1. Absorbance of the organic phase as a function of the duration of extraction, 1-cm cell, 10 μg of LS, one extraction

	Time, *min*	2	5	10	15	20	25	40
Remacrylblau B, 623 nm		0.296	0.312	0.313	0.312	0.316	0.312	0.312
Remacrylrot 2BL, 538 nm		0.125	0.131	0.130	0.128	0.128	0.128	0.128

Table 2. Absorbance of the organic phase as a function of repetition of the extraction, 1-cm cell

	Remacrylblau B, 623 nm			Remacrylrot 2BL, 538 nm		
LS μg	Extr. 1	Extr. 2	Extr. 3	Extr. 1	Extr. 2	Extr. 3
blank	0.005	0.001	0.000	0.002	0.000	0.000
5	0.153	0.010	0.001	0.066	0.003	0.001
10	0.297	0.015	0.003	0.133	0.005	0.001
20	0.612	0.021	0.003	0.294	0.009	0.001
40	1.220	0.036	0.004	0.565	0.018	0.002

Table 3. Absorbance of the organic phase as a function of the time before extraction, 1-cm cell

	Remacrylblau B, 623 nm				Remacrylrot 2BL, 538 nm			
Time, *min*	0	5	10	20	0	5	10	20
blank	0.003	0.006	0.004	0.006	0.001	0.000	0.001	0.001
model	0.022	0.028	0.022	0.028	0.005	0.005	0.006	0.006
1 μg LS	0.036	0.034	0.034	0.036	0.011	0.011	0.012	0.011
10 μg LS	0.302	0.294	0.300	0.307	0.126	0.124	0.127	0.125
model 1 μg LS	0.054	0.058	0.058	0.054	0.014	0.014	0.015	0.015
model 10 μg LS	0.324	0.322	0.321	0.330	0.126	0.126	0.126	0.128

Table 4. Absorbance of the organic phase as a function of the time after the extraction, 1-cm cell

	Time, *hr*					
LS, μg	0	1	3	5	7	24
Remacrylblau B, 623 nm						
2	0.062	0.062	0.058	0.056	0.055	0.052
5	0.136	0.136	0.125	0.122	0.120	0.120
10	0.289	0.289	0.283	0.272	0.275	0.269
40	1.120	1.130	1.130	1.120	1.130	1.130
Remacrylrot 2BL, 538 nm						
2	0.028	0.028	0.027	0.026	0.026	0.025
5	0.067	0.067	0.066	0.066	0.066	0.066
10	0.132	0.132	0.130	0.130	0.130	0.130
40	0.552	0.552	0.552	0.552	0.553	0.552

is without effect (Table 3). The absorbance of the organic phase can be measured immediately after the extraction and remains constant for an hour (Table 4).

Effect of pH

There is a large pH-range over which the absorbance remains constant (pH 1–4 for Remacrylblau B, 1–5 for Remacrylrot 2BL, Fig. 2). In alkaline medium Remacrylblau B is extracted along with its lauryl sulphate complex. This effect is negligible with Remacrylrot 2BL and the determination can be carried out with it in weakly alkaline medium. This is an important advantage of Remacrylrot 2BL in spite of the lower sensitivity, because waters can be analysed without preliminary treatment.

Calibration curves

The equations of the calibration curves calculated by the least-squares method (from 15 values) for 1-cm cells are:

$A = (0.030 \pm 0.0002)\,C$ (at 623 nm, Remacrylblau B)
$A = (0.013 \pm 0.0002)\,C$ (at 538 nm, Remacrylrot 2BL)

where C is the concentration of lauryl sulphate in μg/50 ml.

The lowest quantity of anionic surfactants (expressed as LS), which can be determined with use of a 1-cm cell and an absorbance of 0.020 is 0.014 mg/l. (with Remacrylblau B) and 0.030 mg/l. (with Remacrylrot 2BL). To estimate the reproducibility, every day for a week we made three

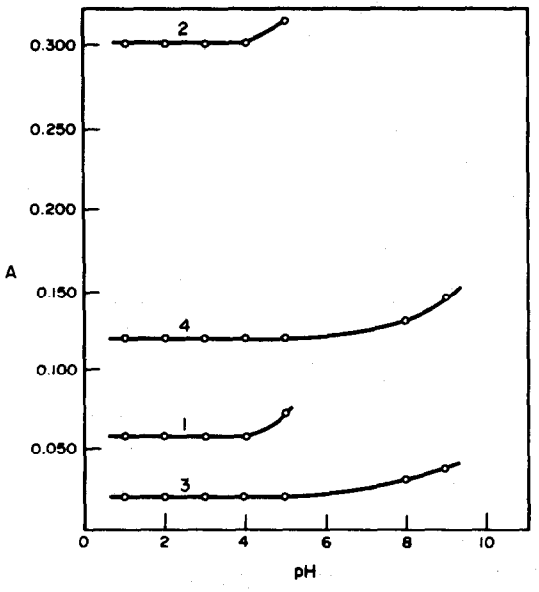


Fig. 2. Absorbance of the organic phase as a function of pH, 1-cm cell, 2 μg of LS (curves 1 and 3) and 10 μg of LS (curves 2 and 4); 1 and 2–Remacrylblau B, 623 nm; 3 and 4–Remacrylrot 2BL, 538 nm.

replicate measurements for each of three samples of the model solution containing different quantities of LS. The calculated standard deviations are given in Table 5.

Interferences

The effect of several ions which are usually present in waters has been studied at two concentrations of LS—0.04 and 0.20 mg/l. The results are shown in Table 6. In our opinion they cannot give a real picture of the individual interferences because they can never represent the effect of only one type of ion, and compensating effects may occur. To estimate the interference at comparatively high concentrations for waters we used a model solution containing (mg/l.): Ca^{2+} 156, Mg^{2+} 55, Na^{+} 283, K^{+} 32, Cl^{-} 250, NO_3^- 100, HCO_3^- 750 and SO_4^{2-} 210. We have found that the degree of interference depends on the quantity of dye used. Thus, with use of 0.25 ml of Remacrylblau B or 0.5 ml of Remacrylrot 2BL (0.04% solutions) for 50 ml of water the absorbance of the model solution is the same as that for 1 μg of LS. The absorbance is only half this when the same volumes of 0.01% solutions are used—enough for the determination of 10 μg of LS. This is suitable for drinking waters. In the surface waters the concentration of the surfactants is higher and the interference when working with 0.04% solutions of the dyes can be neglected.

Table 5. Statistical characteristics

LS, *mg/l.*	Standard deviation, *mg/l.* Remacrylblau B	Remacrylrot 2BL
0.04	0.002	0.003
0.20	0.008	0.005
0.60	0.013	0.016

Procedures

Determination of anionic surfactants in surface waters. Take the sample, containing not more than 30 μg of surfactants, in a separating funnel and dilute it to 50 ml with distilled water. Add 5 ml of 0.1*N* sulphuric acid, 0.25 ml of 0.04% Remacrylblau B solution (or 0.5 ml of Remacrylrot 2BL solution) and 10 ml of chloroform. Shake the mixture for 10 min and transfer the organic phase first into a test-tube and then into the cuvette. Measure the absorbance at 623 nm (for Remacrylblau B) or 538 nm (for Remacrylrot 2BL) against a blank obtained by treating 50 ml of distilled water in the same way as a sample. The calibration curve should cover the range 0–30 μg of lauryl sulphate in 50 ml, which corresponds to 0–0.6 mg/l.

Determination of anionic surfactants in drinking waters. The procedure is the same as for the determination of anionic surfactants in surface waters, but 0.01% solutions of the dyes must be used and the calibration curve covers the range 0–10 μg of lauryl sulphate in 50 ml, which corresponds to 0–0.2 mg/l.

CONCLUSION

To show the applicability of the method the procedures were applied, together with the Methylene Blue[2] and Azur A[7] methods, for analysing several synthetic samples based on the model solution used for the interference studies.

Table 6. Effect of various ions on the determination of LS with Remacrylblau B (623 nm) and Remacrylrot 2BL (538 nm); 1-cm cell

Ion	Concentration *mg/l.*	Absorbance Remacrylblau B LS 0.04 *mg/l.*	LS 0.20 *mg/l.*	Remacrylrot 2BL LS 0.04 *mg/l.*	LS 0.20 *mg/l.*
Only LS	—	0.061	0.297	0.026	0.128
Cl^-	100	0.064	0.297	0.025	0.128
	150	0.069	0.296	0.026	0.128
	250	0.070	0.306	0.028	0.129
NO_3^-	50	0.075	0.298	0.025	0.128
	100	0.080	0.310	0.030	0.128
HCO_3^-	750	0.060	0.300	0.027	0.130
	1000	0.066	0.307	0.028	0.132
PO_4^{3-}	10	0.063	0.298	0.025	0.122
NH_4^+	10	0.064	0.294	0.030	0.129
	20	0.060	0.290	0.031	0.125
Ca^{2+}	250	0.056	0.295	0.025	0.128
Mg^{2+}	200	0.058	0.310	0.025	0.128
Na^+	50	0.066	0.311	0.025	0.126
Fe^{2+}	5	0.060	0.290	0.028	0.128
Fe^{3+}	5	0.058	0.295	0.026	0.128

Table 7.

	LS found *mg/l.*			
	Methylene Blue	Azur A	Remacrylblau B	Remacrylrot 2BL
Model solutions (μg of LS added)				
6	6.9	7.3	7.0	6.5
15	16.1	16.6	16.2	15.4
30	30.8	31.8	31.1	30.4
Natural waters				
1	0.010	0.020	0.016	0.012
2	0.124	0.160	0.134	0.130
3	0.152	0.176	0.160	0.150
4	0.260	0.344	0.256	0.268
5	0.340	0.356	0.348	0.348
6	0.66	0.70	0.69	0.66
7	0.68	0.78	0.70	0.68
8	1.16	1.40	1.27	1.20
9	1.54	1.62	1.54	1.54
10	3.00	3.64	3.60	3.10

and samples of waste and river waters. Some results are shown in Table 7 (means of three results).

The relative standard deviations (%) for the four dyes calculated from 12 results for three quantities of LS added to the model solution are as follows:

	LS 6 μg	LS 15 μg	LS 30 μg
Methylene Blue	7.5	4.2	3.1
Azur A	5.3	2.9	2.3
Remacrylblau B	4.7	2.2	2.2
Remacrylrot 2BL	4.3	3.3	1.3

The Azur A method gives rather higher results than the Methylene Blue method, perhaps because of the higher interferences. The Methylene Blue method requires three extractions followed by three washings of the extracts. The Remacrylblau B and Remacrylrot 2BL methods need only one extraction, without washing, and are simpler samples and faster, with good reproducibility. These methods are suitable for quick integral estimation of the degree of pollution of water with anionic surfactants.

REFERENCES

1. J. Longwell and W. Maniece, *Analyst* 1955, **80**, 167.
2. *Standard Methods for the Examination of Water and Waste-Water*, 12th Ed., p. 296. APHA, AWWA and WPCF, New York, 1965.
3. L. K. Wang, *J. Am. Water Works Assoc.*, 1975, **67**, (1), 19.
4. J. Rodier, *L'Analyse Chimique et Physico-Chimique de l'Eau*, Paris, 1971, p. 326.
5. D. C. Abbot, *Analyst*, 1962, **87**, 286.
6. C. Taylor and B. Fryer, *ibid.*, 1969, **94**, 1125.
6. C. Tonkelaar and G. Bergshoeff, *Water Res.*, 1969, **3**, 31.
8. A. M. Arsov and B. K. Mesrob, *J. Chromatog.*, 1973, **81**, 181.

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DETERMINATION OF WATER IN THIOLS BY KARL FISCHER TITRATION

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Summary—Water in thiol-containing samples may be determined by titration with Karl Fischer reagent after conversion of the thiol into a thioether. Both acrylonitrile and *N*-ethylmaleimide have been found to be suitable reagents.

The determination of water in thiols is complicated by the fact that the Karl Fischer reagent reacts essentially quantitatively with thiols. To obviate this interference, Mitchell and Smith[1] recommend the boron trifluoride catalysed addition of the thiol to the double bond of octene, producing the thioether, or sulphide, which is inert to the Karl Fischer reagent. This method, while satisfactory for materials containing relatively large amounts of water, at least a few tenths of a per cent, is unsatisfactory for determination of small amounts of water in that the reagents themselves usually contribute amounts of water to the system in excess of that contained in the sample.

Table 7.

	LS found *mg/l.*			
	Methylene Blue	Azur A	Remacrylblau B	Remacrylrot 2BL
Model solutions (μg of LS added)				
6	6.9	7.3	7.0	6.5
15	16.1	16.6	16.2	15.4
30	30.8	31.8	31.1	30.4
Natural waters				
1	0.010	0.020	0.016	0.012
2	0.124	0.160	0.134	0.130
3	0.152	0.176	0.160	0.150
4	0.260	0.344	0.256	0.268
5	0.340	0.356	0.348	0.348
6	0.66	0.70	0.69	0.66
7	0.68	0.78	0.70	0.68
8	1.16	1.40	1.27	1.20
9	1.54	1.62	1.54	1.54
10	3.00	3.64	3.60	3.10

and samples of waste and river waters. Some results are shown in Table 7 (means of three results).

The relative standard deviations (%) for the four dyes calculated from 12 results for three quantities of LS added to the model solution are as follows:

	LS 6 μg	LS 15 μg	LS 30 μg
Methylene Blue	7.5	4.2	3.1
Azur A	5.3	2.9	2.3
Remacrylblau B	4.7	2.2	2.2
Remacrylrot 2BL	4.3	3.3	1.3

The Azur A method gives rather higher results than the Methylene Blue method, perhaps because of the higher interferences. The Methylene Blue method requires three extractions followed by three washings of the extracts. The Remacrylblau B and Remacrylrot 2BL methods need only one extraction, without washing, and are simpler samples and faster, with good reproducibility. These methods are suitable for quick integral estimation of the degree of pollution of water with anionic surfactants.

REFERENCES

1. J. Longwell and W. Maniece, *Analyst* 1955, **80**, 167.
2. *Standard Methods for the Examination of Water and Waste-Water*, 12th Ed., p. 296. APHA, AWWA and WPCF, New York, 1965.
3. L. K. Wang, *J. Am. Water Works Assoc.*, 1975, **67**, (1), 19.
4. J. Rodier, *L'Analyse Chimique et Physico-Chimique de l'Eau*, Paris, 1971, p. 326.
5. D. C. Abbot, *Analyst*, 1962, **87**, 286.
6. C. Taylor and B. Fryer, *ibid.*, 1969, **94**, 1125.
6. C. Tonkelaar and G. Bergshoeff, *Water Res.*, 1969, **3**, 31.
8. A. M. Arsov and B. K. Mesrob, *J. Chromatog.*, 1973, **81**, 181.

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DETERMINATION OF WATER IN THIOLS BY KARL FISCHER TITRATION

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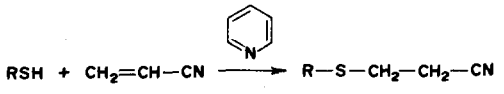
Summary—Water in thiol-containing samples may be determined by titration with Karl Fischer reagent after conversion of the thiol into a thioether. Both acrylonitrile and *N*-ethylmaleimide have been found to be suitable reagents.

The determination of water in thiols is complicated by the fact that the Karl Fischer reagent reacts essentially quantitatively with thiols. To obviate this interference, Mitchell and Smith[1] recommend the boron trifluoride catalysed addition of the thiol to the double bond of octene, producing the thioether, or sulphide, which is inert to the Karl Fischer reagent. This method, while satisfactory for materials containing relatively large amounts of water, at least a few tenths of a per cent, is unsatisfactory for determination of small amounts of water in that the reagents themselves usually contribute amounts of water to the system in excess of that contained in the sample.

For the determination of disulphides in the presence of thiols, Earle[2] utilized the alkali-catalysed addition of the thiol to the double bond of acrylonitrile. In a similar manner, Jaselskis[3] used the same reaction in the determination of mixtures of thiols and sulphides. Both these workers used potassium hydroxide as the alkali. This, of course, is not feasible in the Karl Fischer titration. Obtemperanskaya *et al.*[4] used the addition of thiols to acrylonitrile for the indirect quantitative determination of the thiol group.

It was found by Hurd and Gershbein[5] that some amines are sufficiently basic to catalyse this addition, and as we already incorporate a large excess of pyridine in the Karl Fischer titration system this amine was evaluated as the basic catalyst for the addition of thiols to acrylonitrile. Tests have demonstrated that pyridine is indeed usable, but both the pyridine and the acrylonitrile must be kept completely anhydrous to ensure small "blanks" in the determination.

The reaction of thiols with acrylonitrile may be expressed as:



EXPERIMENTAL

Reagent

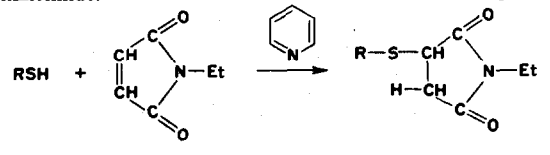
A mixture of 80% acrylonitrile, 10% pyridine, and 10% methanol, v/v, dried and stored over 4-Å molecular sieve in a container suitable for anhydrous dispensing.

Procedure

Weigh, into a dry 25-ml standard flask, sufficient sample to require a large enough volume of Karl Fischer reagent for accurate determination. Add 20 ml of the acrylonitrile–pyridine–methanol reagent and allow to stand for 10 min at room temperature. Quickly transfer the contents of the flask to the pretitrated solvent in the Karl Fischer titration cell. Complete the titration as usual. Perform a "blank" determination on the same quantity of the acrylonitrile–pyridine–methanol reagent.

This procedure has been successful in the determination of water in the range from a few ppm to several per cent in primary thiols and some secondary thiols, but not at all with tertiary thiols or with low molecular-weight mercaptocarboxylic acids.

Another reagent for blocking the thiol group is *N*-ethylmaleimide.[6]



The use and reactions of this reagent are similar to those of acrylonitrile with the exception that *N*-ethylmaleimide will also successfully block the thiol group of low molecular-weight mercaptocarboxylic acids such as mercaptoacetic acid and mercaptopropionic acid.

Procedure

Dissolve 12.5 g of *N*-ethylmaleimide in 50 ml of pyridine which has been predried over 4-Å molecular sieve. Make up to 100 ml with dry methanol. Store under dry nitrogen.

Weigh, into a dry 25-ml volumetric flask, sufficient sample for accurate determination by titration with Karl Fischer reagent. Add 20 ml of the *N*-ethylmaleimide reagent and allow to stand for 10 min at room temperature, then quickly transfer the contents of the flask to the pretitrated solvent in the Karl Fischer titration cell and complete the titration as usual. Perform a "blank" determination on the same quantity of the *N*-ethylmaleimide reagent.

RESULTS

The absolute accuracy is impossible to determine since there is no independent method for determining the water content of the sample substances. However, the precision is very good, the range being ±0.02% absolute for thiol samples containing between 0.2 and several per cent of water. By use of large samples the determination has been carried out at the level of 0.01% water.

Recovery of water was determined by adding known amounts of water to the sample while it was in the titration cell. In all cases the recovery agreed with the added amount plus that found in the sample directly. Thiols that had been rigorously dried over the molecular sieve yielded no titration.

Water has been determined, by both methods, in normal straight-chain thiols from C_2 to C_{12}, and by the *N*-ethylmaleimide procedure in low molecular-weight mercapto acids and their esters.

REFERENCES

1. J. Mitchell Jr. and D. M. Smith *Aquametry*, 2nd Ed., Interscience, New York, 1977.
2. T. E. Earle, *Anal. Chem.*, 1953, **25**, 769.
3. B. Jaselskis, *ibid.*, 1959, **31**, 928.
4. S. I. Obtemperanskaya, A. P. Terent'ev and N. M. Buzlanova, *Vest. Mosk. Univ.* **12**, *Ser. Mat. Mekh. Astron. Fiz. Khim.*, 1957 No. 3.
5. C. D. Hurd and L. L. Gershbein, *J. Am. Chem. Soc.*, 1947, **69**, 2328.
6. E. Friedmann, D. H. Marrian and I. Simon-Ruess, *Brit. J. Pharmacol.*, 1949, **4**, 105.

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SELECTIVE GRAVIMETRIC METHOD FOR DIRECT DETERMINATION OF TIN(IV) WITH *N-o*-TOLUOYL-*N-o*-TOLYLHYDROXYLAMINE AND ITS APPLICATION TO BRASS AND BRONZE ANALYSES

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Summary—A selective gravimetric method for determination of tin(IV) with *N-o*-toluoyl-*N-o*-tolylhydroxylamine by direct weighing as $Sn(C_{15}H_{14}NO_2)_2Cl_2$ is recommended. The metal complex, dried at 110–120°, gives reproducible results. The method is simple, rapid and quantitative over a wide range of acidity (1–4*N* sulphuric acid) and is superior to existing gravimetric methods. The method works satisfactorily for determining tin in brass and bronze.

Determination of tin in its alloys and other samples is a long standing analytical problem because of interferences from other elements. The metastannic acid procedure[1] has a poor conversion factor and is slow, and a small amount of tin always escapes into the filtrate. There is also extensive co-precipitation. The resulting impurities (other than those that give volatile products at the temperature used) can be dealt with by heating the ignited mixed oxides with ammonium iodide but this adds to the analysis time.

The cupferron and phenylarsonic acid procedures[2] also need ignition of the product to stannic oxide and are even less selective. Ryan introduced BPHA[3] (*N*-benzoylphenylhydroxylamine) for the gravimetric estimation of tin by direct weighing as $(Sn(C_{13}H_{10}NO_2)_2Cl_2$ and eliminated the difficulties associated with earlier ignition procedures. The method works well in presence of the elements such as copper, zinc, lead that are found in brass and bronze, but has several disadvantages, *e.g.*, the unusually long cooling period (4 hr), narrow acidity range (0.1–0.6*M* hydrochloric acid), close control of reagent addition because of insolubility of the reagent over the prescribed acidity range. The literature[4] also shows that the BPHA method in the present form is subject to interference from many other cations. Since publication of the BPHA method in 1953, no attempt to use the numerous analogues of BPHA has been reported. This prompted us to try OTOTHA (*N-o*-toluoyl-*o*-tolylhydroxylamine) which has already proved better than BPHA for determination of molybdenum[5] and vanadium.[6] The result is a rapid, selective, direct gravimetric method for determination of tin(IV) over a wide range of acidity (1–4*N* sulphuric acid) with practically none of the disadvantages of earlier methods. The improved selectivity may be attributed to steric hindrance. The method has been successfully used to determine tin in brass and bronze.

EXPERIMENTAL

Reagents

A standard solution of stannic chloride was prepared by dissolving a known weight of pure tin in *aqua regia* and diluting to known volume with doubly distilled water. Stannic sulphate was prepared by dissolving metallic tin in 18*N* sulphuric acid.

Standard solutions of niobium, titanium, zirconium, hafnium and tantalum were prepared as described previously.[5] Soluble salts of other ions were used; all the chemicals were analytical-reagent grade. Tartaric acid was used to prevent hydrolysis of salts such as those of arsenic and bismuth. The reagent (OTOTHA) was prepared as previously described,[5] and used as a 1% solution in glacial acetic acid.

General procedure

The test solution should contain chloride and tin(IV) in at least 4:1 molar ratio. Its volume should be about 150 ml and its acidity 1–4*N* in sulphuric acid. To this solution 1% reagent solution is added dropwise with stirring until no further precipitation occurs and then 5 ml in excess. The mixture is stirred well for 15–20 min and kept in an ice-bath for about 1 hr with occasional stirring. The white precipitate is then filtered off on a weighed sintered-glass crucible (porosity 4), washed with about 100 ml of cold wash solution (reagent solution diluted 100-fold with water) and finally with about 50 ml of cold water. The precipitate is dried at 110–120°C to constant weight. The complex contains 17.72% of tin.

Determination of tin in brass and bronze

A sample weighing 0.5–2 g (depending on the tin content) is accurately weighed and transferred into a 250-ml beaker and treated with 20 ml of *aqua regia*. When the brisk reaction has ceased, the solution is heated gently on a hot-plate for about 5 min, diluted to 100 ml with water, almost neutralized with conc. ammonia solution and then acidified by addition of 30 ml of 50% v/v sulphuric acid. About 500 mg of ascorbic acid are added to reduce any Fe^{3+} to Fe^{2+}, the solution is filtered through Whatman No. 41 filter paper to remove any $PbSO_4$, and the paper is washed with water. Tin is then determined in the filtrate according to the general procedure. Typical results are shown in Table 2.

RESULTS AND DISCUSSION

Effect of acidity

Sulphuric acid medium. Stannic chloride solution gives quantitative precipitation with the reagent in 1–4*N* sulphuric acid media. At higher acidities the reagent is also precipitated[5] and direct determination is not suitable. In the absence of chloride, a white precipitate is obtained in very poor yield, and addition of sodium chloride to the filtrate gives quantitative precipitation of the remainder of the tin. The two precipitates differ in nature and composition.

Hydrochloric acid medium. Precipitation is quantitative up to an acidity of 1*M*; at acidity >2*M* there is no precipitation at all, but addition of a large excess of ammonium sulphate completely precipitates the metal complex (at 2–4*M* acidity) along with an appreciable amount of re-

Table 1. Effect of acidity [a = H_2SO_4; b = HCl; c = HCl + $(NH_4)_2SO_4$]

[Acid], N	Sn taken, *mg*	Sn found, *mg*	
		Direct method	Ignition method
0.5 *a*	10.68	1056	10.7
b	10.68	10.56	10.6
1.0 *a*	10.68	10.69	10.7
b	10.68	10.41	10.4
2.0 *a*	10.68	10.69; 10.72	
b	10.68	no precipitation	
c	21.70		27.7
3.0 *a*	10.68	10.73	
b	10.68	no precipitation	
c	17.30		17.3; 17.2
4.0 *a*	10.68	10.73; 10.81	
b	10.68	no precipitation	
c	21.70		21.8; 21.7
5.0 *a*	8.92	9.16; 9.11	
b	21.70		21.7

Table 2. Alloy analysis

Alloy	Composition, %	Sn found, %
BAS—5G	Cu 67.4, Zn 28.6, Sn 1.09 Pb 2.23, Fe 0.32, P 0.01 Ni 0.33	1.08, 1.09 1.08
BAS—10G	Cu 60.8, Zn 32.0 Sn 0.21, Pb 0.23 Fe 1.56, Mn 1.36 Ni 0.16, Al 3.34	0.21, 0.21 0.22
BAS—10f (Mn-bronze)	Cu 57.2, Zn 35.8, Sn 0.56 Pb 0.16, Fe 1.40, Mn 2.14 Ni 0.49, Al 2.56	0.56, 0.56, 0.57

Table 3. Effect of diverse ions (2–4N H_2SO_4)

Ion added, *mg*	Sn taken, *mg*	Masking agent, *mg*	Sn found, *mg*
Fe^{3+} (100)	11.25	ascorbic acid (500)	11.30
Cr^{3+}, Mn^{2+}, Al^{3+} (50)	11.25	—	11.37
V^{5+} (50)	9.92	ascorbic acid (200)	9.97
Zr^{4+}, Hf^{4+} (50)	13.40	oxalic acid (500)	13.44
As^{5+}, Bi^{3+} (50 each)	13.40	—	13.57
Cu^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} (100)	8.92	—	9.07
Ga^{3+}, Sc^{3+}, Mg^{2+} (50)	13.40	—	13.41
Ce^{4+}, Ce^{3+}, Th^{4+}, La^{3+} (50)	11.25	—	11.42
U^{6+}, Re^{7+} (100)	13.40	—	13.64
Zn^{2+}, Cd^{2+}, Hg^{2+} (100)	13.40	—	13.48
Tartrate (500)	11.25		11.37
Oxalate (500)	13.40		13.41
Thiocyanate (500)	13.40		13.64
F^- (100)	9.72		masks tin completely

agent. Hence direct determination fails, but ignition to stannic oxide shows that precipitation is quantitative. This observation has been utilized in removing interference by niobium, molybdenum, tungsten *etc.* Addition of sulphuric acid in place of ammonium sulphate, however, does not precipitate the tin complex.

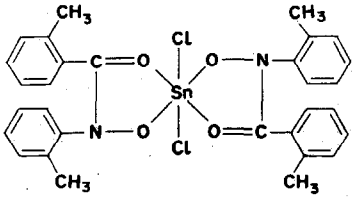
The results are shown in Table 1.

Solvent for reagent

Disubstituted hydroxylamines are usually sparingly soluble in aqueous media, and precipitation of the excess of reagent makes it difficult to be sure when all the metal ion has been precipitated and creates the problem of removal of the reagent from the product. In the case of OTOTHA, however, if a 1% solution of the reagent in glacial acetic acid is diluted 20-fold with water the reagent does not precipitate even after prolonged standing if the pH is <3.[5]

Composition of the complex

Analysis of the dried tin(IV) OTOTHA chelate for tin, chlorine and nitrogen showed that its composition was $Sn(C_{15}H_{14}NO_2)_2Cl_2$. Found: Sn 17.5%, Cl 10.8%, N 4.3%; $Sn(C_{15}H_{14}NO_2)_2Cl_2$ requires Sn 17.72%, Cl 10.60%, N 4.18%. The probable structure is



The complex is white, soluble in all common organic solvents, and insoluble in cold water. The thermolysis curve shows that the complex is thermally stable up to 260°.

Effect of other ions

In 2–4*N* sulphuric acid, a considerable number of cations and anions were found not to interfere (Table 3). In certain cases, masking agents were added. Large amounts of nitrate, sulphate, chloride, alkali and alkaline earth metals give no interference. Only niobium, tantalum, titanium, molybdenum, tungsten and antimony interfere. The interference of niobium, tungsten and molybdenum can easily be eliminated by precipitating them from 2–4*M* hydrochloric acid medium, washing the precipitate with reagent solution, then adjusting the acidity of the filtrate to 4*M* in hydrochloric acid, and adding 40–50 g of ammonium sulphate in portions with stirring. Stirring is continued for another 15–20 min then the mixture is kept in an ice-bath for 1 hr with occasional stirring. The precipitate is filtered off on paper (Whatman No. 41) and washed with 1% reagent solution diluted 20-fold with water. The paper and precipitate are placed in a silica crucible, the paper is charred over a low flame and finally the product is ignited to SnO_2 at 800° in a muffle furnace. Results are shown in Table 3. Any TiO_2 and Ta_2O_5 present are dealt with by removal of SnO_2 by ignition with ammonium iodide, and measurement of the resultant loss in weight.

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REFERENCES

1. I. M. Kolthoff and E. B. Sandell, *Text Book of Quantitative Inorganic Analysis*, 3rd Ed., Macmillan, New York, 1952.
2. J. F. Flagg, *Organic Reagents Used in Gravimetric and Volumetric Analysis*, Interscience, London, 1948.
3. D. E. Ryan and G. D. Lutwick, *Can. J. Chem.*, 1953, **31**, 9.
4. A. K. Majumdar, N-*Benzoylphenylhydroxylamine and its Analogues*, Pergamon, Oxford, 1972.
5. S. Chattopadhyay, B. K. Pal and B. K. Mitra, *Talanta*, 1975, **22**, 431.
6. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 260. Longmans, London, 1960.

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MATRIX EFFECTS ON THE DETERMINATION OF MANGANESE IN GEOLOGICAL MATERIALS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY UNDER DIFFERENT FLAME CONDITIONS

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Summary—Suppression caused by five of the seven matrix elements studied (Si, Al, Fe, Ca and Mg) was observed in the atomic-absorption determination of manganese in geological materials, when synthetic solutions and the recommended oxidizing air–acetylene flame were used. The magnitude of the suppression effects depends on (1) the kind and concentration of the interfering elements, (2) the type of acid medium, and (3) the concentration of manganese to be determined. All interferences noted are removed or alleviated by using a reducing nitrous oxide–acetylene flame. The atomic-absorption method using this flame can be applied to the determination of total and extractable manganese in a wide range of geological materials without interferences. Analyses of six U.S. Geological Survey rock standards for manganese gave results in agreement with the reported values.

Atomic-absorption spectrophotometry has become a popular technique for the determination of trace as well as major elements in geochemical analysis. Recent work in this laboratory on rock coatings, soils, and stream sediments, in which several trace elements associated with iron and manganese oxides were determined by atomic absorption, has prompted an investigation of possible interelement interferences. When the recommended[1,2] oxidizing air–acetylene flame was used, interference in manganese determinations was found to be caused by elements commonly present in geological materials. The general literature on atomic absorption has rarely given adequate coverage to the causes or extent of interferences in manganese determinations. References are often made to the method of standard additions or the preparation of standards in the same matrix as the samples, as means to minimize interferences. Since this may not be feasible for most geochemical work in which speed of analysis is important in order to handle a large number of samples, an alternative approach should be explored.

Attempts were made in this study to demonstrate the kind and degree of interferences in determinations of total and extractable manganese in geological materials, by using synthetic solutions containing various matrix elements, and to determine whether the interference effects can be alleviated or eliminated by using different flame conditions. It was assumed that the residue from sample decomposition involving hydrofluoric acid and other mineral acids for total analysis would be taken up in hydrochloric or nitric acid and diluted to 1% or 10% (v/v) acid concentration.

Solutions obtained from soils and sediments by partial dissolution techniques using ammonium oxalate–oxalic acid[3] or dithionite[4,5] were adjusted to the desired activity. Interelement studies were therefore carried out at two concentration levels of hydrochloric and nitric acid. The flame condition that gave interference-free results was then tried on several U.S. Geological Survey reference rock samples.

EXPERIMENTAL

Apparatus

A Varian AA-6 atomic-absorption spectrophotometer was used for the determination of manganese. The AA-6 was equipped with a simultaneous background corrector, an automic gas-control unit, a variable nebulizer, and a manganese hollow-cathode lamp. The manganese lamp was operated at 5 mA, with a band-width of 0.2 nm and a monochromator setting of 279.5 nm. Flame conditions obtained by varying fuel- and oxidant-flow settings and used in manganese determinations are given in Table 1. All measurements were made by use of the digital absorbance and 3-sec integration modes. The aspiration rate and the position of the burner head were adjusted for optimum sensitivity and minimal noise.

Reagents and standards

All reagents and standards used were prepared from either Baker reagent-grade or "Specpure" chemicals.

Manganese stock and standard solutions. A manganese stock solution (Mn 1000 μg/ml) was prepared by dissolving 1.291 g of MnO in 10 ml of concentrated hydrochloric acid and diluting to 1 litre with water. A tenfold dilution of the stock solution with 1% (v/v) hydrochloric acid gave a 100-μg/ml solution. For manganese working standard solutions (0, 1, 5, 10 and 20 μg/ml) in either 1% or 10% (v/v) hydrochloric acid, 0, 1, 5, 10 and 20 ml of the 100-μg/ml solution were transferred to 100-ml standard flasks and diluted to volume with water and calculated amounts of hydrochloric acid. A similar procedure was followed to prepare manganese working standard solutions in 1% or 10% (v/v) nitric acid, starting with manganese stock solution prepared in nitric acid.

Matrix elements. Stock solutions of the matrix elements aluminium, iron, calcium, magnesium, sodium and potassium (10.0 mg/ml) were prepared from the chloride or nitrate salts and used accordingly in hydrochloric or nitric acid medium for interference studies. Stock solution of silicon was prepared from sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$).

Procedure

Matrix interferences in manganese determinations were studied in 1% and 10% hydrochloric and nitric acid media under the three flame conditions (Table 1). Matrix elements at ranges of concentration which may occur in geological materials were added to manganese standard solutions individually or in combination. The solutions were then aspirated into the spectrophotometer and the manganese absorbance readings on the digital scale (with and without

Table 1. Flame conditions and burner height

	Oxidizing Air–C_2H_2	Oxidizing N_2O–C_2H_2	Reducing N_2O–C_2H_2
Fuel, *l./min*	2	4.5	6
Oxidant, *l./min*	11.5	8.5	8.5
Burner height (*mm* below light-path)	1	1	3

background correction) were compared with those obtained without the matrix elements.

For the determination of manganese in several U.S. Geological Survey rock standards, a 0.20–0.50 g sample (finer than 100-mesh) was weighed into a 100-ml Teflon beaker and wetted with 2 ml of water. Then 5 ml of concentrated nitric acid and 10 ml of 50% hydrofluoric acid were added. The solution was evaporated to dryness on a hot-plate preset at 130°. The acid decomposition step was repeated once more. The residue in the beaker was dissolved with hydrochloric acid and transferred to a 50-ml standard flask with water so that the concentration of hydrochloric acid in the final solution was 10% (v/v). The manganese in the solution was determined with the reducing nitrous oxide–acetylene flame.

RESULTS AND DISCUSSION

A considerable number of manganese determinations were performed, with different flame conditions. Manganese in standard solutions (1–20 μg/ml) was determined in the presence of the seven individual matrix elements (Si, Al, Fe, Ca, Mg, Na and K) individually or in combination. Only those results considered pertinent to the problem of matrix interferences are presented and discussed.

Interferences when an oxidizing air–acetylene flame is used

Table 2 shows the interference caused by five major rock-forming elements at two concentration levels of hydrochloric and nitric acids, when an oxidizing air–acetylene flame is used, as generally recommended. All the interferences are manifested as a suppression of the manganese absorbance (negative sign). Interference was regarded as negligible if the error caused was consistently less than twice the standard deviation obtained in the absence of interfering elements;[3] this is indicated by N in the Table.

The extent of interference depends on (1) the kind and concentration of interfering elements, (2) the type of acid medium, and (3) the concentration of manganese to be determined. In general terms, the order of decreasing interference is Si > Al > Fe > Ca > Mg; HNO_3 > HCl. The interference increases as the manganese concentration decreases.

The degree of interference can readily be visualized if calibration curves obtained with various amounts of interfering elements present are plotted, e.g., Fig. 1. The effect of the type and concentration of interfering elements and acid media is very clear.

The interference effect of silicon is substantial (Fig. 1 and Table 2). The atomic-absorption determination (by use of an oxidizing air–acetylene flame) of manganese extracted by ammonium oxalate–oxalic acid[4] or dithionite[5,6] from soils and sediments in presence of appreciable amounts of co-extracted non-crystalline silica[7–9] would be in error.

The best method to use for determination of manganese in geological materials seems to be to remove silicon by adjust the conditions so that a 1% (v/v) hydrochloric acid and then to take up the residue in hydrochloric acid and adjust the conditions so that a 1% v/v hydrochloric acid medium is used.

These results were obtained without the use of the background corrector. Using it made no difference, however, except in the case of calcium, which deserves some further comments. With the oxidizing air–acetylene flame, the in-

Table 2. Interference* (%) by five major rock-forming elements in manganese determinations at two concentration levels of hydrochloric and nitric acids, when an oxidizing air–C_2H_2 flame is used

Interfering elements, μg/ml		Mn, 1 μg/ml HCl 1%	HCl 10%	HNO_3 1%	HNO_3 10%	Mn, 10 μg/ml HCl 1%	HCl 10%	HNO_3 1%	HNO_3 10%
Si	50	−47	−30	−47	−43	−25	−20	−26	−18
	100	−57	−39	−62	−57	−36	−28	−39	−32
	500	−74	−51	−64	−70	−60	−47	−57	−56
	1000	−70	−50	−65	−70	−58	−47	−55	−65
Al	100	N	−15	−9	−15	N	−11	−7	−6
	500	N	−28	−33	−29	N	−20	−18	−18
	2000	N	−23	−21	−21	N	−15	−14	−14
Fe	100	N	N	N	N	N	N	N	N
	1000	N	−8	−25	−14	N	N	−11	−6
	8000	−23	−19	−43	−21	−8	−9	−20	−15
Ca	100	N	N	N	N	N	N	N	N
	1000	N	N	−21	−22	N	N	−9	−10
	8000	−8	N	−17	−18	−5	N	−23	−23
Mg	100	N	N	N	N	N	N	N	N
	500	N	N	N	−12	N	N	N	N
	2000	N	N	−12	−18	N	N	−6	−7

* Interference = [(Mn absorbance with interferent present/Mn absorbance with interferent absent) − 1] × 100%.
N = insignificant

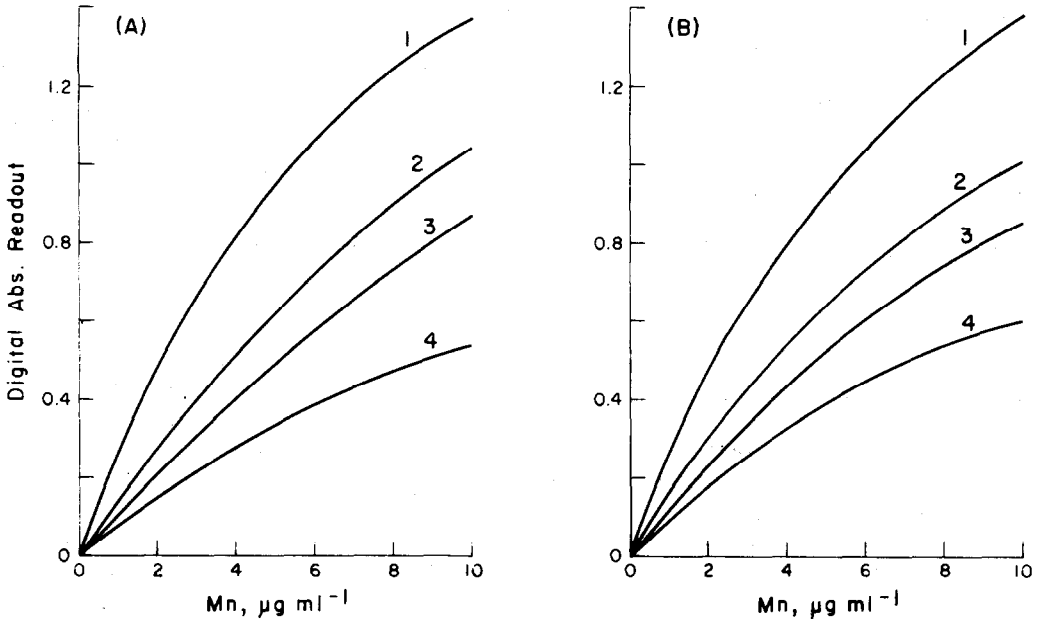


Figure 1. Effect of different amounts of Si on digital manganese absorbance read-out, for the oxidizing air–C_2H_2 flame. (A) In 1% HCl and (B) in 1% HNO_3. [Si]: 1—0 μg/ml, 2—50 μg/ml, 3—100 μg/ml, 4—500 or 1000 μg/ml.

terference of calcium was of two types: an enhancement attributable to light scattering and/or molecular absorption, which can be removed by background correction, and a more pronounced chemical interference, which causes suppression of the manganese signal (see Table 2). As the chemical suppression exceeds the background enhancement, the net result is a suppression. Using a background corrector would increase the suppression.

No interferences were observed from sodium and potassium in concentrations up to 2.0 mg/ml.

It should be emphasized that these results were obtained by adjusting the spectrophotometer to give optimum signal-to-noise ratio. If the operating conditions are varied, *e.g.*, by altering the position of the burner head or changing the ratio of oxidant to fuel in the gas flow, the interference of a given element may be altered. Thus, results different from those presented here may be obtained.

Removal of interferences when a nitrous oxide–acetylene flame is used

All the interferences caused by the five major rock-forming elements in an oxidizing air–acetylene flame can be removed or greatly alleviated by changing to either the reducing or the oxidizing nitrous–oxide acetylene flame (Table 1), whether the interfering elements are present individually at the concentrations shown in Table 2, or in combination at the concentrations expected for geological materials after acid decomposition and dilution to adjust the concentration of manganese to within the range 1–20 μg/ml. The ranges of combined concentrations used (μg/ml) were: Al 400–1600, Fe 250–1000, Ca 200–800, Mg, Na and K 125–500. The reducing nitrous oxide–acetylene flame seems to be better than the oxidizing flame in terms of noise level and sensitivity, especially with the two nitric acid media.

A calibration curve of absorbance *vs.* manganese concentration, for the reducing nitrous oxide–acetylene flame, was linear up to 20 μg/ml. This is an additional advantage over the oxidizing flame, for which the calibration curve tends to level off above 10 μg/ml. Although the effect of the kind and concentration of acid medium on the calibration curve is not significant when a reducing nitrous oxide–acetylene flame is used, the same acid medium should be used for the calibration as for the sample solution.

The reducing nitrous oxide–acetylene flame is less sensitive than the oxidizing air–acetylene flame (0.07 μg/ml for 1% absorption, against 0.02), but this is not a serious problem in the determination of manganese in geological materials, because the crustal abundance of manganese is about 1000 ppm.[10]

Table 3 presents results of replicate analyses of six rock samples for manganese with the reducing nitrous oxide–

Table 3. Replicate determination of manganese in six U.S. Geological Survey rock standards, by use of the reducing nitrous oxide–acetylene flame

		This work		Flanagan's values[5]
Sample	Material	MnO, %	R.S.D.,* %	MnO, %
G-2	Granite	0.03	4.4	0.03–0.06
BSP-1	Granodiorite	0.04	3.9	0.03–0.06
AGV-1	Andesite	0.10	2.5	0.08–0.10
PCC-1	Peridotite	0.11	1.5	0.10–0.14
DTS-1	Dunite	0.12	2.5	0.09–0.17
BCR-1	Basalt	0.17	1.8	0.17–0.21

* Relative standard deviation

acetylene flame. They are in agreement with values reported by Flanagan.[11]

REFERENCES

1. *Analytical Methods for Atomic Absorption Spectrophotometry*, Perkin–Elmer Corporation, 1976.
2. *Analytical Methods for Flame Spectroscopy*, Varian Techtron, 1972.
3. J. Ramírez-Muñoz, *Talanta*, 1973, **20**, 705.
4. A. S. de Endredy, *Clay Minerals*, 1963, **5**, 218.
5. O. P. Mehra and M. L. Jackson, *7th Natl. Conf. on Clays and Clay Minerals*, 1960, 317.
6. D. D. Coffin, *Can. J. Soil. Sci.*, 1963, 1.
7. H. H. Le Riche, *Geoderma*, 1977, **18**, 279.
8. Y. La Flamme, *At. Abs. Newsletter*, 1968, **7**, 101.
9. P. M. Huang, M. K. Wang, M. H. Wu, C. L. Liu and T. S. C. Wang, *Geoderma*, 1977, **18**, 251.
10. H. J. Rosler, *Geochemical Tables*, Elsevier, New York, 1972.
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COLORIMETRIC DETERMINATION OF SOME PHARMACEUTICAL PRIMARY AROMATIC AMINES

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(*Received* 28 *September* 1976. *Revised* 2 *December* 1977. *Accepted* 12 *January* 1978)

Summary—A method for determination of amines of pharmaceutical interest is based on diazotization of the amine and coupling of the product with ethyl acetoacetate.

Photometric methods for the determination of primary aromatic amines are of great interest to the pharmaceutical analyst, owing to their high sensitivity and wide applicability. The most widely used are based on coupling the diazotized amines with phenols and amines.[1–4]

This coupling reaction, being an electrophilic substitution, may also occur with carbanions associated with active hydrogen, such as ethyl acetoacetate. A colorimetric method for the determination of acetoacetic acid has been based on the coloured product given with diazotized 4-nitroaniline.[5,6] In the present work this reaction is applied to the determination of some primary aromatic amines.

EXPERIMENTAL

Reagents

Ethylacetoacetate solution in ethanol, 3% *v/v*.

Standard solutions of the drugs investigated. Stock solutions were prepared in 0.1*M* hydrochloric acid to contain 1 mg of the drug per ml, a few ml of ethanol being added to aid dissolution when necessary. Working standards were prepared by diluting the stock standards with 0.1*M* hydrochloric acid [to give 0.005% for all drugs except for *p*-aminobenzoic acid (0.002%)].

Procedure

Transfer 0.02–0.1 mg of *p*-aminobenzoic acid or 0.05–0.35 mg of *p*-aminosalicylic acid, benzocaine or procaine hydrochloride, or 0.025–0.25 mg of sulphacetamide sodium, or a suitable portion of a pharmaceutical preparation, into a 25-ml standard flask. Add 1 ml of 1*M* hydrochloric acid, followed by 1 ml of 3% sodium nitrite solution, and cool in an ice-bath for 3 min. Add 2 ml of 2% urea solution, shake, and allow to stand for 2 min. Add 1 ml of ethyl acetoacetate solution, and 2 ml of 20% sodium hydroxide solution. Shake well and dilute to volume with water. Measure the absorbance in a 1-cm cell against a reagent blank at the wavelength of maximum absorption (Table 1).

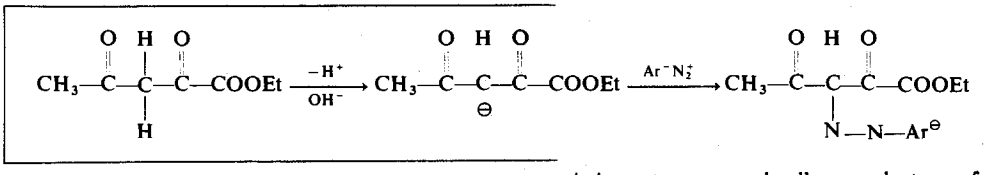
Eye drops and injections. The preparation is suitably diluted with 0.1*M* hydrochloric acid to give a concentration of about 0.005%. A suitable portion of this solution is treated as described above.

Tablets. A 500-mg portion of the powdered tablets is extracted by shaking with five successive 25-ml portions of 1*M* hydrochloric acid, the extracts being filtered into a 250-ml standard flask and diluted to volume with water. An appropriate portion is then treated as above.

Ointment. A suitable weight of ointment is shaken with 20 ml of petroleum ether (40–60°) in a separatory funnel and then extracted with four portions of 5 ml of ethanol plus 10 ml of 1*M* hydrochloric acid. The aqueous extracts are transferred to a 100-ml standard flask and diluted to volume, then the assay is completed as described above.

RESULTS AND DISCUSSION

The amines tested were procaine hydrochloride, *p*-aminobenzoic acid, *p*-aminosalicylic acid, benzocaine and sulphacetamide sodium. The coupling reaction



is instantaneous, and yellow products are formed.

The amine is diazotized with excess of nitrous acid, but the surplus affects the stability of the colour and must be removed with urea, which has no effect on the products. The coupling reagent is then added as its ethanolic or methanolic solution, 1 ml of 3% solution being adequate.

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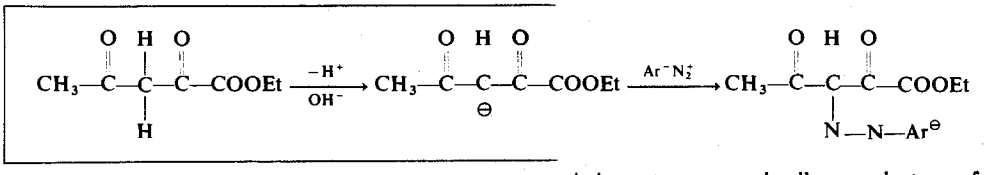
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Table. 1. Absorption maxima and $E^{1\%}_{1cm}$ of the coloured products obtained from the drugs tested

Compound	λ max, nm	$E^{1\%}_{1cm}$
Procaine hydrochloride	365	700
Benzocaine	385	700
Sulphacetamide sodium	405	967
p-Aminobenzoic acid	365	1564
p-Aminosalicylic acid	360	500

Table 2. Determination of the test amines in pharmaceutical preparations*

Pharmaceutical preparation	Recovery: B.P. 1973 method[7]	Recovery: Proposed method
Procaine hydrochloride injection	98.8 ± 0.2	99.0 ± 0.4
Sulphacetamide eye drops	98.1 ± 0.3	97.6 ± 0.7
p-Aminobenzoic acid tablets	98.7 ± 0.4	98.3 ± 0.2
p-Aminosalicylic acid tablets	97.5 ± 0.4	98.7 ± 0.3
Benzocaine ointment	97.2 ± 0.2	97.9 ± 0.2

* Means of 5 experiments ± standard deviation

The concentration of the alkali used in the coupling reaction affects the accuracy. The most intense colour is obtained when the final sodium hydroxide concentration is about 0.4*M*. Lower concentrations give incomplete colour development, and higher ones tend to decrease the stability of the colour.

The absorption maxima are in the region 365–405 nm. The $E^{1\%}_{1cm}$ values are shown in Table 1. Beer's law is obeyed for these amines in the concentration range 0.002–0.015 mg/ml. The sensitivity is about the same as that of the other colorimetric methods.

Common tablet excipients and additives which usually accompany these drugs in pharmaceuticals do not interfere, and the procedure was successfully applied to analysis of pharmaceutical preparations. The recoveries obtained were satisfactory and in reasonable agreement with those obtained by the B.P. 1973 method (Table 2).

REFERENCES

1. F. J. Bandelin and C. R. Kemp, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 470.
2. W. Eissner, *Arch. Pharm.*, 1930, **268**, 322.
3. D. T. Englis and H. A. Fiess, *Ind. Eng. Chem.*, 1944, **36**, 604.
4. A. C. Bratton and E. K. Marshall Jr., *J. Biol. Chem.*, 1939, **128**, 537.
5. M. S. Rosenthal, *ibid.*, 1949, **179**, 1235.
6. T. E. Friedemann and G. E. Haugen, *ibid.*, 1943, **147**, 415.
7. *British Pharmacopoeia*, 1973, p. 446. Pharmaceutical Press, London.

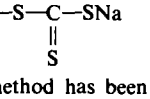
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ALKALIMETRIC DETERMINATION OF MERCAPTANS THROUGH TRITHIOCARBONIC ACID FORMATION

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(*Received* 6 *June* 1977. *Accepted* 18 *November* 1977)

Summary—A simple and rapid alkalimetric method for the determination of mercaptans through trithiocarbonic acid formation is described. The mercaptans are titrated in tert.-butanol in the presence of carbon disulphide with standard aqueous sodium hydroxide, with phenolphthalein as indicator. The –SH group is smoothly, rapidly and quantitatively transformed into the



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6. T. E. Friedemann and G. E. Haugen, *ibid.*, 1943, **147**, 415.
7. *British Pharmacopoeia*, 1973, p. 446. Pharmaceutical Press, London.

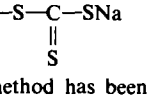
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group under the specified conditions. The method has been extended to the analysis of mercaptan–carboxylic acid and mercaptan–trithiocarbonate mixtures.

Amines react with carbon disulphide in the presence of an alkali to form dithiocarbamates

$$RNH_2 + CS_2 + KOH \longrightarrow RNH{-}C(=S){-}SK + H_2O$$

$$R_2NH + CS_2 + KOH \longrightarrow R_2N{-}C(=S){-}SK + H_2O$$

On the basis of these reactions, Critchfield and Johnson[1] described a method for the determination of primary and secondary amines by reacting them with carbon disulphide in isopropyl alcohol or isopropyl alcohol–pyridine medium and titrating the resulting dithiocarbamic acids with standard sodium hydroxide.

$$RNH_2 + CS_2 \longrightarrow RHN{-}C(=S){-}SH$$

$$R_2NH + CS_2 \longrightarrow R_2N{-}C(=S){-}SH$$

Recently Reddy and Boparai[2] determined amino-acids by treating them with carbon disulphide in water–tert.-butanol mixture and titrating the resulting dithiocarbamic acids with sodium hydroxide.

Mercaptans react with carbon disulphide in the presence of an alkali to form organotrithiocarbonates.[3-5]

$$RSH + CS_2 + NaOH \longrightarrow RS{-}C(=S){-}SNa + H_2O$$

A simple, rapid, accurate and reliable method has been developed for the determination of mercaptans, which consists of treating them with carbon disulphide in tert.-butanol and titrating

$$RSH + CS_2 \longrightarrow RS{-}C(=S){-}SH$$

the resulting trithiocarbonic acids with standard aqueous sodium hydroxide, with phenolphthalein as indicator. A blank titration indicates that no xanthic acid is formed through the reaction of the solvent (tert.-butanol) with carbon disulphide under the experimental conditions (a pink colour develops on addition of the first drop of titrant).

The method has been extended to the analysis, in the same sample solution, of mercaptan–carboxylic acid mixtures. The mixture, in tert.-butanol medium, is first titrated with standard sodium hydroxide solution (phenolphthalein as an indicator) to the appearance of a pink colour. The volume of titrant used corresponds to the amount of carboxylic acid in the sample mixture. The titrated solution is then mixed with carbon disulphide. The solution becomes colourless and is again titrated with standard alkali to the appearance of a yellowish-pink colour. The volume of titrant used in the latter titration corresponds to the amount of mercaptan in the sample mixture.

EXPERIMENTAL

Reagents

Mercaptans. Ethyl, isopropyl, n-propyl, isobutyl, n-butyl, n-amyl and benzyl mercaptans were distilled before use. Thiophenol, *o*-aminothiophenol, thioglycollic acid (80% solution) and thiomalic acid were used as received.

Carboxylic acids. Acetic, propionic and butyric acids were purified according to published procedures.[6]

Carbon disulphide. Used as received.

Tert.-butanol. Distilled before use.

Sodium hydroxide solution, 0.1*N*.

Phenolphthalein solution, 0.5%, in tert.-butanol.

In the determination of mercaptans or mercaptan–carboxylic acid mixtures, the substances were not weighed individually, but a single large sample of each was weighed and dissolved in a known volume of tert.-butanol, and aliquots were taken for analysis.

Procedures

Determination of mercaptans. Aliquots of solutions of each compound in tert.-butanol were taken in conical flasks and diluted to 30–40 ml with the solvent. Each solution was mixed with 1 ml of carbon disulphide and 2 or 3 drops of phenolphthalein indicator. Each solution was titrated at room temperature (~30°) with 0.1*M* aqueous sodium hydroxide. During the titrations the solutions became yellow, indicating the formation of the sodium salts of the trithiocarbonic acids. The colour changed to yellowish-pink at the end-point. The colour change was extremely sharp.

Analysis of mercaptan–carboxylic acid mixtures. Aliquots of the solutions (in tert.-butanol) of the synthetic mixtures with different ratios of mercaptan and carboxylic acid were taken in titration flasks and diluted to 30–40 ml with the solvent. The solutions were mixed with 2 or 3 drops of phenolphthalein indicator and titrated at room temperature (~30°) with 0.1*M* aqueous sodium hydroxide to the appearance of a pink colour. The titrated solutions were mixed with 1 ml of carbon disulphide and the colourless solutions thus obtained were titrated again with the same titrant until the colour changed sharply from yellow to yellowish-pink.

From the volumes of titrant used in the first and the second titrations, the amounts of carboxylic acid and mercaptan respectively were calculated.

Analysis of mercaptan–trithiocarbonate mixtures. The sample was diluted to 30–40 ml with tert.-butanol, mixed with 1 ml of carbon disulphide and titrated with sodium hydroxide as before (phenolphthalein as indicator). The titrated solution was then diluted with 50–60 ml of water, neutralized with 0.1 *M* acetic acid (to the yellow colour), mixed with about 1 g of sodium carbonate and titrated with 0.05 *N* iodine to the blue end-point with amylose as indicator (or to the sharp colour change to deep yellow in the absence of amylose). The second titration gives the sum of the two components, and the trithiocarbonate content is found by difference.

RESULTS AND DISCUSSION

The results recorded in Table 1 show that mercaptans (ethyl, isopropyl, n-propyl, isobutyl, n-butyl, n-amyl and benzyl), thiophenol, *o*-aminothiophenol, thiomalic acid and thioglycollic acid can be successfully determined by converting them into the corresponding organotrithiocarbonic acids through reaction with carbon disulphide in tert.-butanol and titrating the resulting acids with aqueous sodium hydroxide, with phenolphthalein as indicator. The overall standard deviation calculated from the pooled data of all the titrations performed with 8 mg of each mercaptan is 0.037 mg. For 20-mg samples it is 0.051 mg. The end-points were stable for about 5 min.

In the case of thioglycollic acid and thiomalic acid which contain respectively both carboxylic acid and thiol groups, the carboxylic group(s) will be titrated first, followed by titration of the thiol group. This conclusion is based on the following observations. Two colour changes are observed during the titration if carbon disulphide is added at the beginning. The first, from colourless to yellow, corresponds to the neutralization of carboxylic acid group(s), the appearance of the yellow colour being due to formation of the sodium salt of the trithiocarbonic acid produced by the first excess of titrant beyond that needed to neutralize the carboxylic acid group(s). This colour change is not sharp, however. The second colour change, from yellow to yellowish-pink, is due to imposition of the pink colour of the basic form of the

Table 1. Determination of mercaptans

Compound	Amount found,* *mg*	Amount found,† *mg*
Ethyl mercaptan	8.02 (0.042)	20.06 (0.047)
Isopropyl mercaptan	7.96 (0.038)	19.93 (0.055)
n-Propyl mercaptan	8.01 (0.033)	20.05 (0.052)
Isobutyl mercaptan	7.97 (0.036)	20.08 (0.046)
n-Butyl mercaptan	8.00 (0.038)	19.95 (0.048)
n-Amyl mercaptan	8.02 (0.041)	20.04 (0.053)
Benzyl mercaptan	7.99 (0.036)	19.93 (0.049)
Thiophenol	8.01 (0.038)	20.06 (0.055)
o-Aminothiophenol	8.03 (0.034)	20.07 (0.052)
Thiomalic acid	7.99 (0.032)	19.94 (0.047)
Thioglycollic acid	8.02 (0.037)	19.92 (0.053)

* Amount taken, 8 mg; mean of 10 results, standard deviation in brackets.
† Amount taken, 20 mg; mean of 10 results, standard deviation in brackets.

Table 2. Determination of n-propyl mercaptan and n-propionic acid in admixture

n-Propionic acid		n-Propyl mercaptan		Ratio of $CH_3CH_2CH_2SH$: CH_3CH_2COOH
Taken, *mg*	Found, *mg**	Taken, *mg*	Found, *mg**	
7.00	6.98 (0.042)	7.00	7.02 (0.033)	1:1
7.00	7.01 (0.034)	14.00	14.05 (0.049)	2:1
7.00	6.97 (0.037)	21.00	21.08 (0.066)	3:1
7.00	7.02 (0.035)	28.00	28.05 (0.074)	4:1
14.00	13.96 (0.058)	7.00	6.99 (0.041)	1:2
21.00	21.07 (0.071)	7.00	6.98 (0.038)	1:3
28.00	27.92 (0.078)	7.00	7.01 (0.037)	1:4

* Mean of ten determinations, standard deviation in brackets.

indicator on the yellow of the trithiocarbonate. The result was calculated from the total volume of titrant used.

In the case of *o*-aminothiophenol it might be expected that both the amino and the thiol group would react with carbon disulphide in tert.-butanol, to form the corresponding dithiocarbamic and trithiocarbonic acids respectively. It is observed that the thiol group is titrated first, followed by titration of the amino group. However, whereas the reaction corresponding to the titration of the thiol group is rapid and quantitative, that involving the titration of the amino group is too slow to be analytically useful. The end-point corresponding to the titration of the thiol group is marked by a sharp colour change from yellow to a yellowish-pink which remains stable for 1–2 min. The volume of titrant corresponding to this end-point is used to calculate the amount of *o*-aminothiophenol in the sample.

Acetonitrile, dimethylformamide, dioxan, methanol, ethanol and isopropyl alcohol were also tried as solvents, but the transformation of thiol group into the sodium salt of the corresponding trithiocarbonic acid was not quantitative in any of them. Amines interfere owing to the formation of dithiocarbamates.

The proposed method for the determination of mercaptan–carboxylic acid mixtures is simple, accurate and reliable, and has the added advantage that the analysis can be conducted on the same sample solution, thus saving time and effort. The addition of carbon disulphide to the mixture at the beginning of the titration is not recommended, because though the carboxylic acid will still be preferentially titrated, the corresponding end-point will be difficult to detect (a change from colourless to pink is easier to detect than that from colourless to pale yellow). The results in Table 2 show that synthetic mixtures of n-propyl mercaptan and n-propionic acid with ratios in the range from 1:4 to 4:1 can be analysed with an average relative standard deviation of 0.44% for both components. Mixtures of ethyl mercaptan and acetic acid or n-butyl mercaptan and n-butyric acid have been analysed with almost the same accuracy as that for the n-propyl mercaptan and n-propionic acid mixture.

Various mixtures of mercaptan and trithiocarbonate in ratios from 4:1 to 1:4 have been successfully analysed, with a maximum relative standard deviation of 0.5%.

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REFERENCES

1. F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, 1956, **28**, 430.
2. J. V. K. Reddy and K. S. Boparai, *Indian J. Chem.*, 1976, **14A**, 721.
3. E. E. Reid, *Organic Chemistry of Bivalent Sulphur*, Volume IV, p. 178. Chemical Publishing Co., New York, 1962.
4. B. C. Verma and S. Kumar, *Microchem. J.*, in the press.
5. B. C. Verma and V. Sharma, *J. Indian Chem. Soc.*, 1976, **53**, 1190.
6. J. J. Lagowski, *The Chemistry of Non-aqueous Solvents*, pp. 243, 361, 364. Academic Press, New York, 1970.

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PRELIMINARY COMMUNICATION

ULTRAMICRO SOLVENT EXTRACTION AND FLUORIMETRY BASED ON THE FLOW-INJECTION METHOD

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A novel automatic solvent extraction on the microlitre scale has been achieved by means of rapid injection of an aqueous sample into the continuously flowing-stream of a solution of the extracting agent in an organic solvent.

The present communication describes the extraction of potassium into 1,2-dichloroethane by use of macrocyclic compounds. Neutral macrocyclic compounds such as dibenzo-18-crown-6 and naturally occurring polynactin react selectively with potassium ions. The cationic complex formed can be extracted into 1,2-dichloroethane as an ion-pair with anilino-naphthalene sulphonate (ANS).[1] If a flow-injection system is used the ion-pair is extracted during the travel of the injected aqueous plug through the tubing. A fluorimetric detector is used to measure the amount of complex by means of the ANS. ANS is practically non-fluorescent in water but becomes strongly fluorescent when extracted into the organic phase.

Because of this fluorescence characteristic of ANS, it is unnecessary to separate the phases. Potassium at the ppm-level can be easily determined by the proposed extraction-fluorimetry method.

EXPERIMENTAL

Reagents and apparatus

Dibenzo-18-crown-6 (DB18C6) was synthesized from catechol and bis(2-chloroethyl)ether by the method described by Pedersen.[2] The crude DB18C6 was purified by recrystallization several times from benzene. Polynactin, a 1:3:6 mixture of dinactin, trinactin and tetranactin,[3] was kindly supplied by Chugai Pharmaceutical Co. Ltd. It was recrystallized from ethanol before use. Fluorescence intensity measurements were made with a Hitachi 204 spectrofluorophotometer fitted with a 150-W xenon arc lamp. The organic carrier stream was pumped at a rate of 1.23 ml/min with a single-plunger pump (Kyowa Seimitsu KHU-52 type).

Procedure

The experimental arrangement is shown as a flow diagram in Fig. 1 and is based on flow-injection analysis developed by Růžička *et al.*[4,5]

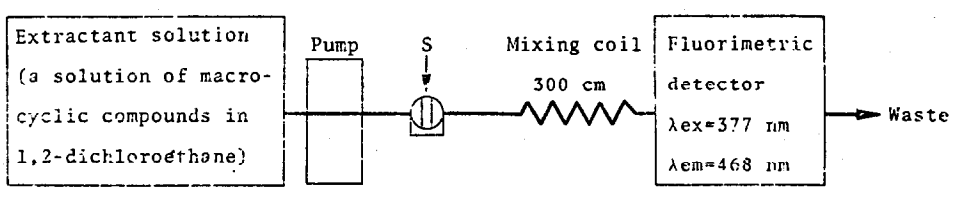


Fig. 1 Flow diagram for solvent extraction fluorimetry

A 10-µl volume of the aqueous sample (S) is injected into the carrier stream of the solution of macrocyclic compounds in 1,2-dichloroethane through a silicone-rubber septum. The injection samples have a potassium concentration of $2 \times 10^{-4} - 1 \times 10^{-3}$ M and an ANS concentration of 1×10^{-3} M. The fluorescence intensity is measured continuously in a flow-through cell at 468 nm with excitation at 377 nm. Teflon tubing (0.5 mm bore) is used as the mixing coil.

RESULTS

The aqueous sample is rapidly injected into the flowing organic stream, which is transported through the mixing coil to the detector. During transport the sample solution is mixed with the carrier stream and the potassium complex is extracted into the organic phase with ANS as counter-ion. The fluorescence intensity is recorded. It is necessary to use a sufficiently long mixing coil to obtain high reproducibility of the peak height. Too long a mixing coil, however, results in a lower peak height owing to the longitudinal dispersion of the complex. In our work, 300 cm of 0.5-mm bore Teflon tubing was found suitable.

DB18C6, which is known as one of the crown ether compounds effective for binding potassium ions, was tried as an extracting agent. Samples of potassium solutions (2, 4, 6, 8 and 10×10^{-4} M) containing the magnesium salt of ANS in 1×10^{-3} M concentration were injected into the carrier stream (0.01M DB18C6 solution in 1,2-dichloroethane). For extractions on the microlitre scale, the response of the detector is satisfactory, as shown in Fig. 2.

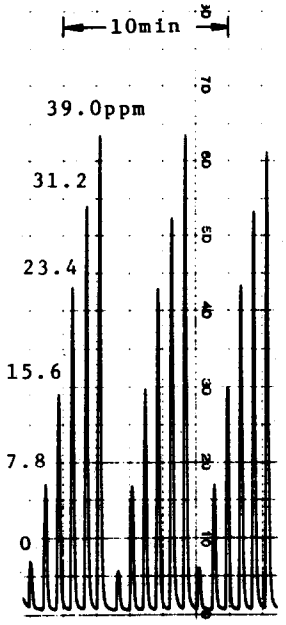


Fig. 2. Fluorescence signal in flow-injection of 10-µl samples of potassium-ANS mixture into a flowing stream of a 0.01M solution of DB18C6 in 1,2-dichloroethane.
Flow-rate : 1.23 ml/min, chart-speed : 0.5 mm/min.

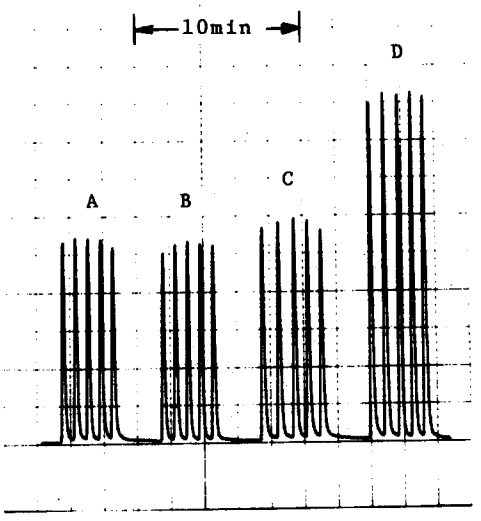


Fig. 3. Influence of sodium content on the peak height for determination of potassium. Volume of sample (4×10^{-4} M K^+) 10 µl. $[Na^+]/[K^+]$ ratios: A: 0, B: 1, C: 10, D: 100.

The selectivity of this extraction system with respect to sodium was examined. As can be seen in Fig. 3, sodium scarcely interferes with the potassium determination provided that molar ratio of sodium to potassium is below 10.

Polynactin was also found useful as binding agent for potassium. A calibration curve is shown in Fig. 4. Although the flow-stream passing through the detector was turbid, the fluorimetric detection gave good reproducibility, as is shown in Fig. 4. The proposed automatic method can be applied to various analyses using fluorogenic chelate extraction.

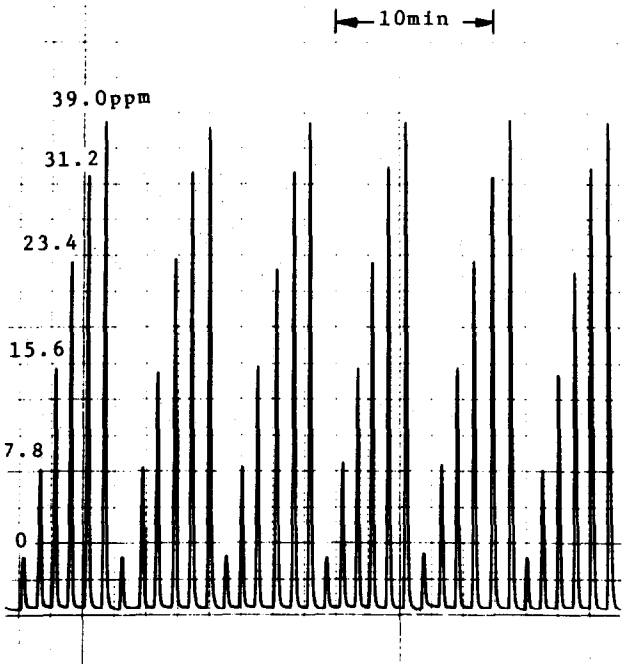


Fig. 4. Reproducibility of automatic solvent extraction of potassium ion with polynactin. The carrier stream is a 10^{-3}M solution of polynactin in 1,2-dichloroethane. The experimental conditions are identical to those of Fig. 2.

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REFERENCES

1. K. Kina, K. Shiraishi and N. Ishibashi, Bunseki Kagaku, 1978, in the press.
2. C.J. Pedersen, J. Am. Chem. Soc., 1976, 86, 7071.
3. K. Suzuki, private communication.
4. J. Růžička and E.H. Hansen, Anal. Chim. Acta, 1975, 78, 145.
5. D. Betteridge and J. Růžička, Talanta, 1976, 23, 409.

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TALANTA MINI-REVIEW*

GAS-CHROMATOGRAPHIC DETERMINATION OF ORGANOMERCURY(II) COMPOUNDS

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Summary—Gas chromatography has proved to be an invaluable technique not only for the identification and determination of organomercury(II) compounds but also for differentiating inorganically bound from organically bound mercury. It also offers a possible route for determining various inorganic species through their conversion into organomercury(II) compounds. These procedures and the chemical and instrumental problems associated with them are reviewed.

The organic chemistry of mercury has been for many years the subject of extensive work resulting in the preparation and characterization of a large number of organomercury(II) compounds, some of which have since found extensive use in agriculture, as fungicides, in the paint, wood-pulp and paper industries to prevent slime formation, and as antiseptics, diuretics and preservatives in pharmaceutical products. These products, together with inorganic and organic mercury compounds from industrial processes, account for most of the mercury released into the biosphere by human activity.

The toxicity of some of these compounds, especially of the alkylmercurials, was noticed several decades ago.[1–3] This knowledge, added to an understanding of the ecological transformation of mercury into potentially more hazardous compounds, has motivated an increased concern in the last ten years about the mercury levels in our environment. Several studies conducted in various parts of the world have shown that mercury can be converted in biological systems into toxic methylmercury(II) compounds and that much of the mercury assimilated into plant and animal tissues is present in this form.[4] The ecological implications of the presence of organomercury compounds, particularly of methyl and phenylmercurials, in the human food chain, were strongly emphasized by Fishbein in a recent review.[5]

It is therefore of considerable importance to be able not only to detect small amounts of mercury but also to identify the compounds containing it, as the toxicity depends very much on the state of chemical combination. Methylmercury compounds, for instance, are far more toxic than their phenylmercury(II) analogues, and the methyl and ethyl forms are also more volatile than the corresponding phenyl derivatives. Thus analytical methods which are capable of distinguishing between inorganic and the various organic forms of mercury are of special interest.

Most of the procedures commonly used for the determination of traces of mercury require its conversion into the metallic or the ionic form, by wet chemical digestion of the sample, followed by determination of the resultant inorganic mercury either as the dithizonate[6] or by flameless atomic-absorption spectrophotometry.[7] Neutron-activation analysis has also been employed to determine nanogram quantities of mercury, but while this technique offers very high specificity and sensitivity, it is expensive and the procedures are rather lengthy.[8] Various other methods making use of several techniques are summarized in recent reviews.[9,10]

Comparatively little work has been done on the identification and determination of individual organomercury(II) compounds. Some methods based on solvent extraction and differential reduction can be used to distinguish inorganically bound from organically bound mercury.[11–17] Organic mercury may be estimated as the difference between total and ionic mercury(II) present.[18–22] Paper and thin-layer chromatography have also been employed, and allow a more specific identification of the compound in which the mercury is present.[23–30]

There has been a growing interest over the last decade in the use of gas–liquid chromatography (GLC) for the detection, identification and determination of organomercury compounds in en-

*For reprints see Publisher's announcement near the end of this issue TALMR 9.

vironmental samples and it is today probably the most widely employed technique for the evaluation of the methylmercury content of biological materials. Very recently the potential utility of some organomercury compounds for the determination at trace level of various inorganic species by means of GLC after their conversion into organic derivatives has been shown.

The present review aims at covering these GLC systems. Before the procedures are surveyed, some practical aspects such as choice of column and detection system will be considered. Owing to peculiarities in the behaviour of organomercury compounds, gas-chromatographic conditions are critical if these substances are to be determined successfully, and if the problems are not taken into consideration, serious errors may arise in the analyses.

GENERAL CONSIDERATIONS

Thermal stability of the compounds

Though thermogravimetric studies of some phenylmercury(II) compounds have provided no evidence of decomposition during volatilization,[31] and it might therefore be assumed that the corresponding alkyl derivatives, which are more volatile, might behave similarly, the GLC determination of a number of organomercurials of the general form RHgX has proved to be difficult. Thermal degradation and exchange reactions of several organomercury(II) salts in the gas chromatograph have been reported, with dialkyl or diarylmercury as the major product.[31-35] Gas-chromatographic analyses of various methyl, ethyl and phenylmercury(II) salts, including acetates, hydroxides, benzoates, borates, chlorides, bromides, iodides and sulphides, in diverse organic solvents, have indicated in some instances a high degree of conversion into the corresponding dimethyl, diethyl and diphenylmercury compounds; the halide salts were also produced to an extent related to the halide content of the sample.[33-35] These results are in agreement with those obtained by other approaches, such as the action of various reducing agents, pyrolysis and electrochemical reduction.[2,36,37] In all cases the organomercurial salts yielded predominantly the bis-organomercurial, mercury and/or the corresponding salt HgX_2, as decomposition products.

The mechanistic pathways by which these compounds react have been discussed by Dessy and Kitching.[38] They propose that in the overall reaction

$$2RHgX \rightleftharpoons R_2Hg + HgX_2 \quad \text{(and/or Hg)}$$

the following pathways seem likely

$$RHgX \rightleftharpoons RHg^{\cdot} + X^{\cdot} \qquad \text{slow}$$

$$RHgX + RHg^{\cdot} \rightleftharpoons RHgR + HgX^{\cdot} \qquad \text{fast}$$

$$HgX^{\cdot} + X^{\cdot} \rightleftharpoons X_2Hg \qquad \text{fast}$$

and perhaps involve a binuclear RHgHgR species.

In a recent paper Dressmann[34] proposed the following possible pathways for the degradation reaction:

$$RHgX \rightleftharpoons RHg^{\cdot} + X^{\cdot} \qquad \text{initiating step}$$

$$X^{\cdot} + RHgX \rightleftharpoons X_2Hg + R^{\cdot} \qquad \text{propagating step}$$

$$R^{\cdot} + RHg^{\cdot} \rightleftharpoons RHgR \qquad \text{terminating step}$$

where X is benzoate and R a phenyl group.

According to Dressmann the free-radical reaction takes place in the heated injection block, which supplies the energy required to break the Hg–X bond, under ideal high-temperature gas-phase conditions.

Although electrolytic and polarographic studies have indicated that $RHg^{\cdot}$ radicals may be intermediates in such reactions in solution,[37,38] other radicals may be generated when decomposition occurs in the gas phase.

The degradation of RHgX compounds may also be predicted from their properties, which primarily depend on the tendency of the group X to form an ionic (fluoride, nitrate, sulphate, *etc.*) or a covalent bond (chloride, bromide, iodide, sulphide, *etc.*); the first type of compound will decompose more easily than the second and this will be reflected in the rates of decomposition of compounds of the two classes. Thus for halomercury derivatives the rate constants for the decomposition reactions in various solvents increase on going from chloride through bromide to iodide, suggesting that the Hg–X bond weakens in the sequence RHgCl > RHgBr > RHgI.[39] This also explains the exchange or displacement type of reaction, by nucleophilic attack, of the type

$$RHgX + A^{-} \rightleftharpoons RHgA + X^{-}$$

where X is an anion or group and A a halide, usually chloride. This type of reaction has been reported to occur either in the chromatograph or before sample injection.[32-35] Though the media are different, these reactions are similar to those taking place in acidic aqueous solution, such as displacement of acetate, nitrate or hydroxide by a halide (chloride, bromide or iodide). Thus the weaker mercury–oxygen bond is replaced by the stronger mercury–halide bond.

Impurities or metallic surfaces appear to act as catalysts for these reactions and thus to be responsible for these degradation and replacement phenomena during GLC analyses and in fact they are more noticeable when metallic injection ports and stainless-steel columns are employed. Some compounds which were stable when injected directly into glass columns were found to decompose to some extent when even a very short stainless-steel lining was fitted in the injection port. Peaks in the chromatograms were identified as corresponding to RHgX (where X is a halide) and R_2Hg, and a dark brown deposit was formed in the glass-wool plug on top of the column. The operating conditions in the two series of experiments were otherwise kept strictly unchanged.[40]

From these considerations it is clear that attention must be paid not just to normal operating conditions,

but also to the choice of apparatus, particularly the use of glass columns rather than metal ones. Prior conversion of all organomercury salts into their corresponding chlorides may also be helpful in some cases, but not when mixtures of compounds with the same R group have to be analysed.

Columns

Adsorption and displacement phenomena resulting in severe tailing have been reported, and it has been found necessary to condition columns for a long time before use and then to analyse replicate samples to obtain reproducible peaks. The nature of the column packing accounts for these effects. The solid supports most usually employed are specially treated diatomaceous earths, which give a high-quality support with a moderate degree of non-linear adsorption; even so, adsorption on the support can be a problem, particularly at low levels. Porous polymers and PTFE materials are occasionally utilized.

Several liquid phases on various supports have been evaluated for the separation of organomercury(II) compounds. A number of difficulties were encountered when high molecular-weight hydrocarbon greases (*e.g.*, Apiezon L), silicone gums and oils (*e.g.*, SE-30, QF-1, OV-17) and non-polar or moderately polar compounds were used. The most satisfactory in terms of peak shape and number of plates were the more polar polyesters PEGS [poly(ethyleneglycol) succinate], HI-EFF-4BP (butanediol succinate), DEGA and DEGS (diethyleneglycol adipate and succinate) and the poly(ethyleneglycol) Carbowax 20M. The amount of liquid phase used on the column depends mainly on the compounds to be chromatographed; it varies over a wide range, *e.g.*, 3–20% w/w, for the alkyl derivatives and 1–5% w/w for the aryl derivatives. The optimum liquid-phase loading also depends on the column length, which usually lies in the range 0.5–2.0 m. Borosilicate glass tubing should be used for the columns. The column temperature is usually in the range 140–190°, depending on the nature of the compounds to be chromatographed, with injection and detection ports being held at somewhat higher temperatures.

Detectors

Electron-capture detectors are the most widely used as they are very sensitive for halogenated compounds, being able to detect as little as 10^{-12} g of methylmercury chloride.[41] However, as the sensitivity towards the dialkyl and diarylmercurials is relatively low, these should be converted into the halide salts before injection, when very small amounts are to be determined. The high sensitivity of the electron-capture detector makes careful clean-up of all reagents, solvents, *etc.*, essential if interferences are to be avoided. Some of these problems can be overcome by using a microwave emission detector, first described by Bache and Lisk,[42] or a cold-vapour mercury detector,[43–46] both of which offer very high selectivity and simplify the analytical procedure considerably. A properly adjusted microwave emission device can show an absolute sensitivity ranging from 0.5 to 10 pg for many organomercury derivatives, including dialkyl compounds.[47] The cold-vapour mercury detector has a sensitivity of 20 and 10 pg for dimethylmercury and methylmercury chloride.

Thermal-conductivity, flame-ionization and mass-spectrometric detectors have also been applied in both survey and actual analytical studies. Flame-ionization detection limits of about 2 ng for phenylmercury halides have been achieved, these limits being essentially those of the flame-ionization detector itself. Methylmercury(II) chloride has been identified at the pg level by a combined gas chromatograph–mass spectrometer system.

It can be concluded that glass columns, high-quality supports and liquid phases and on-column injection, coupled with electron-capture detection form the best practical combination for the successful gas-chromatographic determination of organomercury(II) halides at the ultratrace level. An all-glass flow system and direct on-column injection technique with microwave-emission or mass-spectrometric detection might be nearer the ideal combination.

METHODS FOR THE DETERMINATION OF ORGANOMERCURIALS

A number of alkyl and arylmercury(II) compounds of the general form RHgX exhibit good thermal stability, while the largely covalent substances such as the halides and bis-organomercurials are even more stable. They are sufficiently volatile to be sublimed under reduced pressure, have sharp melting points and are soluble in a range of organic solvents. These properties suggest that gas–liquid chromatography might be a good technique for separating and determining the various compounds alone or in mixtures.

GLC was probably first used for the analysis of organomercury(II) compounds by Brodersen and Schlenker[48] who in 1961 separated various alkylmercury(II) compounds, dissolved in tetrahydrofuran, at 190–220° on silicone grease with hydrogen as carrier gas. A few years later some Japanese workers employed this technique for the microdetermination of various alkyl and arylmercury(II) salts such as the sulphates, halides, borates, phosphates and acetates, using both flame-ionization and electron-capture detection.[49]

Its widespread acceptance, however, particularly for determining toxic organomercury(II) substances, is due to the successful attempts of some Japanese and Scandinavian workers who independently, at about the same time and for the same reason, *i.e.*, following serious mercury toxicity problems in their respective countries, applied the technique to the evaluation of methylmercury in biological samples such as hair and fish.[29,50] Separation of methyl, ethyl and

butylmercury(II) chlorides was also achieved. Methylmercury in fish was determined after acidification of the homogenized sample with hydrochloric acid in order to form the corresponding chloride salt, which was extracted into benzene and then back-extracted into an aqueous solution of cysteine. This solution was in turn acidified with hydrochloric acid and extracted with benzene. The benzene extract was reduced to one tenth of the initial volume and an aliquot was injected into the chromatograph. Recoveries of methylmercury added to samples of foods and separated by this procedure were better than 90%. With electron-capture detection about 0.07–4 ppm of mercury as methylmercury was detected in the samples of fish. Whilst methylmercury in hair can be determined without purification of the extracts, the given method for fish outlines the clean-up procedure which, with some modifications, is nowadays most widely used.

Redistribution equilibria of some organomercurials were also studied by means of this technique, equilibrium constants for the exchange of organic groups in various systems being calculated.[51] The chromatographic evaluation of numbers of theoretical plates and separation factors for several alkylmercurials in the temperature range 120–200° for a number of column packings has been reported. The compounds were generally eluted in order of increasing carbon number of the alkyl group but retention volumes were not markedly influenced by a change in the halogen atom.[52]

The combined gas–liquid and thin-layer chromatographic method first proposed by Westöo[29] was later modified and improved by him in order to apply it to a wider range of materials. Thiol groups present in biological substances prevented the formation of the water-soluble methylmercury(II) hydroxide, and this difficulty was solved by adding an excess of mercury(II) ions. The methylmercury(II) compound was also extracted into the aqueous phase with a 1% aqueous solution of cysteine acetate. When modified by precipitation of proteins with molybdic acid at the first extraction and increase in the cysteine acetate concentration from 1 to 10%, the method could be utilized to determine methylmercury(II) in a wide variety of biological and environmental samples.[53–55]

Isolation of organic mercury(II) after acidification with 1*M* hydrochloric acid, three extractions into benzene, purification by back-extraction into an aqueous solution of glutathione and re-extraction into benzene which was then concentrated to a small volume, led to a successful determination of ultratrace amounts of alkyl and arylmercurials.[41] Detection limits for methylmercury(II) and phenylmercury(II) chloride with electron-capture detection were 1 and 10 pg respectively. Several columns and column-packing materials were tried with various organic mercury(II) compounds. Carbon numbers and retention volumes were measured in two columns and the plot of the log of retention volume against carbon number of the alkyl radical gave good linearity for carbon number 1, 3, 4 and 5. The method was used for the determination of these compounds in rat liver, fish, vegetables, rice and human hair samples. The need for using glass columns, on-column injection and a long conditioning time was also stressed.[56]

Nishi and Horimoto studied the gas-chromatographic behaviour of alkylmercury(II) and dialkylmercury(II) compounds at low levels on stainless-steel and glass columns at 140–150°.[32] For sample sizes above 10^{-5} g various compounds were fairly well separated, showing characteristic retention times and no evidence of decomposition. However, when the sample size was decreased below 10^{-8} g and stainless-steel columns were used, the compounds decomposed completely, with all those having the same R group showing the same retention time regardless of differences in the X group (where X = 1 chloride, bromide, iodide, acetate, sulphate, hydroxide and dithizonate). These phenomena were not observed when glass columns were used. The same authors reported a method for determining trace amounts of organomercurials in aqueous solutions. Methyl, ethyl and phenylmercury(II) chloride at concentrations >0.4 μg/l. were extracted twice with benzene, back-extracted into an aqueous solution of cysteine and again extracted into benzene after acidification with hydrochloric acid. The concentrations of cysteine and hydrochloric acid affected the efficiency of extraction, which under optimal conditions was 97.6%. With this technique levels of 0.41 μg/l. for methylmercury chloride, 0.43 μg/l. for ethylmercury chloride and 0.86 μg/l. for phenylmercury chloride were concentrated by factors of up to 50 and successfully determined by gas chromatography with electron-capture detection.[57]

Gas–liquid and thin-layer chromatographic characteristics of a number of organomercury(II) fungicides as their dithizonates were studied by Tatton and Wagstaffe.[30] In this study several liquid phases were tried, the most satisfactory being poly(ethyleneglycol) succinate; the retention volumes of the dithizonates under investigation were calculated; about 0.05 ng of each of these species could be detected by electron-capture. Owing to the poor recovery of alkoxyalkylmercury(II) compounds a modification of the Westöo extraction procedure was required. The method was applied to the extraction, identification and determination of these compounds in various vegetables and fruits. Biological methylation of mercury(II) in aquatic organisms has been investigated by means of electron-capture gas chromatography of methylmercury(II) halide.[58] Bottom sediments and dead fish were able to methylate inorganic mercury(II) over periods of time ranging from 4 days up to 7 weeks. Errors arose mainly from too low an acid concentration being used during hydrolysis; elemental sulphur and inorganic mercury(II) salts were also reported to interfere in the gas-chromatographic determination of methylmercury(II) compounds; mass spectrometric detection at *m/e* =

215 corresponding to the methylmercury(II) ion was used.[59]

A combined gas chromatograph–mass spectrometer system was employed to identify and determine methylmercury(II) compounds in fish samples containing 0.15–3.2 ppm of mercury(II). The results, when compared with those obtained with a standard gas chromatograph–electron-capture detection system and by neutron-activation analysis, gave agreement within ±10%. During this study it was found that exchange conversion of methylmercury(II) iodide into methylmercury(II) chloride does occur but neither destruction of these compounds nor their transformation into other molecules was observed.[33]

The presence of sulphide, thiosulphate or organic thio-groups in the sample renders difficult the determination of methylmercury(II) and other mercurials of the RHgX type. To overcome these interferences copper(II) chloride can be added to sample solutions containing sulphide. The compound is then extracted in the usual way but with either glutathione or cysteine–sodium sulphate solution as stripping reagent.[60,61] The interfering species can, however, be satisfactorily utilized for identification of organomercurials by means of a gas-chromatographic peak-subtraction technique in which the peaks corresponding to a given compound are subtracted from the chromatogram of the sample after comparison with the chromatograms obtained from samples which have first been treated with an aqueous solution of an organic thio-compound, an inorganic sulphide, or thiosulphate and metal powder. This may be achieved very simply by packing a small precolumn with the reagent and switching it in as required. This method serves also to remind us of the need to eliminate metallic surfaces in the flow system so as to avoid decomposition.[62] Samples of freshwater and marine fish have been analysed for methylmercury by the Westöo procedure:[63] the presence of the compounds was confirmed by thin-layer chromatography and high-resolution mass spectrometry. Recovery of methylmercury chloride at relatively high levels was 82%, with a precision of ±10%.

Newsome modified the Westöo procedure by incorporating a filtration step and using hydrobromic rather than hydrochloric acid so as to enhance the partition ratio.[64] Overall recoveries of 94 ±6% and 98 ±6% from two classes of fish samples and a mean recovery above 95% from some cereal and grain products were achieved. In the last case interfering species were eliminated by column chromatography and extraction with cysteine acetate solution; the method is useful in the 0.01–0.9 ppm range. The determination of alkylmercury(II) compounds by this technique was also studied by Ross and Moore.[65] Extraction systems, types of columns and different detectors were evaluated.

Bache and Lisk[42] developed a very selective gas-chromatographic method for organomercury(II) compounds, using emission spectrometry in a microwave inert-gas plasma as the detection system. The selectivity ratio for methylmercury(II) chloride relative to eicosane was at least 10^4 and the signal response was linear, when peak heights were measured, from 10^{-10} g to about 10^{-7} g of injected methylmercury chloride. When applied to the determination of this compound in some fish samples it gave a limit of detection of about 0.05–0.1 ppm, depending on the operating conditions.

Methylmercury(II) can be extracted as the bromide into toluene, then stripped as the thiosulphate complex into aqueous ethanol and finally re-extracted as methylmercury(II) iodide into benzene and determined by gas chromatography with electron-capture detection. Recoveries of 99 ±5% of the added methylmercury(II) have been reported for this method, and the peak-height is proportional to the amount of methylmercury over the range 10^{-11} – 2×10^{-9} g. The species detected is the iodide, and the columns are kept conditioned by the intermittent injection of aqueous 3*M* potassium iodide, which helps to prevent breakdown of the mercury compounds. As the electron-capture detector is easily contaminated, its design was modified by introduction of a concentric tube device; the performance was not affected and cleaning was facilitated.[66] The Westöo procedure for determining methylmercury(II) as its chloride salt has been tested over a one-year period, being used for the estimation of this substance in fish. During the testing period good performance characteristics, with a limit of detection of 0.02 ppm, were obtained.[67] Homogenized fish tissue was digested with either papaine or pepsin at 37° and the methylmercury(II) was continuously extracted into benzene in a reflux extractor. Purification was by stripping into aqueous cysteine acetate solution in 2–3*M* hydrochloric acid. Average recoveries were about 93% with a relative standard deviation smaller than 1.7%.[68]

A study of the behaviour of methylmercury compounds in aqueous solution indicated that in acidic media dimethylmercury(II) dissociated into monomethylmercury(II). Both species were determined after solvent extraction.[69] However, it was found that at pH 8.2 this hydrolysis did not occur, and that both monomethylmercury(II) and dimethylmercury could be determined. Monomethylmercury is kept in solution as the water-soluble cysteine complex, while dimethylmercury is extracted into toluene, converted into monomethylmercury(II) bromide and estimated by gas chromatography. The determination of different alkylmercury compounds by GLC has been the subject of an interlaboratory comparison. Over 80% of the analyses were within ±10% of the mean value and all of them were within ±20%.[70] A microwave discharge detector has been employed in the gas-chromatographic determination of dimethylmercury for an evaluation of its selectivity with respect to different compounds (selectivity ratio 514 relative to carbon tetrachloride, 4.0×10^4 relative to triethyl phosphite). The sensitivity for dimethylmercury was

3×10^{-10} g and the relative standard deviation 6.8%. This detection system has the advantage of being able to discriminate between organic mercury compounds.[71]

Gas chromatography with temperature programming and flame-ionization detection has been utilized to study the suspected conversion of some phenylmercury(II) salts submitted to this technique.[34] Infrared and mass-spectrometric analysis of the eluted compounds revealed that all the salts investigated were converted in the injection block into diphenylmercury as the main product of what appeared to be a free-radical reaction. When phenylmercury(II) chloride was chromatographed this conversion took place on a very reduced scale, suggesting that phenylmercury salts should preferably be converted into phenylmercury(II) chloride first, before determination by GLC.

When trace amounts of dialkylmercurials are to be determined, they should also first be converted into the corresponding halide salts if electron-capture detection is to be used. However, by using a combustion/cold-vapour mercury-detection system, it is possible to determine microamounts of those substances without having to convert them into a salt suitable for sensitive electron-capture detection. After separation, the compounds are combusted either in a furnace or in a flame-ionization detector and the resulting free mercury is passed through the optical cell of an atomic-absorption instrument tuned to the mercury resonance line at 253.7 nm. The limit of detection is 0.1 ng of mercury, with a linear response from 50 pg to 0.1 μg of diethylmercury. River water and sediment samples have been analysed for dialkylmercury compounds at the nanogram level by this method.[43–46] Gas-liquid chromatography with mass-spectrometric detection (GLC–MS) has been employed to identify methylmercury(II) chloride in aqueous solution at the 1 part per milliard (1 ppM) level after solvent extraction into benzene and concentration of this extract to a few μl.[72]

Methylmercury present in fish, sediment and water has been determined by this technique after extraction as the bromide (from fish and sediments) or chloride (from water) and purification by stripping into aqueous sodium thiosulphate solution followed by conversion into the iodide salt for analysis by GLC with electron-capture detection.[73,74] Recovery of added methylmercury(II) ranged from an average of 88.5% for water samples to averages of 95.5 and 96.3% for fish and sediment samples. The limit of detection of the method was 10 ppM for fish, 1 ppM for sediments and 20 ppM for water samples, respectively. Periodic reconditioning of the columns used, involving injection of microamounts of methylmercury(II) chloride and large amounts of aqueous potassium iodide solution, was required in order to obtain reproducible peaks. An interlaboratory programme for determining the methylmercury(II) content of fish and aquatic mammals by the Westöo procedure showed a coefficient of variation of ±20% for recovery of spikes to fish tissue, the mean recovery being 103%.[75] A procedure for the isolation of methylmercury(II) from biological tissues and its determination at the ppm level has been described.[76] The species is first converted into the cyanide salt in a diffusion cell and then trapped on cysteine-impregnated filter paper. The organomercurial is then extracted from the paper into benzene and determined by gas chromatography. The method has been applied to a wide variety of samples and because of the concentration factor achieved in the isolation step, as little as 1 ng of compound per g of sample can be measured.

Ealy *et al.*[77] investigated the separation, identification and determination of methyl, ethyl and methoxyethylmercury(II) halides in biological materials. The procedure they developed involves a solvent-extraction purification step and injection of an aliquot of the benzene phase. Extraction of the compounds remained constant for hydrogen concentrations up to 10*M* but decreased at high pH with halide concentrations higher than 1*M*. Partition coefficients for methyl and ethylmercury(II) halides were reported and several overall formation constants for the anionic complexes $RHgCl_n^{1-n}$ ($n = 2, 3$) were determined. Good separation of the chromatographic peaks was obtained, but the relative retention times of the chloride, bromide and iodide compounds were identical. An apparent increase in detector sensitivity towards the substances chromatographed was paralleled by the increase in the atomic weight of the halide. The plot of peak-height *vs.* mass of compound gave a straight line, calculated by regression analysis, over the range 7–32 ng. The relative standard deviation varied from 8.2% at the lowest concentrations to 1.1% for the highest.

GLC–MS investigations of several alkyl and arylmercury(II) compounds have also indicated that these substances undergo decomposition during chromatographic analysis and that the fraction decomposed is larger when smaller amounts of material are taken.[35] This seems to be particularly important in the case of phenylmercury salts such as the acetate, borate and hydroxide, which decompose even when large samples are taken, to give diphenylmercury as the major product. The authors concluded that because of this behaviour GLC was not a good method for the determination of these compounds; reliable results for methylmercury(II) salts may, however, be achieved if a column treatment, such as injection of some halide salts, is employed. Both flame-ionization and electron-capture detection were used in this study.

A sensitive method has been described[78] for the determination of methylmercury(II) in small samples of whole blood, to which oxalic acid is added as acidifying agent, and potassium iodide as the source of halide. The combined use of both substances is claimed to increase the average recovery by 10%. A sodium hydroxide wash helps to remove impurities. The chloride derivative of the compound is extracted into

benzene, urea being used instead of distilled water as haemolysing agent, as it increases the number of methylmercury(II) binding sites and helps to give clear benzene extracts. Aliquots of the benzene extracts are injected into a column which has a small portion of finely powdered potassium iodide at the top. The amount of the organomercurial is finally evaluated by measurement of the peak-height of the methylmercury(II) iodide produced in the exchange reaction on the column. As little as 1 ng of the compound could be determined in a sample of blood by this method. The relationship between total mercury content, determined by flameless atomic-absorption spectrophotometry, and the methylmercury, indicated that at least 89% of the mercury in some fish samples was present as methylmercury(II).[79]

Sumino has discussed the problems encountered in determining methylmercury(II) by GLC and presented detailed information on each process involved: sample pretreatment, extraction and purification of the compounds under various circumstances and gas chromatographic conditions.[80] While the isolation step must be carefully controlled to ensure that all the methylmercury will finish up in the final extract, the conditions for gas chromatography are also critical if the compounds are to be eluted without any degradation. The need to use an all-glass system with on-column injection is stressed.

Sample pretreatment usually involves homogenization and acidification, but some modifications are intended to liberate the methylmercury(II) ion before the acidification step.[81-84] One of these employs alkaline digestion of the homogenized sample with 2–3*M* ethanolic potassium hydroxide which, apart from easing liberation of methylmercury, also prevents the formation of emulsions, common during the acid extraction, at the same time providing more homogeneous digests and uniform sample distribution. After the alkaline hydrolysis the Westöo method of determination is generally followed. This procedure was employed successfully in the determination of the organomercury compounds in hair and other biological products.[81-83] In another variation of sample pretreatment, a foam is created on the sample by addition of a small amount of potassium n-butylxanthate and cetyltrimethylammonium bromide at pH 9.0 and passage of nitrogen. The foam is collected with a small volume of butanol and extracted with benzene, a small portion of it then being injected into the chromatograph column. In this manner a concentration factor of 150–300 may be achieved, permitting determination at the ppM level. Interfering heavy metal ions can be separated by ion-exchange.[84]

A procedure has been described for the determination of trace amounts of volatile organomercurials in aqueous and biological samples by gas chromatography, with a microwave-emission spectrometric detection system, which does not require a clean-up step,[47] with the consequent advantage of being faster than most other methods for methylmercury(II). The limit of detection under optimum conditions was quoted as 0.5 pg for methyl or ethylmercury(II) chloride and 2 pg for dimethylmercury. The selectivity of this detection system for methylmercury halide or dimethylmercury relative to chloroform or hexadecane was well above 10^4. The recovery for a single extraction step was $76 \pm 5\%$. Recoveries of methylmercury(II) chloride added to several biological samples varied from $77 \pm 4.5\%$ to $98 \pm 3.5\%$ with relative standard deviations in the range 2–20%. Results for low levels of methylmercury(II) halide in biological samples showed very good agreement with those obtained by the Westöo procedure. Direct determinations of these compounds by injecting aliquots of the aqueous samples, at pH 5–9, are also possible.

The Westöo procedure has been modified by Schafer *et al.*[85,86] so as to improve the determination of alkylmercury(II) in various foods by gas chromatography with electron-capture detection. The methyl and ethylmercury ions, liberated by alkaline hydrolysis from the samples, are extracted as the chloride derivatives into benzene, after tying up of sulphur groups with mercury(II) chloride and adjustment of the acidity of the solution to 0.8*M* in hydrochloric acid. Purification is achieved by stripping into cysteine solution and re-extracting as the chloride into benzene. The benzene phase is dried and a small volume is injected into the column. Mean recoveries ranged from 73.3 to 87.2% with a coefficient of variation of 8–14%. Calibration curves of peak-height *vs.* concentration were linear in the range 0.012–0.12 μg/ml, the limit of detection being 0.02 ppm. Comparative inter-laboratory studies using both acidic and alkaline hydrolysis, and with eight samples of fish, showed standard deviations in the range 0.05–0.15 ppm and coefficients of variation from 8 to 23%.

Recent studies have demonstrated the possibility of extracting some organomercury(II) compounds with quaternary and tertiary amines dissolved in simple solvents. When 0.5% solutions of some tertiary amines (Alamine 336-S and Adogen 464) in benzene were employed, $95 \pm 3\%$ of the methylmercury chloride was extracted from aqueous solutions at pH 6.5–9.0, even for aqueous–organic phase-volume ratios as high as 400. Aliquots of the benzene layer were submitted to gas-chromatographic analysis with a microwave-emission detector, thus greatly simplifying the procedures commonly used for the determination of methylmercury. The methylmercury chloride is instantly released from its amine adduct in the injection port and then separated on the GLC column. Concentrations as low as 1 ng/l. in various fresh and synthetic sea-water samples were determined with a relative standard deviation of 10–15%.[87]

Cappon and Smith have used gas chromatography with electron-capture detection to determine both organomercurials and inorganic mercury present at the ppM level in various biological materials.[88] Whole samples, samples homogenized with water, or alkaline

digests, after addition of urea, are subjected to a purification procedure by acid-extraction into benzene and stripping into aqueous sodium thiosulphate. The organomercurials are finally extracted again into benzene with a recovery of 80–90% and determined as the bromide derivatives. Inorganic mercury(II) is then converted into methylmercury by adding methanolic tetramethyltin to the aqueous phase left after the first extraction of the organomercurials, followed by conversion into the chloride derivative, extraction and measurement as before. The two procedures may be carried out sequentially, or simultaneously if methylmercury is known to be absent. The mean deviation and relative standard deviation averaged 3.2 and 2.2% respectively.

Several phenylmercury(II) compounds, derived from the treatment of dilute aqueous solutions of diverse anions with aqueous solutions of phenylmercury(II) nitrate, have been examined by thermogravimetric and gas-chromatographic analysis.[31] Thermogravimetric results indicated favourable volatilization characteristics for phenylmercury chloride, bromide and iodide, there being no evidence of decomposition during volatilization. In contrast, phenylmercury(II) sulphide and thiocyanate showed a markedly different behaviour, thermal degradation being clear from the breaks on the thermogram. Whilst a single, narrow and well-defined peak was obtained for the halide derivatives, phenylmercury(II) sulphide and thiocyanate showed broadened major peaks and substantial solvent tailing, characteristic of thermal degradation on the column. The results obtained indicated the potential usefulness of GLC for the determination of the halides at the submicrogram level

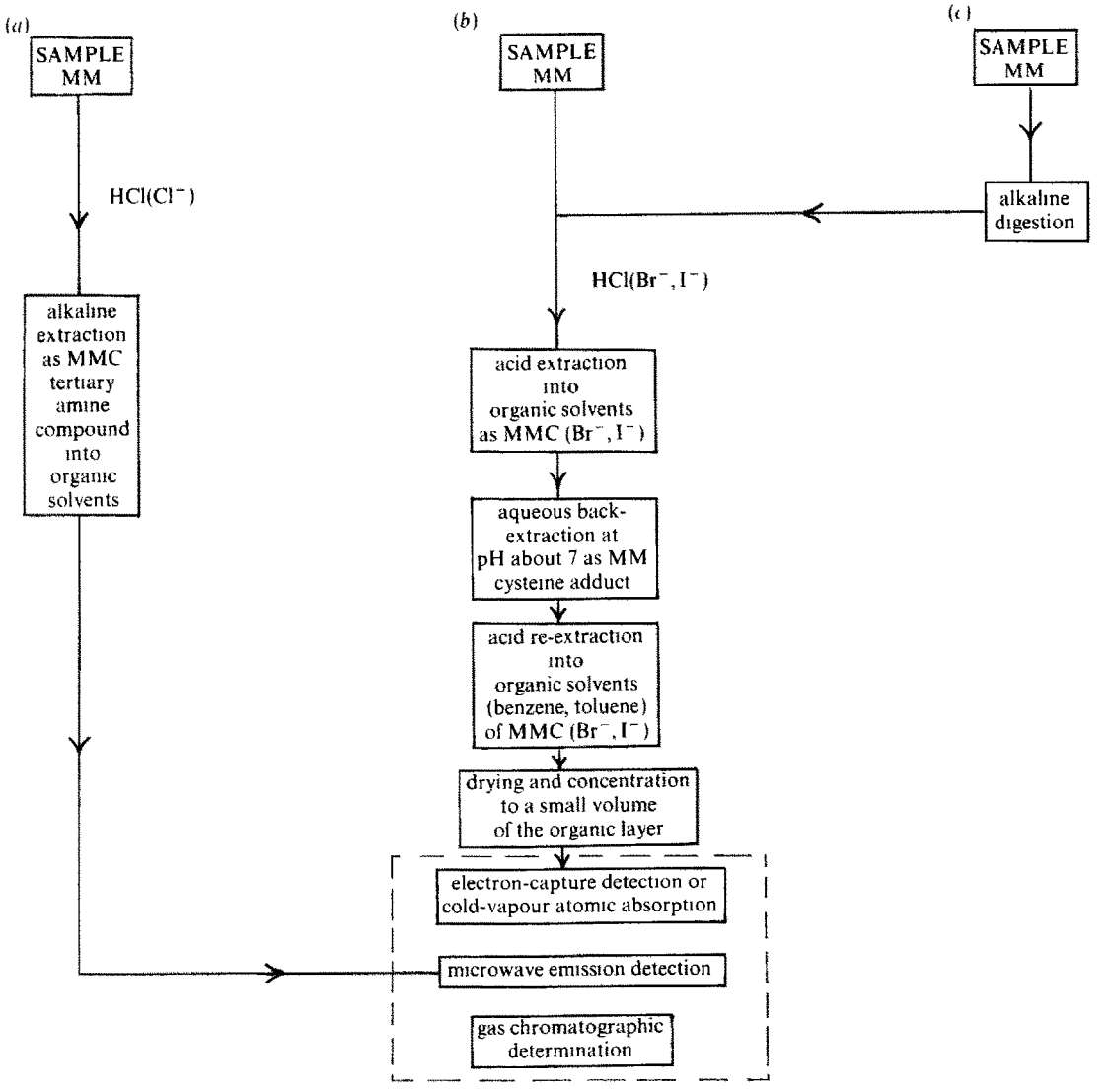


Fig. 1. Schematic diagram for determination of methylmercury in biological systems by gas chromatography: (*a*) rapid procedure with microwave-emission detection, after Talmi;[47,87] (*b*) Westöo/Sumino basic procedure; (*c*) sample pretreatment by alkaline digestion.[81–86,88] These processes are also applicable to other organomercurials.

after a solvent-extraction step, electron-capture detection being used. With a flame-ionization detector, a decrease in sensitivity was noticed ($Cl^- > Br^- > I^-$).

Figure 1 outlines the main variants of the procedures for determining organomercurials. Most methods are based on the Westöo procedure.[55] Applications to various types of samples are summarized in Table 1.

METHODS FOR THE DETERMINATION OF INORGANIC SPECIES

The successful determination of several organomercurials, notably methylmercurials, by a derivative formation–solvent extraction–gas chromatography technique, together with the knowledge of various ways of preparing these substances (such as mercuration, replacement of functional groups and displacement reactions) suggested that a study should be made of their usefulness for the determination of some inorganic species, particularly halides and mercury(II). This has been the aim of a number of investigations which have been reported in the last few years.

The first such method to be reported was developed for determining trace levels of chloride.[89] The halide ion is allowed to react with phenylmercury(II) nitrate in a perchloric acid medium at about pH 1.5 and the phenylmercuric(II) chloride formed is extracted into chloroform. With flame-ionization detection and injection of large samples it is possible to detect as little as 0.23 ng of chloride. Calibration graphs obtained by plotting peak-areas or heights are linear in the chloride ranges 5–100 and 0.4–7.0 μg/ml, respectively. Aqueous solutions containing 8 ppM of this anion can be analysed with a mean relative error of 25% (by peak-height) or 21% (by peak-area). With electron-capture detection a tenfold increase in sensitivity can be achieved and about 30 pg of chloride can be detected. The method was successfully applied to the measurement of the chloride content of drinking and high-purity water.[90,91]

One of the procedures for synthesizing organomercury compounds is based on the Peters reaction[92] between arylsulphinic acids and mercuric(II) chloride:

$$ArSO_2H + HgCl_2 \rightleftharpoons ArHgCl + SO_2 + HCl$$

Jones and Nickless[93] developed a method, based on this reaction, for the determination of mercury(II) as phenylmercury chloride, after reaction of mercury in a weakly acidic medium at near boiling point, with sodium benzenesulphinate. The product was extracted

Table 1. Some applications of gas chromatography to the determination of organomercury(II) compounds in several specimens

Species	Determined as	Matrix	Ref.
Methylmercury	MMC	Hair, fish, aqueous solutions, biological and environmental samples	29, 33, 42, 50, 54, 55, 66–68
Methylmercury Ethylmercury Phenylmercury	MMC EMC PMC	rat liver, fish, vegetables, rice, hair and aqueous solutions	41, 56, 57
Methylmercury Ethylmercury Methoxyethylmercury Ethoxyethylmercury Phenylmercury Tolylmercury	MMDz EMDz MEMDz EEMDz PMC TMC	vegetables, fruit	30
Methylmercury	MMC	fish, cereal and grain	64
Dimethylmercury Diethylmercury	MMB, DMM DEM	aqueous solutions	43–46, 69, 71
Methylmercury	MMC, MMI	fish, sediments, whole blood, hair, biological tissues, aqueous solutions	72–76, 78–84, 87
Methylmercury Ethylmercury Methoxyethylmercury	MMC EMC MEMC	biological materials	77
Methylmercury Ethylmercury Dimethylmercury	MMC EMC DMM	fish and water samples	47
Methylmercury Ethylmercury	MMB EMB	foods and biological samples	85, 86, 88

Abbreviations: MMC, methylmercury chloride; MMB, methylmercury bromide; MMI, methylmercury iodide; EMC, ethylmercury chloride; EMB, ethylmercury bromide; MEMC, methoxyethylmercury chloride; EEMC, ethoxyethylmercury chloride; DMM, dimethylmercury; DEM, diethylmercury; PMC, phenylmercury chloride; TMC, tolylmercury chloride; Dz, dithizonate.

into toluene and an aliquot of the extract was injected for analysis. With an electron-capture detector the calibration graphs were linear over three ranges of mercury level: 5.0–20.0 μg; 0.5–5.0 μg and 0.05–0.2 μg; the limit of detection was about 0.2 ng of phenylmercury chloride. When the method was used for the determination of mercury in biological materials the Westöo clean-up procedure was followed, primarily to prevent sulphur compounds from being injected into the gas chromatograph.

The methylation of mercury by means of a trimethylsilyl derivative has also been utilized for the evaluation of this element in various environmental samples.[94,95] The reaction proceeds quantitatively at high acidity and high temperature over the range 0.03–10 ppm. A clean-up step, for use when interfering peaks were present, followed the Westöo procedure, with sodium thiosulphate as stripping agent for the methylmercury ion. The final benzene extract was dried with sodium sulphate and an aliquot injected into the chromatograph. Electron-capture detector response was linear from 0.04 to 0.16 ppm of mercury(II) in the final extract. Total mercury in sediments and fish samples determined by this method and by cold-vapour atomic-absorption spectrophotometry gave a relative standard deviation ranging from 0.8 to 22%, depending on the amount of mercury present.

The Peters reaction also provided the basis for a procedure reported by Mushak *et al.*[96] Lithium pentafluorobenzenesulphinate serves as the reagent, and the product, pentafluorophenylmercury(II) chloride, formed in acidic medium, is extracted into xylene and submitted to gas-chromatographic analysis. Inorganic mercury can be evaluated by this method when present in water, urine and sera. It is claimed that mercury can be determined at the 50-ppM level in water, the limit of detection with electron-capture detection being 20 ppM. Recoveries of added mercury were 70% for water, 81% for urine and 51% for blood serum; the relative standard deviations were 6.8, 10.5 and 9.4%, respectively. Other mercurials can be determined in the presence of inorganic mercury in several ways, as for example by sequential analysis of the sample at different column temperatures.

Quantitative measurements of inorganic mercury in the presence and absence of organomercurials in water and biological media have been achieved by gas–liquid chromatography.[97] Several agents have been used for forming alkyl and aryl derivatives, the best being pentacyanocobaltate(III) and tetraphenylborate, which react in acidic media with inorganic mercury(II) to give the corresponding methyl and phenylmercurials. Limits of detection of mercury with these reagents were in the range $1–3 \times 10^{-8}$ g/ml. Inorganic mercury and various organomercurials in mixture were determined by sequential or simultaneous procedures, by varying the column temperatures and packings. Tetraethyltin, forming ethylmercury, was less than satisfactory for derivative formation, but better results were obtained with methanolic tetramethyltin. Under mildly acidic conditions, after 10 min of shaking, methylmercury was produced in 85–90% yield,[88] and was simultaneously converted into the chloride derivative:

$$(CH_3)_4Sn + Hg^{2+} \overset{HCl}{\rightleftharpoons} CH_3HgCl + (CH_3)_3SnCl$$

This was extracted into benzene and determined by GLC with electron-capture detection. Recovery of mercury(II) chloride added to blood, faeces and liver ranged from 81.5 to 88.2% with a relative standard deviation of 1.3–2.2%. A comparison of gas-chromatographic and atomic-absorption results for several representative samples containing methyl, ethyl and inorganic mercury(II) indicated good agreement between the two methods.

The GLC method for chloride mentioned previously[89] has been further developed into a procedure for bromide and iodide.[98] Extraction studies showed that both phenylmercury(II) bromide and iodide could be recovered quantitatively by extraction into chloroform from aqueous solution in the pH range 0–4, after acidification with various mineral acids,

Table 2. Gas chromatographic determination of inorganic species after conversion into an organomercury(II) compound

Species	Determined as	Matrix	Ref.
Chloride	PMC	drinking and high-purity water	90, 91
Mercury(II)	PMC	biological materials	93
Mercury(II)	MMC	environmental and biological samples	88, 94, 95
Mercury(II)	PFPMC	water, urine and blood serum	96
Mercury(II)	MMC PMC	water and biological media	97
Bromide	PMB	aqueous solutions	98
Iodide	PMI	aqueous solutions	98

Abbreviations: MMC, methylmercury chloride; PMC, phenylmercury chloride; PMB, phenylmercury bromide; PMI, phenylmercury iodide; PFPMC, pentafluorophenylmercury chloride.

perchloric acid being preferred. The degree of extraction diminished as the pH increased, becoming negligible at *ca.* pH 10. Linear calibrations were obtained for the range 3–80 μg/ml when peak-height was plotted against concentration of either bromide or iodide. The limit of detection for the flame-ionization detector under optimal operating conditions was established as 2.4 and 2.6 ng for bromide and iodide respectively. Both halides were extracted quantitatively from large volumes of aqueous solution with concentrations as low as 0.01 ppm, and were determined after concentration of the organic phase to a small volume. Smaller amounts might well be evaluated by using electron-capture detection.

Table 2 summarizes the determinations of inorganic species by gas liquid chromatography of organomercury compounds.

REFERENCES

1. E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, pp. 107–123. Wiley, London, 1957.
2. G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Vol. I, 3rd Ed., pp. 147–176. Methuen, London, 1967.
3. L. G. Makarova and A. N. Nesmeyanov, eds., *The Organic Compounds of Mercury (Methods of Elemental-Organic Chemistry, Vol. IV)*, North-Holland, Amsterdam, 1967.
4. T. Fagerström and A. Jernelöv, *Water Research*, 1972, **6**, 1193.
5. L. Fishbein, *Chromatog. Rev.*, 1970, **13**, 83.
6. Analytical Methods Committee of the Society for Analytical Chemistry, *Analyst*, 1965, **90**, 515.
7. W. R. Hatch and W. L. Ott, *Anal. Chem.*, 1968, **40**, 2085.
8. B. Sjostrand, *ibid.*, 1964, **36**, 814.
9. S. Chilov, *Talanta*, 1975, **22**, 205.
10. M. López-Lamas and E. Fernández-Gómez, *Quim. Anal.*, 1976, **30**, 251.
11. V. L. Miller, D. Polley and C. J. Gould, *Anal. Chem.*, 1951, **23**, 1286.
12. D. Polley and V. L. Miller, *ibid.*, 1952, **24**, 1622.
13. V. L. Miller and D. Polley, *ibid.*, 1954, **26**, 1333.
14. Y. Kimura and V. L. Miller, *ibid.*, 1960, **32**, 420.
15. J. C. Gage, *Analyst*, 1961, **86**, 457.
16. J. C. Gage and J. M. Warren, *Ann. Occup. Hyg.*, 1970, **13**, 115.
17. T. W. Clarkson and M. R. Greenwood, *Anal. Biochem.*, 1970, **37**, 236.
18. S. Ishikura and K. Yokota, *Chem. Pharm. Bull. Tokyo*, 1963, **11**, 939.
19. S. Ehrlich-Rogozinsky and R. Spesling, *Anal. Chem.*, 1970, **42**, 1089.
20. A. E. Moffitt, Jr. and R. E. Kupel, *At. Absorption Newslett.*, 1970, **9**, 113.
21. P. E. Doherty and R. S. Dorsett, *Anal. Chem.*, 1971, **43**, 1887.
22. Y. Umezaki and K. Iwatomoto, *Bunseki Kagaku*, 1971, **20**, 173.
23. J. Kanazawa and R. Sato, *ibid.*, 1959, **8**, 322.
24. J. N. Bartlett and G. W. Curtis, *Anal. Chem.*, 1962, **34**, 80.
25. S. Takitani, S. Ishikura and Y. Nagao, *Eisei Kagaku*, 1964, **10**, 151.
26. S. Kitamura and H. Nakayama, *Jap. J. Ind. Health*, 1965, **7**, 276.
27. G. W. Johnson and C. Vickers, *Analyst*, 1970, **95**, 356.
28. R. Takeshita, H. Akagi, M. Fujita and Y. Sakagami, *J. Chromatog.*, 1970, **51**, 283.
29. G. Westöo, *Acta Chem. Scand.*, 1966, **20**, 2131.
30. J. O'G. Tatton and P. J. Wagstaffe, *J. Chromatog.*, 1969, **44**, 284.
31. R. Belcher, J. A. Rodriguez-Vazquez, W. I. Stephen and P. C. Uden, *Chromatographia*, 1976, **9**, 201.
32. S. Nishi and Y. Horimoto, *Bunseki Kagaku*, 1968, **17**, 75.
33. B. Johansson, R. Ryhage and G. Westöo, *Acta Chem. Scand.*, 1970, **24**, 2349.
34. R. C. Dressman, *J. Chromatog. Sci.*, 1972, **10**, 468.
35. G. I. Baughman, M. H. Carter, N. L. Wolf and R. G. Zepp, *J. Chromatog.*, 1973, **76**, 471.
36. H. V. Caster, E. I. Chappell and E. Warhurst, *J. Chem. Soc.*, 1956, 106.
37. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1957, 2114.
38. R. E. Dessy and W. Kitching in *Advances in Organometallic Chemistry*, Vol. 4, F. G. A. Stone and R. West, eds., pp. 289–309. Academic Press, New York, 1966.
39. R. E. Dessy and F. E. Paulik, *J. Am. Chem. Soc.*, 1963, **85**, 1812.
40. J. Areses-Trapote, A. Concheiro-Nine and J. A. Rodriguez-Vazquez, unpublished work.
41. K. Sumino, *Kobe J. Med. Sci.*, 1968, **14**, 115.
42. C. A. Bache and D. J. Lisk, *Anal. Chem.*, 1971, **43**, 950.
43. R. C. Dressman, *J. Chromatog. Sci.*, 1972, **10**, 472.
44. J. E. Longbottom, *Anal. Chem.*, 1972, **44**, 1111.
45. J. G. Gonzalez and R. T. Ross, *Anal. Lett.*, 1972, **5**, 683.
46. J. E. Longbottom and R. C. Dressman, *Chromatog. Newslett.*, 1973, **2**, 17.
47. Y. Talmi, *Anal. Chim. Acta*, 1975, **74**, 107.
48. K. Brodersen and U. Schlenker, *Z. Anal. Chem.*, 1961, **182**, 421.
49. S. Kitamura, T. Tsukamoto, K. Hayakawa, K. Sumino and T. Shibata, *Med. Biol. Tokyo*, 1966, **72**, 274; 1966, **73**, 276.
50. Y. Takizawa and T. Kosaka, *Acta Med. Biol. Niigata*, 1966, **14**, 153.
51. G. F. Reynolds and S. R. Daniel, *Inorg. Chem.*, 1967, **6**, 480.
52. S. Ishikura and S. Onodera, *Bunseki Kagaku*, 1967, **16**, 15.
53. K. Teramoto, M. Kitabatake, M. Tanabe and Y. Noguchi, *Kogyo Kagaku Zasshi*, 1967, **70**, 1601.
54. G. Westöo, *Acta Chem. Scand.*, 1967, **21**, 1790.
55. *Idem, ibid.*, 1968, **22**, 2277.
56. K. Sumino, *Kobe J. Med. Sci.*, 1968, **14**, 131.
57. S. Nishi and Y. Horimoto, *Bunseki Kagaku*, 1968, **17**, 1247.
58. S. Jensen and A. Jernelov, *Nature*, 1969, **223**, 753.
59. S. Jensen, *Nord. Hyg. Tidskr.*, 1969, **50**, 85.
60. M. Fujiki, *Bunseki Kagaku*, 1970, **19**, 1507.
61. S. Nishi, Y. Horimoto and Y. Umezawa, *ibid.*, 1970, **19**, 1646.
62. S. Nishi and Y. Horimoto, *ibid.*, 1971, **20**, 16.
63. V. Zitko, B. J. Finlayson, D. J. Wildish, J. M. Anderson and A. C. Kohler, *J. Fisheries Res. Board Can.*, 1971, **28**, 1285.
64. W. H. Newsome, *J. Agr. Food Chem.*, 1971, **19**, 567.
65. R. T. Ross and L. Moore, *162nd ACS National Meeting*, Washington DC, 12–17 September, 1971.
66. J. F. Uthe, J. Solomon and B. Griffitt, *J. Assoc. Off. Anal. Chem.*, 1972, **55**, 583.
67. L. R. Kamps and B. McMahon, *ibid.*, 1972, **55**, 590.
68. K. Tanaka, T. Shimada, S. Fukui and S. Kanno, *Eisei Kagaku*, 1972, **18**, 256.
69. R. Hartung and B. D. Dinman, eds., *Environmental Mercury Contamination*, Ann Arbor Science Publishers, Ann Arbor, 1972.
70. G. Lindstedt and G. Skerfving in *Mercury in the Environment*, pp. 11–13. CRC Press, Cleveland, Ohio, 1972.
71. W. E. L. Grossman, J. Eng and Y. C. Tong, *Anal. Chim. Acta*, 1972, **60**, 447.
72. S. Ohkoshi, T. Takahashi and T. Sato, *Bunseki Kagaku*, 1973, **22**, 593.

73. J. E. Longbottom, R. C. Dressman and J. J. Lichtemberg, *J. Assoc. Off. Anal. Chem.*, 1973, **56,** 1297.
74. H. C. Freeman and D. A. Hoene, *J. Fisheries Res. Board Can.*, 1973, **30,** 454.
75. A. V. Holden, *Proc. Soc. Anal. Chem.*, 1973, **10,** 31.
76. V. Zelenko and L. Kosta, *Talanta*, 1973, **20,** 115.
77. J. A. Ealy, W. D. Shults and J. A. Dean, *Anal. Chim. Acta*, 1973, **64,** 235.
78. R. von Burg, F. Farris and J. C. Smith, *J. Chromatog.*, 1974, **97,** 65.
79. E. T. Hall, *J. Assoc. Off. Anal. Chem.*, 1974, **57,** 1068.
80. K. Sumino, *Water Technology*, Vol. VII, pp. 35–45. Pergamon, New York, 1974.
81. T. Giovanoli-Jakubczak, M. R. Greenwood, J. C. Smith and T. W. Clarkson, *Clin. Chem.*, 1974, **20,** 222.
82. M. Takeuchi, K. Ebato, K. Ito, T. Amemiya, H. Harada and T. Totani, *Tokyo Toritsu Eisei Kenkyusho Kenkyu Nempo*, 1974, **25,** 113; *Chem. Abstr.*, 1975, **82,** 150028.
83. T Ueta, R. Yamazoe, H. Yamanobe and T. Totani, *ibid.*, 1975, **26,** 110; *Chem. Abstr.*, 1976, **84,** 160202e.
84. T. Hobo, T. Ogura, S. Suzuki and S. Araki, *Bunseki Kagaku*, 1975, **24,** 288.
85. M. L. Schafer, U. Rhea, J. T. Peeler, C. H. Hamilton and J. E. Campbell, *J. Agr. Food Chem.*, 1975, **23,** 1079.
86. M. L. Schafer, U. Rhea and J. E. Campbell, *ibid.*, 1976, **24,** 1078.
87. Y. Talmi and V. E. Norvell, *Anal. Chim. Acta*, 1976, **85,** 203.
88. C. J. Cappon and J. C. Smith, *7th ACS Northeast Regional Meeting*, Albany, New York, August 1976.
89. R. Belcher, J. R. Majer, J. A. Rodriguez-Vazquez, W. I. Stephen and P. C. Uden, *Anal. Chim. Acta*, 1971, **57,** 73.
90. R. Belcher, J. A. Rodriguez-Vazquez and W. I. Stephen, *ibid.*, 1972, **61,** 223.
91. R. Belcher, A. Nadjafi, J. A. Rodriguez-Vazquez and W. I. Stephen, *Analyst*, 1972, **97,** 993.
92. W. Peters, *Ber.*, 1905, **38,** 2567.
93. P. Jones and G. Nickless, *J. Chromatog.*, 1973, **76,** 285.
94. *Idem, Proc. Soc. Anal. Chem.*, 1973, **10,** 270.
95. *Idem, J. Chromatog.*, 1974, **89,** 201.
96. P. Mushak, F. E. Tibbetts, P. Zarnegar and G. B. Fisher, *ibid.*, 1973, **87,** 215.
97. P. Zarnegar and P. Mushak, *Anal. Chim. Acta*, 1974, **69,** 389.
98. L. Garea-Rodriguez and J. A. Rodriguez-Vazquez, unpublished work.

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ANALYTICAL APPLICATIONS OF CONDENSED PHOSPHORIC ACID—I

DETERMINATION OF FERROUS AND TOTAL IRON IN IRON ORES AFTER DECOMPOSITION WITH CONDENSED PHOSPHORIC ACID

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Summary—A simple method is described for the determination of ferrous and total iron in iron ores. Iron ores are dissolved by condensed phosphoric acid (CPA) very rapidly without any tedious and time-consuming manipulations such as elimination of silica and filtration. Under the proposed conditions (amount of sample 100 mg, amount of CPA added 10 g, heating temperature 290°, heating time 30 min), magnetite, limonite and hematite are completely dissolved. The iron content can be determined in the presence of condensed phosphoric acid by titration with dichromate solution, if a slight modification is made. The total iron in iron ores, determined by the present method, is in agreement with that found by the JIS method. The ferrous iron in iron ores can be determined by dissolving the samples with CPA in a nitrogen atmosphere and titrating with dichromate solution. Chelatometric titration of iron after solvent extraction with MIBK from solutions prepared by use of CPA is found to be accurate for samples such as pyrite cinder. The ability of CPA to dissolve various materials has been investigated.

The decomposition of solid samples is still a very time-consuming operation.[1–3] In this operation, various mineral acids are used and the acids are volatilized, usually into the atmosphere. It is therefore desirable that methods for decomposing solid samples, especially rocks, should be actively explored, to establish "rapid and clean analysis".[4]

It is well known that the analytical methods based on use of condensed phosphoric acid (CPA) as a reaction medium have been studied by Kiba and his co-workers, who have established methods for determination of such volatile elements as sulphur,[5,6] halogens,[7,8] mercury,[9] selenium,[10,11] *etc.* It is widely accepted that CPA is a very powerful agent for dissolution of solid materials, but there are few analytical methods in which this property of CPA is fully utilized.

We have therefore been investigating the dissolution of various kinds of minerals in CPA. The present paper is concerned with the decomposition of iron ores and the methods for determination of ferrous and total iron in them. The ability of CPA to dissolve various compounds is also described.

EXPERIMENTAL

Reagent

Condensed phosphoric acid (CPA). According to the method proposed by Kiba *et al.*,[5] 250 g of orthophosphoric acid (85%) are heated to 300° in a 300-ml quartz flask on an electric heater. The temperature is measured by means of an alumel–chromel thermocouple protected by a quartz tube.

Standard iron(III) solution, 0.1*M*. About 24 g of ferric alum dissolved in 400 ml of 0.1*M* hydrochloric acid, diluted to 500 ml with 0.1*M* hydrochloric acid and standardized against a standard potassium dichromate solution.

Standard potassium dichromate solution, 0.1*N*. About 2.5 g of primary-standard grade potassium dichromate, weighed accurately, dissolved in water and then diluted to 500 ml with water.

Standard zinc solution, 0.01*M*. About 0.66 g of primary-standard grade metallic zinc, weighed accurately and dissolved in 150 ml of 0.1*M* nitric acid; after addition of 3 ml of concentrated nitric acid, the volume is made up to 1 litre with water in a standard flask.

Standard EDTA solution, 0.01*M*. About 3.8 g of EDTA (disodium salt), dissolved in 1 litre of water and standardized against the standard zinc solution, with Xylenol Orange as indicator.

Tin(II) chloride solution. Ten g of tin(II) chloride dihydrate dissolved in 20 ml of hot concentrated hydrochloric acid and diluted to 100 ml with water; stored in an amber-coloured bottle together with a small amount of metallic tin.

Nitrogen. Commercial product purified by passage through an alkaline pyrogallol solution and a silica gel column.

Unless otherwise stated, all chemicals used were analytical-reagent grade. Distilled and demineralized water was used throughout.

Samples

Iron ore samples were supplied by the Department of Mining and Mineral Engineering, Faculty of Engineering, Tohoku University. The X-ray diffraction patterns for these samples are shown in Fig. 1. The main iron-bearing mineral in sample B is goethite. The content of goethite, however, is as low as about 60%, many other minerals being considered present. Accordingly, this iron sample is conventionally referred to as "limonite" in the present paper.

Apparatus

The apparatus used for the decomposition of samples is shown in Fig. 2. The temperature at the sensing point was kept constant within ±2° by using a Chino thermoregulator, model BE121.

Procedures

Decomposition of ores with CPA. Weigh about 0.1 g of the finely powdered sample in a quartz test-tube and add 10 g of

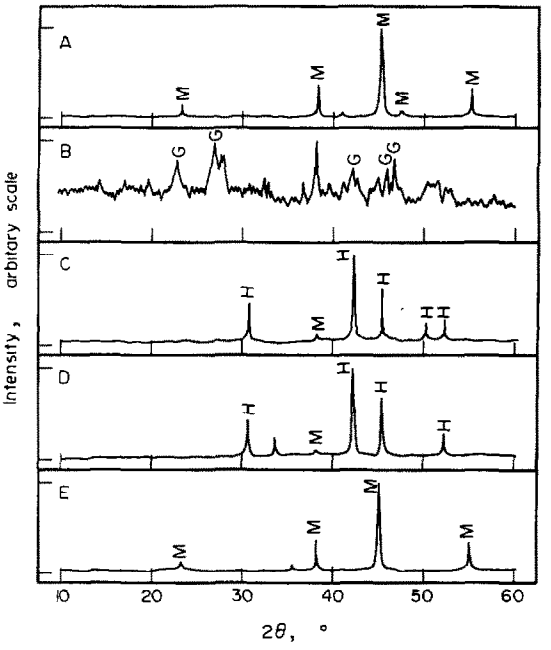


Fig. 1. X-ray diffraction patterns for iron ore samples. Target Fe, scanning speed 2°/min. A: magnetite, B: limonite, C: hematite, D: pyrite cinder, E: iron sand, G: goethite, H: hematite, M: magnetite.

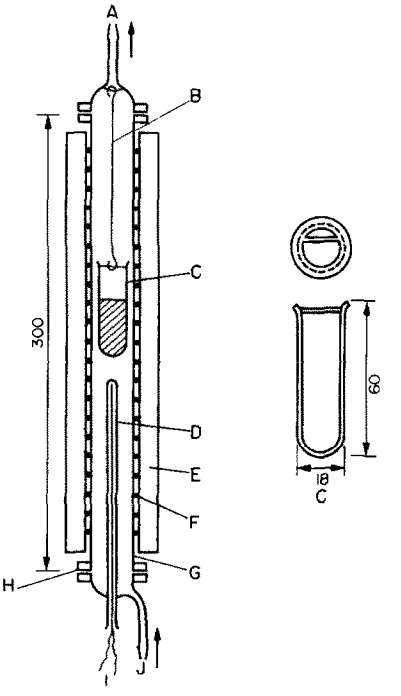


Fig. 2. Apparatus for the decomposition of samples. A gas outlet, B hanger (Pyrex glass rod), C reaction vessel (quartz test-tube), D protective tube, E asbestos, F nichrome heater, G Pyrex glass tube (28 mm bore), H glass flange, I alumel–chromel thermocouple, J gas inlet. Dimensions in mm.

CPA. Suspend the tube in an electric furnace regulated at 290°. After 30 min, remove the tube from the furnace and cool it to room temperature.

Determination of the degree of decomposition of iron ores. Add about 3 ml of water to the tube containing the reaction mixture, and mix. Pour the contents into a beaker and wash the tube with water. Fill the tube with water and apply ultrasonic waves for 5 min to recover the insoluble materials quantitatively. Filter off and wash all the insoluble materials. Transfer the filter-paper and residue into a platinum crucible, dry and ignite. After elimination of silica with hydrofluoric acid, fusion of the residue with potassium pyrosulphate and separation of the platinum dissolved, determine the iron content in the residue colorimetrically with 1,10-phenanthroline.[12] Carry out a blank determination on the reagents and correct the result. Calculate the amount of iron dissolved by subtracting the amount of iron in the residue from the total amount of iron. Determine the degree of decomposition from the amount of iron dissolved and that in the sample taken.

Determination of total iron by redox titration. After the decomposition, add about 3 ml of water to the tube, mix, transfer the contents into a beaker and wash the tube with 15–20 ml of water. Add 5 ml of concentrated hydrochloric acid to the sample solution (total volume < 30 ml) and heat the solution to boiling. Reduce the iron(III) by dropwise addition of tin(II) chloride solution until the solution is colourless, add 2 drops in excess, boil gently for 2 min, cool to room temperature in an ice-bath, add rapidly 8 ml of saturated mercury(II) chloride solution and allow to stand for 2 min. Dilute to about 100 ml with water and add several drops of sodium diphenylaminesulphonate indicator solution, Titrate immediately with standard potassium dichromate solution to a permanent purple end-point.

Determination of total iron by chelatometric titration after solvent extraction. To the reaction mixture, transferred into a 100-ml beaker, add 5 ml of concentrated hydrochloric acid and 2.5% potassium permanganate solution dropwise until a purple colour appears. Heat the solution to boiling to reduce excess of permanganate and expel the chlorine formed. Boil for 2 min more, cool to room temperature and then transfer the solution into a 100-ml standard flask. Take an aliquot of this solution, containing ~0.15 mmole of iron, in a 50-ml separatory funnel. Add 2 ml of 1*M* sodium sulphate and 14 ml of concentrated hydrochloric acid, and dilute to about 30 ml with water. Add 20 ml of methyl isobutyl ketone (MIBK) and extract the chloro-complex of iron by shaking for 1 min. Discard the aqueous phase and wash the organic phase by shaking for 1 min with 15 ml of 6*M* hydrochloric acid and 1 ml of 1*M* sodium sulphate. Discard the aqueous phase and strip the iron complex from the organic phase by shaking (for 1 min each time) first with 15 ml of water, then with 10-ml portions. Collect these aqueous phases in a 200-ml beaker. Add an excess of 0.01*M* EDTA, adjust the pH to 5–6 with hexamine and then titrate the excess of EDTA with standard zinc solution (0.01*M*), using Xylenol Orange as indicator.[13]

Determination of ferrous iron. Decompose the sample as described above but with a flow of nitrogen through the reactor throughout. Cool the test-tube to below 100° in the furnace, then transfer it into a 200-ml Erlenmeyer flask containing about 100 ml of 0.3*M* sulphuric acid (freshly boiled and kept in an atmosphere of nitrogen). Swirl the flask well to disperse the reaction mixture and cool to room temperature, leaving the nitrogen gas flowing. Add several drops of sodium diphenylaminesulphonate indicator solution and titrate with standard dichromate solution.

The terms "titrimetry or solvent extraction in the presence of CPA" will be used to describe the processes in which the CPA has been used, even when most of the CPA has been hydrolysed by dilution.

RESULTS AND DISCUSSION

Dissolution of various inorganic compounds in CPA

The solubilities of various compounds in CPA, which provide the basic data for dissolution reactions of minerals with CPA, are mainly unknown. An amount of compound containing 20 mg of an element of interest was put into the reaction vessel together with 10 g of CPA and kept at 290° for 30 min. The presence of insoluble material was judged visually. Chlorides, nitrates or oxides were used as model compounds, because the non-metallic moiety, *e.g.*, hydrogen chloride, nitrogen oxides, is easily expelled during the dissolution in CPA.

From the results shown in Table 1, it is seen that compounds of many metals are sufficiently soluble in CPA to give concentrations of at least 20 mg of the metal per 10 g of CPA, *i.e.*, amounts adequate for titrimetry and gravimetry.

Table 1. Dissolution of various inorganic compounds in CPA

	Elements
Group A	Ag(I),[a] Al(III),[b] Ba(II),[b] Bi(III),[c] Ca(II),[c] Cd(II),[b] Co(II),[a] Cr(III),[c] Cu(II),[a] Fe(III),[c] K(I),[b] Mg(II),[a] Mn(II),[b] Na(I),[b] Pb(II),[a] Sn(II),[b] Sr(II),[a] Te(VI),[d] V(V),[e] W(VI),[f] Zn(II)[a]
Group B	As(III),[c] Mo(VI),[g] Ni(II),[b] Sb(III),[c] Si(IV),[c] Ti(IV)[c]

Group A: Insoluble material was not detected.
Group B: Insoluble material was detected.
Compounds used: [a]nitrate, [b]chloride, [c]oxide, [d]K_2TeO_4, [e]NH_4VO_3, [f]$Na_2WO_4 \cdot 2H_2O$, [g]$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$.

Under the same conditions as those described in Table 1, 200 mg of iron(III) oxide are easily dissolved. Judging from the solubility of iron in CPA, it follows that an analytical method consisting of dissolution of iron ores with CPA and redox titration of iron with 0.1*N* dichromate is practicable.

Decomposition of iron ores with CPA

Effect of heating time. The degree of decomposition at 290° was determined for three kinds of iron mineral, as a function of the heating time. From the results shown in Fig. 3, it is clear that all of the iron ores tested were decomposed quantitatively within 20 min, and that limonite is decomposed more easily than magnetite and hematite. A decomposition time of 20 min is far shorter than that in the JIS (Japanese Industrial Standard) method,[14] in which iron ores are opened out in 3 hr or longer by decomposition with hydrochloric acid and removal of silica, followed by fusion of the insoluble residues with potassium pyrosulphate.

Effect of heating temperature. Three kinds of iron ore were decomposed at various temperatures. From the results shown in Fig. 4, it is seen that each sample is almost completely decomposed at 270° and 290°. If the CPA is kept for long at above 300°, it may solidify, so a decomposition temperature of 290° is recommended. At temperatures below 230° limonite is decomposed with CPA to leave a large amount of solid. The degree of decomposition of limonite at 210° and 230°, however, is as high as 74 and 90%, respectively. The reason may be that limonite reacts with CPA even at temperature as low as 210°, to form iron phosphates which dissolve during the transfer of the reaction mixture with water.

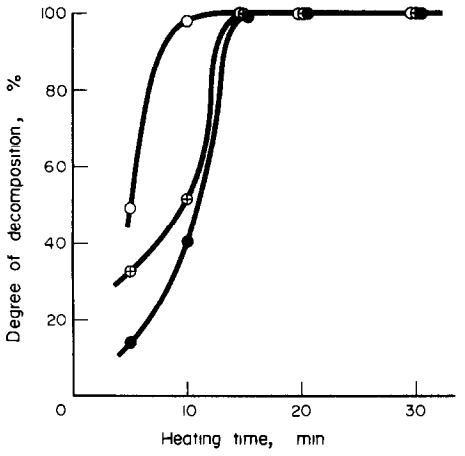


Fig. 3. Effect of heating time on the decomposition of iron ores with CPA. Heating temperature 290°, sample taken 100 mg, CPA added 10 g. ⊕ Magnetite, ○ limonite, ● hematite.

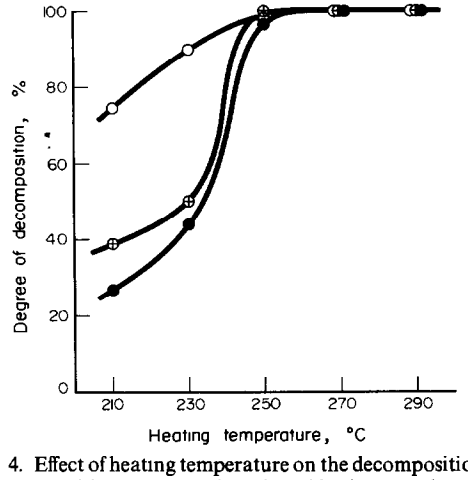


Fig. 4. Effect of heating temperature on the decomposition of iron ores with CPA. Heating time 30 min, sample taken 100 mg, CPA added 10 g. ⊕ Magnetite, ○ limonite, ● hematite.

The composition and fluidity of CPA depend on the temperature at which it is prepared. Accordingly, it is considered that the decomposition of samples is affected by the preparation temperature as well as the decomposition temperature. This aspect, however, was not investigated in this study.

Permissible amount of iron ore samples. The degree of decomposition of various amounts of sample was also examined; the results are shown in Table 2. It is seen that regardless of the kind of mineral, 99.9% or more of the iron is recovered when samples of 0.1–0.2 g are used. When the degree of decomposition

Table 2. Effect of the amount of sample on the decomposition of iron ores with CPA

Amount of sample, *mg*	Degree of decomposition, %		
	Magnetite	Limonite	Hematite
100	>99.9	100.0	>99.9
200	>99.9	>99.9	>99.9
400	99.1	>99.9	>99.9
600	ND	99.7	99.8

ND: not determined.

was below 99.9%, insoluble materials were seen to be present on the upper part of the test-tube but not in its bottom. The reason is that the larger the sample, the more vigorously the decomposition reaction spatters it. An amount of sample as large as 0.4 g or more must be decomposed at lower temperature with prolonged heating time. A heating time of 30 min, temperature of 290° and sample amount of 0.1 g were decided on as the optimum conditions, on the basis of these results (Figs. 3 and 4, Table 2). Under these conditions decomposition was at least 99.9% complete.

Redox titration of iron with potassium dichromate

It has been reported by Saeki *et al.*[15] that ferric iron is not reduced quantitatively with metallic aluminium in the presence of condensed phosphoric acids. The factors affecting the reduction of ferric iron with stannous ion were investigated and the results are shown in Figs. 5–7. It is seen that when the concentration of hydrochloric acid is too low, the reduction does not proceed quantitatively (Figs. 5 and 6). Consequently, it is concluded that the amount of concentrated hydrochloric acid added should be 5 ml, and that the volume of sample solution should be 30 ml or less at the reduction stage. Under these conditions, iron can be determined accurately by titrimetry with dichromate even in the presence of 10 g of CPA (Fig. 7). The volume of titration solution was also varied, and recovery of iron was constant at 99.9%

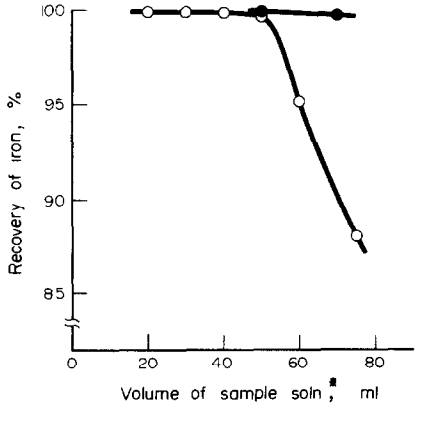


Fig. 5. Effect of the volume of sample solution at the reduction stage. Iron(III) taken 83.7 mg, CPA added 10 g, hydrochloric acid added ○ 5 ml, ● 7.5 ml.

* Includes the volume of hydrochloric acid added. This also applies to Figs. 6 and 7.

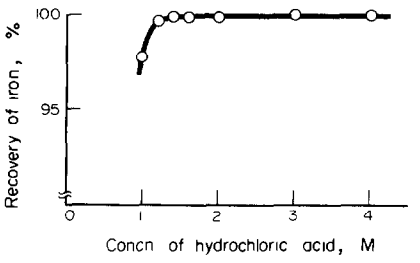


Fig. 6. Effect of the concentration of hydrochloric acid at the reduction stage. Iron(III) taken 83.7 mg, CPA added 10 g, volume of sample solution 30 ml.

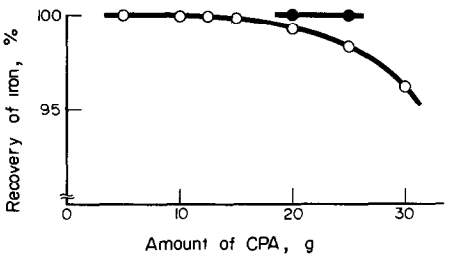


Fig. 7. Effect of CPA on the titration of iron with dichromate. Iron(III) taken 83.7 mg. ○ Hydrochloric acid added 5 ml, volume of sample solution 30 ml, ● hydrochloric acid added 7.5 ml, volume of sample solution 40 ml.

Table 3. Effect of diverse ions on the titrimetry of iron with dichromate solution

Ion	Added as	Amount added, *mg*	Iron recovered, *mg*
None	—	—	85.2
Ag(I)	Ag_2SO_4	5	85.3
Al(III)	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	5	85.2
As(III)	As_2O_3(NaOH)	1	85.4
		5	87.2
Cd(II)	$CdSO_4$	5	85.1
Co(II)	$CoSO_4 \cdot 7H_2O$	5	85.0
Cr(III)	$K_2Cr_2(SO_4)_4 \cdot 24H_2O$	5	85.1
Cu(II)	$CuSO_4 \cdot 5H_2O$	0.25	84.6
		0.50	84.4
		1.0	83.8
		2.5	84.1
		5.0	84.7
		7.5	86.8
		10.0	88.9
Mn(II)	$MnCl_2 \cdot 4H_2O$	5	85.2
Mo(VI)	$Na_2MoO_4 \cdot 2H_2O$	1	86.0
		5	88.3
Ni(II)	$NiCl_2 \cdot 6H_2O$	5	85.2
Pb(II)	$PbCl_2$	5	85.2
Sb(III)	$SbCl_3$	1	85.6
		5	89.4
Ti(IV)	$TiO_2(H_2SO_4)$	5	85.0
V(V)	NH_4VO_3(HCl)	0.5	85.3
		1.0	86.2
		2.5	87.4
		5.0	90.6
W(VI)	$Na_2WO_4 \cdot 2H_2O$	5	85.2
Zn(II)	$ZnSO_4 \cdot 7H_2O$	5	85.1

Iron(III) taken 85.2 mg, CPA added 10 g.

for the range 50–300 ml. Table 3 shows the effect of diverse ions on the recovery of iron. Assuming that 85 mg of iron are determined in the presence of 5 mg of foreign ions and that the acceptable deviation is ±1%, species such as Sb(III), As(III), Mo(VI), V(V) and Cu(II) interfere. These do not commonly occur in commercial iron ores, however.

It is seen that the recovery of iron shows a minimum when about 1 mg of copper is present. The reason may be related to two separate properties of copper. On the one hand, copper(II) catalyses the air-oxidation of ferrous iron[16] to decrease the recovery of iron, but on the other hand, is reduced to copper(I) by stannous chloride in the presence of CPA and is titrated with dichromate, thus increasing the apparent recovery of iron. Further studies (including electrochemical ones) are necessary to clarify the details of this phenomenon.

Chelatometric titration of iron, combined with solvent extraction

Several methods for the determination of iron have been proposed, to prevent pollution of drainage by the mercury used in the stannous chloride method.[15,17] Chelatometric titration has the merit of dispensing with mercury and chromium compounds. However, it must be combined with a separation, *e.g.*, by solvent extraction, to eliminate the influence of phosphates and to enhance the selectivity for iron.

The extraction of iron with MIBK in the presence of CPA was studied with variation in the concentration of hydrochloric acid. The results shown in Fig. 8 are almost the same as those obtained by Goto *et al.*[18] for the system without CPA present. If the concentration of hydrochloric acid is fixed at 5.6*M*, variation of the amount of CPA up to 8 g does not affect the results.

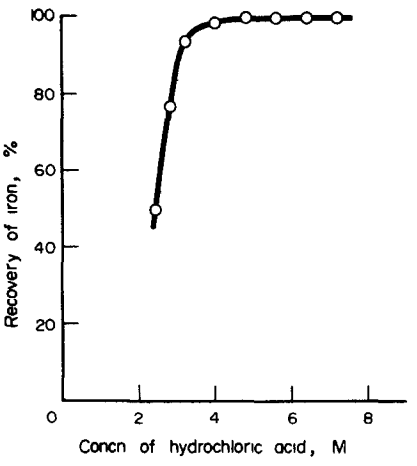


Fig. 8. Effect of the concentration of hydrochloric acid on the solvent extraction of iron with MIBK in the presence of CPA. Iron(III) taken 5.66 mg, CPA added 1 g. The concentration of hydrochloric acid for the first extraction of iron was varied. The ensuing manipulation was the same as that described under *Procedures*.

The effect of diverse ions on the recovery of iron was also studied. The ions which interfered with the redox titration, including As(III), Cu(II), Mo(VI) and V(V), were found not to affect the chelatometric determination of iron.

Determination of total iron in ores

The two types of method described above have been applied to the determination of total iron in several samples. The results obtained are shown in Table 4 together with those obtained by the JIS method.[14] The results obtained for the first three samples are all in

Table 4. Determination of total iron in iron ores

Decomposition of sample	JIS M 8212*		CPA method			
Determination of total iron	JIS M 8212†‡		Titrimetry with dichromate		Chelatometry after solvent extraction§	
Samples	Sample taken g	Iron found, %	Sample taken, g	Iron found, %	Sample taken, g	Iron found, %
Magnetite	0.5500	69.4	0.1272	69.6	0.1160	69.2
	0.5855	69.5	0.1064	69.4	0.1255	69.1
	0.5832	69.6	0.1081	69.3	0.1086	69.1
Limonite	1.0209	38.8	0.1946	38.8	0.1991	38.8
	0.9956	38.9	0.1920	38.8	0.2080	38.8
	1.0001	38.9	0.2046	38.7	0.2081	38.6
Hematite	0.5560	69.2	0.1091	68.9	0.1061	68.9
	0.5401	69.1	0.1043	68.8	0.1119	68.6
	0.5281	69.2	0.1110	68.9	0.1146	68.7
Pyrite cinder (Cu content, 0.34%)	0.6447	56.3	0.1150	55.9¶	0.1154	56.4¶
	0.6489	56.7	0.1019	56.1¶	0.1171	56.4¶
	0.6646	56.7	0.1015	55.8¶	0.1155	56.4¶

* Decomposition with hydrochloric acid, removal of silica with hydrofluoric acid and fusion with potassium pyrosulphate.
† Titrimetry with potassium dichromate solution in the presence of H_2SO_4–H_3PO_4 mixture.
‡, § One fifth and one tenth of the sample solutions were used, respectively.
¶ Heating time 1 hr.

Table 5. Determination of the ferrous iron in iron ores and related compounds

Decomposition of sample	JIS M 8213*†		CPA method	
Determination of iron(II)	JIS M 8213‡		Titrimetry with dichromate	
Samples	Sample taken, g	Iron(II) found, %	Sample taken, g	Iron(II) found, %
Limonite	0.5072	0.07	0.2892	0.10
	0.6027	0.06	0.3265	0.12
	0.5079	0.07	0.2159	0.13
Hematite	0.5187	0.44	0.2337	0.68
	0.5493	0.47	0.2886	0.67
	0.5109	0.38	0.2159	0.66
Magnetite	0.4955	23.1	0.2319	23.3
	0.3231	23.2	0.2163	23.1
	0.4894	23.0	0.2119	23.2
Iron sand	0.4358	24.1	0.2405	24.4 (30)§
	0.2088	24.2	0.2069	24.8 (45)§
	0.5033	23.9	0.2027	24.9 (60)§
Iron(II) iron(III) oxide (reagent grade)	0.3865	20.4	0.2453	20.3
	0.4576	20.3	0.2079	20.2
	0.5082	20.4	0.2115	20.2

* Decomposition with hydrochloric acid in atmosphere of nitrogen.
† The degrees of decomposition by this method were as follows: limonite 99.9, hematite 97.4, magnetite 99.8 and iron sand 97.4%.
‡ Titrimetry with potassium dichromate solution in the presence of H_2SO_4–H_3PO_4 mixture.
§ The numbers in parentheses represent heating time in minutes.

acceptably close agreement. Redox titration gave a lower result than the JIS method for pyrite cinder, which may be attributed to the copper contained in it (see Table 3). The chelatometric finish may be more accurate for such samples.

The decomposition of iron ores with CPA is rapid, free from such tedious and time-consuming manipulations as elimination of silica and filtration, and is therefore suitable for analysis of large numbers of samples. When the samples are decomposed successively in the same furnace, five samples can be analysed within 3 hr.

Determination of ferrous iron in iron ores

The ferrous iron in several samples was determined by the procedure described above; the results are shown in Table 5. It is evident that in general the values obtained by the present method are slightly higher than those for the JIS method.[19] The reason may be that samples such as limonite, hematite and ilmenite cannot be decomposed quantitatively with hydrochloric acid alone.

Many methods have been proposed for the determination of iron(II).[20] The present method may be superior to these in that samples are brought into solution quantitatively and the oxidation of iron(II) during the process is easily prevented.

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REFERENCES

1. H. Bennett, *Analyst*, 1977, **102**, 153.
2. K. Nagashima, *Bunseki Kagaku*, 1972, **21**, 129.
3. O. Kammori, *ibid.*, 1972, **21**, 140.
4. O. P. Bhargava, *Analyst*, 1976, **101**, 125.
5. T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, *Bull. Chem. Soc. Japan*, 1955, **28**, 641.
6. T. Kiba, I. Akaza and N. Sugishita, *ibid.*, 1957, **30**, 972.
7. K. Terada, S. Hirakawa and T. Kiba, *ibid.*, 1977, **50**, 396.
8. T. Kiba and I. Akaza, *Nippon Kagaku Zasshi*, 1960, **81**, 449.
9. T. Kiba, I. Akaza and O. Kinoshita, *Bull. Chem. Soc. Japan*, 1960, **33**, 329.
10. T. Kiba, I. Akaza and H. Hachino, *ibid.*, 1959, **32**, 454.
11. K. Terada, T. Ooba and T. Kiba, *Talanta*, 1975, **22**, 41.
12. *Muki Ōyōhishoku Bunseki*, Vol. 2, p. 334. Kyōritsu Shuppan, Tokyo, 1974.
13. K. Ueno, *Kireito Tekiteihō*, p. 248. Nankodo, Tokyo, 1972.
14. JIS M 8212-1971 *Method for Determination of Total Iron in Iron Ores.*
15. M. Saeki, K. Nishizaka, M. Iwamoto and A. Adachi, *Tetsu to Hagane*, 1974, **60**, 2045.
16. A. B. Lamb and L. W. Elden, *J. Am. Chem. Soc.*, 1931, **53**, 137.
17. T. Hata, T. Hagiwara and K. Sumi, *Bunseki Kagaku*, 1973, **22**, 886.
18. H. Goto, Y. Kakita and K. Furukawa, *Nippon Kagaku Zasshi*, 1958, **79**, 1513.
19. JIS M 8213-1971 *Method for Determination of Ferrous Oxide in Iron Ores.*
20. H. N. S. Schafer, *Analyst*, 1966, **91**, 755.

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COMPOSITIONAL ANALYSIS OF SINGLE CRYSTALS OF FLUX-GROWN MAGNETIC GARNETS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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Summary—A method of determining the chemical composition of single crystals of flux-grown magnetic garnets $(R_1, R_2)_3(Fe, Ga)_5O_{12}$ (R_1 and R_2 = Y, Eu, Gd, or Er) is described. Elements to be determined were rare earths, iron and gallium as main constituents, and lead as an impurity introduced from the flux. Lanthanum chloride was added to the samples and the standard solutions to remove the interference effects of concomitant foreign elements on the atomic-absorption measurement of the rare earths and to improve the measurement precision for iron, gallium and lead. The atomic-absorption measurements in the lanthanum chloride matrix are discussed. Finally, results for some garnets are presented and problems regarding the composition of the materials are described.

Rare-earth iron garnets have been investigated for their applications in magnetic bubble domain devices by a number of workers. The single crystals are usually grown by the flux method and the crystal composition is usually expressed as a "nominal" formula determined empirically by use of data on phase equilibria and distribution coefficients of components between the liquid (flux) and solid (garnet) phases; the nominal composition differs from the crystal component ratio in the melt.[1] Chemical analyses for all the constituents have not been reported and only a partial analysis has been described.[2,3]

In garnets with the general formula $R_3Fe_5O_{12}$, where R is a rare-earth metal, the R sites can be occupied by combinations of several kinds of rare-earth and the Fe sites can be partially substituted with tervalent ions such as Al^{3+} and Ga^{3+}. The variation of rare-earth atom ratios causes a change in the lattice parameter[3] and the Fe substitutions change the saturation magnetic moment.[4] It is also known that lead from the flux agent is incorporated as an impurity in the crystal and that the lattice parameter increases with increasing lead content.[3] A complete chemical analysis is desirable in interpretation of the physical properties of materials; a partial analysis fails to detect compositional variation of components other than the elements of interest. In this paper a method for determining the chemical composition of the flux-grown single crystals is described.

The materials analysed were single crystals of magnetic garnets with the composition $(R_1, R_2)_3(Fe, Ga)_5O_{12}$ (R_1 and R_2 = Y, Eu, Gd, or Er). The garnets were grown from a flux consisting of lead oxide, lead fluoride and boron oxide,† so that the elements to be determined were rare earths, iron, and gallium as main constituents, and lead as an impurity in the crystals. Determination of the rare earths has been reported previously.[5] It was found that the addition of lanthanum chloride to the sample solution increased the analytical sensitivity for the rare earths and removed the interference effects of accompanying foreign elements. A discussion on the effects of lanthanum chloride is given here because the major factors contributing to the role of lanthanum chloride were not clearly understood earlier. The effect of lanthanum chloride on the measurement of iron, gallium and lead was also examined in the present work. The addition of lanthanum chloride improved the measurement precision for these elements as well. Accordingly, all the elements were determined in the lanthanum chloride matrix, on the same starting sample. It is recommended that a wide variety of metals in the same sample be determined by a one-solution procedure. To demonstrate the applicability of this method for the analysis of individual single crystals, a maximum sample weight of 20 mg was used. Finally, the results of analysis for various samples are presented.

EXPERIMENTAL

Reagents

Standard solutions. The rare-earth solutions were prepared by dissolving rare-earth chloride hexahydrates in demineralized water and were standardized by titration with EDTA. The iron solution was prepared by dissolving iron metal (99.9% pure) in hydrochloric acid. The gallium solution was prepared by dissolving gallium metal (99.99% pure) in nitric acid, evaporating with hydrochloric acid, and then dissolving the residue in demineralized water. The lead solution was prepared by dissolving lead nitrate in demineralized water. The standard solutions, except for lead, were prepared in 0.1*M* hydrochloric acid medium. The lead solution was prepared in 0.01*M* nitric acid medium. All stock solutions had an analyte concentration of 1 mg/ml. The reagents were of analytical grade.

Lanthanum chloride solution. Lanthanum chloride heptahydrate (reagent grade) was dissolved in demineralized water and the stock solution had an $LaCl_3$ concentration of 50 mg/ml.

* Part of the thesis submitted to the University of Tokyo to fulfil the requirements for the degree of *Rigaku-Hakushi* (Ph.D.).

† Unpublished work by Y. Wada and S. Harada, RCA Research Laboratories, Inc., Tokyo, Japan.

Table 1. Operating conditions for measurements of rare earths, iron, gallium and lead

Analyte	Wavelength,* *nm*	Lamp current, *mA*	Scale expansion	Flow-rate,† *l./min* C_2H_2/N_2O	Burner height‡
Y	410.2	10	0–2.5	5.8–6.0	1–2
Eu	459.4	10	0	5.5–5.8	3
Gd	368.4	10	0–2.5	5.8–6.0	1–2
Er	400.8	10	0–2	5.8–6.0	1–2
Fe	372.0	15	0–1	5.8	3
Ga	287.4	10	0–2	5.8	3
Pb	283.3	10	0–2.5	5.8	3

*Spectral width 0.32 nm. † Pressures were 1.8 kg/cm² for N_2O and 0.8 kg/cm² for C_2H_2; nitrous oxide flowrate 8.0 l./min throughout. ‡The instrument has a 5-cm single-slot burner head and the beam is passed twice through the flame. The burner height is denoted by the numerals 0, 1, 2 and 3. A measurement made with a screen placed on the burner head showed the following relation between these numerals and the height (mm) above the burner head at which the beam-centre enters or leaves the flame:

numeral	beam position			
	1st entry	1st exit	2nd entry	2nd exit
0	14	9	—	—
1	19	14	1	2
2	24	19	6	7
3	29	24	11	12

Working conditions for atomic-absorption measurements

A nitrous oxide–acetylene flame was used, in a Hitachi model 208 atomic-absorption spectrophotometer. Westinghouse hollow-cathode lamps were used for the rare earths and gallium, and Hitachi HLA-3 lamps were used for iron and lead. Table 1 shows the operating conditions for the measurements; they were optimized with use of the standard solutions. Conditions were chosen to prevent a noisy absorption and to avoid blocking of the burner slot by reduced carbon particles.

As indicated in Table 1, measurement at a lower position in the flame was suitable for yttrium, gadolinium and erbium, whereas the use of a higher position was better for other elements. The measurement positions may be related to the dissociation energies of the monoxides of the elements: YO 7.50 eV, EuO 5.85 eV, GdO 7.55 eV, ErO 6.63 eV, FeO 4.29 eV, GaO 3.04 eV, and PbO 4.29 eV. Effects of hydrochloric acid on atomic-absorption measurements of rare earths have been studied by several workers,[6–9] but the effects reported differ. In this work a constant concentration of 0.1*M* for the hydrochloric acid was used; no significant effects of the hydrochloric acid were found for any of the elements.

Procedure

Samples weighing 10–20 mg were dissolved in concentrated hydrochloric acid and the sample solutions were diluted to give appropriate concentrations of the analytes. The final sample solutions were adjusted to be 0.1*M* in hydrochloric acid and to contain 5000 ppm of lanthanum chloride. The same adjustment was carried out for the standards. The nitrous oxide–acetylene flame was used for all the determinations.

RESULTS AND DISCUSSION

Atomic-absorption measurements in the lanthanum chloride matrix

As reported previously,[5] the absorption of the rare earths was enhanced by increasing the lanthanum chloride concentration, and the mutual interference effects were suppressed by the addition of lanthanum chloride. For example, the error in the europium measurement was about 50–80% in the presence of gadolinium or gallium for solutions without lanthanum chloride, but was only 1–2% when it was present. Similar effects with lanthanum chloride were also observed for other rare earths. The error in the measurement of the rare earths, arising from the effects of all the foreign elements examined for the garnet analysis, was reduced to within 1–2% in the presence of 5000 ppm lanthanum chloride.

Figure 1 shows the effects of lanthanum chloride on the atomic absorption of gallium and lead. The absorption of these elements was slightly increased by the presence of lanthanum chloride whereas the iron absorption was not generally affected by the addition of the reagent.[10] Table 2 presents the comparison of measurements for 50 ppm lead with and without the addition of lanthanum chloride. The observed values are the average of three measurements for the same sample solution. As seen from Table 2, the addition of

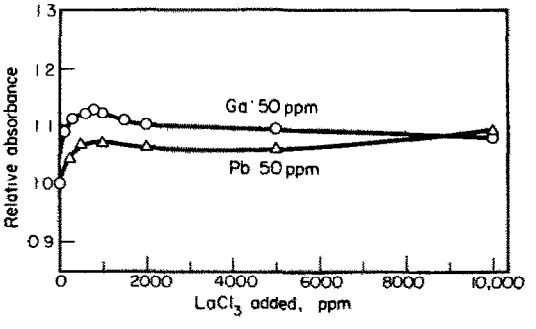


Fig. 1. Effects of lanthanum chloride on absorption of gallium and lead in 0.1*M* hydrochloric acid solution.

Table 2. Comparison of measurements for 50 ppm lead with and without addition of lanthanum chloride

Foreign element,* ppm	Sample solution (in 0.1*M* HCl)			
	No $LaCl_3$		5000 ppm $LaCl_3$	
	obsd., ppm	error, %	obsd., ppm	error, %
Y	1000	52.3	+4.6	+0.4
Eu	2000	52.6	+5.2	+3.0
Gd	500	52.0	+4.0	+1.0
Er	2000	51.3	+2.6	+0.2
Y	1000			
Fe	2000	51.1	+2.2	−0.4
Ga	200			
Eu	2000			
Fe	2000	51.2	+2.4	+0.8
Ga	200			
Gd	500			
Fe	2000	51.4	+2.8	+1.0
Ga	200			
Er	2000			
Fe	2000	51.3	+2.6	+1.2
Ga	200			
av.		51.6_5	$+3.3_0$	$+0.9_0$
std. devn.			3.7_0	1.3_8

* Added as chlorides.

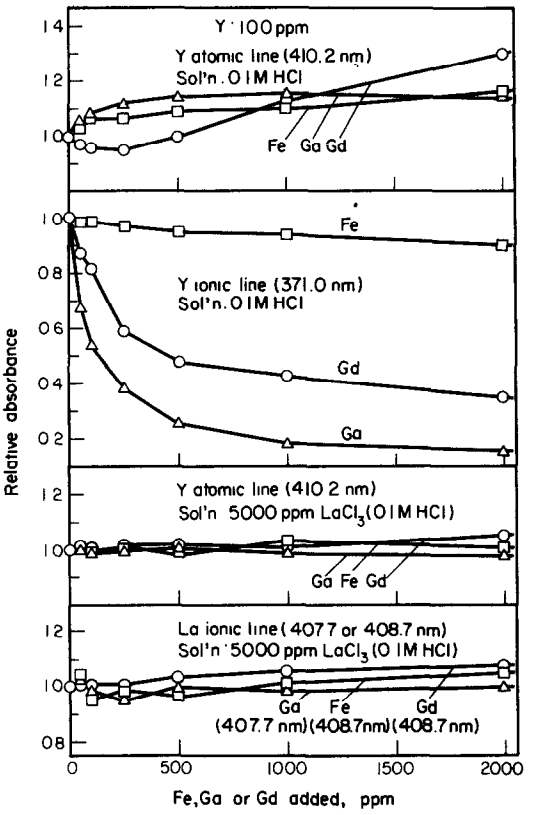


Fig. 2. Variation of absorption intensities of the yttrium atomic and ionic lines and the lanthanum ionic line with and without lanthanum chloride present in the solution.

lanthanum chloride improves the precision. Similar effects were also observed for iron and gallium.

In the case of the alkaline earths, it is known that lanthanum chloride acts as a releasing reagent.[11,12] The effect is generally attributed to formation of lanthanum compounds of the interfering elements that are more stable than the corresponding alkaline earth compounds and so prevent formation of refractory compounds of these analytes. However, the releasing agent may possibly act by a simple sputtering mechanism that leads to production of smaller residual solid particles which can be more easily volatilized. In the case of the rare earths, however, the major factors contributing to the effect of lanthanum chloride have not been reported. The effects of iron, gallium and gadolinium on yttrium atomic and ionic absorption was therefore studied with and without the addition of 5000 ppm of lanthanum chloride. The ionic line used was 371.0 nm. Results are shown in Fig. 2, where the variation of lanthanum ionic absorption at 407.7 or 408.7 nm is also given.

As can be seen from Fig. 2, in solutions without lanthanum chloride, the presence of iron increased the yttrium atomic absorption but had little effect on the ionic absorption. With the addition of lanthanum chloride, the atomic absorption of yttrium was constant over the range 0–2000 ppm of iron and the yttrium ionization was almost suppressed; the lanthanum ionic absorption was unchanged. The presence of gadolinium decreased or increased the yttrium atomic absorption, depending on the gadolinium concentration, but suppressed the yttrium ionic absorption under all conditions in the absence of lanthanum chloride. In the presence of 5000 ppm lf lanthanum chloride, the atomic absorption of yttrium was constant for 0–1000 ppm gadolinium, but slightly increased for the higher concentrations of gadolinium up to 2000 ppm. The 2000 ppm of gadolinium also increased the lanthanum ionic absorption. The presence of gallium increased the yttrium atomic absorption but suppressed the ionic absorption for the solutions without lanthanum chloride. In the presence of 5000 ppm of lanthanum chloride, the atomic absorption of yttrium was constant over the range 0–2000 ppm of gallium, but the yttrium ionization was almost suppressed and the lanthanum ionic absorption did not vary.

The formation of free atoms in the flame is governed by the processes of solvent evaporation, vaporization of solid particles, and the dissociation of gaseous compounds into atoms. The rare earths have a relatively low ionization energy (5.5–6.8 eV; Y 6.38 eV) so that easily ionized elements are usually added to the sample solutions to suppress the ionization and thus increase the measurement sensitivity for the rare earths.[6,7,13–16] However, it seems that not all the interference effects can be explained in terms of only ionization suppression, because the dissociation energies of the rare-earth monoxides are relatively high (6–8.5 eV; YO 7.50 eV). Metals which form monoxides with dissociation energies less than about

6.5 eV are completely atomized if solute vaporization is complete,[17] but most concomitant foreign metal species strongly influence the atomization process of the elements of interest.[18]

As shown in Fig. 2, the increase in the yttrium atomic absorption in the presence of iron cannot be attributed to suppression of the ionization of yttrium. The presence of gadolinium or gallium truly contributes to suppression of yttrium ionization, however, because elements with ionization energies below 6.5 eV are appreciably ionized and suppress ionization of other elements in the flame.[19] The ionization energies are 6.16 and 6 eV for gadolinium and gallium, respectively. However, other factors such as the vaporization of samples and dissociation rate of yttrium compounds in the flame have to be taken into account; increasing the vaporization or dissociation rate would apparently produce the same effect as ionization suppression. If the addition of gadolinium or gallium did not affect the vaporization and dissociation rates for the yttrium measurement, a constant number ratio of yttrium atoms to ions should be obtained for various concentrations of gadolinium or gallium. This relation can be expressed as follows:[20]

$$x+y = ax+by \quad (=1), \tag{1}$$

whence

$$y/x = (1-a)/(b-1), \tag{2}$$

where x and y are the fractions of yttrium present in the flame as atoms and as ions, respectively, without addition of foreign elements. The terms a and b are the ratios of the atomic and ionic absorptions with and without addition of the foreign elements, respectively.

Table 3 shows the ratios of y to x calculated from the data in Fig. 2 for gadolinium and gallium. The ratio for gallium is fairly constant but that for gadolinium varies widely. This indicates that the effect of gallium is mainly the suppression of ionization. Therefore, an easily ionizable element, for example sodium, can eliminate the gallium interference as reported previously.[5] In the case of gadolinium, the variation in values of the ratio suggests that there are contributing factors other than the suppression of ionization. There seems to be a change in dissociation or vaporization rate. The difference between the gallium and gadolinium effects may be due to the dissimilarity in chemical properties, compared to those of yttrium, rather than that in the ionization energies. A change in dissociation or vaporization rate seems to occur also in the presence of iron because the yttrium ionization is not suppressed but the yttrium atomic absorption increases as shown in Fig. 2. This suggests that the interference effects of gadolinium and iron cannot be eliminated by addition of easily ionizable elements, *e.g.*, sodium and potassium.[5] Another reagent, which will control the dissociation or vaporization rate, can be more effective for suppressing the interference effects.

Table 3. Ratios of fractions of yttrium present as ions and atoms in the flame (y/x),* as a function of concentrations of gadolinium or gallium added

Concentration, *ppm*	Gd	Ga
50	−0.162	0.127
100	−0.204	0.165
250	−0.078	0.187
500	−0.004	0.185
1000	0.225	0.174
2000	0.461	0.176

* See equation (2) in the text.

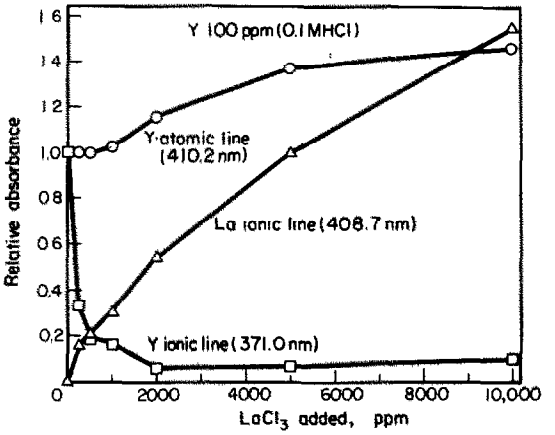


Fig. 3. Variation of absorption intensities of the yttrium atomic and ionic lines and the lanthanum ionic line as a function of concentration of lanthanum chloride added.

The effect of lanthanum chloride on the atomic and ionic absorption of yttrium is shown in Fig. 3, together with the variation in the ionic absorption of lanthanum. From these data, similar calculations were made for various concentrations of lanthanum chloride. Non-constant values were obtained, indicating that lanthanum chloride affects the vaporization and dissociation as well as the ionization process. However, it seems certain that lanthanum chloride acts as an ionization suppressor by producing electrons in the flame, because the lanthanum ionic absorption was not altered by the other species present, in most cases examined, as shown in Fig. 2. Lanthanum itself ionizes in the flame, as shown in Fig. 3.

The vaporization or dissociation rate is a complex function of many factors such as variation of droplet size, and diffusion of vaporized and flame species. Although we do not understand all the phenomena in the present case, lanthanum chloride would appear to affect the volatility of the analytes (rare earths). The most probable explanation for the interference effects is a change in the volatility of the analytes when other metal species are present in the sample solutions.[18] This effect occurs because a high concentration of salts in sample solutions can change the droplet size but does not affect the aspiration rate.[21] In the present work, the sample solutions were aspirated at a flow-rate of $2.00 \pm 0.02_5$ ml/min.

Table 4. Results of mixed-oxides analysis (means of three experiments)

	Sample*	Analyte, % w/w						
		Pb	Y	Eu	Gd	Er	Fe	Ga
1	calcd.	0.27	35.24				28.04	11.05
	obsd.	0.26	35.5	—	—	—	27.8	10.9
	range	0.02	0.4				0.2	0.1
2	calcd.	0.27	30.89	5.87			26.59	11.66
	obsd.	0.25	31.5	5.77	—	—	26.2	11.5
	range	0.02	0.2	0.06			0.1	0
3	calcd.	3.76	25.82		11.42		27.04	8.44
	obsd.	3.70	25.5	—	10.9	—	26.6	8.37
	range	0.05	0.5		0.7		0.2	0.06
4	calcd.	0.53		15.62		34.38	24.68	5.02
	obsd.	0.50	—	15.3	—	34.2	24.4	5.02
	range	0		0.4		0.2	0.2	0.04

* Oxides mixed in the following mole ratios:

	PbO	Y_2O_3	Eu_2O_3	Gd_2O_3	Er_2O_3	Fe_2O_3	Ga_2O_3
1:	0.02	3.0	—	—	—	3.8	1.2
2:	0.02	2.7	0.3	—	—	3.7	1.3
3:	0.30	2.4	—	0.6	—	4.0	1.0
4:	0.05	—	1.0	—	2.0	4.3	0.7

For measurements of iron, gallium and lead, the addition of lanthanum chloride is effective for matching the concentration of salts in the sample solutions nearly to that in the standard solutions. Thus lanthanum chloride can eliminate some of the matrix effects and thereby improve the measurement precision as already described. Interferences due to the formation of lead chloride[22] were not observed.

Analysis of samples

Test analyses were first performed on a mixture of oxides of known composition. Results are given in Table 4 for rare earths (Y, Eu, Gd, and Er), iron, gallium and lead. All the oxides had a purity of at least 99.9%. The atomic absorption was measured with 5000 ppm of lanthanum chloride present, as described in the experimental section. The values shown in Table 4 are the averages from three experiments. The range is also shown. In all cases the results agree with the calculated values, indicating that the procedure is suitable for analysis of single-crystal samples.

The results for single crystals of several magnetic garnets are shown in Table 5, calculated as mole ratios. The average and range of results from three experiments are shown. In all cases both the ratio of rare earth to iron plus gallium, [R/(Fe+Ga) where R = Y, Eu, Gd, and/or Er] and the rare-earth ratio, R_1/R_2, were close to the ratios expected from the nominal compositions. For different crystals grown in the same batch, the observed rare-earth ratios also agreed with each other as shown by the results for samples 2 and 3 and for samples 4 and 5. A similar result was reported by Barns[3] for X-ray fluorescence milliprobe analysis of the $Gd_{2.34}Tb_{0.66}Fe_5O_{12}$ crystal. He reported that application of Vegard's law[23] gave a quantitative estimation of compositional gradients due to varying rare-earth atom ratios, but according to the X-ray fluorescence analysis there was no variation in the rare-earth ratios. He concluded that this discrepancy was due to a variation in the lead content incorporated from the flux, indicating that the application of Vegard's law is unsuitable for such analyses, just as was found for single crystals of chromium chalcogenide spinels.[24]

The ratio of iron to gallium always deviated from that calculated from the nominal composition. In general, the iron content was higher and the gallium content lower than the nominal content. Even in the same batch, the iron:gallium ratios were different for individual crystals, as shown by the results for samples 4 and 5. In this particular case, the lead content differed from crystal to crystal. This variation of lead content may cause the fluctuation in the iron and gallium content because the incorporation of gallium in the $Y_3Fe_{5-x}O_{12}$ crystals is strongly dependent on the ratio of lead fluoride to lead oxide in the flux.[2] Hence the lead fluoride to lead oxide ratio has to be well adjusted to optimize uniformity within crystals.[2] It also became clear that a substantial amount of lead was incorporated into the crystals; the mole ratios for lead content given in Table 5 correspond to 0.4–2.1% w/w. The present results indicate that the crystal-growth conditions must be carefully determined for growing garnets of the desired composition, particularly for iron and gallium, and that the analysis should be performed for all the constituents, including impurities.

The results of the analysis are being utilized to investigate the associated physical properties of these materials. It has been found that the composition

Table 5. Results of single-crystal analysis of magnetic garnets

	Analyte, mole ratio															
	Pb		Y		Eu		Gd		Er		Fe		Ga		R/(Fe+Ga)†	
Sample*	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range	mean	range
1	—		2.98	0.06	—		—		—		4.27	0.06	0.75	0.02	0.592	0.022
2	0.01	0	2.69	0.04	0.30	0.01	—		—		4.05	0.04	0.94	0.01	0.597	0.015
3	0.03	0	2.69	0.04	0.29	0.01	—		—		4.03	0.03	0.96	0.01	0.598	0.015
4	0.02	0	2.48	0.03	0.50	0.01	—		—		4.23	0.04	0.78	0.02	0.594	0.015
5	0.08	0	2.49	0.02	0.47	0	—		—		4.08	0.03	0.88	0.02	0.596	0.008
6	0.02	0	2.35	0.02	—		0.62	0.04	—		4.08	0.03	0.92	0.02	0.594	0.014
7	0.03	0	—		3.00	0	—		—		4.04	0	0.93	0	0.604	0.001
8	—		—		2.02	0.02	—		0.97	0.01	4.40	0.03	0.61	0.01	0.595	0.010

* The crystals grown had the following nominal composition:

1: $Y_3Fe_{3.8}Ga_{1.2}O_{12}$.
2: $Y_{2.7}Eu_{0.3}Fe_{3.7}Ga_{1.3}O_{12}$.
3: $Y_{2.7}Eu_{0.3}Fe_{3.7}Ga_{1.3}O_{12}$.
4: $Y_{2.5}Eu_{0.5}Fe_{3.7}Ga_{1.3}O_{12}$.
5: $Y_{2.5}Eu_{0.5}Fe_{3.7}Ga_{1.3}O_{12}$.
6: $Y_{2.4}Gd_{0.6}Fe_{3.7}Ga_{1.3}O_{12}$.
7: $Eu_3Fe_4GaO_{12}$.
8: $Eu_2ErFe_{4.3}Ga_{0.7}O_{12}$.

† R designates rare earths (Y, Eu, Gd, and Er), and the expected value of the ratio is 0.6 for each sample.

determined by the present method is consistent with the physical measurements such as the saturation magnetization and the Curie temperature.* For example, in the case of the system $Eu_{3-x}Er_xFe_{5-y}Ga_yO_{12}$ $(x=0,1,2,3, \quad y=0.6-1.2)$ the saturation magnetization at room temperature increases linearly with increasing iron to gallium ratio and does not depend primarily on the rare-earth ratio. The Curie temperature for the system also increases with increasing iron to gallium ratio. The correlation between the physical properties and the composition is useful for characterizing garnet films prepared by liquid-phase epitaxial growth.

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REFERENCES

1. See for example, L. G. Van Uitert, W. A. Bonner, W. H. Grodkiewicz, L. Pictroski and G. J. Zydzik, *Mat. Res. Bull.*, 1970, **5**, 825.
2. J. W. Neilsen, D. A. Lepore and D. C. Leo in H. S. Peiser, eds., *Crystal Growth*, p. 457. Pergamon Press, London, 1967.
3. R. L. Barns, *J. Appl. Phys.*, 1971, **42**, 1623.
4. A. H. Bobeck, E. G. Spencer, L. G. Van Uitert, S. C. Abrahams, R. L. Barns, W. H. Grodkiewicz, R. C. Sherwood, P. H. Schmidt, D. H. Smith and E. M. Walters, *Appl. Phys. Lett.*, 1970, **17**, 131.
5. K. Ametani, *Bull. Chem. Soc. Japan*, 1974, **47**, 2238.
6. M. Satō, H. Matsui and T. Matsubara, *Bunseki Kagaku*, 1971, **20**, 856.
7. A. M. Szaplonczay, *Analyst*, 1972, **97**, 29.
8. T. Ishizuka and H. Sunahara, *Bunseki Kagaku*, 1973, **22**, 59; *Anal. Chim. Acta*, 1973, **66**, 343.
9. T. Ishizuka, Y. Uwamino and H. Sunahara, *Bunseki Kagaku*, 1973, **22**, 1450.
10. K. Ametani and T. Takahashi, *Bull. Chem. Soc. Japan*, 1975, **48**, 721.
11. J. Yofé, R. Avni and M. Stiller, *Anal. Chim. Acta*, 1963, **28**, 331.
12. I. Rubeška and B. Moldan, *ibid.*, 1967, **37**, 421.
13. R. W. Cattrall and S. J. E. Slater, *ibid.*, 1971, **56**, 143.
14. D. R. Thomerson and W. J. Price, *ibid.*, 1974, **72**, 188.
15. W. Ooghe and F. Verbeek, *ibid.*, 1974, **73**, 87.
16. R. L. Scott, *At. Abs. Newslett.*, 1970, **9**, 46.
17. J. O. Rasmuson, V. A. Fassel and R. N. Kniseley, *Spectrochim. Acta*, 1973, **28B**, 365.
18. J. Y. Marks and G. G. Welcher, *Anal. Chem.*, 1970, **42**, 1033.
19. G. R. Kornblun and L. de Galan, *Spectrochim. Acta*, 1973, **28B**, 139.
20. D. C. Manning and L. Capacho-Delgado, *Anal. Chim. Acta*, 1966, **36**, 312.
21. J. Ramirez-Muñoz, *Anal. Chem.*, 1970, **42**, 517.
22. J. E. Baker, A. J. Kabat and V. G. Mossotti in J. A. Dean and T. C. Rains eds., *Flame Emission and Atomic Absorption Spectrometry*, Vol. 3, p. 191. Dekker, New York, 1975.
23. See for example, R. H. Bragg in E. F. Kaelble ed., *Handbook of X-rays for Diffraction, Emission, Absorption and Microscopy*, p. 12–11. McGraw-Hill, New York, 1967.
24. K. Ametani, *Bull. Chem. Soc. Japan*, 1976, **49**, 450.

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A CRITICAL EXAMINATION OF ANALYTICAL ERROR

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Summary—Errors associated with three of the five basic analytical operations are examined. It is concluded that non-Gaussian distributions of error are to be expected. With greater care and with improved technique such non-Gaussian distributions become more evident. Condensation of experimental data and interpretation of the analytical results should be made with these characteristics in mind.

Chemistry, as an experimental science, necessarily deals with numbers, since the result of an analysis is normally expressed as a number. Such numbers should be evaluated with an awareness of their limitations. This study is concerned with a broad and long-term concern with the best formal processing methods to use for the condensation of experimental data and the interpretation of the condensed information.

Experimentally, data are obtained from a sequence of up to five basic operations: definition of the goal, isolation of the system, manipulation, measurement, and evaluation. Error can be introduced at any stage. In this paper experimental data concerning errors relating to the manipulative and measurement steps are presented and evaluation is discussed.

OBSERVATIONAL (QUANTIZATION) ERROR

As indicated, the fourth major operation in analysis is that of measurement. Numbers are usually generated from an analogue-to-digital conversion or a quantization procedure in which the magnitude of an analogue parameter is represented numerically. (Quantization is the operation of limiting the possible values of a continuous quantity to a discrete set.) This process has been most carefully examined[1,2] in terms of electronic analogue-to-digital conversion of electrical signals. However, such analogue-to-digital conversion, or quantization, is also required in the reading of scales, dials and verniers by humans.

As stated, the observations frequently entail the reading of scales, dials, or verniers. By definition, analogue quantities can take an infinite number of values, whereas a numerical representation of an analogue value is always limited in resolution. Resolution of a number is related to the quantization level, defined as the smallest change in input signal that can be recorded numerically by the system used. In addition to this resolution limitation, a quantizer (the device or human agent, which brings about the analogue-to-digital conversion) may also introduce bias into the numerical representation of the output. Such bias is seldom random. For example, some electronic quantizers always round down to the nearest quantization level. Introduction of bias into the resulting numerical data has been studied and assessed for electronic quantizers.[1,2]

Although the use of electronic quantizers is spreading, in scientific measurement a large number of quantization operations must continue to be carried out by humans. Like electronic quantizers, human scale-readers are seldom unbiased, and the biases are clearly non-random. Existence of such bias has important implications with respect to the statistical evaluation of numerical data.

Observations

I have examined in some detail one of the simplest human quantization operations, that of reading a burette. At the completion of a titration, the meniscus should be at a random position in terms of the final digit in the burette reading (the 7 in a reading of 44.47 ml, for example). Thus a large number of such terminal digits would be expected to be uniformly distributed among the ten digits from 0 to 9. Figure 1 shows three samples of distributions obtained from human quantization of burette meniscus positions.

Figure 1A shows a sample of the distribution of 10000 terminal digits for burette readings recorded by 184 students (between 45 and 65 readings each) during the course of their performance of analyses. In the sample selected there was prior elimination of those few students with pronounced prejudice for zero ($p < 0.01$). A large number of readings were examined so that the expected standard deviation would be reduced to the low level indicated. Presumably, each of the 10000 readings in Fig. 1A had been taken with care; each student had been thoroughly instructed on how to read the burette scale and on the common sources of error, and had been given both practice and a practical test in careful reading. The fact that terminal digits of 0 and 5 do not stand out from the others is evidence that quantization to the nearest 0.01 ml was attempted. It can be seen that nearly all ten digits have an observed frequency clearly lying far outside the expected standard-deviation limits. A chi-square calculation can be used to determine the extent to which data such as these deviate from expected probabilities. In this

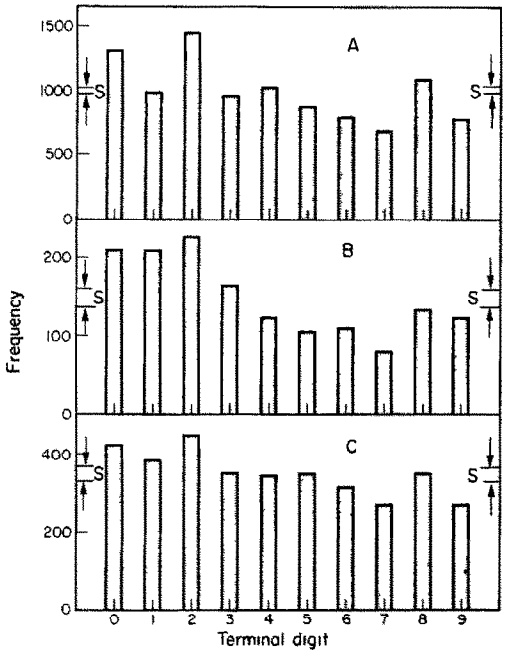


Fig. 1. Frequency of observation of randomly distributed terminal digits in burette readings; *s*, the interval between the arrows, denotes the expected 95% confidence limits (± two standard deviations). (A) 10000 readings of terminal digits taken by 184 students during the performance of analyses; (B) 1500 extraordinarily carefully taken readings by 200 students during a practical test;[3,4] (C) 3500 readings with prior elimination of those from individuals with bias ($p < 0.05$).

case the chi-square value indicates a probability approaching certainty that the distribution observed was not uniform.

Although each of the 10000 readings was presumably taken with care, the question arises as to whether a set of readings with better reliability in terms of the distribution could be expected if even greater care were exercised. Figure 1B shows the distribution of 1500 readings that were taken with painstaking care. They were taken during a practical examination where extraordinary concern for reporting the correct value was shown. The distribution pattern is strikingly similar to that for the 10000 readings. For example, in both cases the digit 2 is observed most frequently and 7 the least frequently. With 1500 readings the expected standard deviation is relatively larger, but still all digits have a frequency lying outside the expected standard deviation limits. A chi-square calculation again indicates with a probability approaching certainty that the distribution of the reported observation is non-uniform.

Figure 1C shows a third independent sample of a distribution of terminal digits. For this sample the chi-square values for the 45–65 readings taken by individuals were calculated, and those with a distribution having a probability of randomness of less than 0.05 were eliminated (about half). This third independent sample was obtained solely from the readings of 72 selected individuals who showed no obvious bias. For these 3500 terminal digits the same distribution pattern persists, and again the probability approaches certainty that the distribution of the reported observations in this highly selected sample is non-uniform.

In distributions such as those illustrated in Fig. 1, three distinct types of group bias can be identified. The first type is bias towards small (0, 1, 2) and away from mid-range (5, 6, 7) terminal digits. The more painstakingly careful readings in Fig. 1B actually appear to show more, not less, of this type of bias.

The second type of group bias is prejudice for even and against odd terminal digits. For all three groups of readings, chi-square calculations for the odd–even distribution give probabilities showing it is highly unlikely that the observed distributions arise from a uniform distribution alone. For the 184 individuals involved in the 10000-reading distribution, the tendency toward odd–even bias was examined; some were found to have bias toward odd numbers, and more to have bias toward even numbers. For individuals, this type of bias appears to be almost as common as the pronounced low–mid-range bias. The overall group distributions as to odd–even bias therefore include some mutual cancellation of individual biases.

The third type of bias can be revealed by examining the deviations of readings from their correct values. Figure 2 shows the distribution of such errors for 200 independent readings. These readings, like those in Fig. 1B, were obtained with painstaking concern and under the controlled conditions of a practical test. This

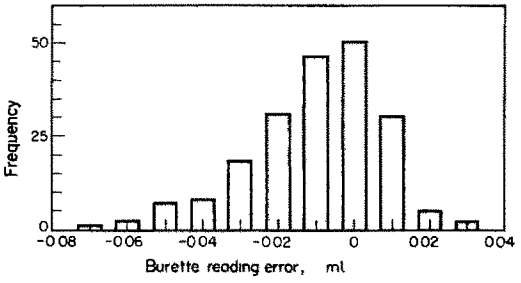


Fig. 2. Distribution of reading errors for 200 independent student observations of over 40 different burettes (errors >0.1 ml omitted). (Correct values were established to a high level of confidence from the readings of 10–15 experienced instructors.)

figure illustrates an obvious non-Gaussian distribution of errors. Negative errors in excess of 0.01 ml outweighed positive ones by almost ten to one.

The simultaneous existence of three types of bias in such a simple operation as quantization of a burette scale seems remarkable. Also remarkable is the observation that the bias is not eliminated through detailed instruction and practice, but rather is brought sharply into focus. We can speculate about the causes for the various types of bias. For example, the third type probably results from incorrect positioning of the reading aid. In spite of prior identification of this as a likely source of error, it was not eliminated even with painstakingly careful readings. Similarly, explanations

might be offered for the sources of error giving rise to the first two types of bias. Their elimination, however, even if the causes were identified, would appear to be unattainable.

The use of a vernier scale decreases, but does not eliminate, number bias in readings. It has been shown[5] that the random terminal digits of weighings from a balance with a vernier read-out exhibit less bias than those from a burette scale (though it is still present). Although digital read-out, where feasible, should further reduce uncertainties introduced by human quantization, it should be recognized that electronic quantization also exhibits bias.[1]

MANIPULATIVE ERROR

The third operation in analysis involves physical and chemical manipulation of the system, including such steps as separation, transfer, reagent addition, and determinate sampling errors. Errors introduced during this operation are called manipulative, and they usually become smaller with increasing competence of the experimentalist.

It is attractive to study observational bias in detail because it is easy to isolate the quantization operation and to obtain large amounts of data. Isolation of the errors associated with physical and chemical manipulations is more difficult.

In a complex set of operations, quantization errors such as those described in the preceding section probably make only minor contributions to the total uncertainty. Most bias and uncertainty is probably introduced through the manipulative operations; that is, in addition to a number of opportunities for introduction of error and bias from quantization operations, there is manipulative error. In general, the several sources of error are difficult to study separately. Consequently, only the overall quality of the results is compared with the correct values. Several such studies have been reported. For example, one study[6] of several hundred chloride determinations indicated no significant bias by the gravimetric technique, positive bias with the Fajans method, and negative bias for the Volhard method. Even though isolation of the errors associated with physical and chemical manipulations is difficult, manipulative bias is probably far more significant than quantization bias and therefore deserves a larger share of attention.

When the number of sources of errors is increased, and provided no one source of error dominates, it would be expected that the distribution of error would become more nearly Gaussian even though the individual sources have non-Gaussian distributions. If a strongly non-Gaussian overall distribution is observed, then it is likely that there is a dominating source of error.

Observations

One simple fundamental manipulative operation, that of taking an aliquot, was adequately isolated from the reading operation and was examined for manipulative bias. Figure 3 shows the distribution of errors in the taking of aliquots by a group of 700 students (over a 5-year period). Those aliquots with gross errors were excluded. To obtain the data, a procedure was used that allowed the error to be estimated to the nearest 0.01 ml. Scale-reading errors were reduced to a negligible level and were certainly at least an order of magnitude smaller than the average errors shown in the figure. In Fig. 3 the errors have been collected into 0.1-ml intervals to show the group distribution. The aliquots were carefully taken under the conditions of a practical test and after detailed instruction and practice. It seems probable that an individual may tend toward either positive or negative manipulative bias; on a group basis, however, this figure clearly demonstrates a much higher probability of positive than of negative errors of moderate magnitude. Chi-square calculations indicate with a probability approaching certainty that the distribution is non-Gaussian.

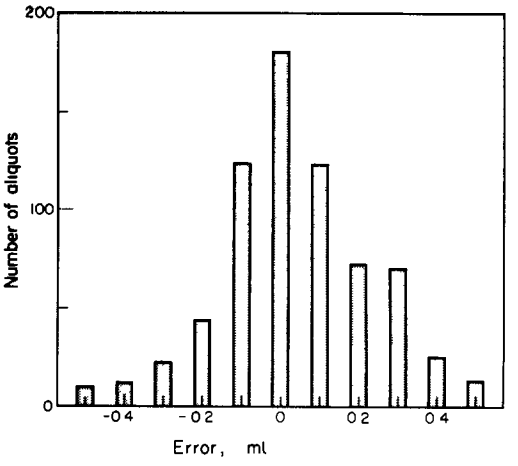


Fig. 3. Distribution of errors for the taking of an aliquot which would require about 40 ml of titrant. The manipulative operations are those involved in the procedure "pipette 10 ml of the concentrated solution ($3M$ H_2SO_4) from the 50-ml flask into the 250-ml volumetric flask; dilute to volume; pipette a 10-ml aliquot of the diluted solution into the 200-ml conical flask". Each student was given a fresh portion of $3M$ H_2SO_4, which has little tendency to absorb or lose water. The pipettes and volumetric flasks were matched so that the calibration error was negligible—normally less than 1 part in 3000. The aliquot supplied by the student was titrated by the instructor to a highly precise end-point. The error plotted in the graph is the difference between the expected and observed volumes of titrant used.

The operations involved in the taking of an aliquot gave no obvious evidence of bias until after refinement of the instructions and improvement of the techniques for using a pipette and volumetric flask. After such improvement, uncertainty in the operation was reduced and bias became clear.

Less direct evidence of overall bias, observational plus manipulative, relates to evaluation of the results of analyses performed by students. Minimization of the adverse effect of bias is basic to a systematic approach to making student's marks agree as closely

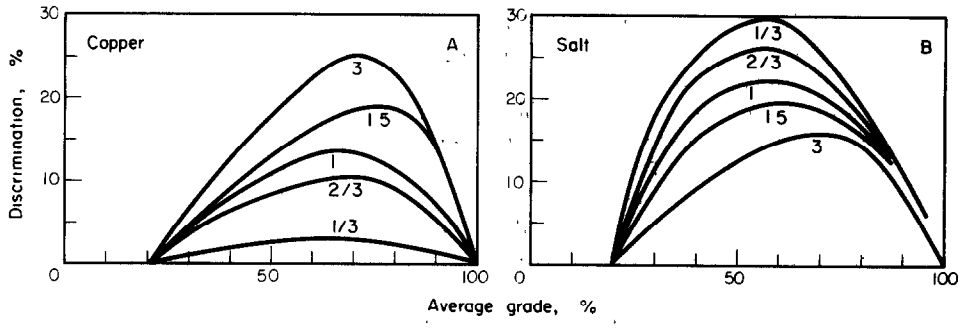


Fig. 4. Smoothed curves showing the effect of varying degrees of skew (1/3, 2/3, 1, 1.5 and 3) on the relation between average grade and discrimination for two analyses by a class in introductory quantitative analysis. (Arbitrarily, a skew of 3 is much more lenient toward results that show positive deviation from correct values than toward ones that show negative deviations, a skew of 1/3 much more lenient toward negative deviations, and a skew of unity equally lenient toward both.) These curves relate to a 5-point grading scale described elsewhere.[4] (A) Determination of copper iodiometrically; (B) determination of total salt by ion-exchange.

as possible with the quality of their experimental work. Thus, the significance of an error in technique represented by a result that is high by a given amount may be greater or less than that of a result that is low by the same amount.

The best index of the reliability of grades is the quantity called discrimination.*[7] It has been observed that grading scales that allow different ranges for high and for low results usually give better values of discrimination. The most desirable skew factors to be used in setting up grading scales cannot be theoretically predicted. Figure 4 shows plots of discrimination against average grade for two such experiments. They are chosen for purposes of illustration because they are closely similar in many respects. In both cases samples and standards are weighed, then subjected to appropriate chemical manipulations, and finally samples and standards are titrated alternately. It is clearly shown that a skew factor greater than unity is desirable in setting up the grading scale for copper, whereas skew in the opposite direction is desirable for grading the results for the determination of total salt. The significance of results such as those in Fig. 4 would seem to have implications for the evaluation of data from interlaboratory comparisons of analyses and from clinical testing. However, the findings are given here mainly to indicate that we should expect real data to show bias.

EVALUATIVE ERROR

The final operation in analysis is the complex matter of evaluation. Significant error can result from inadequate or improper exercise of judgment about the data collected. In a formal sense, evaluation involves (1) selection of the most valid value(s) to represent the data collected, (2) determination of the reliability of the selected value(s), and (3) an attempt to assess the validity of the usually unstated prior assumptions about non-random errors.

Evaluation is and must partly remain an ill-defined and elusive process. In the context of scientific measurement, it involves two stages: the processing of data and the exercise of judgment.

Data-processing has as its aim the condensation of observations to furnish results free from irrelevant information. Such condensation is carried out according to formalized rules. Thus calculation of the average, median and confidence limits, or the application of graphical, minmax, least-squares, maximum-likelihood and Bayesian methods have formalized rules by which an estimate of the "real" value is produced. We need not be concerned further with such formalities except to note that their estimates and validities may differ. The exercise of judgment is another matter. It enters the evaluative process, first in the decision as to the method of data-processing to be applied, and secondly in the interpretation of results. In reality, two separate acts of judgment are not consciously made since a decision about the method of processing establishes the rules by which the results are interpreted.

Almost inevitably, data-processing techniques are chosen that involve quantities such as the average (arithmetic mean) and standard deviation. For these quantities to be good estimates of the central tendency and its validity, a Gaussian distribution of error is required, and experimentalists usually tacitly assume that this is the case. This is the point at which substantial evaluative error is often introduced. (It is taken here that evaluative error includes the use of assumptions that lead to a biased central value.)

If a Gaussian distribution of error could be ensured then the average would be the most efficient estimate of the central value, and confidence limits the most efficient estimate of its reliability, but as Schmitt[8] has said, "No physical process or collection of observations has ever followed or will ever follow the Gaussian distribution exactly." Therefore one part of the exercise of judgment in evaluation must be to

* It is a measure of the difference between the performance of the best and poorest students in a class, for an item such as a test question or an experiment. It is calculated from the top and bottom end-fractions of a class. The size of the end-fraction chosen is a compromise between including as many students as possible for statistical validity and maintaining as great a difference as possible between these fractions.

weigh the convenience of the use of the Gaussian assumption against the consequent probability of introduction of substantial evaluative error.

Non-Gaussian distributions decrease the reliability of averages and also makes conclusions about their reliability conform less with "reality". The frequency of non-Gaussian distributions makes questionable the nearly universal practice of using the average as the best estimate of the true value. Nevertheless the use of a value other than the average meets with widespread prejudice and is likely to be viewed with strong suspicion. It is often believed that somehow, if an experimentalist would simply exercise more care, faith in the fantasy of the Gaussian distribution would be justified. Actually, as pointed out earlier, with greater care, non-Gaussian distributions become more clearly evident.

It is instinctively difficult to accept non-Gaussian distributions and bias because, from a utopian point of view, a Gaussian distribution of error is a persistently attractive model. In fact, it is so attractive that the term "normal distribution" is used. The use of "normal" as synonymous with "Gaussian" is unfortunate because of its misleading connotation (in the sense of "customary" or "usual").

In real measurements, high and low results of the same magnitude are unlikely to occur with the same frequency. Each operation is likely to have its own characteristic biases, and their combination can only fortuitously lead to a Gaussian distribution of error. Although sources of bias may be uncovered, in many cases the best that can be hoped for is to minimize their effects.

The median is more robust than the average as an indicator of the true value in that it is less dependent on the nature of the distribution of the results.[5] In real analyses and particularly those involving only a few measurements it is probably superior to the average.

The data presented here demonstrate that several types of bias can be encountered in even the most elementary operations. Such bias makes it more difficult to arrive at the truth. For example, in Fig. 2 the median of the deviations from correct burette-reading values is substantially smaller than the average of the deviations from correct values. This is so for even the median obtained without prior elimination of gross errors and the average obtained with such elimination. Similarly, with the manipulative bias exhibited in Fig. 4, the median appears to be more reliable than the average in that the median deviation from correct values is only half as large as the average deviation.

The curves shown in Fig. 4 also appear to confirm more broadly that non-Gaussian distributions are the norm for the overall results of a series of operations.

In the exercise of judgment during evaluation, the most significant error is probably that made by confusing the estimation process with the interpretation process. One conclusion reached here is that a prior assumption should be made that significant deviation from a Gaussian distribution is customary. Another conclusion is that these deviations may be of such magnitude as to make the average less valid than the median and that non-parametric methods of data-reduction should be used more extensively. Caution in the use of averages and confidence limits is recommended, and the prior assumption of a Gaussian distribution should be avoided if possible.

REFERENCES

1. G. Horlick, *Anal. Chem.*, 1975, **47**, 352; P. C. Kelly and G. Horlick, *ibid.*, 1973, **45**, 518.
2. H. V. Malmstadt, C. G. Enke, S. R. Crouch and G. Horlick, *Optimization of Electronic Measurements*, p. 18. Benjamin, Menlo Park, California, 1974.
3. W. E. Harris and B. Kratochvil, *J. Chem. Educ.*, 1971, **48**, 543.
4. *Idem, Teaching Introductory Analytical Chemistry*, p. 78. Saunders, Philadelphia, 1974; *Rev. Anal. Chem.* 1977, **3**, 249.
5. H. A. Laitinen and W. E. Harris, *Chemical Analysis*, 2nd Ed., p. 547. McGraw-Hill, New York, 1975.
6. B. Kratochvil, T. J. Bydalek and W. J. Blaedel, *J. Chem. Educ.*, 1965, **42**, 430.
7. R. L. Ebel, *Essentials of Educational Measurements*, 2nd Ed. Prentice-Hall, Englewood Cliffs, N.J., 1972; W. E. Harris, *Anal. Chem.*, 1975, **47**, 1046A.
8. S. A. Schmitt, *Measuring Uncertainty. An Elementary Introduction to Bayesian Statistics.* Addison-Wesley, Reading, Mass., 1969.

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DERIVATIVES OF 2-THIOHYDANTOIN AS SPECTROPHOTOMETRIC ANALYTICAL REAGENTS

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Summary—The synthesis, characteristics, properties and reaction with metallic ions of four pyridine derivatives of 2-thiohydantoin have been studied. 5-(2-Pyridyl)methylene-2-thiohydantoin, 5-(6-methyl-2-pyridyl)methylene-2-thiohydantoin, 5-(di-2-pyridyl)methylene-2-thiohydantoin and 5-[1-(2-pyridyl)-1-methyl]methylene-2-thiohydantoin have been synthesized. The substances exhibit three p*K* values in aqueous solution and with Ag(I), Au(III), Cu(II), Pd(II) and Zn(II) form complexes with high molar absorptivities.

Hydantoins have been isolated from a number of natural sources and have been the subject of numerous physiological studies. There is a close relationship between hydantoins and α-amino-acids and it has been suggested that hydantoic acids[1] and hydantoins[2] might be present in proteins. Their biochemical significance is obvious and, therefore, they have been used in medicine. 5,5-Diphenylhydantoin and 5,5-diphenylthiohydantoin have been frequently employed as anticonvulsant agents;[3–6] other derivatives of hydantoin have been recommended for the treatment of tuberculosis and other infectious diseases.[7]

Hydantoins, thiohydantoins and their substitution products have been used for other than medicinal purposes: in textile printing,[8,9] as catalysts for polymerization,[10] in the production of resins and plastics[11,12] and in photographic compositions.[13] Halogenated hydantoins and thiohydantoins have been recommended for use as bleaching and vulcanizing agents and germicides.[14–17]

The condensation of hydantoins, which have a free methylene group in the C-5 position, with aromatic aldehydes, was first reported by Wheeler and Hoffman;[18] 2-thiohydantoins also undergo condensations of this type and they frequently condense more than the corresponding oxygen-containing hydantoins.[19,20] Another method of synthesis was developed by Boyd and Robson.[21] Successful condensations have been carried out with a number of different heterocyclic compounds, among them aldehyde derivatives of furan, thiophene, pyrrole, pyridine, quinoline, indole and imidazole; several cyclic ketones have also been condensed with hydantoins, including isatin, parabanic acid and cyclohexanone.

Hydantoins, thiohydantoins and their derivatives have rarely been used as analytical reagents. Dubsky *et al.*[22,23] have verified that some derivatives of 2-thiohydantoins are useful as qualitative reagents for silver, mercury and copper ions. In addition, it was observed by Turkevich[24] that compounds obtained by condensation of rhodanine with 2-thiohydantoin at the C-5 position and some of their derivatives with benzaldehyde and salicylaldehyde could be used as qualitative reagents for Ag(I), Hg(I) and (II), Cu(I) and (II), Tl(I), Pd(II), Pt(IV) and Au(III), and, in a later paper,[25] that the derivatives of rhodanine, 2-thiohydantoin and 2,4-thiazoldienedione (25 combinations) were good spot-test reagents for these ions. 5,5-Diphenyl-2-thiohydantoin has been studied as a gravimetric reagent for Cu(II) and Co(II)[26,27] in ammoniacal medium; finally, 5-vanillin-2-thiohydantoin has been used[28] for the colorimetric determination of Ce(IV). Other reports have dealt with the organic analysis of hydantoin itself.[29,30]

2-Thiohydantoin has the same molecular grouping as rhodanine (S=C–NH–C=) and it is surprising that it has not been studied extensively, especially in spectrophotometric analysis.

The present paper is the first of a series which will essay the spectrophotometric use of the condensation products of 2-thiohydantoin in the C-5 position with pyridine aldehydes and ketones. We have studied the 2-thiohydantoin derivatives of pycolinaldehyde, 6-methylpycolinaldehyde, methyl 2-pyridyl ketone and di-2-pyridyl ketone.

The picolinaldehyde derivative has already been synthesized[31] but not for this purpose.

EXPERIMENTAL

Apparatus

Unicam SP800, Unicam SP600, and Beckman DU spectrophotometers equipped with 1.0-cm glass or quartz cells; Perkin-Elmer 621 infrared spectrophotometer, and a Phillips PW9408 digital pH-meter with glass-calomel electrodes.

Table 1. Characteristics of the reagents studied

Compound	Abbreviation	Molecular formula	m.p., °C	Colour and appearance	Yield, %
5-(2-Pyridyl)methylene-2-thiohydantoin	**A**	$C_9H_7N_3OS$	276	yellow-orange scales	60
5-(6-Methyl-2-pyridyl)-2-thiohydantoin	**B**	$C_{10}H_9N_3OS$	245–7	yellow fibres	63
5-(Di-2-pyridyl)methylene-2-thiohydantoin	**C**	$C_{14}H_{10}N_4OS$	205 dec.	white-yellow microcrystals	83
5-[1-(2-Pyridyl)-1-methyl]methylene-2-thiohydantoin	**D**	$C_{10}H_9N_3OS$	285 dec.	microcrystals yellow	40

Reagents

Salts and solvents of analytical-reagent grade purity or better were used throughout. All metal ion solutions were standardized.

Buffer solution, pH 4.7. Dissolve 56.0 g of sodium acetate and 25.0 ml of glacial acetic acid in water and dilute to one litre.

Preparation of reagents

The reagents were prepared by a modification of Wheeler and Hoffman's method. Both 2-picolinaldehyde and 6-methyl-2-picolinaldehyde derivatives of 2-thiohydantoin (compounds **A** and **B** respectively) were obtained by the same method. 2-Thiohydantoin (0.014 mole) was dissolved in 20 ml of 0.4*M* sodium hydroxide and a solution of the pyridine aldehyde (0.014 mole) in 20 ml of ethanol was added; 5 ml of glacial acetic acid were slowly added to the mixture and the product rapidly began to appear. The mixture was heated for 5 min at 60°, then allowed to stand overnight at 2°, and the crystalline product was filtered off under suction, drained well, dried in a desiccator and recrystallized from ethanol.

Di-2-pyridyl ketone and methyl 2-pyridyl ketone derivatives (compounds **C** and **D**) were obtained by the same method, but the mixtures were heated under reflux for 30 min.

The colours, melting points and yields of these compounds are summarized in Table 1. The elemental analyses agreed with the values calculated for the empirical formulae.

Procedures

Spectrophotometric determination of dissociation constants. One ml of a solution of **A** or **B** ($4 \times 10^{-3}M$) or **C** ($7 \times 10^{-3}M$) or **D** ($8 \times 10^{-3}M$) in dimethylformamide was placed in a 25-ml standard flask and 5 ml of 0.3*M* potassium chloride was added to give an ionic strength of 0.1. The pH value was adjusted with sodium hydroxide solution and hydrochloric acid and the solution was diluted with water to the mark. The absorbance was measured at 410 nm against water as blank (1-cm cells).

The dissociation constants were determined by the methods of Phillips and Merritt[32] and Hildebrand and Reilley.[33]

Reactions with metal ions. The reactions of 36 ions with the reagents were tested in acetic acid–acetate medium. The solutions were prepared in 25-ml standard flasks, with 5 ppm of metal ion, a five-fold molar ratio of reagent (dissolved in dimethylformamide), 1 ml of buffer solution and dilution to volume with distilled water; the spectrum from 200 to 700 nm was measured against a reagent blank.

Influence of reducing and oxidizing agents. One ml of a solution of **A** or **B** ($4 \times 10^{-3}M$) or **C** ($7 \times 10^{-3}M$) or **D** ($8 \times 10^{-3}M$) in dimethylformamide was placed in a 25-ml standard flask and 5 ml of 0.5*M* potassium chloride to give an ionic strength of 0.1 and 0.1 g of ascorbic acid or potassium persulphate were added. The flask was filled to the mark and the absorption spectra were recorded every 5 min against water as blank.

RESULTS AND DISCUSSION

The ultraviolet spectra of the reagents in some common solvents were measured. The results are summarized in Table 2. The reagents show a band with two peaks between 350 and 400 nm. These results are in agreement with those reported by Cook *et al.*,[34] who have found a maximum at 370 nm for the benzaldehyde derivative.

The infrared spectra of the derivatives are extremely complicated and the extensive overlapping of bands makes detailed interpretation very difficult. The assignments for the spectrum of pyridine are well established,[35–37] as are those for 2-thiohydantoin.[38] The spectra of these individual compounds have several absorption bands in similar regions, which leads to extensive overlapping of the bands in the reagent spectra and the corresponding complexity. The bands assigned to the characteristic vibrations are shown in Table 3.

The well-defined band at about 3200 cm^{-1} is characteristic of N–H stretching frequencies. According to Elmore,[38] the thioureide band for thiohydantoins is situated at 1500 cm^{-1} when the substituents are not at the N-1 or N-3 positions. This author asserts that the thioureide band results from the coupling of a stretching frequency of a CN band modified by resonance, as suggested by Randall *et al.*[39] or Chatt *et al.*,[40] of a ν^{NH} mode. Mecke and Mecke[41] and Hadzi[42] have attributed bands at lower frequencies to ν^{CN}, so it may be correct to assign the band at about 1350 cm^{-1} to a ν^{CN} mode. Finally, we have assigned the band situated at approximately 1300 cm^{-1} to a $\nu^{C=S}$ vibration, in accordance with Lieber *et al.*[43]

Stability of the reagents

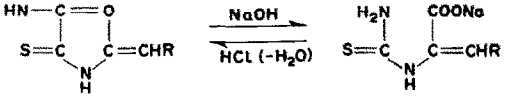
***A* and *B*.** These are both very soluble in dimethylformamide and the solutions (4×10^{-5} *M*) are stable for at least a month.

The stability of the reagents in aqueous solution at the same concentration shows a pH-dependence. They are stable for at least 100 hr in acid medium (pH 1.7), but in alkaline medium (pH 9.1) the absor-

Table 2. Ultraviolet spectra of the reagents in common solvents

	A		B		C		D	
	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$
Water	384	2.00×10^4	384	3.07×10^4	375	320	365	1.55×10^4
	365	1.85×10^4	368	3.02×10^4				
			295	9.0×10^3				
Ethanol	384	1.72×10^4	384	3.35×10^4	385	322	370	1.67×10^4
	369	1.65×10^4	369	3.27×10^4	370	314	300	1.80×10^4
	305	4.5×10^3	300	9.5×10^4				
Acetone	385	1.97×10^4	385	3.45×10^4	385	300	385	1.72×10^4
	367	1.87×10^4	365	3.30×10^4	370	342	368	1.88×10^4
Ethyl acetate	380	1.77×10^4	385	3.50×10^4	380	351	385	1.70×10^4
	360	1.66×10^4	365	3.45×10^4	370	348	370	1.86×10^4
	300	4.7×10^3	300	8.5×10^3			300	5.7×10^3
Dimethyl-formamide	382	1.55×10^4	387	3.10×10^4	385	328	370	1.63×10^4
	365	1.45×10^4	370	3.47×10^4	370	308	388	1.65×10^4
	300	3.5×10^3	300	7.2×10^3			300	5.0×10^3
Chloroform	384	1.80×10^4	387	3.77×10^4	385	328	388	1.71×10^4
	365	1.65×10^4	368	3.25×10^4	375	320	370	1.75×10^4
	300	5.0×10^3	300	8.5×10^3			300	6.0×10^3
Dioxan	340	1.00×10^4	385	1.67×10^4	385	317	385	1.58×10^4
					370	331	370	1.72×10^4
							300	6.3×10^3
Benzene	386	1.72×10^4	388	3.60×10^4	390	362	392	1.68×10^4
	368	1.57×10^4	370	3.50×10^4	368	342	375	1.67×10^4
	300	4.7×10^3	300	9.5×10^3			300	$5.7 + 10^3$
Carbon tetrachloride	392	1.82×10^4	390	3.47×10^4	390	331	392	1.70×10^4
	375	1.72×10^4	370	3.25×10^4	375	317	375	1.70×10^4
	300	5.5×10^3	300	1.00×10^4	315	325	300	6.0×10^3

bance at 350–400 nm decreases by about 17% in 100 hr for **A** and 36% for **B**. This behaviour can be attributed[44] to the equilibrium with conversion into the corresponding thiohydantoic acid.



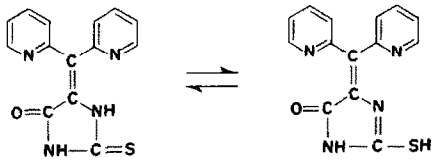
(**A**: R = C_5H_6N
B: R = CH_3, C_5H_5N)

C. The behaviour of **C** in solution is different. A 0.1% aqueous solution is not stable; the absorbance at 350–400 nm increases by about 40% in 117 hr, another band appearing simultaneously at 425–475 nm. The instability is pH-dependent, the absorbance increasing by only about 5% in acid medium in 117 hr. Solutions in dimethylformamide (0.1%) are unstable at room temperature (the absorbance increases about 46% in 117 hr) but stable if kept in the refrigerator (2°). Solutions in benzene are stable for at least 138 hr.

Table 3. Infrared spectra of thiohydantoin derivatives (cm^{-1})

Assignment	A	B	C	D	Thiohydantoin
ν^{NH}	3220 m	3300 m	3225 s	3200 m	3225 s
$\nu^{C=O}$	1715 vs	1730 vs	1770 vs	1725 vs	1740 vs
(Amide I band)					
$\nu^{C=C}$	1655 s	1660 s	1600 m	1635 m	
δ^{NH}	1580 s	1580 m	1585 m	1590 w	1570 s
(Amide II band)					
Thioureide band	1560 sh	1562 m	1545 s	1510 s	1545 s
Aromatic ring (multiplet)	1500–1400 s	1500–1400 s	1500–1400 s	1500–1400 s	
δ^{CH_2}					1430 s
ν^{CN}	1350 s	1360 s	1365 m	1360 m	1310 s
(Amide III band)					
$\nu^{C=S}$	1260 s	1275 m	1300 s	1275 m	1180 s
Pyridine in-plane C–H deformations (multiplet)	1200–950	1200–950	1200–950	1200–950	
Pyridine out-of-plane deformations (multiplet)	900–200	900–200	900–200	900–200	

This behaviour can be explained by a tautomeric equilibrium caused by the greater conjugation in the second structure.

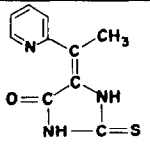


C

D. Interpretation of the behaviour of **D** is very difficult. An $8 \times 10^{-5}M$ aqueous solution is not stable: the maximum at 370 nm undergoes a hypsochromic shift to 330–325 nm in 60 hr and the absorbance decreases by about 50% in the first 48 hr. In alkaline medium (pH 12.7) the change is complete in 24 hr. In acid medium, the maximum undergoes only a small hypsochromic shift (from 362 to 355 nm) and the absorbance remains constant for 109 hr.

The spectral band of $8 \times 10^{-5}M$ **D** solutions in dimethylformamide and benzene undergoes a hypsochromic shift from 370–390 nm to 240–360 nm in 7 hr.

This hypsochromic shift can be explained in terms of geometrical isomerism. According to Hahn and Evans,[45] the absorption maxima of *cis-trans* isomers occur about 20 nm apart and we can attribute the shift of the spectrum to this phenomenon. This assumption is supported by the small variation in the spectrum in acid medium and the greater change in alkaline medium, since, according to Hahn *et al.*,[46,47] the *trans* isomer is preferentially formed in acid medium and may be transformed into the *cis* isomer in alkaline solution.



D

Geometrical isomerism

The existence of geometrical isomerism among the C-5 unsaturated derivatives of hydantoin has been reported.[46–48] These forms differ in their melting points.

The yellow *trans* product obtained by Wheeler and Hoffman's method can readily be transformed into the *cis* form (which has a different melting point) if the *trans* compound is dissolved in aqueous alkali and the solution neutralized immediately with mineral acid, the crystalline *cis* compound being precipitated. If, on the other hand, the *cis*-compound is boiled for some time in glacial acetic acid, the yellow product is formed again. This transformation can also be induced by suspending the *cis* form in ethanol and saturating the mixture with hydrogen chloride.

Table 4. Melting points of *cis-trans* isomers (°C)

Compound	*trans* synthesis	*trans* from cis (AcH)	*cis* from cis (HCl)	*cis* from trans
A	275	275	275	220
B	285	284	285	270
C	205	205	205	205
D	280–5	280–5	280–5	235–40

In Table 4 the melting point of the *cis-trans* isomers obtained by these procedures are summarized.

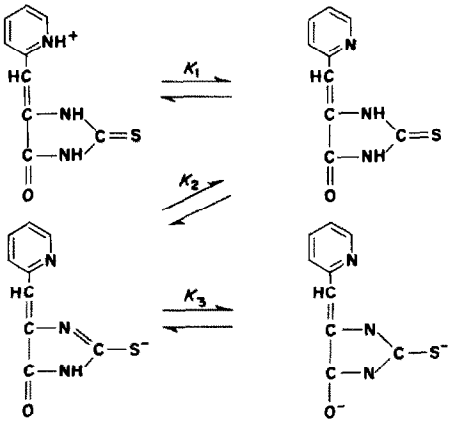
Influence of reducing and oxidizing agents

Reducing agents (such as ascorbic acid) do not perceptibly affect the spectra of the aldehyde derivatives. Their effect on the keto-derivatives is greater (the absorbance of **C** increases by about 5% in 3 hr and that of **D** decreases by about 13% in the same time). Oxidizing agents (such as potassium persulphate) decrease rapidly (by about 40% in 30 min). All measurements were made at 370 nm.

Acid–base behaviour

The equilibria are marked by isosbestic points on the absorption spectra of each reagent (Fig. 1). Figure 2 shows the plot of pH *vs.* absorbance at 410 nm.

The pK values obtained by the spectrophotometric method[32] are listed in Table 5. The reagents show three pK values, indicating four possible forms in solution. The dissociation equilibrium of **A**, for example, may be formulated as follows:



The acid–base behaviour can be explained by the existence of tautomeric forms of the 2-thiohydantoin

Table 5. Dissociation constants of reagents in 4% v/v dimethylformamide solution (0.1M KCl, 25°C)

Reagent	pK_1	pK_2	pK_3
A	4.2	7.6	12.05
B	3.9	7.3	11.75
C	2.2	8.2	13
D	2	8.75	13.25

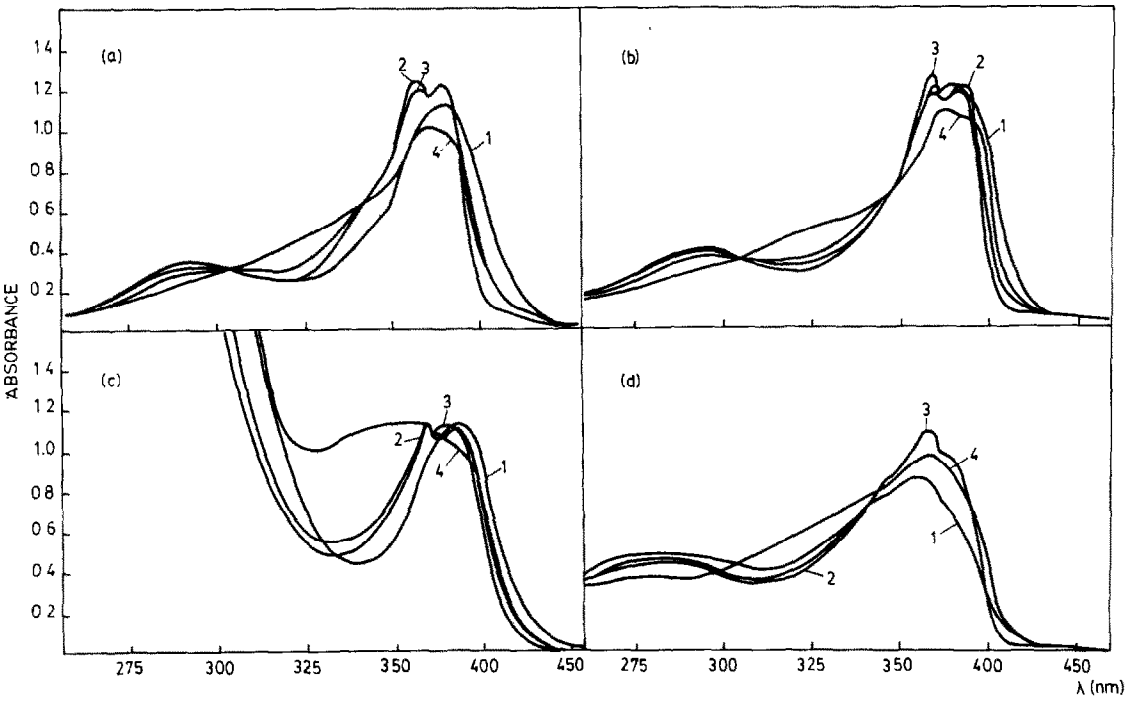


Fig. 1. Absorption spectra of the reagents in aqueous 4% v/v dimethylformamide solution. (a) **A**, (b) **B**, (c) **C**, (d) **D**. (1) pH 1.5, (2) pH 5.7, (3) pH 7.5, (4) pH 11.6.

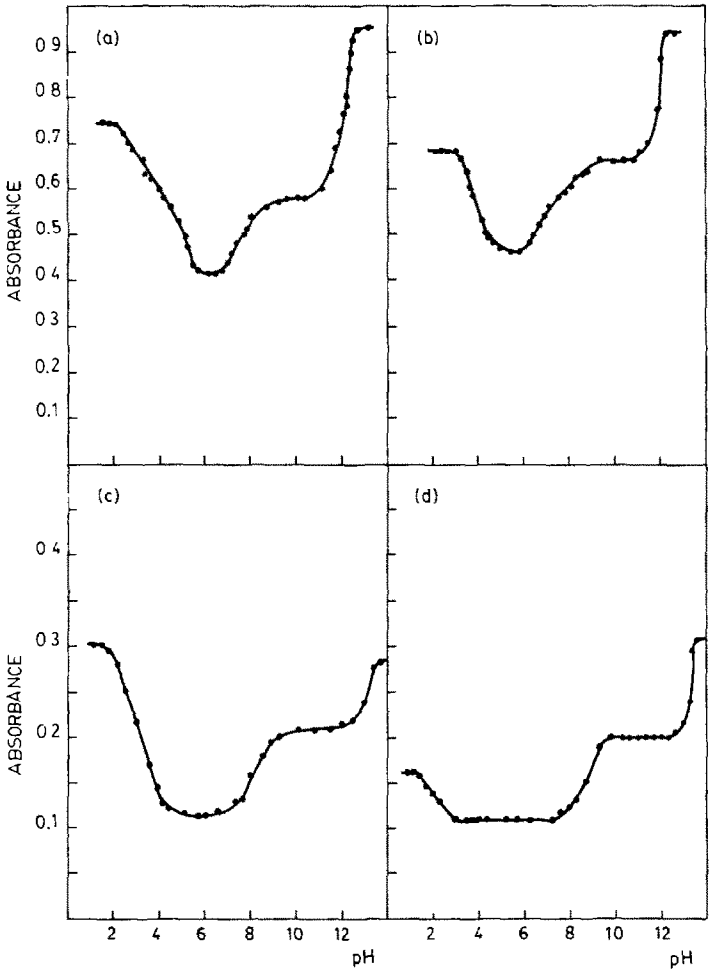
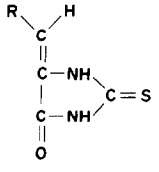


Fig. 2. Plots of absorbance (at 410 nm) *vs.* pH of the reagents. (a) **A**, (b) **B**, (c) **C**, (d) **D**.

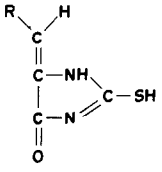
Table 6. Photometric characteristics of the complexes in solution

Cation	A		B		C		D	
	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$	λ_{max} nm	ϵ_{max} $l.mole^{-1}.cm^{-1}$
Ag(I)	415	3.75×10^3	420	3.5×10^3	290	1.25×10^4	415	7.5×10^3
Au(III)	410	9.5×10^3	410	1.10×10^4	295	2.40×10^4	412	1.30×10^4
Cu(II)	415	9.1×10^3	406	1.52×10^4	290	2.14×10^4	425	1.00×10^4
Pd(II)	440	8.5×10^3	412	1.60×10^4	200	1.65×10^4	415	1.50×10^4
Co(II)	412	5.5×10^3	402	2.2×10^3	280	1.5×10^3		
Ni(II)	419	1.90×10^4			380	6.0×10^3		
Hg(II)					289	1.40×10^4	420	9.0×10^3
Fe(II)	400	2.2×10^3			300	2.8×10^3		
Fe(III)	412	2.2×10^3			290	5.3×10^3		
Zn(II)	419	2.22×10^4	420	1.97×10^4				
Pt(IV)					290	5.0×10^3		

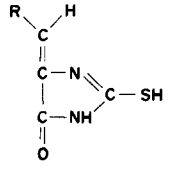
molecule.[44] The forms proposed are:



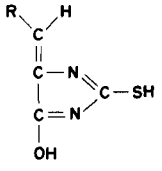
I



II



III



IV

There is no certainty as to which form is mainly present in solution, but **III** seems most probable. This assumption is supported by Komatsu's findings[49] in relation to the desulphuration of 2-thiohydantoin, which involves reaction in form **III**, and by the p*K* values, which suggest that form **III** must be the precursor for the first deprotonation of the neutral molecule in order to provide the –CO–NH– grouping necessary for the second deprotonation at higher pH.

Also, the greater acidity of the thioimidol group formed between the N-1 and C-2 atoms, in relation to the imidol group formed between the N-3 and C-4, can be explained by the decreasing acidity of the groupings –S–CS–NH– > –O–CO–NH– > –S–CO–NH–,[50] and the increase of the acidity of the –SH group by the action of the double bond at C-5.[51]

Reaction with metal ions

The reactions of 36 ions with the reagents were tested in acetic acid–acetate medium, and the results are summarized in Table 6. Generally, aqueous solutions of the chelates formed are yellow or orange-yellow and the absorption spectra show a band with a maximum at 400–420 nm for chelates of **A**, **B** and **D** and 290–300 nm for those of **C**.

Most of the reagents react well with Ag(I), Au(III), Cu(II) and Zn(II). **A** would be expected to be the best chromogenic reagent for Ag(I), Ni(II) and Zn(II). **B** is a good reagent for Au(III), Cu(II), Pd(II) and Zn(II), and **C** reacts well with Ag(I), Au(III), Cu(II), Pd(II), Hg(II) and Pt(IV), but the absorption maxima are situated at short wavelengths.

REFERENCES

1. F. Lippich, *Z. Physiol. Chem.*, 1914, **90**, 442.
2. T. D. Johnson, *Proc. Natl. Acad. Sci. U.S.*, 1916, **2**, 69.
3. H. H. Merritt, T. J. Putnam and W. G. Bywater, *J. Pharmacol.*, 1945, **84**, 67.
4. T. J. Putnam and H. H. Merritt, *Science*, 1937, **85**, 525.
5. H. B. Lewis, *J. Biol. Chem.*, 1912, **13**, 347.
6. *Idem, ibid.*, 1913, **14**, 245.
7. W. Bockmühl and W. Persch, *U.S. Pat.* 2323445, 1944.
8. Société pour l'industrie chimique à Bâle, *Swiss Pat.* 296688, 1939.
9. *Idem, Brit. Pat.* 330883, 1942.
10. W. D. Stewart, *U.S. Pat.* 2430591, 1947.
11. E. I. du Pont de Nemours and Co. and J. F. Walker, *Brit. Pat.* 564424, 1944.
12. H. V. Wood and W. O. Drake, *U.S. Pat.* 3560470, 1971.
13. E. I. du Pont de Nemours and Co., *French Pat.* 1410426, 1965
14. A. O. Rogers, *U.S. Pat.* 2398598, 1946.
15. *Idem, U.S. Pat.* 2398599, 1946.
16. *Idem, U.S. Pat.* 2404096, 1946.
17. D. L. Cottle and L. S. Minckler, *U.S. Pat.* 3177182, 1965.
18. H. L. Wheeler and C. Hoffman, *Am. Chem. J.*, 1911, **45**, 368.
19. T. B. Johnson and W. M. Scott, *J. Am. Chem. Soc.*, 1915, **37**, 1846.
20. H. L. Wheeler and C. Brautlecht, *Am. Chem. J.*, 1911, **45**, 446.
21. W. J. Boyd and W. Robson, *Biochem. J.*, 1935, **29**, 542.
22. J. V. Dubský, *Mikrochem. Mikrochim. Acta*, 1940, **28**, 145.
23. J. V. Dubský, V. Šindelář and V. Černák, *ibid.*, 1938, **25**, 124.
24. N. M. Turkevich and U. F. Gerlich, *Zh. Analit. Khim.*, 1956, **11**, 180.
25. B. M. Turkevich, *Farm. Zh.*, 1959, **14**, 9.
26. M. Lora and J. Garrido, *Anal. Fis. y Quim.*, 1947, **43**, 54.
27. J. Garrido, *ibid.*, 1947, **43**, 1195.
28. F. Pino, F., Burriel and J. Valero, *Inf. Quim. Anal.*, 1961, **15**, 1.

29. M. J. de Faubert Maunder, *Analyst*, 1975, **100**, 878.
30. F. Feigl, *Spot Tests in Organic Analysis, 7th Ed.*, p. 545. Elsevier, Amsterdam 1966.
31. H. Thielemann, *Sci. Pharm.*, 1971, **39**, 8.
32. J. P. Phillips and L. L. Merritt, Jr., *J. Am. Chem. Soc.*, 1943, **70**, 410.
33. G. P. Hildebrand and C. N. Reilley, *Anal. Chem.*, 1957, **29**, 258.
34. A. H. Cook, G. D. Hunter and J. R. A. Pollock, *J. Chem. Soc.*, 1950, 1892.
35. C. H. Kline and J. Turkevich, *J. Chem. Phys.*, 1944, **12**, 300.
36. L. Corssin, B. J. Fax and H. J. Bernstein, *Can. J. Chem.*, 1957, **35**, 1185.
37. I. M. Hunsberger, *J. Am. Chem. Soc.*, 1950, **72**, 5626.
38. D. T. Elmore, *J. Chem. Soc.*, 1858, 3489.
39. H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, *Infrared Determination of Organic Structures*, p. 5. Van Nostrand, New York, 1949.
40. J. Chatt, L. A. Duncanson and L. M. Venanzi, *Suomen Kem.*, 1956, **29B**, 75.
41. R. Mecke and R. Mecke, *Chem. Ber.*, 1956, **89**, 343; R. Mecke, R. Mecke and A. Lüttringhaus, *ibid.*, 1957, **90**, 975.
42. D. Hadži, *J. Chem. Soc.*, 1957, 847.
43. E. Lieber, C. N. R. Rao, C. N. Pillai, J. Ramachandran and R. D. Hites, *Can. J. Chem.*, 1958, **36**, 801.
44. E. Ware, *Chem. Rev.*, 1950, **46**, 403.
45. D. A. Hahn and J. Evans, *J. Am. Chem. Soc.*, 1928, **50**, 806.
46. D. A. Hahn and M. M. Endicott, *ibid.*, 1937, **59**, 2740.
47. D. A. Hahn and E. Gilman, *ibid.*, 1925, **47**, 2953.
48. T. B. Johnson and I. S. Bates, *ibid.*, 1915, **37**, 333.
49. S. Komatsu, *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1915, **1**, 69.
50. H. Erlenmeyer and A. Kleiber, *Helv. Chim. Acta*, 1939, **22**, 851.
51. L. W. Pickett and M. McLean, *J. Am. Chem. Soc.*, 1939, **61**, 423.

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DOSAGES THERMOMETRIQUES DE QUELQUES SUBSTANCES A INTERET PHARMACEUTIQUE DERIVEES DU NOYAU PHENOTHIAZINE PAR UNE SOLUTION D'HYDROXYDE DE SODIUM: ENTHALPIE DE NEUTRALISATION, ENTHALPIE ET ENTROPIE D'IONISATION DU CHLORHYDRATE DE PROMETHAZINE

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Résumé—Les acides conjugués de quelques substances à intérêt pharmaceutique, dérivées du noyau phénothiazine, sont titrés directement par une solution standard d'hydroxyde de sodium, à l'aide d'un appareillage automatique de titrage thermométrique. On obtient des diagrammes avec des points d'inflexion très nets, qui permettent des déterminations analytiques aisées. La netteté de cette cassure est discutée, dans le cas du chlorhydrate de prométhazine, en fonction de différents paramètres comme le pK_A, la solubilité du produit et l'enthalpie de neutralisation que nous déterminons dans ce travail.

Les titrages thermométriques n'ont été qu'assez peu utilisés pour le dosage de substances à intérêt pharmaceutique, bien qu'ils puissent, comme les autres méthodes d'étude, être exploités en solution aqueuse ou en solvants non aqueux. Les dosages en milieu non aqueux font presque tous appel aux techniques dites de titrages thermométriques catalytiques. Citons le dosage d'un grand nombre de sulfamides,[1] de dérivés de l'acide barbiturique,[2] de catécholamines,[3] d'alcaloïdes,[4,5] de substances diverses comme l'antipyrine ou la vitamine B_6,[6–8] de dérivés du type benzodiazepines[9] et de l'isoniazide.[10] Pour les dosages en milieu aqueux, mentionnons la détermination de quelques alcaloides et de la vitamine B_1 par précipitation à l'aide d'acide silicotungstique en milieu acide,[11] le dosage direct de sulfamides par une solution de nitrate d'argent,[12] par diazotation[13] ou par l'hypochlorite de sodium.[14] La diazotation est également employée pour doser la nicotine.[15] L'acide ascorbique est titré en milieu aqueux par le monochlorure d'iode.[16] Enfin, sont mentionnés des dosages acide–base de quelques substances présentant un ou plusieurs azotes basiques.[17,18] Nous constatons que les dosages thermométriques n'ont pas été appliqués à la détermination de la grande classe chimique des médicaments dérivés du noyau phénothiazine, à l'exception du chlorhydrate de chlorpromazine, qui a été titré en milieu aqueux par une solution d'hydroxyde de sodium.[18] Celui-ci donne un diagramme avec un point de neutralisation parfaitement net, et la méthode paraît plus simple que les autres méthodes de dosage publiées.[19] C'est pourquoi il nous semble intéressant de vérifier si ce type de dosage peut être étendu à d'autres phénothiazines.

D'autre part, un autre avantage de la méthode thermométrique est que l'on peut déterminer, dans certaines conditions, l'enthalpie de la réaction mise en jeu et éventuellement les constantes d'équilibre correspondantes à partir d'un seul enthalpogramme.[20–32] Les valeurs des différentes fonctions thermodynamiques peuvent être en effet intéressantes dans le cadre d'une approche pharmacologique moderne. Les composés étudiés sont le chlorhydrate de prométhazine (A), le bisméthane sulfonate de thiopropérazine (B), le fumarate d'aminopromazine (C), et le tartrate d'alimemazine (D) (Trimeprazine) (Tableau 1).

PARTIE EXPERIMENTALE

Appareillage

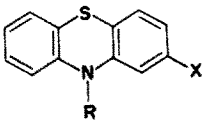
L'appareillage comporte une burette automatique à débit constant, une enceinte réactionnelle isolée thermiquement, un agitateur, un groupe de thermistances, un pont de Wheatstone, un dispositif d'amplification et un enregistreur.

La burette automatique est une burette "Tacussel" à commande électronique du type électroburap. Elle est commandée par le bloc "BC.VRE" pour fonctionnement autonome. Le vase réactionnel est isolé thermiquement par du polystyrène expansé. L'agitation est magnétique. Nous utilisons un groupe de 4 thermistances (COPRIM RTC) chacune d'une résistance $R_c = 100\,k\Omega$ à 25°, montées en parallèle et dont la résistance équivalente est de 25 kΩ. Le pont de Wheatstone est un pont M.P. 1010 dont l'alimentation M.P. 1008b, stabilisée à une valeur de 4 V, est modifiée en supprimant la liaison de l'un de ses pôles avec la masse commune (Fig. 1).

Le dispositif d'amplification est constitué par un amplificateur opérationnel M.P. 1006C, dont le montage est du

* Avec la collaboration technique de J. P. Cognec.

Tableau 1. Phénothiazines étudiées



Composé étudié		R	X
Prométhazine chlorhydrate	(A)	$-CH_2-CH(CH_3)-N(CH_3)_2$	-H
Thiopropérazine bis-methane sulfonate	(B)	$-CH_2-(CH_2)_2-N\langle\rangle N-CH_3$	$-SO_2N(CH_3)_2$
Aminopromazine fumarate	(C)	$-CH_2-CH(N(CH_3)-CH_3)-CH_2-N(CH_3)_2$	-H
Alimémazine tartrate	(D)	$-CH_2-CH(CH_3)-CH_2-N(CH_3)_2$	-H

type "sans inversion" à grande impédance d'entrée et à gain réglable par la résistance de contre-réaction R_f. L'enregistreur est un appareil "Tacussel", type EPL 1B, équipé du tiroir T.U. 11G dont la gamme de mesure s'étend de 12,5 mV à 3,75 V. Un dispositif de filtrage (capacitif en T) est intercalé entre l'amplificateur et l'enregistreur.

Caractéristiques de l'appareillage. Une variation de température $\Delta\theta = 0{,}01°$ correspond à un déplacement d'environ 1 cm de la plume sur une sensibilité de 12,5 mV pleine échelle de l'enregistreur (25 cm) et 1 mm de déviation correspond à 0,6 J.

Réactifs

Les quatre phénothiazines (A) (B) (C) (D) nous ont été fournies à l'état de pureté analytique. Elles sont mises en solution dans de l'eau distillée. Les solutions d'hydroxyde de sodium sont préparées par dilution de solutions étalon avec de l'eau distillée. Leur titre est vérifié systématiquement après chaque série de mesures et est environ 2*M*. Toutes les solutions titrées sont gardées en flacons bien bouchés.

Méthode

La solution contenant la substance à doser est introduite à l'aide d'une pipette de 100 ml dans l'enceinte réactionnelle. L'agitation, le pont où sont incorporées les thermistances et l'enregistreur sont branchés. Le pont est équilibré. Après 5 à 10 mn le pont est rééquilibré et la burette est mise en marche. La courbe de titrage est alors enregistrée. Le débit de la burette automatique est vérifié en déter-

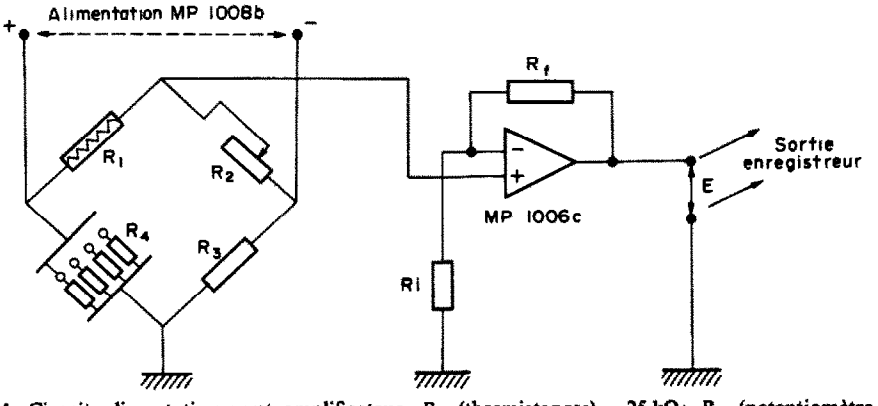


Fig. 1. Circuit alimentation-pont-amplificateur. R_1 (thermistances) = 25 kΩ; R_2 (potentiomètre 10 tours de réglage fin du zéro) = 0,255 kΩ; R_3 (résistance fixe) = 1 kΩ; R_4 (commutateur de réglage grossier de zéro) = 100 kΩ; R_f (résistance de contre-reaction) = 200 kΩ; R_i (résistance fixe) = 10 kΩ.

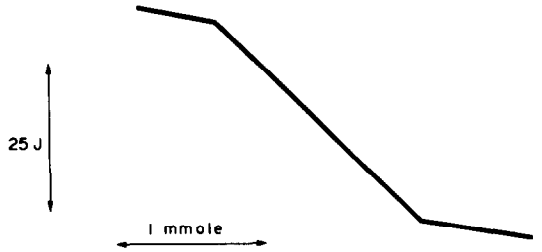


Fig. 2. Dosage d'une solution $1{,}6 \cdot 10^{-3} M$ de chlorhydrate de promethazine par une solution aqueuse d'hydroxyde de sodium $2M$.

minant systématiquement avant et après chaque série de mesures le volume versé en un temps déterminé. Pour les mesures calorimétriques concernant le chlorhydrate de prométhazine, on effectue en alternance avec chacune des déterminations anlytiques de celle-ci, un dosage de 100 ml d'une solution d'acide chlorhydrique $0{,}01 M$ par la même solution d'hydroxyde de sodium. La neutralisation de l'acide chlorhydrique sert d'étalon calorimétrique interne et permet d'évaluer les chaleurs de neutralisation. La vitesse de déroulement du papier enregistreur est de 30 mm/24 s. Les diagrammes obtenus sont pratiquement linéaires. Les variations d'enthalpie sont mesurées par la méthode d'extrapolation de Jordan et Alleman[33] plutôt que par la méthode de la tangente initiale. Pour l'évaluation des chaleurs de neutralisation, on détermine pour chaque concentration de la substance à tester, la déviation moyenne que l'on compare à la déviation moyenne due à la neutralisation de l'acide chlorhydrique. Pour l'évaluation des concentrations, on prend la moyenne des mesures.

Tous les titrages sont effectués à la température ambiante (23 ± 2°). L'enthalpie d'ionisation de l'eau est prise égale à 55740 J/mole.[34,35]

RESULTATS

Les enthalpogrammes correspondant aux dosages du chlorhydrate de prométhazine, du fumarate d'aminopromazine, du bis-méthane sulfonate de thiopropérazine et du tartrate d'alimemazine présentent une seule cassure extrêmement nette (Fig. 2), du méme type que celle correspondant au dosage du chlorhydrate de chlorpromazine.[18] Dans le Tableau 2, nous regroupons les données analytiques:

Dans le Tableau 3, nous mentionnons les chaleurs de neutralisation Q_n du chlorhydrate de prométhazine par une solution d'hydroxyde de sodium $2M$, en fonction des concentrations. Nous y regroupons également les résultats des calculs des fonctions thermodynamiques.

Le report des chaleurs de neutralisation Q_n en fonction du nombre de moles de produit à doser, fournit des points quasi-alignés. Mais la droite, ajustée d'après la méthode des moindres carrés intercepte l'ordonnée légèrement en-dessus de l'origine. Ceci indique qu'une erreur presque constante apparaît pour chaque titrage, correspondant à une valeur trop élevée de la chaleur de neutralisation. Nous ne cherchons pas plus avant une explication, d'autres auteurs ayant déjà mentionné un phénoméne proche.[32]

L'enthalpie de dissociation acide ΔH_a^0 est calculée par la relation:

$$\Delta H_a^0 = C + \Delta H_n^0$$

Tableau 2. Titrage des acides (A) (B) (C) (D) par une solution d'hydroxyde de sodium $2M$

Composé		Quantité, *mmole*	Rapport trouvé/mis	Nombre d'essais	Déviations standards relatives, %
Prométhazine*		0,46	1,00	5	8,0
chlorhydrate	(A)	1,02	0,97	6	6,8
		1,60	0,99	5	4,0
		2,17	1,01	5	1,8
		3,41	1,01	5	3,2
Thiopropérazine†		0,276	0,97	6	3,7
bis-méthane sulfonate	(B)				
Aminopromazine†					
fumarate	(C)	0,303	1,03	4	3,6
Alimemazine†					
tartrate	(D)	0,236	1,04	4	7,4

* Débit de la burette: 1 ml/mn.
† Débit de la burette: 1,90 ml/mn.

Tableau 3. Chaleurs de neutralisation du chlorhydrate de prométhazine par solution d'hydroxyde de sodium; données thermodynamiques

Quantité, *mmole*	Nombre d'essais	Q_n, *J*	ΔH_n^0, *kJ/mole*	ΔH_a^0, *kJ/mole*	ΔG_i^0, *kJ/mole*	ΔS_i^0, *J. mole*$^{-1}$ *deg*$^{-1}$
0,46	5	−9,49				
1,02	6	−19,31				
1,60	5	−32,02	−1,72	−38,5	−51,8	−45
2,17	5	−39,12				
3,41	5	−60,69				

*Analyse par la méthode des moindres carrés: ordonnée à l'origine −2215 J.

où la constante C est l'enthalpie d'ionisation de l'eau à 25° (55,74 kJ/mole). La variation d'énergie libre est calculée d'aprés la relation:

$$\Delta G_i^0 = RT\log K_i$$

La valeur $10^{-9,1}$ de la constante d'ionisation thermodynamique K_i est prise dans la littérature[36, 37] (elle est déterminée par une methode potentiométrique en milieu hydroalcoolique avec des concentrations variables de méthanol et extrapolation des valeurs obtenues à 0% d'alcool). Enfin l'entropie d'ionisation est calculée par la relation:

$$\Delta S_i^0 = \frac{\Delta H_i^0 - \Delta G_i^0}{T}.$$

DISCUSSION

Les points équivalents, dans un titrage thermométrique, consistent en des changements de pente des courbes des températures en fonction du volume d'agent titrant ajouté. La facilité d'estimation du point final est évidemment dépendante de la netteté de la cassure. Cette netteté est reliée à deux facteurs fondamentaux: la valeur du changement d'énergie libre de la réaction et la valeur du changement d'enthalpie qui accompagne la réaction. La valeur du changement d'énergie libre est fondamentale car c'est elle qui détermine si une réaction est totale au point équivalent. La valeur du changement d'enthalpie est également importante, car en supposant un changement d'énergie libre favorable, c'est elle qui conditionne la netteté de la cassure. Plus importante elle sera, et plus visible sera le changement de pente au point équivalent. Si le changement d'énergie libre n'est pas favorable, il y aura un point équivalent arrondi dû à la réaction incomplète quelle que soit la valeur du changement d'enthalpie. Cet arrondi, inversement, permet d'atteindre la constante d'équilibre, et par là même, la variation d'énergie libre et d'entropie (cf. introduction). La valeur du pK du chlorhydrate de prométhazine[36,37] pouvait laisser, *a priori*, prévoir un arrondi de la courbe de neutralisation par la solution d'hydroxyde de sodium, et par là même, atteindre la valeur de K_A et confirmer celles de la littérature. Or les enthalpogrammes de neutralisation du chlorhydrate de prométhazine ont une cassure très nette, sans arrondi, comme ceux du chlorhydrate de chlorpromazine,[18] permettant des déterminations analytiques aisées. Cette contradiction apparente doit être attribuée à la très grande insolubilité de la prométhazine base (0,0012M à pH = 7,4 et 37,5°)[38] qui précipite dès le début du titrage et déplace ainsi l'équilibre. Il en ressort que la variation d'entropie calculée au paragraphe précédent, ne s'applique que tant que la prométhazine base ne précipite pas, c'est à dire, pour des concentrations très faibles. Dans la détermination de la valeur d'enthalpie de neutralisation, nous négligeons, d'une part la fraction de l'acide dissociée, ce qui est légitime, étant donnée la valeur de K_A, et d'autre part, la chaleur de précipitation. Ceci est justifié par le fait que les chaleurs mesurées s'alignent bien en fonction des concentrations des solutions à doser. Une chaleur de précipitation non négligeable, entraînerait un non-alignement surtout pour les concentrations les plus faibles, pour lequelles la fraction de produit encore en solution ne serait pas négligeable.

Du point de vue analytique, les diagrammes correspondent à la neutralisation des azotes des groupements amino tertiaires des chaînes latérales. La réaction correspond à la neutralisation d'un proton pour le chlorhydrate de prométhazine (A) (comme pour le chlorpromazine[18]), à deux protons identiques pour le fumarate d'aminopromazine (C) et le tartrate d'alimemazine (D). La thermométrie titrimétrique ne permet pas de différencier les deux protons, en principe différents de la chaîne latérale du bis-méthane sulfonate de thiopropérazine (B), les deux protons étant dosés globalement.

Les titrages thermométriques en milieu aqueux, par une solution étalon d'acide chlorhydrique, du chlorhydrate de prométhazine (A) et du bis-méthane sulfonate de thiopropérazine, ne présentent pas de points équivalents, l'azote du cycle phénothiazine étant trop peu basique pour devenir protoné en solution aqueuse. Les dosages du fumarate d'aminopromazine [et du tartrate d'alimemazine (D)] par une solution d'acide chlorhydrique, bien qu'entraînant des effets thermiques notoires, correspondent à des courbes arrondies et il n'y a pas de cassures nettes. Ceci provient du fait que pour le fumarate d'aminopromazine (C), il y a à la fois protonation du deuxième groupe amino tertiaire de la chaîne latérale et des fonctions carboxyliques du reste fumarate, cette dernière n'étant pas quantitative. Il en va de même lors de la neutralisation du reste tartrate du tartrate d'alimemazine (D).

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BIBLIOGRAPHIE

1. E. J. Greenhow et L. E. Spencer, *Anal. Chem.*, 1975, **47**, 1384.
2. L. S. Bark et O. Ladipo, *Analyst*, 1976, **101**, 203.
3. E. J. Greenhow et L. E. Spencer, *ibid.*, 1973, **98**, 485.
4. G. A. Vaughan et J. J. Swithenbank, *ibid.*, 1967, **93**, 364.
5. E. J. Greenhow et L. E. Spencer, *ibid.*, 1973, **98**, 98.
6. V. J. Vajgand et F. F. Gaál, *Talanta*, 1967, **14**, 345.
7. V. J. Vajgand, A. K. Tibor, F. F. Gaál et I. J. Zsigrai, *ibid.*, 1968, **15**, 699.
8. V. J. Vajgand, F. F. Gaál et S. S. Brusin, *ibid.*, 1970, **17**, 415.
9. P. Marcu et I. Grecu, *Pharmazie*, 1976, **31**, 167.
10. E. J. Greenhow, *Chem. Ind. London*, 1973, 697.
11. L. S. Bark et J. K. Grime, *Anal. Chim. Acta*, 1973, **64**, 276.
12. *Idem, Analyst*, 1973, **98**, 452.
13. J. Jordan, R. A. Henry et J. C. Wasilewski, *Microchem. J.* 1966, **10**, 260.
14. H. Scafer et E. Wilde, *Z. Anal. Chem.* 1949, **130**, 396.

15. R. D. Daftary et B. C. Haldar, *Anal. Chim. Acta*, 1961, **25**, 538.
16. L. S. Bark et J. K. Grime, *Analyst*, 1974, **99**, 38.
17. A. B. Deleo et M. J. Stern, *J. Pharm. Sci.*, 1964, **53**, 993.
18. *Idem, ibid.*, 1966, **55**, 173.
19. J. Blazek, A. Dymes et Z. Stejskal, *Pharmazie*, 1976, **10**, 681.
20. J. Jordan, *J. Chem. Educ.*, 1963, **40**, A5.
21. L. D. Hansen, J. J. Christensen et R. M. Izatt, *Chem. Commun.*, 1965, **3**, 36.
22. J. J. Christensen, R. M. Izatt, L. D. Hansen et J. A. Partridge, *J. Phys. Chem.*, 1966, **70**, 2003.
23. J. J. Christensen, D. P. Wrathall et R. M. Izatt, *Anal. Chem.*, 1968, **40**, 175.
24. R. M. Izatt, L. D. Hansen, J. H. Rytting et J. J. Christensen, *J. Am. Chem. Soc.*, 1965, **87**, 2760.
25. *Idem, ibid.*, 1966, **88**, 2641.
26. J. J. Christensen, J. H. Rytting et R. M. Izatt, *J. Phys. Chem.*, 1967, **71**, 2700.
27. J. Barthel, F. Becker et N. G. Schmahl, *Z. Physik. Chem. (Frankfurt)*, 1961, **29**, 58.
28. F. Becker, J. Barthel et N. G. Schmahl, *ibid.*, 1963, **37**, 33.
29. S. T. Zenchelsky et P. R. Segatto, *J. Am. Chem. Soc.*, 1958, **80**, 4796.
30. F. J. Cioffi et S. T. Zenchelsky, *J. Phys. Chem.*, 1963, **67**, 357.
31. E. Cudey, *Bull. Soc. Chim. France*, 1968, 3177.
32. R. J. Raffa, M. J. Stern et L. Malspeis, *Anal. Chem.*, 1968, **40**, 70.
33. J. Jordan et T. G. Alleman, *ibid.*, 1957, **29**, 9.
34. J. D. Hale, R. M. Izatt et J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.
35. C. E. Vanderzee et J. A. Swanson, *ibid.*, 1963, **67**, 2608.
36. A. L. Green, *J. Pharm. Pharmacol.*, 1967, **19**, 10.
37. L. G. Chatten et L. E. Harris, *Anal. Chem.*, 1962, **11**, 1495.
38. N. G. Lordi et J. E. Christian, *J. Am. Pharm. Ass.*, 1956, **5**, 300.

Summary—Acids conjugated to various phenothiazine derivatives are titrated directly with sodium hydroxide, by means of an automatic thermometric titrimeter. The titration curves have sharp breaks, suitable for analytical use, and these are discussed, in the case of promethazine hydrochloride, as functions of various parameters such as pK_a the solubility of the product and the enthalpy of neutralization (determined in this work).

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC METHOD FOR ASSESSING OXIDATION OF CHALCOPYRITE-BEARING ORES AND CONCENTRATES

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Summary—The short-term oxidation of chalcopyrite ores and concentrates, during storage, can be monitored by measuring the absorbance of the purple Cu(I)–biquinoline complex that is formed when powdered samples are agitated directly with a water–acetone solution of 2,2′-biquinoline.

In the Canadian Certified Reference Materials Project (CCRMP), a number of sulphide-bearing ores and concentrates have been, or are being, certified for a variety of elements.[1,2] Because such mineralogically complex materials are liable to undergo oxidation under certain conditions of storage, it is necessary to have available simple analytical methods that permit the ready, periodic monitoring of their condition.[3–5] Obviously a useful parameter for chalcopyrite-bearing materials is the concentration of the oxidation products formed by chalcopyrite under ambient conditions, among which copper sulphate is expected to predominate.[6]

A relatively simple and commonly-used empirical method for determining "oxide" or "acid-soluble" copper involves leaching the sample with dilute sulphuric acid saturated with sulphur dioxide,[7] then finishing by an appropriate technique such as atomic absorption. Although this method could be used in many cases for the monitoring purposes mentioned above, the author has considered an alternative approach to the problem which is an analytical extension of one of his earlier co-ordination studies.[6]

This communication describes a method in which chalcopyrite-bearing ores, concentrates, *etc.* are shaken directly with an acetone–water solution of 2,2′-biquinoline (biq) to form the Cu(I)–biq complex. After centrifugation of the resulting suspension, the absorbance of the solution gives a direct and sensitive measure of the oxidation product of chalcopyrite in the sample. Evidence is given to show that the copper found by use of the proposed method, herein referred to as "oxy-copper", can be related directly to the overall effects of oxidation on samples of complex zinc–lead–copper ores for example. The term "oxy-copper" is used to include all copper species that react to form the Cu(I)–biq complex.

EXPERIMENTAL

Reagent

2,2′-Biquinoine (Cuproine), 0.3%(~1.2M). Prepared by dissolving the requisite quantity in reagent-grade acetone. Such a solution is practically saturated and dissolution of the reagent can be facilitated by placing the containing vessel in an ultrasonic bath for a minute or two.

Mineralogical materials

Chalcopyrite. Transvaal, Messina, South Africa, finer than 325-mesh, 34.4% Cu. A portion of this specimen was treated with 10*M* phosphoric acid solution to remove oxidation products[3] prior to experimentation.

Partially oxidized chalcopyrite. The original specimen was from Ajo, Arizona, and contained 33.5% Cu. Three samples of this material (200–325-mesh), previously cleaned in 10 *M* phosphoric acid,[3] were oxidized at 52° and 68% relative humidity for three, four and five weeks respectively.

Zinc–lead–copper ore MP-1. This reference ore[1] (finer than 200-mesh) contains approximately 16% Zn, 2% Pb and 2% Cu in the form of sphalerite, galena and chalcopyrite respectively. Three bottles were chosen that were known to have been oxidized to various degrees by repeated exposure to a corrosive laboratory atmosphere during the course of use. Because this study was initiated after distribution of the samples, details of their history cannot be given.

Calibration curve

A calibration curve was constructed by use of an aqueous, standardized copper solution with a pH in the range 1.5–9.[8] Aliquots of the stock solution were transferred to 50-ml flasks and each was diluted to approximately 10 ml with water. Approximately 35 ml of acetone and 5 ml of 0.3% 2,2′-biquinoline solution were added, followed by approximately 25 mg of crystalline ascorbic acid to reduce copper(II) to copper(I).[8] The test solutions were diluted to the mark with acetone and the absorbance of each was measured at 545 nm against acetone or a reagent blank.

Procedure

Using a small funnel, transfer 50–1000 mg of powdered sample of ore or concentrate, expected to contain not more than ~350 μg of "oxy-copper", to a 50-ml volumetric flask. Add in succession, 10 ml of water, 30 ml of acetone and 5 ml of the 0.3% reagent solution. Using a mechanical shaker, agitate the stoppered flask for 1 hr (±5 min) at room temperature. Make up to volume with acetone. Next, centrifuge the suspension in a 15-ml cone, decant the clear purple solution into a 1-cm cuvette and measure the absor-

bance at 545 nm against acetone or a reagent blank. Determine the copper content of the solution from a calibration curve.

RESULTS AND DISCUSSION

Conditions for colour formation—sulphide minerals as reducing agent

From earlier work[8] it was known that for complete formation of the Cu(I)–biq complex the water–acetone system must contain 20–50% by volume of water, and that a reducing agent such as ascorbic acid is required. However, it was observed in preliminary experiments that the purple colour of the Cu(I)–biq complex was evident immediately on mixing powdered partially oxidized chalcopyrite with a water–acetone solution containing excess of biq but no added reducing agent. It was also observed that the intensity of the colour was dependent both on the history of the sample and contact time (Fig. 1).

Additional experiments with chalcopyrite, using the procedure described above, showed that after an arbitrarily selected leaching time (*e.g.*, 1 hr) the addition of ascorbic acid crystals did not increase the absorbance of the centrifuged solution. This indicated that chalcopyrite itself was acting as the reducing agent. Confirmation was obtained in experiments using samples of freshly cleaned chalcopyrite that had been "salted" with known amounts of a copper sulphate solution (Fig. 2).

Theoretically the "oxy-copper" values found in this way should be too high because additional copper will be released from the chalcopyrite that is oxidized during the colour development, and the calibration curve is prepared by use of a different reduction system. However, ascorbic acid gives virtually immediate reduction, whereas chalcopyrite takes a considerable time to react (Fig. 1) and it is necessary to find empirically a reaction time that will give the "correct" value for a known amount of added copper.

That other sulphides likely to be associated with chalcopyrite are also effective reducing agents was proved in tests in which complete colour formation was obtained from added Cu^{2+} by use of ore samples containing various proportions of sphalerite, galena, pyrite and pyrrhotite, and essentially no chalcopyrite.

For most applications of the proposed method, the ratio of chalcopyrite to its oxidation product(s) will be greater than 10:1 and therefore no tests were performed to determine the minimum ratio of sulphide mineral to Cu^{2+} that would effect complete reduction.

Because of this uncertainty as to the reductant that will be operative, the results for a given sample will be uncertain in absolute terms, but will be in correct relation to each other in relative terms. Thus for the purpose stated (assessment of changes on aging), the method is adequate, but for an absolute determination it would be better to use a standard addition method.

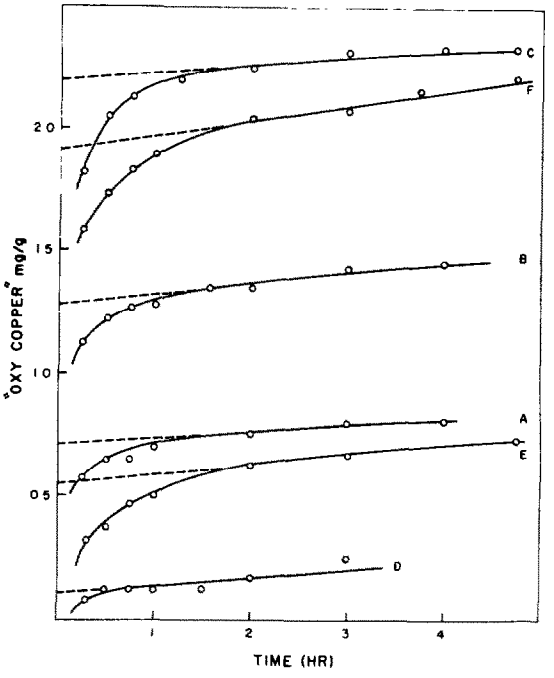


Fig. 1. "Oxy-Cu" *vs.* reaction time for Arizona chalcopyrite oxidized at 52° and 68% relative humidity for three, four, and five weeks, A, B, and C respectively; South African chalcopyrite, freshly cleaned (D) and uncleaned (E); and bottle No. 3 of reference ore MP-1(F).

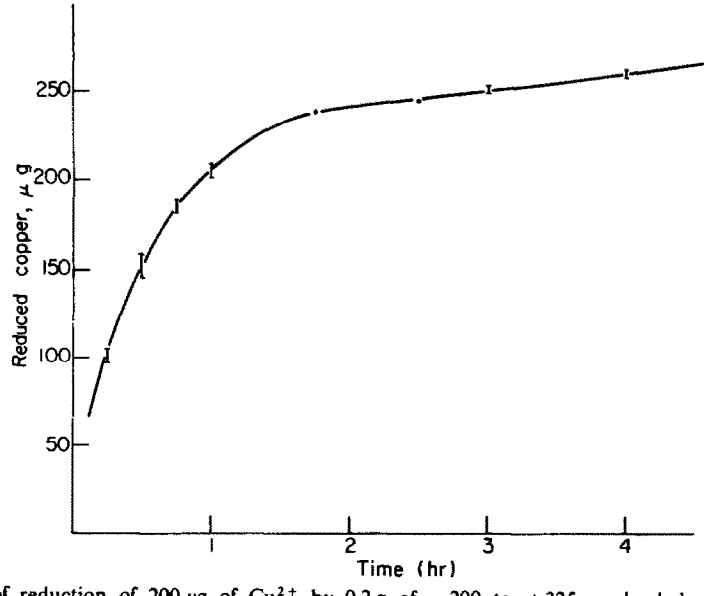


Fig. 2. Rate of reduction of 200 μg of Cu^{2+} by 0.2 g of −200 to +325 mesh chalcopyrite. Each point is the mean of two results.

Table 1. Repeatability of results for "oxy-copper" in Messina chalcopyrite and bottle No. 3 of ore MP-1 (0.2 g samples of both materials)

Chalcopyrite	MP-1 (bottle No. 3)
"Oxy-Cu", *mg/g*	
0.50	1.91
0.50	1.93
0.49	1.90
0.47	1.99
0.52	2.04
s = 0.02	s = 0.06

Effect of leaching time

Figure 1 shows the effect of leaching time on the "oxy-copper" values obtained for a number of chalcopyrite specimens that had been oxidized to various degrees, and the partially-oxidized zinc–lead–copper ore MP-1. Obviously, the rate of increase of colour is essentially linear after approximately 1 hr. Moreover, the intercept of the extrapolation (to zero time) of the linear portion of all six curves yields an "oxy-copper" value that is practically the same as that obtained after 1 hr of leaching. Therefore, a 1 hr leaching or reaction time was selected for all applications of the proposed method.

The slope of the linear portion of the curves suggests that there may be further attack on unoxidized chalcopyrite and/or that residual "oxy-copper" trapped in fissures *etc.* may not be readily available for reaction with biq.

Amount of biq

It is known that biq forms a 2:1 complex with Cu(I),[8] thus 5 ml of $\sim 10^{-2} M$ biq, as used in this work, reacts, theoretically, with ~2 mg of copper—a quantity that greatly exceeds the amount of oxidized copper expected to be present in 50–500 mg of an ore or concentrate sample. If necessary, as much as 40 ml of reagent solution, *i.e.*, ~120 mg of biq could be used for unusual cases; however, this would be wasteful of reagent in normal applications.

In unpublished work the author has estimated the formation constant of the Cu(I)–biq complex in the water–acetone medium to be $\sim 10^{12}$. Although it cannot be established conclusively here, this value is probably substantially higher than that for corresponding complexes formed between biq and other metal ions such as Zn^{2+}, Pb^{2+}, Fe^{2+} and Fe^{3+} that can be present also in partially oxidized base-metal sulphide ore samples. This assumption is supported by the results of tests with samples of bottle No. 3 of the partially oxidized zinc-lead ore MP-1 which was known to contain 26, 8 and 25 mg/g of "oxy" zinc, lead and iron, respectively. In four tests the molar ratio of (Zn + Pb):biq was varied from 0.44 to 3.3, however the corresponding "oxy copper" values remained in the range, 1.93 to 2.06 mg/g, indicating that the base metal ions did not interfere.

Repeatability of method

Because the proposed method is empirical and required for the periodic monitoring of reference materials in storage, it was desirable to establish its repeatability. Table 1 shows replicate results obtained in the analysis of 0.2-g samples of "uncleaned" Messina chalcopyrite (E in Fig. 1) and bottle No. 3 of the partially oxidized ore MP-1 (F in Fig. 1). Their precision is well within the limits expected for the variability of subsampling.

Comparison of results of proposed method and H_2SO_4–SO_2 method

To establish the validity of the proposed method, it was applied to samples of partially oxidized Messina chalcopyrite and ore MP-1, both of which were also analysed by the H_2SO_4–SO_2 method[7] in conjunction with either atomic absorption or the biq method.[9]

Table 2 shows that the proposed method gives results that are in reasonable agreement with those of the H_2SO_4–SO_2 method. Because the H_2SO_4–SO_2 leaching method may introduce unknown amounts of matrix constituents into sample solutions, there is a possibility of interference in the atomic-absorption finish. For many materials this problem could perhaps be overcome by use of the standard addition technique, but this would be a disadvantage of the atomic-absorption finish.

"Oxy-copper" as an indicator of bulk composition of complex ores

When a mineralogically complex ore such as MP-1 is appreciably affected by oxidation during storage, the component sulphides, sphalerite, galena, chalcopyrite, *etc.*, are partially oxidized, mainly to the corresponding metal sul-

Table 2. Comparison of results of proposed method with those of the H_2SO_4–SO_2 method

	"oxy-Cu" *mg/g*		
		H_2SO_4–SO_2 method	
Nature of sample	Proposed method	A.A.	Spectrophotometric[9]
Arizona chalocopyrite, three-week oxidation	0.70	0.9	—
Arizona chalcopyrite, four-week oxidation	1.30	1.7	—
Arizona chalcopyrite, five-week oxidation	2.16	2.2	—
Messina chalcopyrite, uncleaned	0.50	0.4	—
Messina chalcopyrite, two-week oxidation	0.72	0.7*	0.72*
MP-1, bottle No. 1 (see Fig. 2)	0.40	0.4*	0.36*
MP-1, bottle No. 2 (see Fig. 2)	0.77	0.7*	0.76*
MP-1, bottle No. 3 (see Fig. 2)	1.95	2.2(6)*	2.07(6)*

* Values obtained on aliquots of same sample solution. All results in duplicate except those for which number of replicates is given in parentheses.

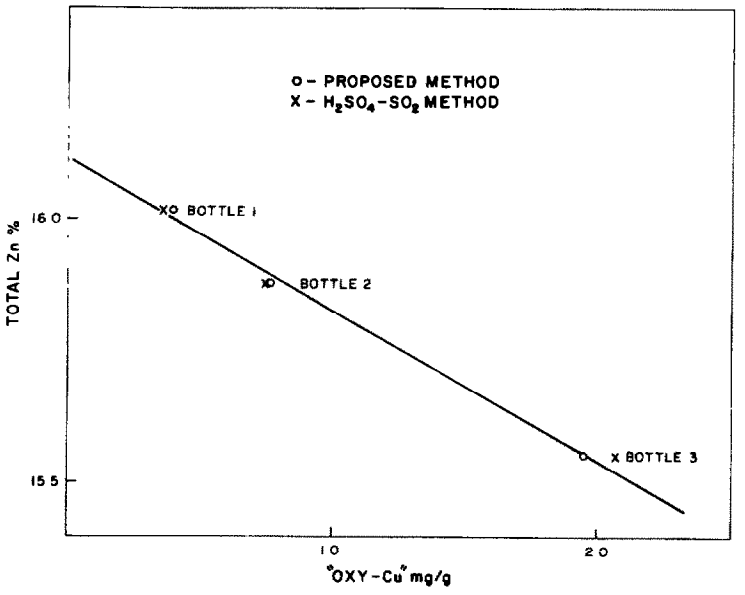


Fig. 3. "Oxy-Cu" *vs.* total zinc in bottles of partially oxidized samples of reference ore MP-1.

phates. For a given sample there is, of course, a weight increase and the bulk composition changes so as to lower the metal values.

Figure 3 shows that for three samples of MP-1 that had been partially oxidized, inadvertently, by exposure to the laboratory atmosphere, both total zinc and "oxy-copper" are direct measures of change in the overall composition of the samples during use and storage. However, monitoring such change by the proposed "oxy-copper" method is more sensitive, simpler, and much less time-consuming than by the methods used to determine total zinc.

The range of applicability of the "oxy-copper" method is indicated by the fact that it is being used currently in the CCRMP to assess the condition of a commercial-grade chalcopyrite concentrate (~25% Cu) and a low-grade zinc-copper ore (~0.85% Cu) as well as the ore MP-1.

Effect of secondary copper minerals

Chalcopyrite is essentially the only copper sulphide in the ores and concentrates of current interest in the CCRMP, and it is the most common mineral in copper deposits in Canada. However, for more general application of the proposed method it is necessary to consider the effect of the presence of secondary sulphides, oxides or hydroxy-carbonates that could be associated, usually in subordinate concentration, with chalcopyrite.

Experiments with specimens (finer than 200-mesh) of the sulphides bornite, chalcocite and covellite, which had been cleaned (of oxidation products) with 15% ammonium acetate–3% acetic acid[4] immediately before analysis, gave approximately 0.05, 0.4 and 0.03% by weight of "oxy-copper" after the recommended 1-hr reaction period. These values compare with approximately 0.01% for freshly cleaned chalcopyrite (D in Fig. 1).

Obviously, the presence of these secondary sulphides would contribute to a background value for "oxy-copper". However, because their concentration would usually be low and constant relative to chalcopyrite, their presence would not be important in the periodic monitoring of the alteration of specific samples, under storage for example, where extent of change is the desired parameter.

Semi-quantitative experiments with very small samples of unknown purity of the oxide, cuprite, and the hydroxy-carbonates malachite and azurite, gave high values of "oxy-copper". Therefore, in the unusual cases where these naturally occurring minerals are present, they too would contribute to the background. The results of these tests also suggest that the products of short-term oxidation of bornite, chalcocite and covellite, which are probably oxides or hydroxides, would be reported as "oxy-copper" along with the copper sulphate from chalcopyrite. Again, it is the concentration of the products of alteration that would change significantly under ambient conditions during the monitoring period, not that of the parent mineral(s).

CONCLUSION

For chalcopyrite ores and concentrates, the short-term oxidation which can affect the bulk composition of samples in storage, for example, can be successfully monitored by measuring the absorbance of a water–acetone solution of 2,2′-biquinoline placed in direct contact with the powdered sample for 1 hr. This empirical method is essentially free from interference and is applicable to both relatively low-grade ores and concentrates in which copper occurs mainly as chalcopyrite.

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REFERENCES

1. G. H. Faye, *Canmet Report 76-3*, Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, 1976.
2. G. H. Faye and R. Sutarno, *Geostandards Newsletter*, 1977, **1**, 31.
3. H. F. Steger, *Talanta*, 1977, **24**, 251.
4. *Idem, ibid.*, 1977, **24**, 268.
5. H. F. Steger and L. E. Desjardins, *ibid.*, 1977, **24**, 675.
6. H. F. Steger, *Chem. Geol.*, 1977, in the press.
7. R. S. Young, *Chemical Phase Analysis*, Wiley, New York, 1974.
8. G. H. Faye, *Can. J. Chem.*, 1966, **44**, 2729.
9. R. J. Guest, *Anal. Chem.*, 1953, **25**, 1484.

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PHARMACEUTICAL ANALYSIS OF SOME TRANQUILLIZERS AND ANTIDEPRESSANTS WITH IODINE MONOCHLORIDE

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Summary—A titrimetric method for the evaluation of some tranquillizers and antidepressants is proposed. The method is based on the oxidation of these drugs by iodine monochloride, in strong acid medium, the iodine liberated being titrated with potassium iodate by the Andrews method. The proposed method is applied successfully for the determination of 9 phenothiazines, 1 thioxanthene, 2 acid hydrazides and 1 dibenzazepine containing a double bond (Opipramol). Tablets, solutions for injection, and drops are also determined by the proposed method. The mechanism of oxidation for each species is suggested and the results obtained agree with these suggestions. Some official and non-official methods for the evaluation of the drugs have been compared with the iodine monochloride method, which is found to be superior in specificity, sensitivity and speed.

Various methods have been reported for the estimation of tranquillizers and antidepressants. The most widely used are those depending on the determination of the basic nitrogen by non-aqueous[1] or two-phase[2–4] titrations or with tetraphenylborate[5–7] or ammonium reineckate.[8]

Titration with the picrates of lead, copper, cadmium or zinc,[9] potassium iodobismuthate,[10] or the thiocyanate complex of chromium[11] or zinc[12] has also been used for the evaluation of the phenothiazine derivatives. Photometric titration with ceric sulphate (monitored at 420 nm) has also been applied to phenothiazine analysis.[13]

Titan Yellow is found to form a yellow complex with phenothiazines, which can be extracted into ethyl acetate and measured at 405 nm.[14] Eriochrome Black T is also used for spectrophotometric evaluation of phenothiazine derivatives. The complex formed is extracted with chloroform and the colour measured at 510–520 nm.[15] Various oxidizing agents have been used for the colorimetric determination of phenothiazine derivatives: ferric chloride,[16] potassium bromate,[17] hydrogen peroxide[18] and *p*-benzoquinone.[19]

Isocarboxazid can be reacted with ammoniacal silver nitrate and the precipitated silver dissolved in nitric acid and titrated with thiocyanate.[20] Polarography,[21] nitrosation[22] or colorimetry with tetrazolium[23] have also been used for the evaluation of isocarboxazid.

Iproniazid has been determined with tetrazolium,[23] molybdic acid,[24] thiobarbituric acid[25] and ammonium vanadate.[26]

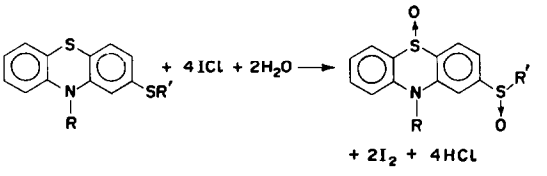
In this work some tranquillizers and antidepressants, either in pure form or in pharmaceutical preparations, are determined with iodine monochloride. The iodine liberated is titrated with potassium iodate by the Andrews method.

RESULTS AND DISCUSSION

The reactions involved differ according to the nature of the compound, and can be explained as follows.

Phenothiazine derivatives

The sulphur atom present in the nucleus of these compounds or in the side-chain is oxidized by iodine monochloride to give the mono or the disulphoxide derivative.



Thioxanthene derivatives

The reaction is the same as for phenothiazine derivatives.

Acid hydrazides

In these compounds the hydrazide moiety is cleaved, then oxidized to nitrogen.

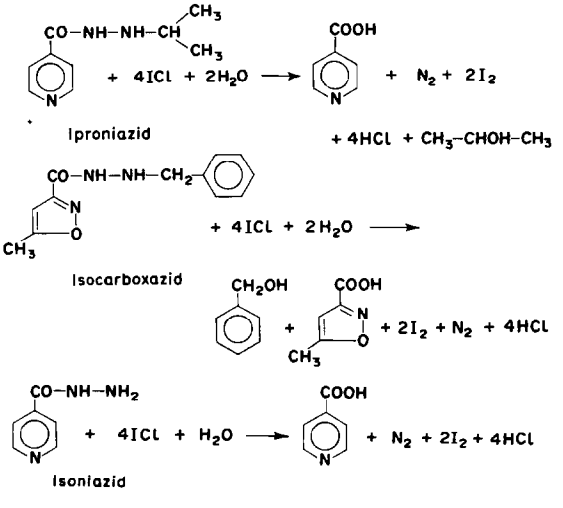


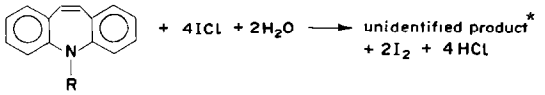
Table 1. Results obtained by the iodine monochloride method and the B.P. 1973 method

Compounds in pure form or in pharmaceutical preparations	Iodine monochloride method		B.P. 1973	
	Taken, *mg*	Mean recovery, %*	Taken, *mg*	Mean recovery, %*
1. Chloropromazine hydrochloride ("Neurazine")[3] ("Promacid")[8]				
Powder	25–100	100.9 ± 0.3	50	98.1 ± 0.1
Tablets (25 mg/tab.)[3]	50	98.4 ± 0.4	0.5	97.3 ± 0.5
Ampoules (50 mg/2 ml)[3]	40	104.6 ± 0.9	0.5	104.1 ± 1.5
Drops (4%)[5]	40	104.5 ± 0.9		
2. Acetophenazine dimaleate[4]	25–100	100.8 ± 0.5	50	98.2 ± 0.3†
3. Promethazine hydrochloride ("Promantine")[3]				
Powder	25–100	100.3 ± 0.4	50	98.1 ± 0.3
Ampoules (25 mg/ml)	50	102.2 ± 1.0	0.5	104.2 ± 0.9
4. Perphenazine ("Trilafon")[4]				
Powder	25–100	99.2 ± 0.2	50	98.8 ± 0.4
Tablets (4 and 8 mg/tab.)[4]	40	101.5 ± 0.4	0.5	102.2 ± 0.9
5. Fluphenazine dihydrochloride[4]	25–100	100.6 ± 0.1	50	98.1 ± 0.4
6. Thioridazine hydrochloride ("Melleril")[5]				
Tablets (10, 25 and 100 mg/tab.)[5]	50	105.0 ± 0.3		
7. Promazine hydrochloride ("Sparin")[6]				
50-ml vials (50 mg/ml)	50	104.0 ± 0.2		
"Prozine" capsules (Promazine HCl[6] 25 mg and meprobamate 200 mg)	25	103.4 ± 0.3		
8. Trifluperazine dihydrochloride[7]				
Tablets ("Stelazine") (5, 10 and 15 mg/tab.)	50	102.7 ± 1.0	8	105.1 ± 0.9
9. Thiethylperazine ("Torecan")[5]				
Ampoules (6.5 mg/ml)	52	103.6 ± 1.1		
10. Chlorprothixene ("Taractan")[2]				
Powder	25–100	99.4 ± 0.1	50	98.2 ± 0.3†
Tablets (5, 15 and 50 mg/tab.)	45	97.7 ± 0.4	45	97.0 ± 0.4†
11. Iproniazid dihydrochloride ("Marsilid")[2]				
Powder	25–100	99.7 ± 0.4	50	98.3 ± 0.1§
Tablets (25 and 50 mg/tab.)	50	100.9 ± 0.2	50	101.4 ± 0.3‡
12. Isocarboxazid ("Marplan")[2]				
Powder	25–100	99.4 ± 0.0	40	101.6 ± 0.3
Tablets (10 mg/tab.)	50	101.0 ± 0.2	1–3	102.2 ± 0.5
13. Opipramol dihydrochloride ("Insidon")[1]				
Powder	25–100	100.0 ± 0.7	40	99.2 ± 0.6†
Tablets (50 mg/tab.)	50	101.0 ± 0.3	50	103.0 ± 0.6†

* Average of 6 experiments.
† Non-aqueous titration.
§ Official nitrosation method.
‡ General bromide–bromate method.
¶ Tablets prepared in laboratory with the tablet filler described in text.
(1) Geigy, (2) Roche, (3) Misr, (4) Schering, (5) Swiss-pharma, (6) Wyeth, (7) Kahira, (8) Cid.

Dibenzazepine derivatives

The reaction is thought to involve the double bond in the azepine nucleus.



In the case of phenothiazine derivatives, it was found that the black oxidation product formed on adding iodine monochloride interfered with the detection of the end-point. This problem was solved by adding alcohol to the reaction mixture before the titration. The amount of acid used in the general procedure was found to be insufficient in the case of promazine, promethazine and thioridazine. For these drugs the amount of acid had to be increased (to 30 ml) for concordant results to be obtained. The reaction time was found to be 5 min for the compounds mentioned, except for thioridazine, which required 15 min for complete oxidation.

The coloured sugar-coated tablets were evaluated by the proposed method without prior removal of the coatings, *e.g.*, "Melleril" (Swiss-pharm) "Promacid" (Cid), "Trilafon" (Schering), and "Stelazine" (Kahira) tablets. In addition to these tablets, other tablets were prepared in our laboratory, containing tablet fillers composed of lactose, starch, talc and magnesium stearate (90:7:2.7:0.3 w/w). These fillers were found not to interfere.

The results obtained (Table 1) were compared with those of the official and some non-official methods. The pro-

* The structure of this product is under investigation.

Table 2. Results obtained by the standard addition method

Preparation	Added, *mg*	Found, *mg*	Recovery, %
1. Chlorpromazine tablets	24.0	23.8	99.0
	48.0	47.5	99.1
	60.0	59.6	99.3
ampoules	24.0	23.8	99.2
	48.0	47.7	99.4
	60.0	59.6	99.4
drops	24.0	23.8	99.3
	48.0	47.7	99.4
	60.0	59.6	99.4
2. Promethazine ampoules	24.0	24.1	100.4
	48.0	48.5	101.1
	72.0	72.5	100.3
3. Perphenazine tablets	24.0	23.8	99.6
	48.0	47.7	99.2
	60.0	59.8	99.6
4. Chlorprothixene tablets	24.0	23.8	99.5
	48.0	47.8	99.5
	60.0	59.5	99.4
5. Iproniazid tablets	20.0	19.9	99.3
	25.0	24.8	99.1
	50.0	49.5	99.1
6. Isocarboxazid tablets	24.0	23.8	99.5
	48.0	47.8	99.5
	60.0	59.5	99.4
7. Opipramol tablets	24.0	23.9	99.5
	48.0	47.2	99.2
	60.0	59.7	99.5

posed method was found to be more selective than the official non-aqueous methods, rapid and sensitive. The standard addition method was also applied for assaying these drugs and the results obtained (Table 2) were accurate and concordant.

EXPERIMENTAL

Reagents

Iodine monochloride.[27] Prepared by mixing 6.5 g of potassium iodate and 10 g of potassium iodide in a mixture of 75 ml of water and 75 ml of conc. hydrochloric acid, adding chloroform and adjusting by adding either potassium iodate or potassium iodide solution.

Potassium iodate solution, 0.05*M*.

General procedure

A solution containing 20–100 mg of the compound in 10 ml of water (Note 1) is transferred to a 250-ml glass-stoppered flask, 10 ml of alcohol (Note 2), 15 ml of conc. hydrochloric acid (Note 3), 10 ml of iodine monochloride solution and 5 ml of chloroform are added. The reaction mixture is set aside for 5 min (Note 4) and the iodine liberated is titrated (with vigorous shaking) with 0.05*M* potassium iodate (microburette) till the violet colour disappears from the chloroform layer.

Tablets, injections and drops. A portion of sample containing about 50 mg of the active compound is assayed by the general procedure.

Notes

1. Isocarboxazid is dissolved in alcohol and perphenazine in hydrochloric acid.
2. Alcohol is used only for phenothiazine derivatives.
3. For promethazine, promazine and thioridazine 30 ml of hydrochloric acid are used.
4. The reaction time is increased to 15 min for thioridazine.

The standard addition method

The standard addition method was applied by taking constant amounts of sample, adding various known amounts of the pure compound, assaying by the general procedure and calculating the recovery for the added material.

Analytical factors

One ml of 0.05*M* potassium iodate is equivalent to:
35.54 mg of chlorpromazine HCl (m.w. 355.4)
64.37 mg of acetophenazine dimaleate (m.w. 643.7)
32.09 mg of promethazine HCl (m.w. 320.9)
40.39 mg of perphenazine (m.w. 404.0)
51.05 mg of fluphenazine 2 HCl (m.w. 510.5)
48.04 mg of trifluperazine 2 HCl (m.w. 480.4)
19.98 mg of thiethylperazine (m.w. 399.6)
32.09 mg of promazine HCl (m.w. 320.9)
20.35 mg of thioridazine HCl (m.w. 407.0)
31.59 mg of chlorprothixene (m.w. 315.9)
11.56 mg of isocarboxazid (m.w. 231.3)
12.61 mg of iproniazid (m.w. 252.2)
21.82 mg of opipramol 2 HCl (m.w. 436.5)

REFERENCES

1. J. Milne, *J. Pharm. Assoc.*, 1959, **48**, 117.
2. J. Blazek and M. Travnicková, *Cesk. Farm.*, 1975, **24**(3), 100.
3. S. Rolski and Z. Zakrzewski, *Farm. Pol.*, 1969, **25**, 621.
4. F. M. Albert, H. Aftalion and R. Simionovicic, *Rev. Chem. (Bucharest)*, 1968, **19**, 283.
5. Gh. Morait, V. Turculat and Gh. Ciogolea, *Farmacia (Bucharest)*, 1970, **18**, 267.
6. J. Dobrecky and B. E. Gonzalez, *Rev. Asoc. Bioquim. Argent.*, 1969, **34**, 168.
7. S. Prinzanti and V. Dal Piaz, *Boll. Chim. Farm.*, 1972, **111**, 512.
8. A. Olech, *Acta Pol. Pharm.*, 1972, **29**, 57.
9. M. Gajewska, *Chem. Anal. (Warsaw)*, 1973, **18**, 651.
10. H. Basinska and M. Tarasiewicz, *Acta Pol. Pharm.*, 1969, **26**, 343.
11. A. Olech. *ibid.*, 1973, **30**, 505.
12. B. Dembinski and K. Novakowski, *Farm. Pol.*, 1974, **30**, 423.
13. S. P. Agarwal and M. I. Blake, *J. Pharm. Sci.*, 1969, **58**, 1011.
14. H. Puzanowska-Tarasiewicz and M. Tarasiewicz, *Farm. Pol.*, 1973, **29**, 1009.
15. F. Pellerin, J. A. Gautier, O. Barat and D. Damay, *Chim. Anal. (Paris)*, 1963, **45**, 395.
16. M. K. Youssef and I. A. Attia, *Indian J. Pharm.*, 1975, **37**(5), 121.
17. M. Tarasiewicz and H. Puzanowska-Tarasiewicz, *Farm. Pol.*, 1970, **26**, 393.
18. H. Basinska, H. Puzanowska-Tarasiewicz and M. Tarasiewicz, *Chem. Anal. (Warsaw)*, 1970, **15**, 405.
19. J. Mounier and B. Viossat, *Ann. Pharm. Franc.*, 1968, **26**, 429.
20. R. Soliman and S. A. Belal, *J. Drug Res. (Egypt)*, 1974, **6**, 7.
21. Z. I. El-Darawy, H. K. El-Makkawi and T. M. H. Saber, *Pharmazie*, 1975, **30**, 94.
22. *British Pharmacopoeia*, 1973.
23. J. Rieder and M. Roth, *Biochem. Pharmacol.*, 1963, **12**, 445.
24. J. Colarusso, M. Schmall, E. G. Wollish and E. G. E. Shafter, *Anal. Chem.*, 1958, **30**, 62, 451.
25. P. Mesnard, G. Devaux and J. Fauquet, *Sci. Pharm. Proc.*, 1965, **2**, 77.
26. A. F. Fartushnyi, Ya. A. Mikhailovskii and E. D. Kuzmenko, *Farm. Zh. (Kiev)*, 1974, **29**, 60.
27. *British Pharmacopoeia*, 1963, p. 935.

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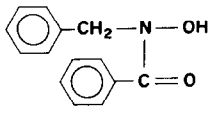
SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN BIOLOGICAL MATERIALS WITH *N*-BENZYLBENZOHYDROXAMIC ACID

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Summary—A spectrophotometric method for the determination of vanadium in biological materials with *N*-benzylbenzohydroxamic acid is proposed. The method is highly selective for vanadium and is free from rigid control of reaction conditions. No separation of iron prior to the determination of vanadium is necessary. Cu(II), Co(II), Ni, Mn(II), Cr(III), Ce(IV), Zr, Mo(VI), Ca, Sr, Ba, UO_2(II) and many others metal ions do not interfere. Fairly large quantities of Ti(IV) and W(VI) are tolerated.

The toxic effects due to industrial exposure to vanadium compounds are followed by different ailments in man.[1–3] Determination of the quantity of vanadium accumulated in body tissues and blood and that excreted in the urine is important for study of the toxicity of vanadium. The present work describes use of *N*-benzylbenzohydroxamic acid (**I**) (BBHA) as a highly selective reagent for the determination of vanadium in blood, tissues and urine.



(I)

Earlier, Talvitie[4] estimated vanadium in biological samples with 8-hydroxyquinoline, but the permissible pH-range was comparatively narrow, and a series of extractions was necessary to avoid the interference of iron and other metal ions. In the method using benzohydroxamic acid[5] the greatest interference comes from iron. Other ions such as niobium, cobalt, mercury and titanium also interfere. The *N*-arylhydroxamic acids give an increased selectivity for vanadium in fairly concentrated hydrochloric acid medium and interference from iron, cobalt, nickel and many other metal ions is completely eliminated.[6–10] However, when the phenyl group is directly connected to the nitrogen atom of the hydroxamic acid functional group, Ce(IV), Zr, Ti(IV), Mo(VI) and W(VI) interfere seriously. In *N*-benzylbenzohydroxamic acid the presence of a methylene group between the phenyl group and the hydroxamic acid nitrogen atom causes a further increase in selectivity. Hence, in the present method, in addition to that of iron the interference of Ce(IV), Zr and Mo(VI) is completely eliminated and that of Ti(IV) and W(VI) is minimized.[11]

In fairly concentrated hydrochloric acid solution vanadium(V) forms a violet-red complex with BBHA extractable into chloroform. The complex is stable in ethanol-free chloroform for several days and its absorbance obeys Beer's law at 510 nm, the wavelength of maximum absorption, the molar absorptivity being $4.30 \pm 0.05 \times 10^3$ $l.mole^{-1}.cm^{-1}$ at 510 nm.

EXPERIMENTAL

Reagents

N-Benzylbenzohydroxamic acid. A 0.1% solution in ethanol-free chloroform.

Ammonium metavanadate solution. A stock solution was prepared by dissolving a weighed quantity in distilled water, and diluted as required.

Hydrochloric acid. For maintaining the acidity, analytical-reagent or C.P. grade hydrochloric acid, standardized with potassium hydrogen phthalate.

Ethanol-free chloroform. Obtained by washing commercial chloroform 5 or 6 times with half its volume of water and drying over fused calcium chloride, then distilling. Stored in amber-coloured bottles.

Solutions of diverse ions. Prepared from analytical-grade salts, according to West.[12] The concentration was 20 mg/ml unless otherwise stated.

Wet-ashing of biological materials

The preparation of sample solution depends upon the nature of the sample. The general directions given in the literature[4,5,13] for attacking vanadium-bearing materials were followed. Care must be taken that polyphosphates produced during wet-ashing are hydrolysed to orthophosphates. Polyphosphates have a tendency to complex with vanadium and if they are not hydrolysed may cause low results. Vanadium "spikes" were added to bio-samples prior to ashing.

Procedure for urine. Transfer 100–150 ml of urine and 20 ml of concentrated nitric acid to a 250-ml Kjeldahl flask fitted with a loose stopper. Heat gently; when fuming subsides, increase the temperature and evaporate to dryness at just below the boiling point, on a hot-plate. Cool, add 1 ml of concentrated sulphuric acid and 5 ml of nitric acid and evaporate gently to fumes. Repeat the procedure 3–6 times until a light-coloured mass is obtained.

To the ash add 2 ml of nitric acid and 25 ml of water and digest on a water-bath for 30 min to hydrolyse polyphosphates to orthophosphates. Dilute the solution to 20 ml and oxidize vanadium to the quinquevalent state with a dilute solution of potassium permanganate at 70°. A persistent faint pink colour indicates complete oxidation. Cool and add the solution and the washings from the Kjeldahl

flask to a separatory funnel. Determine vanadium by the recommended procedure.

Blood and soft tissues. Transfer 5 g of blood or soft tissue to a 100-ml Kjeldahl flask fitted with a loose stopper. Add 0.5 g of potassium sulphate and 5 ml of concentrated nitric acid. Heat gently until foaming subsides. Evaporate nearly to dryness. Cool and add 1 ml of concentrated sulphuric acid and 3 ml of concentrated nitric acid and evaporate gently to fumes. Repeat the evaporation three times, with addition of 3 ml of nitric acid each time. Proceed as for urine.

Procedure

Transfer an aliquot of the sample solution containing 15–100 μg of vanadium(V) into a 125-ml separatory funnel. Add distilled water and concentrated hydrochloric acid so that the total volume and acidity of the aqueous phase are 25 ml and 5*M* respectively. Immediately after addition of the acid add 10 ml of 0.10% chloroform solution of *N*-benzylbenzohydroxamic acid, shake vigorously for about 2 min and allow the two phases to separate. Collect the violet-red organic phase in a beaker and dry it by addition of 1 g of anhydrous sodium sulphate, and transfer to a 25-ml standard flask. Wash the aqueous phase in the separatory funnel with 3–5 ml portions of chloroform and use the washing to recover any extract trapped in the anhydrous sodium sulphate. Make the solution up to the mark with chloroform and read the absorbance at 510 nm against ethanol-free chloroform. Prepare a calibration curve in the same way. Use a 2-cm cell for >60 μg of vanadium and a 4-cm cell for <60 μg.

Run a blank test on the reagents under the conditions used for sample preparation (the blank is usually negligible).

RESULTS AND DISCUSSION

Absorption spectrum

Figure 1 shows the absorption characteristics of the complex in chloroform solution. The absorption maximum is at 510 nm when the complex is extracted from 1–10*M* hydrochloric acid. Maximum colour is developed when the hydrochloric acid concentration is 3–6*M* (Fig. 2). The coloured complex is completely extracted into chloroform within 2 min and is stable for at least 10 days at room temperature.

Beer's law and sensitivity

The absorbance of the complex obeys Beer's law over the range 0.7–12 ppm of vanadium at 510 nm. The reaction is moderately sensitive, the molar absorptivity at 510 nm being $4.30 \pm 0.05 \times 10^3$ l. mole^{-1}.cm^{-1}.

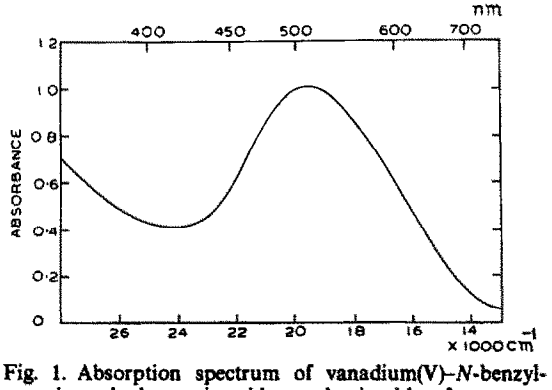


Fig. 1. Absorption spectrum of vanadium(V)–*N*-benzylbenzohydroxamic acid complex in chloroform.

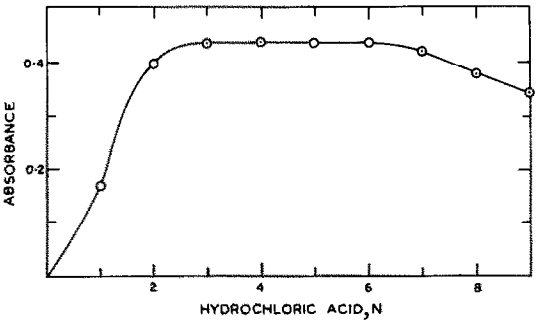


Fig. 2. Effect of hydrochloric acid concentration on the extraction of vanadium(V) with BBHA (measurement at 510 nm).

Selectivity

The effect of several metal ions on determination of 100–130 μg of vanadium in 25 ml of aqueous solution was studied. The ratio of vanadium to diverse ion was generally 1:200. Many metal ions, including Fe(III), Co(II), Ni, Cu(II), UO_2(II), Ca, Sr, Ba, Ce(IV), Zr and Mo(VI), do not interfere. Under the recommended conditions Ce(IV) does not form a complex with BBHA; the chloroform extracts of Zr(IV) and Mo(VI) are practically transparant at 510 nm, but when these ions are present the vanadium complex should be extracted with several portions of 0.3% BBHA solution in chloroform. Fairly large quantities of Ti(IV) (10 mg) and W(VI) (15 mg) are tolerated by the system provided the extraction of vanadium is repeated with several small portions of reagent.

Table 1. Recovery of vanadium from bio-samples

Sample*	Vanadium, μg Added	Vanadium, μg Recovered	Relative error, %
Blood			
3 g	60	61.0	+1.6
	60	60.5	+0.8
	60	59.0	−1.6
	60	60.0	0.0
5 g	100	101.0	+1.0
	100	99.7	−0.3
	110	110.0	0.0
	110	109.0	−0.9
Soft tissue (liver)			
3 g	70	69.5	−0.7
	70	70.5	+0.7
	100	99.7	−0.3
	100	100.5	+0.5
	100	100.8	+0.8
5 g	100	100.0	0.0
	100	99.3	−0.7
	100	100.5	+0.5
Urine			
100 ml	100	100.5	+0.5
	100	99.2	−0.8
	100	99.4	−0.6
	100	100.5	+0.5
	100	99.5	−0.5

* The normal vanadium content of the sample was negligible.

Recovery

A known quantity of vanadium was added to the biosample before ashing, and the procedure was then applied. The recovery is illustrated by the results given in Table 1.

Conclusion

The proposed method is satisfactory for the determination of microquantities of vanadium in biological materials. The method is precise and accurate and is free from rigid control of reaction conditions. The outstanding selectivity is the most attractive quality of the method. Thus a large number of metal ions do not interfere and the time-consuming removal of iron prior to the determination of vanadium is eliminated. The higher tolerance of the method for titanium extends its applicability to feed, faeces and other materials where titanium may be present in small quantities.

Acknowledgements—Grateful acknowledgement is made to U.G.C., New Delhi, for financial support and to Principal P.R. Khandekar for providing facilities.

REFERENCES

1. S. G. Sjoberg, *Acta Med. Scand.*, 1956, **154**, 381.
2. F. J. Vintinner, R. Vallenas, C. E. Carlin, R. Weiss, C. Marcher and R. Ochoa, *A.M.A. Arch. Ind. Health*, 1955, **12**, 635.
3. F. A. Patty, *Industrial Hygiene and Toxicology*, Vol. II, 2nd Ed., Interscience, New York, 1963.
4. N. A. Talvitie, *Anal. Chem.*, 1953, **25**, 604.
5. F. H. Hulcher, *ibid.*, 1960, **32**, 1183.
6. U. Priyadarshini and S. G. Tandon, *ibid.*, 1961, **33**, 435.
7. S. G. Tandon and S. C. Bhattacharya, *ibid.*, 1961, **33**, 1267.
8. S. C. Shome, *ibid.*, 1951, **23**, 1186.
9. U. Priyadarshini and S. G. Tandon, *Analyst*, 1961, **86**, 544.
10. D. C. Bhura and S. G. Tandon, *Anal. Chim. Acta*, 1971, **53**, 379.
11. R. R. Nanewar and U. Tandon, *Indian Sci. Congr. Assoc. Calcutta, 65th Session*, 1978 in the press.
12. P. W. West, *J. Chem. Educ.*, 1941, **18**, 523.
13. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. IIA, Chap. XXIV. Van Nostrand, London 1959.

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2-HYDROXY-1-NAPHTHALDOXIME AS AN ANALYTICAL REAGENT FOR TITANIUM(IV)

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(*Received* 28 *March* 1977. *Accepted* 8 *September* 1977)

Summary—2-Hydroxy-1-naphthaldoxime is proposed as a new selective and sensitive reagent for titanium. The oxime complex can be dried to constant weight at 105–110° and the conversion factor is 0.1793. The method is sensitive and gives reproducible results. Quantitative separation of titanium(IV) from iron(III) and other metals by this method gives good results. The method has been applied to the gravimetric determination of titanium(IV) in ilmenite and the results are in good agreement with those obtained by the cupferron method. The dried complex has definite composition $[TiO(OH)\text{-}(C_{11}H_8O_2N)]_2$ and is a non-electrolyte. The dimeric structure proposed for the complex is based on evidence from elemental analysis, molecular weight determination, magnetic susceptibility and infrared spectral data.

Several organic reagents[1–17] have been proposed for the gravimetric determination of titanium but very few afford precipitates which can be weighed as such. None of these reagents is specific or selective.

We have found that 2-hydroxy-1-naphthaldoxime yields a crystalline heavy orange-red precipitate at pH 3–5. The sensitivity was determined by Feigl's method[18] and the limits of identification and dilution were found to be 0.5 μg and $1:1 \times 10^5$ respectively, making it superior to hydrogen peroxide (2.0 μg; $1:2.5 \times 10^4$), catechol (2.7 μg; 1.2×10^4) and chromotropic acid (3.0 μg; $1:1 \times 10^4$). Fluoride, oxalate, tartrate, citrate and EDTA prevent the precipitation of titanium(IV) but thioglycollic acid does not. Iron(III) but not iron(II) yields a bluish-violet precipitate and the interference of the former can be prevented by reduction with thioglycollic acid.

EXPERIMENTAL

Reagents

Oxime solution. A 1% solution of 2-hydroxy-1-naphthaldoxime in rectified spirit.

Titanium solution. Potassium titanium oxalate (5.5 g) heated with concentrated sulphuric acid (50 ml) until effervescence ceases, then cooled, diluted to 1 litre and standardized gravimetrically with cupferron.[19]

Sodium acetate solution, 10%.

Procedure

The titanium sulphate solution is transferred into a 250-ml beaker, diluted to about 100 ml with distilled water and heated to about 60°. A small excess of oxime solution is added and the pH adjusted to 3–5 with sodium acetate

Recovery

A known quantity of vanadium was added to the biosample before ashing, and the procedure was then applied. The recovery is illustrated by the results given in Table 1.

Conclusion

The proposed method is satisfactory for the determination of microquantities of vanadium in biological materials. The method is precise and accurate and is free from rigid control of reaction conditions. The outstanding selectivity is the most attractive quality of the method. Thus a large number of metal ions do not interfere and the time-consuming removal of iron prior to the determination of vanadium is eliminated. The higher tolerance of the method for titanium extends its applicability to feed, faeces and other materials where titanium may be present in small quantities.

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REFERENCES

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EXPERIMENTAL

Reagents

Oxime solution. A 1% solution of 2-hydroxy-1-naphthaldoxime in rectified spirit.

Titanium solution. Potassium titanium oxalate (5.5 g) heated with concentrated sulphuric acid (50 ml) until effervescence ceases, then cooled, diluted to 1 litre and standardized gravimetrically with cupferron.[19]

Sodium acetate solution, 10%.

Procedure

The titanium sulphate solution is transferred into a 250-ml beaker, diluted to about 100 ml with distilled water and heated to about 60°. A small excess of oxime solution is added and the pH adjusted to 3–5 with sodium acetate

solution. The precipitate is digested on a hot water-bath for about 30 min with occasional stirring, then filtered off on a weighed sintered-glass crucible (porosity 4) and washed with hot water. The complex is dried to constant weight at 105–110°, cooled and weighed.

Determination of titanium in ilmenite. The finely powdered air-dried ore (about 1 g, accurately weighed) is fused with potassium pyrosulphate (25 g) and the cold melt heated with excess of sulphuric acid to fumes of sulphur trioxide, cooled and treated with 50 ml of distilled water. The solution is filtered and the residue washed with hot dilute sulphuric acid. The filter paper is ignited in a platinum crucible and the residue treated with 1 ml of water, 3 drops of concentrated sulphuric acid and 5 ml of hydrofluoric acid; the resulting solution is evaporated to dryness on the water-bath, then heated over a sand-bath in a fume cupboard and finally over a Méker burner for 15 min. The crucible is cooled and the residue (if any) fused with a minimum of flux, then extracted with dilute sulphuric acid, the solution then being filtered. Both filtrates are transferred to a 500-ml volumetric flask and the solution is made up to the mark.

A suitable volume of the ore solution is transferred into a 400-ml beaker and diluted to about 100 ml with distilled water, 2 ml of thioglycollic acid are added and the titanium content is determined with 2-hydroxy-1-naphthaldoxime according to the procedure above.

Comparison analysis of ilmenite. A 40-ml portion of the ore solution was transferred to a 400-ml beaker, tartaric acid (2 g) was added, the excess of acid was neutralized with 4*M* ammonia and the solution was acidified with sulphuric acid (1 + 1) 2 ml and hydrogen sulphide was passed into it until it was colourless. Ammonia solution was added in excess and the solution again saturated with hydrogen sulphide, then filtered, and the ferrous sulphide was washed with very dilute colourless ammonium sulphide solution. The filtrate was acidified with sulphuric acid (1 + 1, 40 ml) and boiled to expel all hydrogen sulphide. The solution was cooled to room temperature and diluted to about 200 ml with distilled water, then a small excess of fresh cupferron solution (6%) was added slowly with constant and vigorous stirring. The precipitate was filtered off, washed several times with 1*M* hydrochloric acid containing 1.5 g of cupferron per litre, then twice with 5*M* ammonia solution and finally once with water. The precipitate was ignited to constant weight, cooled and weighed.

RESULTS AND DISCUSSION

The gravimetric results showed a maximum error of 0.2% in the determination of 5–30 mg of titanium, and demonstrated that the precipitate can be dried to constant weight. The molecular weight of the oxime complex is high (conversion factor 0.1793), so very small amounts of titanium can be determined with considerable accuracy. The reagent gives a more favourable gravimetric factor than *o*-hydroxyacetophenoneoxime (0.2206), 2-hydroxy-5-methylpropiophenoneoxime (0.1850) and peonoloxime (0.1877). The reagent has no tendency to co-precipitate with the titanium complex and the precipitate is crystalline, heavy and easy to filter off. The oxime can be prepared in a high state of purity and the alcoholic solution is stable for several days.

The complex is thermally stable up to 140°, above which it decomposes rapidly, the pyrolysis product above 500° being titanium dioxide (Fig. 1).

In its infrared spectrum the reagent shows no peak for free –OH but a broad band with its centre at 3340 cm^{-1} is present. This may be attributed to the intramolecular hydrogen bonding of the phenol group with the nitrogen atom of the oxime group. The phenol peak at 3340 cm^{-1} for the ligand is shifted to 3260 cm^{-1} for the titanium

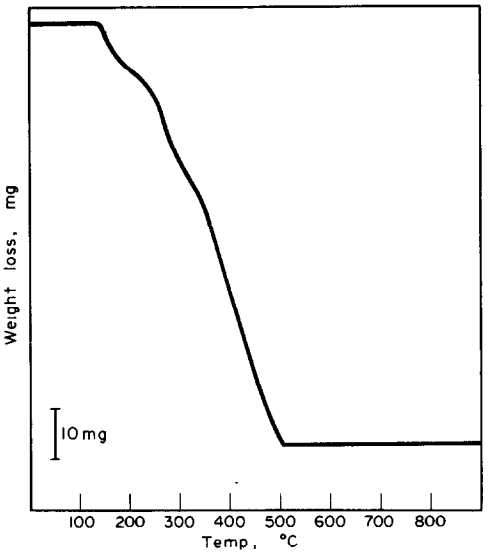
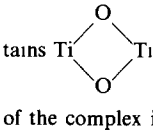
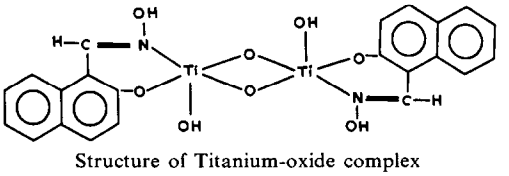


Fig. 1. Thermogram of titanium-2-hydroxy-1-naphthaldoxime complex.

complex. The $\nu_{C=N}$ band observed at 1587 cm^{-1} for the reagent appears at 1518 cm^{-1} for the chelate and a strong band at 1260 cm^{-1} assigned to C–O stretching in the ligand is shifted to 1288 cm^{-1} for the chelate. A strong band at 1235 cm^{-1} ascribed to N–O stretching in the ligand appears at 1185 cm^{-1} for the chelate. The lack of intense bands in the 1000 cm^{-1} region shows the absence of terminal Ti = O stretching modes.[20,21]

Thus on chelation the hydrogen atom of the phenol group has been replaced by Ti, with the nitrogen atom of the oxime group co-ordinating to the metal. The results of the gravimetric method show that the ratio of oxime to metal in the complex is 1:1 and this is supported by the elemental analysis of the complex. Found: C 49.7%; H 3.2%; N 5.1%; Ti 18.0%; $TiO(OH)(C_{11}H_8O_2N)$ requires: C 49.45%; H 3.39%; N 5.24%; Ti 17.93%. The magnetic susceptibility, determined by the Gouy method, shows that the complex is diamagnetic. The molar conductance of the complex in dimethylformamide (~12.7 ohm^{-1}) and in nitrobenzene (0.53 ohm^{-1}) indicates that it is a non-electrolyte. The molecular weight of the complex has been determined in benzene solution by the cryoscopic method and shows the compound to be dimeric. In view of these observations it is assumed that the complex contains  Ti units[20,21] and that the probable structure of the complex is



Structure of Titanium-oxide complex

Interferences

The interference of various other metals which are associated with titanium in its ores and precipitated with it in analysis was studied at pH 3–5. Solutions of the sodium or potassium salts of the anions, and nitrates, chlorides and sulphates of the metals were used. Mercury(II) (50 mg), cadmium (90 mg), tin(II) (60 mg), iron(II) (95 mg), zinc (90 mg), manganese(II) (107 mg), magnesium (120 mg), beryllium (60 mg), bismuth (75 mg), aluminium (93

mg), chromium(III) (90 mg), thorium (75 mg), tungsten (90 mg), molybdenum(VI) (100 mg), uranium(VI) (74 mg), chloride (95 mg) and nitrate (90 mg) cause not more than 0.1 mg error in determination of 15 mg of titanium when present in the amounts shown in brackets. Calcium, strontium, barium and lead do not react with the reagent but form insoluble sulphates during dissolution of the ore. Sulphate does not interfere. Cerium(IV) and zirconium ions do not react with the reagent but the salts are slowly hydrolysed to hydrous oxides at pH 3–5 and cause positive errors. Ferric iron forms a bluish-violet precipitate with the reagent at pH 3–5 but the interference of up to 135 mg or more can be eliminated by reduction with thioglycollic acid. Citrate, fluoride, oxalate, tartrate and EDTA form complexes with titanium and interfere, giving low results.

In the analysis of ilmenite the oxime method gave 45.0, 44.9, 45.1 and 45.0% TiO_2 and the cupferron method 45.0%.

2-Hydroxy-1-naphthaldoxime is a satisfactory reagent for the determination of titanium in ilmenite and the complex can be weighed as such, giving a more favourable conversion factor. The cupferron, oxine and several other methods available for the determination of Ti(IV) require removal of iron and other elements present in ilmenite before precipitation of titanium(IV). In the cupferron method the precipitate cannot be weighed as such but must be ignited to the oxide. The ignition must be done very carefully in the early stages in order to avoid mechanical losses, for the wet precipitate tends to liquefy and effervesce, and the dry precipitate gives off considerable volatile matter. The oxine complex does not give a horizontal break in the thermogravimetric curve and it also partially sublimes on strong heating; its use for the gravimetric analysis is therefore suspect and cannot be recommended.

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REFERENCES

1. K. Schroeder, *Z. Anorg. Chem.*, 1911, **72,** 89.
2. W. M. Thornton, *Am. J. Sci.*, 1913, **37,** 173, 407.
3. *Idem, Z. Anorg. Chem.*, 1914, **87,** 375.
4. R. Berg and M. Tietelbaum, *Z. Anal. Chem.*, 1930, **81,** 1.
5. A. Jilek and J. Kõta, *Collection Czech. Chem. Commun.*, 1932, **4,** 72.
6. R. Berg and H. Kustenmacher, *Z. Anorg. Allgem. Chem.*, 1932, **204,** 215.
7. F. M. Shemyakin, *Zavodsk. Lab.*, 1934, **3,** 986.
8. E. A. Ostroumov, *Z. Anal. Chem.*, 1936, **106,** 170.
9. C. T. Simpson and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, 1938, **10,** 642.
10. M. Ishibashi and M. Shinagawa, *Nippon. Kagaku Zasshi*, 1938, **59,** 1027.
11. S. C. Shome, *Analyst*, 1950, **75,** 27.
12. S. N. Poddar, *Indian J. Appl. Chem.*, 1963, **26,** 153.
13. N. N. Ghosh and A. Bhattacharya, *J. Indian Chem. Soc.*, 1967, **44,** 972.
14. S. N. Tripathi, R. S. Singh, B. V. Agarwala and A. K. Dey, *Z. Anal. Chem.*, 1969, **245,** 323.
15. S. Prakash, Y. Dutt and R. P. Singh, *Indian J. Chem.*, 1970, **8,** 460.
16. A. K. Mujumdar, B. C. Bhattacharya and B. C. Roy, *Anal. Chim. Acta*, 1971, **57,** 425.
17. N. N. Ghosh and G. Siddantha, *Indian J. Appl. Chem.*, 1971, **34,** 288.
18. F. Feigl, *Qualitative Analysis by Spot Tests, (Inorganic Applications)* 4th Ed., p. 4. Elsevier, Amsterdam, 1954.
19. F. J. Welcher, *Organic Analytical Reagents*, Vol. III, p. 371. Van Nostrand, New York, 1955.
20. C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3552.
21. R. E. Collis, *ibid.*, 1969, 1895.

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RAPID METHOD FOR TOTAL IRON DETERMINATION IN IRON ORES, SINTER AND RELATED MATERIALS WITHOUT USE OF MERCURY COMPOUNDS

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Summary—A rapid method for determining total iron in iron ores, sinter and related materials without use of mercury compounds is described. Fusion of the sample with sodium peroxide in a zirconium crucible and subsequent treatment with acid yields total decomposition and a solution amenable to direct reduction to ferrous iron with a silver reductor and subsequent titration with dichromate. Results for NBS, BCS and ISO reference standard ores demonstrate the universal applicability of the method both for routine and referee analysis. There is no interference from vanadium and two samples can be analysed in 30 min.

Mercuric chloride is used extensively (as in the ISO and ASTM methods) in conjunction with stannous chloride for determination of iron in iron ores and other materials. The mercuric chloride (equivalent to about 0.5 g of metallic mercury) used in one iron determination would impart a 2-ppM (parts per milliard) mercury concentration to some 50,000 gallons of water. As this is regarded as the allowable limit, a potential pollution hazard exists. For this reason, the International Standards Organization (ISO) has been seeking methods that do not use mercury compounds.

In 1918 Edgar[1] suggested the use of a silver reductor and Edmonds *et al.*[2] later demonstrated that it gave complete and nearly specific reduction of ferric iron to ferrous at the acidity used for subsequent titration with ceric sulphate with ferroin as indicator. The silver reductor is easily prepared and has the added advantages of self-indication of exhaustion, and easy regeneration. Apart from some academic interest this reduction has not become popular, at least in industrial laboratories.

A rapid method for decomposing iron ores *etc.* by fusion with sodium peroxide in a vitreous carbon crucible has been reported,[3] but the crucible is both heavily attacked and expensive. A zirconium crucible is much more resistant to attack by the peroxide, and is much more economical to use.

EXPERIMENTAL

Silver reductor

Preparation. Dissolve 50 g of silver nitrate in 400 ml of water in a 600-ml beaker. Add 10 ml of conc. nitric acid. Place two zinc rods (15 cm in length and 8 mm in diameter) crosswise in the solution and leave the system for 4 hr or overnight. Wash the precipitated silver thoroughly with 0.2*N* sulphuric acid by decantation. Fit a glass tube (2 cm in diameter, 15 cm in length) with a stop-cock at the bottom and a reservoir cup (about 100 ml capacity, 4 cm in diameter and 9 cm in length) at the top. Lightly pack a little glass wool above the stop-cock, fill the tube with 0.2*N* sulphuric acid and transfer the silver into the tube without trapping any air, until a 9-cm column of silver is obtained. Wash the column several times with 1*M* hydrochloric acid (150 ml are sufficient) at a flow-rate of 30–35 ml/min. The level of acid must never fall below the top of the column. The silver reductor is now ready

Regeneration. With the passage of ferric iron the silver in the reductor darkens at the top, forming a greyish ring which extends downwards by about 1.5 cm per determination. When this ring is about 7 cm deep, regenerate the column as follows. Drain the acid (leaving about 1 ml on the top of the silver) and wash the column with 0.2*N* sulphuric acid until all the hydrochloric acid has been replaced. Finally leave about 3 cm depth of 0.2*M* sulphuric acid above the silver. Gently place a zinc rod in contact with the silver (to avoid compacting it) and leave it for 6 hr or overnight. The dark colour changes to silvery white, indicating complete regeneration of metallic silver. Wash the column several times with 1*M* hydrochloric acid (about 150 ml) at a rate of 30–35 ml/min. The column is now again ready for reuse.

Reagents

All reagents are of analytical grade. Distilled and demineralized water is used throughout.

Mixed acid solution. To about 600 ml of water cautiously add, with stirring, 150 ml of concentrated sulphuric acid and 150 ml of syrupy orthophosphoric acid. Cool the solution and dilute to 1 litre with water.

Procedure

Transfer 2 g of powdered sodium peroxide into a dry 50-ml zirconium crucible. Add about 0.3 g of sample (accurately weighed) to the crucible and mix the contents with a dry stainless-steel spatula. Fuse over a Méker burner (low heat), swirling the crucible until the melt is cherry red and clear. Remove the crucible from the heat and swirl it until the melt solidifies on the crucible wall. Allow the crucible to cool in air for 1–2 min then place it in a dry 250-ml beaker. Add about 10 ml of water to the crucible and cover the beaker with a watch-glass. After effervescence has ceased, empty the crucible contents into the beaker and wash the crucible with 15–20 ml of water. Rinse the crucible into the beaker with 10 ml of concentrated hydrochloric acid and then with water. Boil the solution in the beaker for 3–4 min. Wash down the watch-glass and walls of the beaker with water and continue the boiling for about 30 sec. Cool and dilute the solution to about 60 ml with water.

Place a 400-ml beaker under the reductor. Pass the solution through the reductor at a rate of 35 ml/min, until there is about 1 ml of acid left above the silver. Rinse the reservoir and column 2 or 3 times with 1*N* hydrochloric acid, draining to the same level as before between the rinsings. Finally pass 150 ml of 1*M* hydrochloric acid at 35 ml/min through the column to elute the reduced iron completely, leaving 1 ml of

Table 1. Comparison of silver-reductor results

Sample	Iron content, %		
	ISO or certified value	Found	Mean
Sibley NBS 27e	66.6	66.6_6, 66.5_4, 66.6_1	66.6_0
Nimba BCS 175/2	66.1	66.1_5, 66.1_7	66.1_6
Sinter BCS 377	52.5	52.4_6, 52.4_2	52.4_4
Sinter BCS 303	35.93	35.8_6, 35.9_4	35.9_0
Sweden—2	64.84	64.7_5, 64.8_2	64.7_8
Sweden—7	61.65	61.6_0, 61.6_6	61.6_3
Canadian	65.22	64.9_8, 65.1_5	65.0_6
Marcona	62.66	62.6_1, 62.6_4	62.6_2
Philippine iron sand	60.57	60.6_0, 60.6_2	60.6_1
Minette	31.82	31.7_5, 31.7_6	31.7_6
Krivoj rog	47.32	47.3_2, 47.3_5	47.3_4

Table 2. Effect of vanadium on iron determination

Sample	Weight, *g*	V added, *mg*	Titration, *ml*	Fe found, %	Cert. value, %
NBS 27e	0.30040	nil	35.73	66.5_5	66.6
NBS 27e	0.30084	3*	35.78	66.5_5	66.6

* Vanadium added corresponds to 1% V in the sample.

acid above the silver. Take care not to let the acid level fall below the silver at any time.

To the reduced iron and washings add 25 ml of mixed acid and 5 or 6 drops of 0.3% barium diphenylaminesulphonate indicator solution. Titrate immediately with standard 0.1*N* potassium dichromate to a permanent purple end-point. Only 0.02 ml of titrant is needed to traverse the end-point.

$$\text{Iron} = (5.585 \times T \times N\%)/M$$

where T is the titration volume in ml, N is the normality of the potassium dichromate solution and M is the sample weight in g.

RESULTS

The method was applied to a number of BCS, NBS and ISO reference standard samples with a wide range of composition.[3] The results are recorded in Table 1, which also demonstrates that the method is widely applicable and has excellent precision and accuracy.

Edmonds *et al.*[2] suggested that vanadium would probably be reduced in 1*M* hydrochloric acid medium by the silver reductor. However, at the high acidity they used for the titration of iron with ceric sulphate (ferroin as indicator) no interference from vanadium was encountered. The possible interference of vanadium under the conditions of the method described here was therefore investigated.

Vanadium was added to a reference standard iron ore that had been fused with sodium peroxide (in a zirconium crucible) and dissolved in acid. The solution was passed through the silver reductor and titrated with dichromate. Table 2 shows that up to at least 1% of vanadium does not interfere.

DISCUSSION

As indicated earlier, pollution by mercury may result from the use of the stannous chloride method for the reduction of ferric iron. As an alternative to the use of mercuric chloride to oxidize the excess of stannous chloride, the ISO is considering a method in which most of the ferric iron is reduced with stannous chloride and the rest with titanous chloride, the excess of which is then oxidized by very slow addition of dilute potassium dichromate solution (indigo carmine as indicator). Finally the iron is titrated with 0.1*N* potassium dichromate, with diphenylamine as indicator. The method is tedious and calls for precise and patient judgment on the part of the analyst in the preliminary reduction and oxidation steps. The method is also subject to interference from vanadium, which is not desirable for a standard (reference) method. Moreover, the dissolution method used in the ASTM and ISO methods is quite time-consuming. The method reported in this study, in addition to using no mercury compounds, provides a rapid and complete dissolution of all possible iron, ores, sinters, agglomerates, concentrates, *etc.*, with the wide range of composition encountered in the international trade. It is also rapid (two samples in 30 min).

Although hydrogen peroxide is known to be formed in metal reductor systems in certain circumstances,[4–7] the amount depends on such factors as reductor design, flow-rate, *etc.*, and is usually important only in microanalysis. Blanks run before and after passage of the iron through the reductor were found to amount to only 0.02 ml of 0.1*N* dichromate, which is equivalent to about 0.04% of iron in a 0.3-g sample. For a discussion of the blank see reference 5.

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REFERENCES

1. G. Edgar and A. R. Kemp, *J. Am. Chem. Soc.*, 1918, **40**, 777.
2. G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, *ibid.*, 1934, **56**, 350.
3. O. P. Bhargava, *Analyst*, 1976, **101**, 125.
4. H. A. Liebhafsky, *J. Am. Chem. Soc.*, 1942, **64**, 852.
5. C. C. Miller and R. A. Chalmers, *Analyst*, 1952, **77**, 2.
6. R. A. Chalmers, D. A. Edmond and W. Moser, *Anal. Chim. Acta*, 1966, **35**, 404.
7. M. A. Salam Khan and W. I. Stephen, *ibid.*, 1968, **41**, 43.

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THIOSULPHATE IN THE WOLLAK PROCEDURE—ANALYSIS AND KINETICS IN ACIDIC FORMALDEHYDE MEDIUM

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Summary—The Wollak procedure for the determination of the sum of dithionite and thiosulphate has been investigated. Analytical data and a kinetic study confirm that thiosulphate reacts with formaldehyde under acidic conditions. Both pH and CH_2O concentration affect the results and satisfactory analysis can be performed only if the pH of the initial sample–formaldehyde mixture remains high enough.

The classical method for analysing mixtures of oxy-sulphur compounds such as dithionite, sulphite and thiosulphate, was devised by Wollak.[1] It consists of performing a series of three iodimetric titrations under different reaction conditions. In the first, an aliquot of sample is added to aqueous formaldehyde, which complexes sulphite, cleaves dithionite quantitatively and leaves the thiosulphate unreacted. The sum of the dithionite and thiosulphate is then determined on a second aliquot by iodimetry. The second titration in the procedure determines only the thiosulphate. The difference between the two titration volumes represents the dithionite.

Latimer[2] has studied the procedure for the second titration in detail and found the determination acceptably accurate for high thiosulphate concentrations, whereas Zocher and Saechtling[3] rejected this value for thiosulphate. Of particular interest is the first titration, where thiosulphate and formaldehyde may be present together under acidic conditions.

The decomposition of thiosulphate at low pH to form sulphur and bisulphite has been the subject of numerous papers,[4–12] and a formaldehyde–thiosulphate complex has been reported to exist.[13] In acid solutions of higher pH, at which thiosulphate has been reported to be stable with respect to sulphur formation,[14] addition of formaldehyde decomposes thiosulphate into sulphur and bisulphite quantitatively.[15]

Because of the divergence of opinion in reports concerning the behaviour of thiosulphate and formaldehyde in acidic solution, it was decided to study the kinetics of this system in order to determine the validity of the procedure of the first titration in the Wollak method. If any reaction occurs, then the thiosulphate would not be equivalent in the two titrations and the determination of dithionite would be in error.

EXPERIMENTAL

Reagents

A 37% formaldehyde solution neutralized with sodium hydroxide was used. Fresh thiosulphate solutions were standardized against a standard potassium iodate solution and the iodine solutions were standardized against the thiosulphate. Since the Wollak method uses acetic acid, high capacity sodium acetate–acetic acid buffers, 2*M* in total acetate, were used throughout.

Procedure

Four sets of experiments were performed in order to determine (*a*) whether acidic conditions can arise when oxy-sulphur compounds are added to aqueous formaldehyde solutions, (*b*) the accuracy of determination of thiosulphate in various aqueous formaldehyde solutions, (*c*) the nature of the products of any thiosulphate–formaldehyde reaction under acidic conditions, (*d*) how the kinetics of the reaction (effect of pH, time, *etc.*) influence the determination of thiosulphate.

In the first titration in the Wollak method the sample is added to aqueous formaldehyde that is neutral to Methyl Orange. Since the resulting solution can have a range of pH values, and a reaction between thiosulphate and formaldehyde might be pH-dependent, the pH of solutions of the individual sample components in the recommended solvent mixture was measured. The solvent mixture was 10 ml of formaldehyde (pH ~ 5.0) and 5 ml of water. The pH-values (recorded after 5 min) were 10.5 for 0.1 g and 11.3 for 0.5 g of sodium sulphite dissolved, 7.5 and 7.9 for 0.1 and 0.5 g of sodium thiosulphate pentahydrate, 5.7 and 6.3 for 0.1 and 0.5 g of sodium dithionite (90% dithionite, 2.5% thiosulphate, 7.5% bisulphite).

In order to ascertain how quantitatively thiosulphate could be determined by this procedure, weighed samples of $Na_2S_2O_3 \cdot 5H_2O$ ranging from 0.4 to 2.0 mmole were added to aqueous formaldehyde solutions. The following solutions were prepared:

(*A*)[16] 35 ml of 37% CH_2O (pH ~ 5), 50 ml of H_2O and 0.10 g of anhydrous Na_2CO_3;

(*B*) 10 ml of 37% CH_2O (pH ~ 5) and 5 ml of H_2O;

(*C*) solution (B) plus 1–2 ml of pH-4.76 2*M* acetate buffer.

The thiosulphate was added to 15 ml of solution (*A*) in a small vial and stirred for 2 min, then the solution was transferred to an Erlenmeyer flask, 50 ml of water and 2 ml of 20% acetic acid were added and the solution was titrated with 0.1*N* iodine. With solutions (*B*) and (*C*) the thiosulphate was added, the solutions were let stand in small closed vials for 20 min, then the solutions were diluted to 500 ml in standard flasks, and 50-ml aliquots were diluted with 200 ml of water and titrated with iodine.

The products of the reaction of thiosulphate and formaldehyde were identified as follows. A thiosulphate solution containing excess of formaldehyde and buffered with acetate at pH 4.76 was allowed to react to near completion. Qualitative tests showed the absence of sulphide, dithionite or sulphate. The residue, confirmed by X-ray analysis to be sulphur, was filtered off, washed, dried and weighed. The unreacted thiosulphate was determined iodimetrically on an aliquot of the solution (sulphite did not interfere, because it formed formaldehyde bisulphite complex). Sulphite and the unreacted thiosulphate were determined simultaneously by oxidizing another aliquot of the solution with peroxide in alkaline medium, acidifying, adding barium chloride, and

weighing the sulphate precipitate.

A kinetic study of the reaction was made, by the following general procedure. A known volume of freshly prepared thiosulphate solution was placed in a standard flask, followed by buffer solution and any additional components such as water or salt solutions, and the time recorded at which a known volume of neutral formaldehyde was added. The volume was made up to the mark with buffer and the solution stored in the dark at 26° ±1°. At intervals, an aliquot was removed, diluted with approximately 150 ml of water and titrated with standard iodine to a faint yellow colour. With high formaldehyde concentrations, the iodine colour fades and a 20-sec duration of the yellow colour was taken as indication of the end-point. The pH was found to remain unchanged throughout, regardless of the concentration of formaldehyde.

RESULTS AND DISCUSSION

Preliminary kinetic studies

The stability of thiosulphate solutions in the absence of formaldehyde was studied over a pH range of 4.3–6.0. Aliquots of standard thiosulphate solutions in various buffers were removed at several time intervals, formaldehyde was added to complex any sulphite, and the thiosulphate was titrated with iodine. A small decrease in the apparent thiosulphate concentration was observed over the first few hours, but the apparent concentration returned to its original value after about 8 hr. The maximum decrease (1.5%) occurred at pH 4.76 after 2.5 hr. This unexplained phenomenon may be associated with some of the observations reported by Bassett and Durrant.[14]

By comparing the rates of disappearance of thiosulphate from formaldehyde and formaldehyde–methanol solutions, it was confirmed that the presence of the methanol present as preservative in the formaldehyde did not affect the reaction rate. Methanol was found not to react with standard iodine in pH ~4.76 buffer during a period of 5 hr.

Standard iodine solution in 1.34*M* aqueous formaldehyde buffered at pH 4.76 was found to react at the rate of 4×10^{-4} $eq.l^{-1}.hr^{-1}$ during a 4-hr period. This indicates that the fading end-point observed in the presence of large amounts of formaldehyde is not due to reaction between iodine and formaldehyde.

Solutions with various sulphite and formaldehyde concentrations were prepared in buffers ranging in pH from 1.2 to 9.7. Immediate titration of these solutions with iodine confirmed that the equilibrium

$$HSO_3^- + CH_2O \rightleftharpoons CH_2O \cdot HSO_3^- \qquad (1)$$

is shifted to the right in acidic solution. In acid solution, one drop of iodine gave a permanent yellow colour, showing that no free bisulphite existed. In basic solution the iodine was consumed, since increasing pH favours decomposition of the formaldehyde bisulphite complex. A slow reaction was found to occur at pH 4.76 but its rate was negligible compared to that of the thiosulphate–iodine reaction.

A positive salt effect was observed for the reaction of 0.01*M* thiosulphate and 1.34*M* formaldehyde at pH 4.76 in solutions of low ionic strength. To avoid salt effects, kinetic data were obtained under conditions of constant high ionic strength.

The Wollak procedure

As reported above, dissolution of sodium sulphite in unbuffered aqueous formaldehyde medium (initial pH ~ 5.0), gives a basic solution. Corresponding dithionite solutions are feebly acidic and the resulting pH would presumably be lower but for the sulphite and thiosulphate present as impurities. Unexpectedly, the pH of the thiosulphate solution increases, perhaps due to formation of some formaldehyde bisulphite which then generates sulphite at a pH above 7. Consequently, the pH range of these solutions depends on the following:

(*a*) the pH of the CH_2O—H_2O mixture and

(*b*) the relative amounts of sulphite, thiosulphate and dithionite present in the sample.

Table 1 shows the results obtained when variations of the Wollak procedure are applied to standards containing only thiosulphate. Accurate results are obtained only if the pH of the reaction mixture remains greater than 7.0 before the titration. Solution (*A*) is basic both before and after addition of the thiosulphate and solution (*B*), initially acidic at pH 5, becomes basic upon addition of thiosulphate. However, solution (*C*), buffered to remain acidic upon addition of thiosulphate, gave low values for thiosulphate, generally 5–10% low when the reaction was left for 20 min at pH 5. Dilution of these acidic solutions to 500 ml with water gave rise to a white turbidity.

Table 1. The effect of the pH of CH_2O–H_2O solutions on the recovery of thiosulphate in the Wollak method

Solution*	pH	$Na_2S_2O_3$ recovered, %
A	7–10	100.1 ($n = 4$, $s = 0.4$)
B	7–9	100.2 ($n = 5$, $s = 0.4$)
C	7	90–95

*Prepared as described in the text. Sample size was 2 mmole of $Na_2S_2O_3 \cdot 5H_2O$; n = number of samples; s = standard deviation. The values are pH-dependent.

The thiosulphate–formaldehyde reaction in pH-4.76 buffer proceeds quantitatively to form the products sulphur and formaldehyde–bisulphite complex. Analysis of a standard solution containing 5 mmole of thiosulphate in which 4.9 mmole had been allowed to react showed that 4.9 mmole of sulphur and 4.9 mmole of bisulphite were produced. The nature and extent of the reaction appear to be dependent on the pH and the formaldehyde concentration. For example a compound with the empirical formula CH_2S (corresponding to thioformaldehyde) forms when 12*M* hydrochloric acid is added to concentrated thiosulphate–formaldehyde solutions to give a pH of 1.0.

Kinetics

In this study, reaction rate is defined as the rate of loss of thiosulphate, as determined by iodimetric titration. The experimentally observed pseudo rate-constants, k, were obtained under conditions of constant hydrogen-ion concentration maintained by large buffer capacity and in the presence of excess of formaldehyde. The rate of disappearance of thiosulphate was found to be second order with respect to thiosulphate. The necessary condition that the rate constant should be independent of the thiosulphate concentration in the presence of a large excess of CH_2O is illustrated by the data in Table 2. Plots of the reciprocal of the thiosulphate concentration as a function of time, for 0.01*M* thiosulphate in 1.34*M* formaldehyde, were linear for various pH values from 4.3 to 6.0.

The pseudo rate-constants for the second-order reaction of 0.03*M* thiosulphate at various formaldehyde concentrations and pH-values, and constant ionic strength of 1.07, are listed in Table 3. Since the rate expression is pH-dependent, the slopes of plots of $\log k$ *vs.* pH at constant formaldehyde concentration should give the order with respect to hydrogen ion. Plotting $\log k$ *vs.* pH from the data in Table 3 reveals that increasing the formaldehyde concentration increases the non-linearity of the curves at low pH (Fig. 1). A break in the curves appears between pH 4.30 and 4.76, indicating that there is a complex rate-expression involving the formaldehyde concentration. A least-squares treatment of that portion of the curves above pH 4.76 shows that as the formaldehyde

Table 2. Pseudo second-order rate-constants of thiosulphate decomposition in excess of CH_2O, as a function of concentration of thiosulphate

pH	$[S_2O_3^{2-}]$, M	k, $l.mole^{-1}.min^{-1}$	Ionic strength
4.30	0.01	0.0341	0.51
4.30	0.03	0.0346	0.57
4.30	0.06	0.0343	0.59
4.76	0.01	0.0284	1.1
4.76	0.03	0.0286	1.1
4.76	0.06	0.0280	1.1
4.88	0.01	0.0240	1.1
4.88	0.03	0.0230	1.1
4.88	0.06	0.0234	1.1
5.33	0.01	0.00990	1.4
5.33	0.03	0.0101	1.4
5.33	0.06	0.00980	1.4
6.05	0.01	0.00228	1.6
6.05	0.03	0.00200	1.6
6.05	0.06	0.00201	1.6

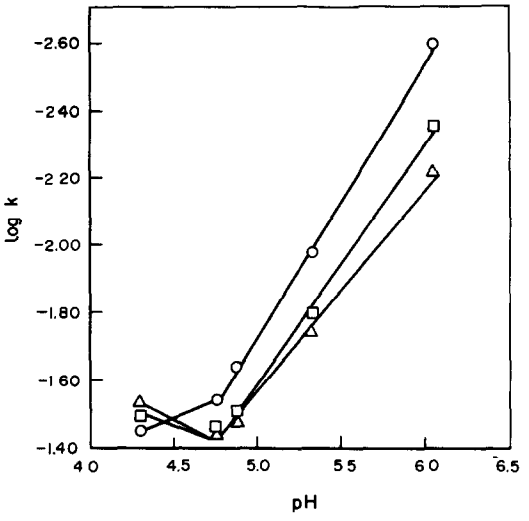


Fig. 1. Log k as a function of pH for 0.03M thiosulphate in the presence of various concentrations of formaldehyde. ○ 1.34M CH_2O; □ 2.68M CH_2O; △ 2.75M CH_2O.

Table 3. Pseudo rate-constants for the second-order decomposition of 0.03M thiosulphate at various CH_2O concentrations at a constant ionic strength of 1.07

pH	$[CH_2O]_1$, M	k, $l.mole^{-1}.min^{-1}$
4.30	1.34	0.0354
4.30	2.68	0.0319
4.30	3.75	0.0293
4.76	1.34	0.0286
4.76	2.68	0.0346
4.76	3.75	0.0356
4.88	1.34	0.0230
4.88	2.68	0.0309
4.88	3.75	0.0330
5.33	1.34	0.0104
5.33	2.68	0.0161
5.33	3.75	0.0179
6.05	1.34	0.00257
6.05	2.68	0.00447
6.05	3.75	0.00609

concentration approaches zero the order with respect to hydrogen ion approaches unity, and the rate expression for the reaction

$$S_2O_3^{2-} + H^+ \xrightarrow{CH_2O} S + CH_2O \cdot HSO_3^- \qquad (2)$$

appears to be

$$\frac{-d[S_2O_3^{2-}]}{dt} = k[H^+][S_2O_3^{2-}]^2 \qquad (3)$$

which is the rate expression obtained by LaMer[6] for low pH with no formaldehyde present.

Increasing the formaldehyde concentration delays the formation of sulphur over the pH range studied and also gives rise to a decreased initial concentration of free thiosulphate.

Table 4 gives the concentration of free thiosulphate present in 0.03M thiosulphate solution at various formaldehyde concentrations and pH-values. The data were obtained from the intercepts of plots of $1/[S_2O_3^{2-}]$ as a function of time and show that increasing the formaldehyde concentration and decreasing the pH favours removal of thiosulphate.

Conclusions

The analytical data presented in Table 1 show that the Wollak procedure used for determining the sum of dithionite and thiosulphate in aqueous formaldehyde medium can be in error if the solution remains acidic. The procedure of neutralizing the formaldehyde to Methyl Orange (pH 5) is insufficient for mixtures containing a large proportion of dithionite. As shown above, the ratio of oxy-sulphur compounds present in the sample determines the pH of the solution in aqueous formaldehyde. At an approximately 4:1 weight ratio of dithionite to thiosulphate the solution can be acidic. Under these conditions, the amount of thiosulphate found is low and not equivalent to the amount determined in the second part of the Wollak procedure. In order to avoid such analytical errors, the aqueous formaldehyde should be adjusted to about pH 8 or 9 with sodium hydroxide or carbonate before the sample is added.

Table 4. Concentration of free thiosulphate (M) in a nominally 0.03M solution at various CH_2O concentrations and pH values

pH	$[CH_2O]$ 5.36M	3.75M	2.68M	1.34M
4.30	0.0234	0.0255	0.0272	0.0291
4.76	0.0266	0.0274	0.0280	0.0298
4.88	0.0269	0.0280	0.0286	0.0299
5.33	0.0287	0.0290	0.0292	0.0299
6.05	0.0297	0.0298	0.0299	0.0300

A kinetic study of the reaction of thiosulphate with formaldehyde in acid medium confirms that the pseudo second-order rate of disappearance of thiosulphate (Table 4) is a function of pH and of formaldehyde concentration, but it is beyond the scope of this paper to discuss the unresolved question regarding the mechanism of this reaction.

REFERENCES

1. R. Wollak, *Z. Anal. Chem.*, 1930, **80**, 1.
2. G. Latimer, *Talanta*, 1966, **13**, 321.
3. H. Zocher and H. Saechtling, *Z. Anal. Chem.*, 1939, **117**, 392.
4. F. Prakke and E. Stiasny, *Rec. Trav. Chim.*, 1933, **52**, 615.

5. J. Scheffer and F. Bohm, *Z. Anorg. Allgem. Chem.*, 1929, **183,** 151.
6. E. Zaiser and V. LaMer, *J. Colloid Sci.*, 1948, **3,** 571.
7. V. LaMer and A. Kenyon, *ibid.*, 1947, **2,** 257.
8. R. Dinegar, R. Smellie and V. LaMer, *J. Am. Chem. Soc.*, 1951, **73,** 2050.
9. R. Dinegar and R. Smellie, *J. Colloid Sci.*, 1952, **7,** 370.
10. H. Taube, *J. Am. Chem. Soc.*, 1943, **65,** 526.
11. G. Latimer Jr. and E. Stetcko, *Talanta*, 1967, **14,** 984.
12. R. Davis, *J. Am. Chem. Soc.*, 1958, **80,** 3565.
13. L. Vanino and A. Schinner, *Ber.*, 1914, **47,** 2562.
14. H. Bassett and G. Durrant, *J. Chem. Soc.*, 1927, 1401.
15. A. Kurtenacker and H. Loeschner, *Z. Anorg. Allgem. Chem.*, 1938, **238,** 338.
16. Committee on Analytical Methods Report, *Am. Dyest. Rep.*, 1957, **46,** 443.

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ELECTROCHEMICAL STRIPPING DETERMINATION OF TRACES OF COPPER, LEAD, CADMIUM AND ZINC IN ZIRCONIUM METAL AND ZIRCONIUM DIOXIDE

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Summary—Procedures have been developed for the determination of copper, lead, cadmium and zinc in zirconium metal and zirconium dioxide, at concentrations of 1 ppm or less. Zirconium metal was dissolved in suphuric acid, and zirconium dioxide decomposed under pressure with hydrofluoric acid. Sample solutions were prepared in dilute sulphuric acid. For the stripping determination, the sample solution was either mixed with a complexing tartrate base electrolyte or the pre-electrolysis was carried out in acid solution, with the acid solution being exchanged for a pure base electrolyte (*e.g.* an acetate buffer) for the stripping step. The stripping step was monitored by d.c., differential pulse and Kalousek commutator voltammetry and the three methods were compared. A stationary mercury-drop electrode can generally be used for all the methods, whereas a mercury-film electrode is suitable only for the d.c. voltammetric determination of copper, lead and cadmium, as pulse measurements with films are poorly reproducible and the electrodes are easily damaged. The relative standard deviation does not exceed 20%. Some samples contained relatively large amounts of copper, which is best separated by electrodeposition on a platinum electrode.

Zirconium materials are now important in many fields of technology and high demands are placed on their purity. Of the many trace impurities which may be present, copper, lead, cadmium and zinc can readily be determined by electrochemical stripping techniques with mercury electrodes (see *e.g.*, ref. 1). The other metals usually present either do not interfere at all in this stripping determination (*e.g.*, Al, Mn, Ni, Co), or the interference can be eliminated without a preliminary separation (*e.g.*, Fe, Mo and Sn).

In developing a method for the electrochemical stripping determination of these metals in zirconium metal and zirconium dioxide, three main problems had to be solved: (1) a decomposition procedure had to be found that would allow the use of a relatively large sample (about 1 g, to attain a sufficiently low limit of determination), not cause contamination or loss of the sample, and not be too tedious; (2) a suitable electrolyte had to be found for the stripping determination, in which hydrolysis of the zirconium would be effectively suppressed; (3) the determination procedure itself had to be sufficiently sensitive, selective and reproducible and not require excessively long pre-electrolysis times.

EXPERIMENTAL

Chemicals and apparatus

All the chemicals employed were of *p.a.* purity, obtained from Lachema, Czechoslovakia; sulphuric acid for semiconductors was obtained from C. Erba, Italy. Stock solutions of metal salts were prepared by dissolving the solid substances in triply distilled water; a mercuric nitrate stock solution was obtained by dissolving mercury in dilute nitric acid. The stock solutions were standardized by EDTA titrations and more dilute solutions were prepared immediately before they were needed. The solutions of base electrolytes were purified from heavy metals by prolonged electrolysis at a mercury pool cathode, with an operational amplifier potentiostat (see *e.g.*, ref. 2).

The solutions were deaerated by passage of nitrogen that had been freed from traces of oxygen in a heated column packed with copper filings and in traps containing solutions of chromium(II) chloride and sodium anthraquinone-β-sulphonate regenerated by amalgamated zinc.

The stripping determinations were carried out with a hanging mercury-drop electrode (HMDE) (Metrohm, Switzerland) and a mercury-film electrode (MFE) on an impregnated graphite support, the preparation of which has been described elsewhere.[3] For direct determinations, a simple commercial cell with a glass stirrer (Radiometer, Denmark) was used. Determinations with exchange of solution after pre-electrolysis were performed in a flow-through cell also described earlier.[4]

The d.c. voltammetric measurements were carried out with polarographs PO-4 (Radiometer, Denmark) and LP-60 (Laboratorní Přístroje, Czechoslovakia), the differential pulse voltammetric (DPV) measurements with an LP-9 polarographic analyser (Laboratorní Přístroje, Czechoslovakia) and the Kalousek commutator voltammetric (KCV) measurements with an instrument of our own construction,[5] which has been modified somewhat and will be described in the section dealing with the results.

For pressure decompositions, steel autoclaves with PTFE crucibles (Kovodružstvo, Czechoslovakia) were employed and were heated in an oven of our own construction.

Small volumes were measured with microsyringes (Hamilton Micromesure, The Netherlands). All potentials are referred to the saturated calomel electrode at laboratory temperature.

Procedure

Sample decomposition. A powdered sample of zirconium metal (about 1 g) is dissolved in hot concentrated sulphuric acid in a PTFE crucible, and the solution is transferred to a 100-ml standard flask and diluted with water to the mark, the sulphuric acid concentration being maintained at about 20%. A sample of zirconium oxide (about 1 g) is placed in a PTFE crucible with 15 ml of concentrated hydrofluoric acid. The crucible is covered with a lid, placed in a steel autoclave and heated for 8 hr at 190°C. After cooling, the solution in the crucible is evaporated several times with small amounts of concentrated sulphuric acid in order to remove the hydrofluoric acid completely, then the residue is dissolved in hot sulphuric acid, transferred to a 100-ml volumetric flask and diluted with water to the mark, the acid concentration being kept at 20% as before. The same procedures are applied to a blank sample and a sample with a suitable standard addition of the trace metals (about the same as the metal content in the sample).

Stripping determination. An aliquot of the sample solution is transferred to the electrolysis flow-through cell, and thoroughly deaerated. Pre-electrolysis onto an HMDE is carried out for 3 min at -1.3 V, then the solution is exchanged for a deaerated 0.5*M* sodium acetate–acetic acid buffer of pH 5–7 (with a 2-min rest period) and the stripping step is carried out by DPV or KCV at a scan-rate not exceeding 120 mV/min for the DPV. The same procedure is performed with the blank sample and with that containing the standard addition: the blank is subtracted and the concentrations of copper, lead, cadmium and zinc are determined by the standard addition technique.

For the determination of only copper and lead, an MFE can be used with the d.c. voltammetric technique, with $E_{el} = -1.0$ V, $t_{el} = 10$ min. The other conditions are the same.

For the determination of zinc alone in zirconium oxide, the hydrofluoric acid resulting from sample decomposition can be neutralized by purified sodium hydroxide to about pH 7 and the determination carried out with an HMDE and $E_{el} = -1.4$ V and t_{el} depending on the concentration and monitoring techniques used.

An alternative procedure for determination of higher concentrations of copper, lead, cadmium and zinc involves diluting 1 ml of the sample solution in sulphuric acid to 10 ml with a purified saturated solution of sodium tartrate, maintaining the resultant pH at 2.0–4.0 by adding purified sodium hydroxide and carrying out the stripping determination without solution exchange, using the HMDE with $E_{el} = -1.2$ V and t_{el} depending on the monitoring technique and the concentrations of the trace metals. For determining copper, lead and cadmium, an MFE and d.c. voltammetry can be used, with $E_{el} = -1.0$ V and $t_{el} = 10$ min.

If a large amount of copper is present, it should be removed electrolytically on a platinum gauze electrode at a potential of -0.4 V in a tartrate solution of pH 2.0–4.0.

RESULTS

Sample decomposition and treatment

Zirconium metal is most often dissolved in sulphuric or hydrofluoric acid.[6] From the point of view of the subsequent determination, it is preferable to decompose the sample in sulphuric acid. We carried out the decomposition of 1-g samples in PTFE crucibles heated on an electric hot-plate and were able to obtain 0.1*M* zirconium solutions in 20% v/v sulphuric acid.

The decomposition of zirconium dioxide is much more difficult. Neither the fusion procedures, which are most frequently employed (see *e.g.*, refs. 6,7) nor the distillation technique[8] are suitable for trace analyses. We did not succeed in dissolving the material in hot mineral acids. It was therefore necessary to employ a pressure decomposition. We tested the method[9] employing a 1:1 mixture of 50% sulphuric acid and hydrofluoric acid. The method leads to complete decomposition, but requires heating at 240° for 12 hr. We found that better results could be obtained when hydrofluoric acid was used alone. Complete decomposition was then achieved by heating a 1-g sample with 15 ml of hydrofluoric acid in an autoclave at 190° for 8 hr.

A solution in concentrated hydrofluoric acid results from this decomposition, which is unsuitable for the determination because of its corrosive effects and the poor separation of the stripping peaks of the metals to be determined. We tested the possibility of converting this solution into a sodium fluoroborate solution by reaction with boric acid and sodium fluoride or into a sodium fluoride solution by neutralization with sodium hydroxide. However, these procedures led to considerable contamination of the solution with the metals to be determined. Moreover, the separation of the stripping peaks was still poor, especially in fluoroborate solution. A sodium fluoride solution is suitable for the determination of zinc, but the lead and cadmium peaks are insufficiently separated and hydrolysis of many metals (e.g., Bi^{3+}, Pb^{2+}, Mn^{2+}, Al^{3+}) occurs. We therefore evaporated the solution with concentrated sulphuric acid in a PTFE dish till the hydrofluoric acid had all volatilized, and then prepared a solution in 20% v/v sulphuric acid analogous to the solution of zirconium metal.

The solution in sulphuric acid is unsuitable for direct stripping analysis, because the acidity is too high. Two approaches can now be taken; the pre-electrolysis can be carried out in the sample solution, which is then replaced by a suitable base electrolyte for the stripping step, or the sample solution can be converted into a solution suitable for both steps of the stripping determination. We tested both of these techniques.

If both pre-electrolysis and the stripping step are to be carried out in a single solution, the base electrolyte must not only permit simultaneous determination of copper, lead, cadmium and zinc, but must also prevent hydrolysis of the zirconium. On the basis of the pertinent stability constants,[10,11] citrate or tartrate would seem to be suitable. Citrate forms a sufficiently stable complex with zirconium, but the stripping peaks of the metals to be determined are not well separated. On the other hand, tartrate is known to be a suitable electrolyte for simultaneous polarographic or stripping determination of copper, lead, cadmium and zinc.[1] To complex the large amounts of

Table 1. Electrical parameters for the stripping voltammetric determination of Cu, Pb, Cd and Zn

pH	Potential range, *V vs. SCE*	$E_{1/2}$, *V vs. SCE*			
		Cu^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}
1.06	0 to −1.1	~ +0.05	~ −0.37	−0.55	→
2.16	0 to −1.2	~ +0.02	−0.38	−0.55	~ −1.05
4.5	+0.1 to −1.4	−0.045	−0.44	−0.59	~ −1.1
6.41	0 to −1.6	*a*	*a*	*a*	*a*
H_2SO_4	+0.1 to −0.6	↑; ~0.0	−0.35	−0.54	→

→—no wave within the potential range available; *a*—poorly developed unresolved waves; ↑—current increases directly from the mercury dissolution anodic wave. Electrolyte was a saturated solution of sodium tartrate containing zirconium at $10^{-2}M$, adjusted to the acidity shown.

zirconium present, as high a concentration of tartrate as possible must be used. Therefore, 1 ml of the sample solution was diluted to 10 ml with a saturated solution of purified sodium tartrate. The potential ranges available and half-wave potentials of the test metals are given in Table 1 for various pH values. It is evident that at low pH values the complexes are dissociated and the half-wave potentials are virtually identical with those in mineral acids. Since at pH values above 4.5 the waves are unresolved, a saturated tartrate solution with pH in the range 2.0–4.0 was thought to be a suitable base electrolyte, in which comparable concentrations of Pb^{2+} and Cd^{2+}, and concentrations of Cu^{2+} and Zn^{2+} up to 50 times those of Pb^{2+} and Cd^{2+}, could be determined. However, as such solutions are not completely stable, with hydrolysis of zirconium becoming apparent after several hours, they must be prepared immediately before the stripping determination.

As some samples of zirconium metal contain rather high concentrations of copper, its electrolytic separation was investigated. The polarization curves (platinum rotating-disk electrode) showed that two waves of copper appear with $E_{1/2} = +0.02$ and -0.3 V in saturated sodium tartrate solutions containing zirconium, at pH values below 4.0. The waves of Pb^{2+}, Cd^{2+} and Zn^{2+} are obscured by the reduction wave of hydrogen ions. Therefore, a potential of -0.4 V and pH 3.25 were selected for the separation of copper from $5 \times 10^{-5}M$ Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} in $0.01M$ zirconium solution in tartrate. The separation was carried out with a platinum-gauze working electrode, an operational amplifier potentiostat and a platinum counter-electrode separated from the test solution by a dense frit, to prevent electrodeposition of PbO_2. The polarographic determination of the metals showed that the separation was complete. However, at pH above 4.5 copper could no longer be electrodeposited on the platinum electrode at the potential used, apparently because of a rapid decrease in the electrode reaction rate.

THE STRIPPING DETERMINATION

Direct current voltammetry

It has been found that it is possible to determine all four metals in zirconium metal and zirconium dioxide with an HMDE in a solution consisting of 1 ml of sample solution diluted to 10 ml with saturated sodium tartrate solution, with pH below 4.0. The pre-electrolysis potential must not be less negative than -1.2 V. As the concentrations of the test metals in the final solution are quite low (of the order of 10^{-9}–$10^{-8}M$), rather long pre-electrolysis times are required (at least 30 min). The MFE permits the determination of only copper, lead and cadmium under these conditions (a pre-electrolysis potential of -1.0 V was generally used), and even the cadmium peak may be distorted by evolution of hydrogen in some samples. On the other hand, the peaks obtained with the MFE are narrower and the measurement is substantially more sensitive, so that pre-electrolysis times of up to 15 min are sufficient. Examples of stripping curves obtained are shown in Figs. 1–3. Generally, the HMDE permits the simultaneous determination of all four metals, up to a 10:1 ratio of Pb^{2+} to Cd^{2+} or *vice versa* and up to a 50:1 ratio of Cu^{2+} or Zn^{2+} to Pb^{2+} and Cd^{2+}. The peak resolution obtained with the MFE is better and the corresponding ratios increase to 20:1 and 70:1, respectively.

The lower limit of determination of Cu^{2+} and Pb^{2+} is about $10^{-9}M$ with pre-electrolysis times of 20 min (MFE) or 45 min (HMDE). To attain the same limit for cadmium, the pre-electrolysis time with the MFE must be doubled, whereas with the HMDE a time of about 50 min suffices. The limit of determination for zinc is higher, about $7 \times 10^{-8}M$ (HMDE, 45 min pre-electrolysis). The sensitivity for zinc can be increased by carrying out the determination in a neutral solution of sodium fluoride (see the previous section), where the lower limit is about $10^{-8}M$ under the same conditions. The sensitivity is sufficient for the present purpose, with the limit of determination about 0.01 ppm of the trace metals in a 1-g sample. One disadvantage is the rather high blank value, which roughly amounts to the value for the samples at our disposal even after electrolytic purification of the solutions.

In view of the complex matrix and rather complicated sample pretreatment, the standard addition must be used, the standard being added to the sample

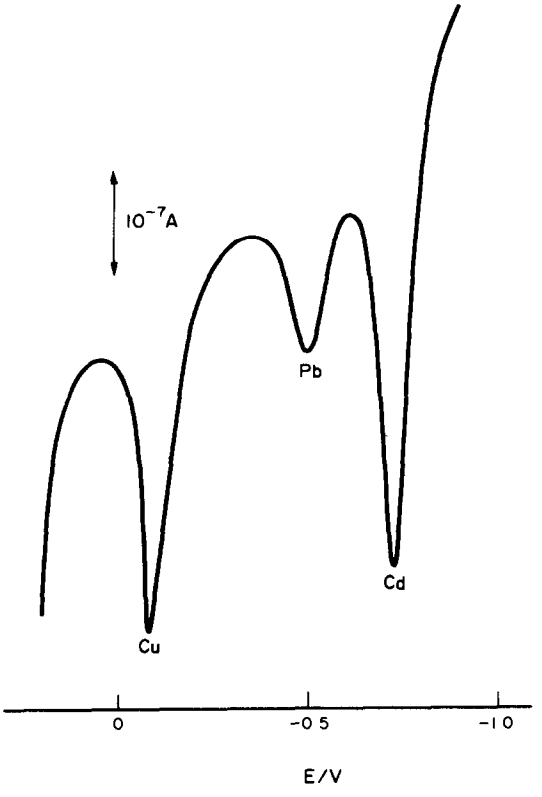


Fig. 1. D.c. stripping voltammetric curve obtained with a solution of 0.01*M* zirconium in sulphuric acid and sodium tartrate at pH 3.73. MFE prepared *in situ*,[12] $2 \times 10^{-5}M$ Hg^{2+}, $E_{el} = -1.4$ V, $t_{el} = 30$ min + 1 min rest period, scan-rate 400 mV/min.

at the beginning of the decomposition step. The reproducibility of the measurements with the HMDE is somewhat better than that of those made with the MFE; typical values of the relative standard deviations are given in Table 2.

Differential pulse voltammetry (DPV) and Kalousek commutator voltammetry (KCV)

The determinations were repeated under similar conditions, by the DPV technique. Typical curves are shown in Fig. 4. A considerable improvement in the sensitivity was found, even with the other parameters remaining the same. Pre-electrolysis times not exceeding 5 min are then sufficient and there are only two drawbacks: first, the MFE cannot be used, as the reproducibility of the measurements is very poor and the electrode is damaged by large current pulses, and secondly the d.c. potential scan must be slow, otherwise the peaks are poorly resolved. Consequently, the time saved compared with d.c. technique is not as large as might at first appear (the potential-scan time is about 3 min in the d.c technique, that in the DPV is more than 10 min).

The first drawback is difficult to overcome; the other can be eliminated by employing a Kalousek commutator, as proposed earlier.[5] During the stripping step, the potential is commutated from the voltage ramp to the pre-electrolysis potential with a frequency of several units or tens of Hz. To eliminate the charging current, the current is sampled just before the end of the pulse. The sensitivity of this method resembles that of DPV and the potential-scan rate can be the same as in d.c. voltammetry. The height of the stripping peak can be doubled by adding the currents sampled on the potential ramp and on the commutated constant potential.

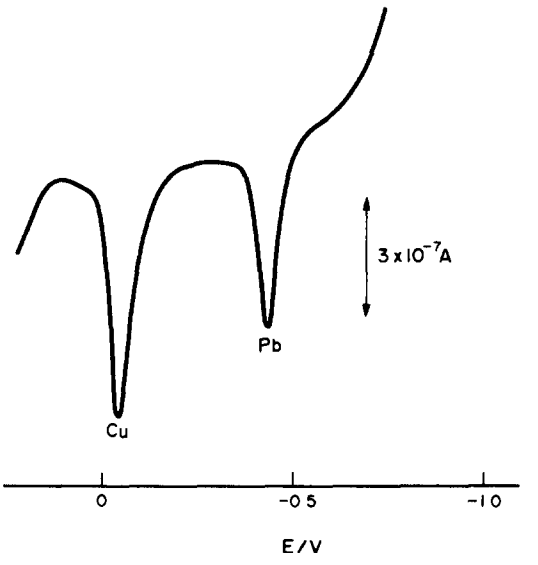


Fig. 2. D.c. stripping voltammetric curve obtained with a solution obtained from decomposition of zirconium oxide; about 0.01*M* zirconium in sulphuric acid and sodium tartrate at pH 3.5. MFE prepared *in situ*,[12] $2 \times 10^{-5}M$ Hg^{2+}, $E_{el} = -1.0$ V, $t_{el} = 10$ min + 1 min rest period, scan-rate 400 mV/min.

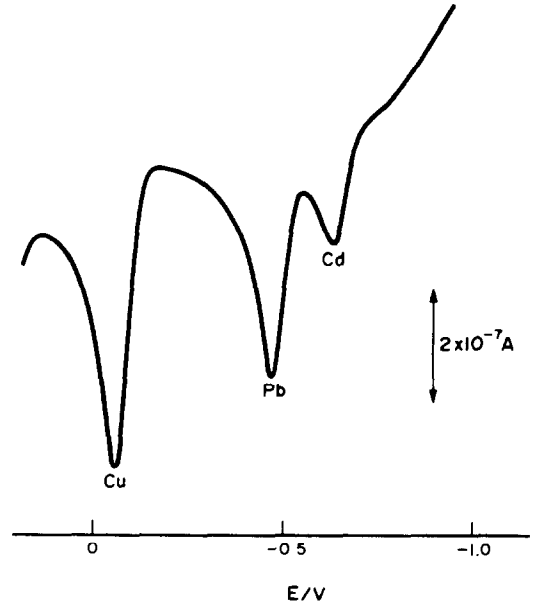


Fig. 3. D.c. stripping voltammetric curve obtained with the same solution as in Fig. 2, but with the HMDE. $E_{el} = -1.2$ V, $t_{el} = 30$ min + 1 min rest period, scan-rate 400 mV/min.

Table 2. Relative standard deviations for the stripping voltammetric determination of $10^{-7}M$ Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}

	s_{rel}, %				
	Blank		$10^{-7}M$ in tartrate		$10^{-7}M$ in NaF
	MFE	HMDE	MFE	HMDE	HMDE
Cu^{2+}	6	5	4	4	—
Pb^{2+}	8	6	13	8	—
Cd^{2+}	—	11	—	7	—
Zn^{2+}	—	24	—	16	8

Saturated sodium tartrate solution at pH 3.5, $E_{el} = -1.0$ V, $t_{el} = 10 + 1$ min (MFE) or $E_{el} = -1.2$ V, $t_{el} = 20 + 1$ min (HMDE), scan-rate 400 mV/min. The determination of Zn^{2+} in 1M NaF, pH 7.5, HMDE, $E_{el} = -1.3$ V, $t_{el} = 20 + 1$ min.

The commutator circuit is shown in Fig. 5. The potential ramp and the constant pre-electrolysis potential are derived from a classical polarograph, the recorder of which is also used for recording the stripping curves. Integrated-circuit switches S_A, S_B and S_C produce function A (commutating of the ramp potential to another, constant, potential) and functions B and C for current sampling. If only the current on the potential ramp is sampled, function B is used and analogue memory M1 always retains the previous value. If the currents on the ramp and at the pre-electrolysis potential are sampled and added, functions B and C and memories M1 and M2 are used.

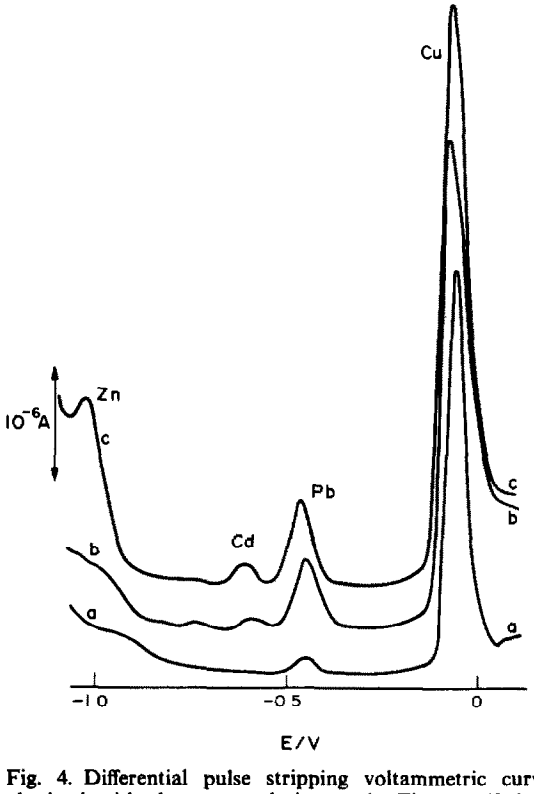


Fig. 4. Differential pulse stripping voltammetric curve obtained with the same solution as in Fig. 2 (pH 2.2). HMDE, $E_{el} = -1.3$ V, $t_{el} = 3$ min + 30 sec rest period, scan-rate 120 mV/min, pulse-height 50 mV. (*a*) blank; (*b*) sample; (*c*) standard addition ($10^{-8}M$) of each metal.

The curves obtained with this apparatus for the samples studied (see Fig. 7 in the following section) have a somewhat less favourable shape from the point of view of peak-resolution than the curves obtained by DPV, but the pre-electrolysis times are similar (not exceeding 5 min) and the stripping step takes a shorter time. The other parameters are the same as in d.c. voltammetry and DPV.

Determinations with solution-exchange

Solution-exchange after pre-electrolysis has several advantages in this determination. By pre-electrolysis from the sample solution in sulphuric acid the tenfold dilution of the sample with the tartrate solution is avoided, and the limit of determination is therefore decreased, the problem with the stability of the sample solution is eliminated and the blank value is decreased, because the sulphuric acid used is of very high purity, while the purity of the base electrolyte in the stripping step is not critical. The disadvantage of this procedure is the loss of the pre-concentrated metals owing to oxidation with atmospheric oxygen during solution-exchange.[4] This disadvantage is eliminated by performing the determination in the flow-through cell described earlier,[4] in which the solutions are exchanged without the electrodes being exposed to the atmosphere.

Stripping curves were recorded, with use of this flow-through cell, with all the techniques described, after pre-electrolysis from the solution of a zirconium dioxide sample in 20% sulphuric acid and stripping into a 0.5M sodium acetate–acetic acid buffer at pH 5. The same average precision was obtained as in determinations without solution-exchange, the blank value decreased to about one third of the initial value and the sensitivity increased, so that the pre-electrolysis times did not need to exceed 15 min with d.c. voltammetry, 2 min with DPV and 4 min with KCV. Two examples of stripping curves obtained with solution-exchange are given in Figs. 6 and 7.

Analysis of samples

The samples were analysed by the procedures described above. A typical set of results obtained from

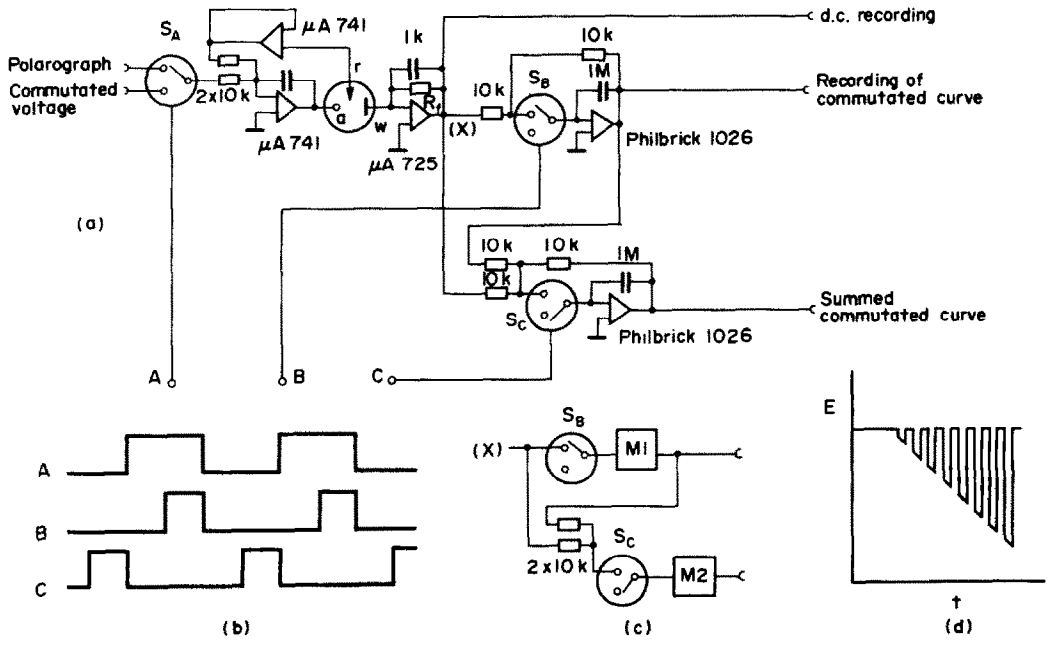


Fig. 5. Modified Kalousek commutator for stripping determinations. For the description see the text. (*a*) commutator circuit; (*b*) logic time functions during stripping current recording; (*c*) simplified schemes of the analogue memories; (*d*) potential function during the stripping step.

four parallel determinations on a ZrO_2 sample is given in Table 3.

DISCUSSION

The results above indicate that the best procedure for the simultaneous determination of all four trace elements is the procedure with solution-exchange and

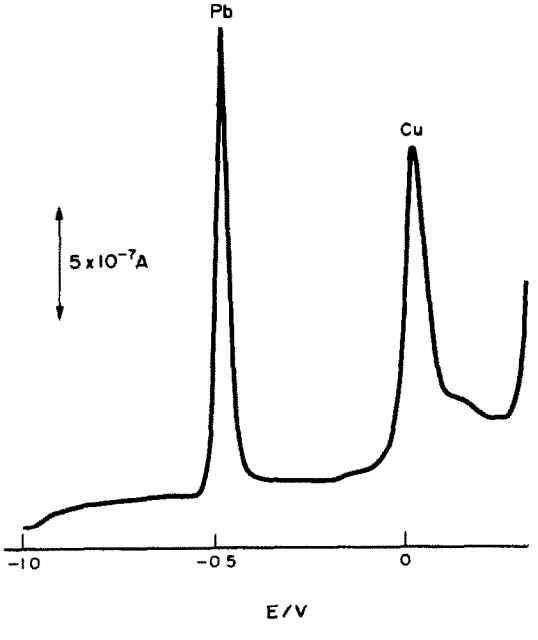


Fig. 6. D.c. stripping voltammetric curve of copper and lead obtained from the solution of a sample of zirconium oxide in 20% sulphuric acid, with solution-exchange for a 0.5*M* sodium acetate–acetic acid buffer at pH 5. MFE, $10^{-4}M$ Hg^{2+}, $E_{el} = -1.0$ V, $t_{el} = 10$ min + 2 min rest period, scan-rate 400 mV/min.

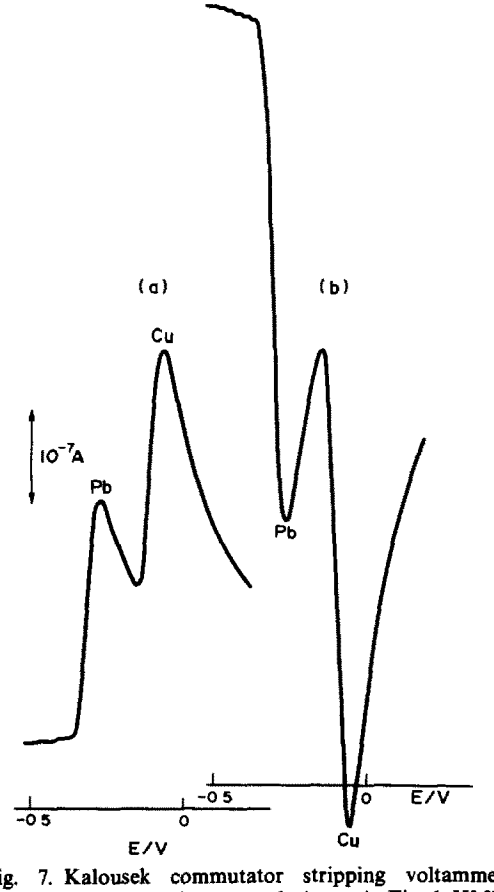


Fig. 7. Kalousek commutator stripping voltammetric curve obtained with the same solution as in Fig. 6. HMDE, $E_{el} = -0.8$ V, $t_{el} = 4$ min + 2 min rest period, voltage commutated to −0.8 V with a frequency of 8 Hz, d.c. potential scan-rate 400 mV/min; (*a*) only ramp current sampled; (*b*) ramp and pre-electrolysis currents sampled and added.

Table 3. Determination of Cu, Pb, Cd and Zn in a ZrO_2 sample. Sample weight, 1.008 g

Metal	Average content, *ppm*	Relative standard deviation, %	Confidence limits (90% probability), *ppm*
Cu^{2+}	1.15	5	1.15 ± 0.07
Pb^{2+}	8.35	19	8.35 ± 1.9
Cd^{2+}	0.68	16	0.68 ± 0.13
Zn^{2+}	undistinguishable from the blank value		

DPV monitoring of the stripping step at an HMDE. The only disadvantages of this procedure are the impossibility of using an MFE and a rather slow stripping step. The use of KCV for the stripping makes the determination faster, but, owing to the less favourable peak shapes (see Fig. 7), may not be sufficiently selective when the contents of the metals are not similar. Furthermore, commutation of the voltage to more negative pre-electrolysis potentials may lead to distortion of the peaks by the hydrogen evolution currents. Nevertheless, this technique will be useful for the determination of copper, lead and cadmium in these materials.

Direct current voltammetry with an MFE has advantages in the determination of copper and lead in the presence of an excess of one of these metals, because of superior selectivity compared with the other methods. The precision of the results obtained with the MFE is generally somewhat poorer than for the HMDE, but the difference is not significant.

The determination without solution-exchange is advantageous for the determination of higher concentrations of the trace metals, where the pre-electrolysis times need not be long and the higher blank value is not critical. Then it is not necessary to use the more complicated flow-through cell, the consumption of chemicals is less and the measurement can be repeated several times on one solution (in measurements with the flow-through cell the sample solution is discarded during the exchange).

If the determination of zinc alone is of interest, then it is preferable to use the sodium fluoride medium, provided that metals undergoing hydrolysis are absent.

As the reproducibility of the determination was the same for all the procedures listed, it can be concluded that the sample decomposition is the decisive source of error. The accuracy of the determination could not be tested sufficiently because of the lack of standard materials, but experiments with multiple addition of the test metals to the samples indicated that there is no significant systematic error.

REFERENCES

1. F. Vydra, K. Štulík and E. Juláková, *Electrochemical Stripping Analysis*, Horwood, Chichester, 1977.
2. R. Kalvoda, *Operational Amplifiers in Chemical Instrumentation*, Horwood, Chichester, 1975.
3. K. Štulík and K. Mařík, *Talanta*, 1976, **23**, 131.
4. L. Zieglerová, K. Štulík and J. Doležal, *Talanta*, 1971, **18**, 603.
5. F. Opekar and K. Štulik, *J. Electroanal. Chem.* 1977, **85**, 207.
6. J. Doležal, P. Povondra and Z. Šulcek, *Decomposition Techniques in Inorganic Analysis*, Iliffe, London, 1969.
7. L. F. Bates and J. S. Rogers, *Nature*, 1928, **112**, 938.
8. M. Borlera, *Ric. Sci.*, 1959, **29**, 1465; *Anal. Abstr.*, 1960, **7**, 1701.
9. J. Ito, *Bunseki Kagaku*, 1962, **35**, 225.
10. L. G. Sillén and A. E. Martell, *Stability Constants*, Special Publ. No. 17, Chemical Society, London, 1964.
11. *Idem*, *Stability Constants*, Suppl. 1, Special Publ. No. 25, Chemical Society, London, 1971.
12. T. M. Florence, *J. Electroanal. Chem.*, 1970, **27**, 273.

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LIQUID–LIQUID EXTRACTION OF ZINC FROM AQUEOUS THIOCYANATE SOLUTIONS WITH 5-(-4-PYRIDYL)NONANE IN BENZENE

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Summary—5-(4-Pyridyl)nonane dissolved in benzene has been applied to the extraction of zinc, down to very low concentration ($<10^{-6}M$), from aqueous thiocyanate solutions. The metal can be quantitatively extracted from neutral and acidic thiocyanate solutions (up to 5*M* HCl, 0.25*M* HNO_3 or 0.25*M* H_2SO_4) in a single extraction. Equilibration times of 5 min are sufficient for almost complete extraction. The optimum thiocyanate concentration range is 0.05–0.5*M*. Among the common anions chloride exerts a slight depressing effect on extraction from neutral solution when present in high concentration. The extraction mechanism and the composition of the extracted complexes of zinc are discussed. The metal is predominantly extracted by means of a solvate mechanism. The effect of chloride, nitrate, sulphate, acetate, citrate, oxalate and ascorbate ions on the extraction of zinc is described. Several elements, including those of interest in separation of zinc, have been tested for extraction from 0.1*M* KSCN at the optimal concentrations of the mineral acids, and the separation factors estimated.

We have studied[1,2] the extraction behaviour of certain high molecular-weight amines. Of the compounds investigated, 5-(4-pyridyl)nonane has been found the most versatile extractant because it extracts through solvation and/or ion-pair formation, depending on experimental conditions. This study is part of a comprehensive programme concerned with the solvent extraction of halides and pseudohalides of bivalent first transition-series metal ions with long-chain alkyl pyridine derivatives. The extraction of thiocyanate complexes of some transition metal ions with pyridine and related lower members of the pyridine series has been investigated.[3–5] The reagents reported suffer from two essential drawbacks: the phases do not separate cleanly when acidic media are used and the reagents themselves have a very pungent odour. In this paper, we report studies on the extraction of zinc from neutral and mineral acid solutions containing thiocyanate ions by a benzene solution of 5-(4-pyridyl)nonane (which is completely free from these defects). In addition, this compound extracts all or most of the metal in a single extraction over a fairly wide range of acidities so the acid concentration of the solution is not a critical factor. The investigation reveals that 5-(4-pyridyl)nonane can be usefully employed for the preconcentration of zinc along with metals of similar properties, which is advantageous in a number of modern multielement techniques.

EXPERIMENTAL

Reagents

5-(4-Pyridyl)nonane (PyN). The reagent was obtained commercially. It is non-hygroscopic, chemically stable, practically odourless, immiscible with water and has no tendency to form emulsions. The other characteristics of this compound are given elsewhere.[6]

Zinc-65 and other tracers. Zinc-65 tracer was obtained by the irradiation of zinc foil (purity >99.9%) with thermal neutrons in the research reactor PARR-I of this institute. A cooling period of 24 hr was allowed to elapse before the can was opened. All other tracers used in this work were obtained either from the Radiochemical Centre, Amersham or were prepared locally by (n, γ) reactions or by separation of the daughter nuclide from the parent, without a carrier.

Apparatus

Radiochemical counting. The γ-emission was counted with a Nuclear Chicago single-channel analyser, model 872, coupled with a 7.5 × 7.5 cm NaI(Tl) well-type scintillation detector. The α and β radiation was counted as reported earlier.[1,7]

Determination of distribution coefficients

Partition experiments were carried out at room temperature (23 ± 3°) in 20-ml glass vials. Mineral acid containing the zinc tracer (^{65}Zn) was put in a glass vial and potassium thiocyanate added to adjust the thiocyanate concentration to the required level. The aqueous phase was equilibrated with an equal volume of the organic phase (a solution of PyN in benzene). The period of equilibration was varied from 0.5 to 15 min and the extraction found to be quantitative with 2-min equilibration or more; a 5-min equilibration time was subsequently used. The concentration of zinc in the original aqueous phases (except in saturation experiments) was $<10^{-6}M$ (generally $\sim 10^{-7}M$).

RESULTS AND DISCUSSION

The extraction of zinc with 0.1*M* PyN in benzene was studied as a function of hydrochloric, nitric and sulphuric acid concentrations in the aqueous phase. Figure 1 shows that in the hydrochloric acid system

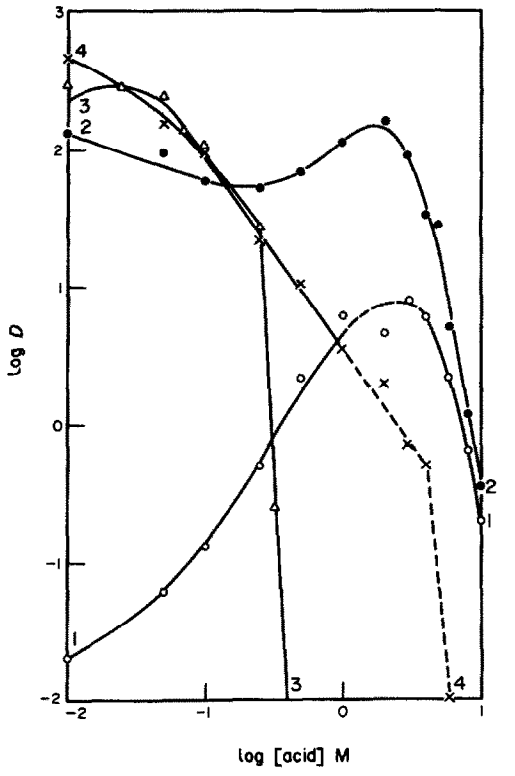


Fig. 1. Variation of the distribution coefficient of zinc *vs.* concentration of the mineral acid solutions containing 0.02*M* KSCN by 0.1*M* PyN solution in benzene. (1) HCl alone, (2) HCl KSCN (3) H_2SO_4 KSCN (4) HNO_3 KSCN.

the distribution coefficient passes through a maximum at an initial acid concentration of *ca.* 1*M*. The extraction of zinc in this region is perhaps due to chloride complexes of the type $ZnCl_3^-$ and $ZnCl_4^{2-}$ which are obviously present since amine extraction in this region is high.[8] However, at 1–5*M* acid concentration the sum of the radioactivity of the organic and aqueous phases did not correspond to the total amount of radioactive zinc taken. This loss of zinc is possibly due to the formation of an invisible third phase caused either by the association of $PyNH^+Cl^-$ with $PyNH^+ZnCl_3^-$ or by mutual immiscibility of the ion-association complexes formed through the following reactions:

$$ZnCl_3^- + PyNHCl \rightleftharpoons (PyNH)^+ZnCl_3^- + Cl^- \quad (1)$$

$$ZnCl_4^{2-} + 2PyNHCl \rightleftharpoons (PyNH)_2^+ZnCl_4^{2-} + 2Cl^-. \quad (2)$$

In the nitric and sulphuric acid systems no extraction was observed.

The influence of the addition of potassium thiocyanate, in solutions of mineral acids, on the extraction of zinc was investigated. Figure 1 also presents the plots of the distribution of zinc *vs.* molarity of aqueous mineral acid (which is 0.02*M* with respect to potassium thiocyanate). It is to be seen that with the addition of thiocyanate, the log D_{Zn} *vs.* log [acid] curves shift markedly towards higher D values. The fact that zinc is extracted to a greater extent from thiocyanate than from chloride, nitrate or sulphate media is presumably because thiocyanate ions lead to the formation of larger and less hydrated complexes. In the nitric acid system, there is an abrupt decrease in D value as the acid concentration in the aqueous phase exceeds 0.25*M*. This can be explained as due to the formation of some inextractable species and/or to the competition of the acid for the pyridylnonane. In the sulphuric acid system, loss of activity was observed at concentrations above 1*M*. This may be due to the formation of a third phase, possibly caused by the lower solubility of $(PyNH)^+HSO_4^-$ in benzene, as the amine hydrogen sulphates are generally less soluble than the corresponding sulphates,[9] perhaps because the former are more aggregated.

The effect of the increase of thiocyanate concentration in nitric, hydrochloric and sulphuric acid solutions is plotted in Fig. 2. The stepwise complex formation of the metal in the aqueous phase seems to affect its distribution. Thus in the lower $[SCN^-]$ region the species may be expected to change progressively from $Zn(SCN)^+$ to $Zn(SCN)_2$ at the maximum log D value, then $Zn(SCN)_3^-$ and finally $Zn(SCN)_4^{2-}$. It is also to be noted that in very dilute solutions of the mineral acids ($\leqslant 10^{-1}M$), the slope of the linear parts of the curves of log D *vs.* log $[SCN^-]_{aqueous}$ is close to 2. In the hydrochloric acid system, the slope decreases from a value of 2 as the initial aqueous acid concentration is increased from 0.1 to 5*M*. This is believed to be due to co-extraction of the acid. In nitric or sulphuric acid systems, the slope of the plots increases as the concentration of the acid increases to 0.25*M*. A possible reason is that nitrate and sulphate, ions of relatively higher electrical potential, could compete favourably with thiocyanate for solvation by water so that the thiocyanate ions become easily attached to the metal complex at the co-ordination sites vacated by the water, resulting in the formation of $Zn(SCN)_3^-$ and $Zn(SCN)_4^{2-}$ complexes. In very dilute (0.01*M*) aqueous acid solutions and water ($D_{Zn} > 100$) the high extraction coefficients are perhaps exclusively due to neutral thiocyanate complexes since the extraction of anionic species by ion-association in acid-deficient systems[10] is unlikely. The extraction reaction in water and weakly acid solutions can be expected to be independent of the nature of the anions of the mineral acids and can be expressed as:

$$ZnX_2nH_2O + yPyN + 2KSCN \rightleftharpoons Zn(PyN)_y(SCN)_2 + 2KX + nH_2O. \quad (3)$$

The value of y in equation (3) was found by plotting log D *vs.* log [PyN] for different concentrations of the acids containing potassium thiocyanate. The equation for the distribution ratio of zinc complexes with the pyridylnonane would take the form $D = K[PyN]_{org}$ if all other variables such as thiocyanate concentration and acidity were held constant. There-

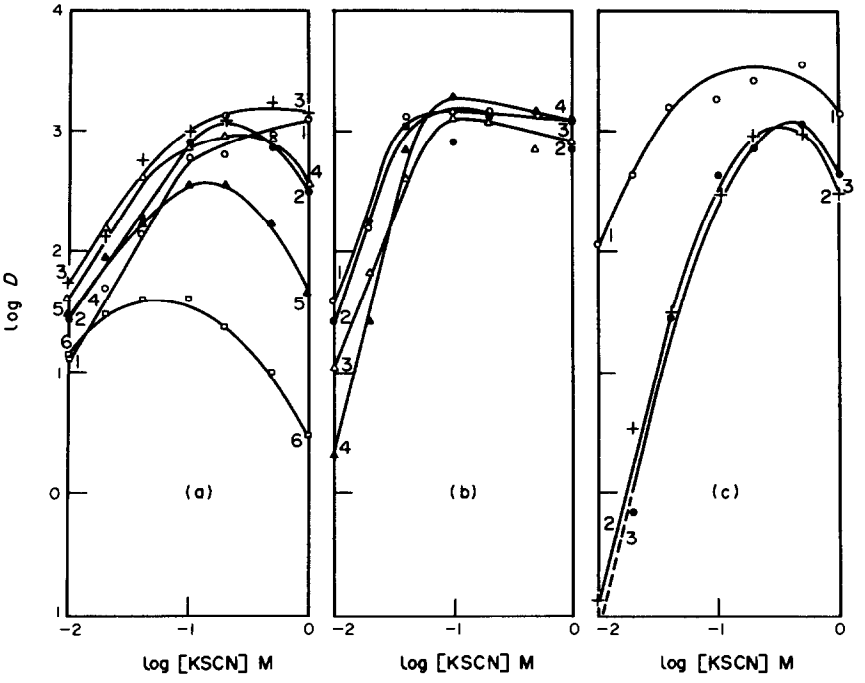


Fig. 2. Dependence of the distribution coefficient of zinc on aqueous thiocyanate concentration for extraction by 0.1*M* PyN solution in benzene.
A. HCl, *M*: (1) 0.1, (2) 1.0, (3) 1.5, (4) 2.5, (5) 3.0, (6) 5.0.
B. HNO_3, *M*: (1) 0.005, (2) 0.05, (3) 0.1, (4) 0.25.
C. H_2SO_4, *M*: (1) 0.01, (2) 0.1, (3) 0.2.

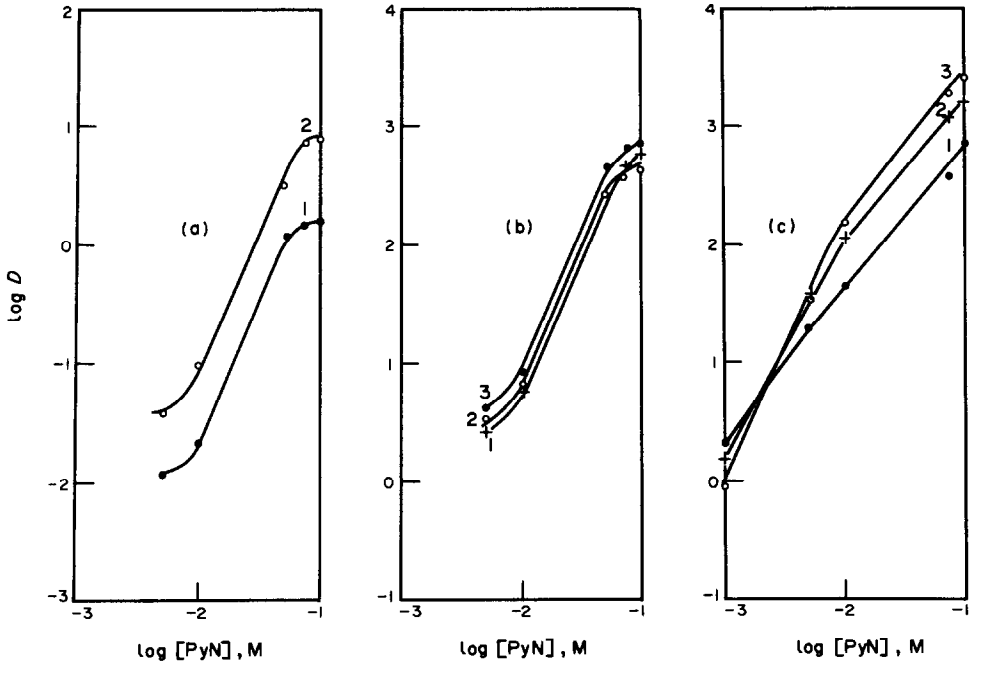


Fig. 3. Variation of the distribution coefficient of zinc with the pyridylnonane concentration, from solutions of varying acidity.
A. (1) 6*M* HCl (2) 6*M* HCl + 0.1*M* KSCN
B. (1) 0.01*M* H_2SO_4 + 0.02*M* KSCN, (2) 0.01*M* HCl + 0.02*M* KSCN, (3) 0.01*M* HNO_3 + 0.02*M* KSCN.
C. (1) 0.1*M* H_2SO_4 + 0.1*M* KSCN, (2) 0.1*M* HCl + 0.1*M* KSCN, (3) 0.1*M* HNO_3 + 0.1*M* KSCN.

Table 1. Distribution coefficients and separation factors for different metal ions between 0.1*M* PyN/benzene and mineral acids (0.1*M* with respect to KSCN) extraction systems

Metal ions	Concentration *M*	Distribution coefficients 0.01*M* HCl	0.01*M* HNO_3	0.01*M* H_2SO_4	Separation factors 0.01*M* HCl	0.01*M* HNO_3	0.01*M* H_2SO_4
TcO_4^-	C.F.*	3.8	3.4	4.5	2.0×10^2	4.1×10^2	3.7×10^2
MoO_4^{2-}	10^{-5}	7.3	1.4	2.5	1.0×10^2	9.9×10^2	6.8×10^2
CrO_4^{2-}	C.F.	0.031	0.061	0.009	2.5×10^4	8.7×10^4	1.8×10^5
UO_2^{2+}	10^{-3}	5.9	5.0	12.0	1.3×10^2	2.7×10^2	1.4×10^2
Mo(V)	10^{-5}	1.9	0.9	7.5	4.0×10^2	1.5×10^3	2.2×10^2
Nb(V)	10^{-5}	0.01	0.01	0.01	10^3	10^3	10^3
Hf^{4+}	10^{-7}	0.058	0.054	0.15	1.3×10^4	2.5×10^4	1.1×10^4
Zr^{4+}	10^{-5}	0.11	0.077	0.14	7.1×10^3	1.8×10^4	1.2×10^4
La^{3+}	10^{-7}	0.011	0.038	0.034	7.1×10^4	3.6×10^4	4.9×10^4
Nd^{3+}	10^{-7}	0.12	0.011	0.073	6.4×10^3	1.2×10^5	2.3×10^4
Y^{3+}	10^{-8}	0.001	0.0001	0.0004	8.7×10^5	1.3×10^7	4.2×10^7
Cr^{3+}	C.F.	0.005	0.008	0.016	1.5×10^5	1.6×10^5	1.0×10^5
Fe^{3+}	10^{-4}	120	52.0	48.0	6.5	26.8	35.4
Au(III)	10^{-6}	0.81	1.5	6.3	9.6×10^2	9.3×10^2	2.7×10^2
As(III)	10^{-5}	0.009	0.004	0.003	8.7×10^4	3.4×10^5	5.6×10^5
Pm^{3+}	10^{-7}	0.001	0.002	0.002	7.8×10^5	9.3×10^5	8.5×10^5
Hg^{2+}	10^{-7}	2.05×10^3	550	860	0.38	2.5	2.0
Sr^{2+}	10^{-8}	0.004	0.05	0.11	1.9×10^5	2.7×10^4	1.5×10^4
Co^{2+}	10^{-7}	520	1.0×10^3	150	1.5	1.4	11
Cs^+	10^{-8}	0.001	0.0008	0.0005	8.0×10^5	1.6×10^6	3.2×10^6
Br^-	10^{-5}	0.002	0.002	0.0034	3.4×10^5	6.6×10^5	5.0×10^5
Ag^+	10^{-8}	6.0	73	60	1.3×10^2	19	28

* C.F. Carrier-free.

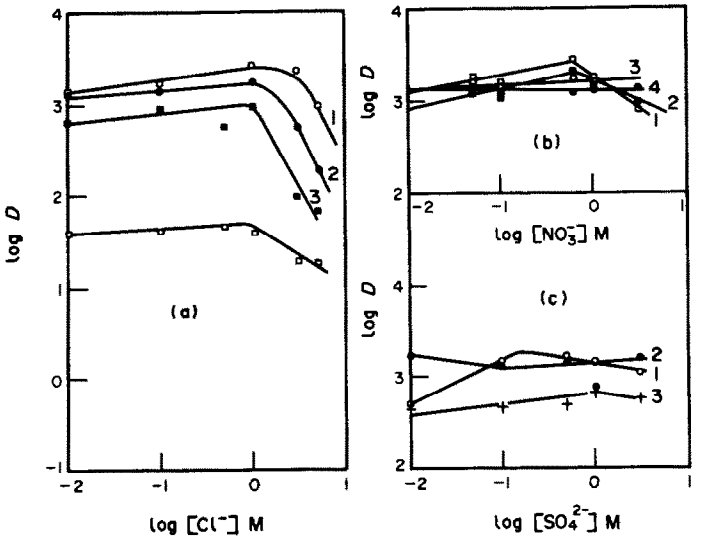


Fig. 4. Variation of the distribution coefficient of zinc with concentration of different salts for extraction by 0.1*M* PyN solution in benzene. Acid concentration fixed as shown below, anion concentration varied as indicated on graph.
A. HCl, *M*: (1) 0.1, (2) 1.0, (3) 2.5, (4) 5.0.
B. HNO_3, *M*: (1) 0.005, (2) 0.05, (3) 0.1, (4) 0.25.
C. H_2SO_4, *M*: (1) 0.01, (2) 0.1, (3) 0.2.

fore, $\log D = y\log [PyN] + \log K$ and a plot of log *D* *vs.* log [PyN] should yield a straight line with a slope of *y* where *y* is the number of PyN molecules per zinc ion in the complex. A test of the dependence of the extraction of zinc on the concentration of PyN was made for 6*M* hydrochloric alone and for 6*M* hydrochloric acid/0.1*M* potassium thiocyanate. The results are shown in Fig. 3A. The linear parts of the curves show that *y* is about 2. Species of the type $ZnCl_4^{2-}$ are perhaps extracted from 6*M* hydrochloric acid through the ion-association reaction given in equation (2). A slope of 2 for 6*M* hydrochloric acid/0.1*M* KSCN also indicates the formation of a disolvate, probably as a mixed chloride–thiocyanate species. Figure 3B shows plots for 0.01*M* nitric, hydrochloric and sulphuric acids which were 0.02*M* with respect to thiocyanate. The slope obtained in all cases, between 0.01 and 0.05*M* PyN, was close to 2, implying the formation of disolvates. Therefore, the reaction can be expressed as

$$ZnX_2nH_2O + 2PyN + 2KSCN \rightleftharpoons Zn(PyN)_2(KCN)_2 + 2KX + nH_2O. \quad (4)$$

Figure 3C shows the logarithmic dependence of the distribution coefficients on the pyridylnonane concentration for hydrochloric, nitric and sulphuric acid media that are 0.1*M* in potassium thiocyanate. In all three systems a slope of around 2 is obtained, when the reagent concentration is between 10^{-3} and $10^{-2}M$, and decreases above this concentration. The non-ideal nature is perhaps mainly due to the molecular association of the organic-phase species.

The loading capacity data for the extraction of zinc were also determined for several concentrations of mineral acid (0.5–3.5*M* for hydrochloric acid, 0.0025–0.25*M* for nitric and 0.01–0.1*M* for sulphuric) and also for water by 0.1*M* benzene solutions of the pyridylnonane. The concentration of thiocyanate ions was kept constant at 0.1*M*. The concentration of zinc was varied from 5 to 65 g/l and the maximum attainable concentration in the organic phases was around 3 g/L, suggesting the formation of disolvates, complying with the slope-analysis data.

The effect of common salts on the extraction of zinc was investigated and the results are presented in Fig. 4. The addition of various amounts of neutral chloride ions (sodium chloride), to solutions of hydrochloric acid of constant concentration and 0.1*M* in KSCN, appears to have a salting-out effect up to about 1*M* concentration of added chloride. A further increase in the salt concentration leads to a decrease in the extraction, possibly due to the formation of less extractable chloride complexes. In the case of nitrate and sulphate ions added to the corresponding solutions of constant acidity, the degree of extraction remains more or less constant, indicating that common salts do not affect it.

The extraction of zinc from 0.01*M* mineral acid that was 0.1*M* in KSCN and contained various other anions was investigated. The results are presented in Fig. 5. Chloride, nitrate, sulphate and ascorbate ions do not have much effect on the extraction. Acetate decreases the extraction but the decrease is not very pronounced. Citrate and oxalate almost completely suppress the extraction when present in concentrations up to 0.1*M* in the original aqueous solutions.

The selectivity of the extraction of zinc by 0.1*M* PyN/benzene from aqueous mineral acid solutions (0.01*M*) containing 0.1*M* KSCN, was evaluated. A number of elements, including fission products and

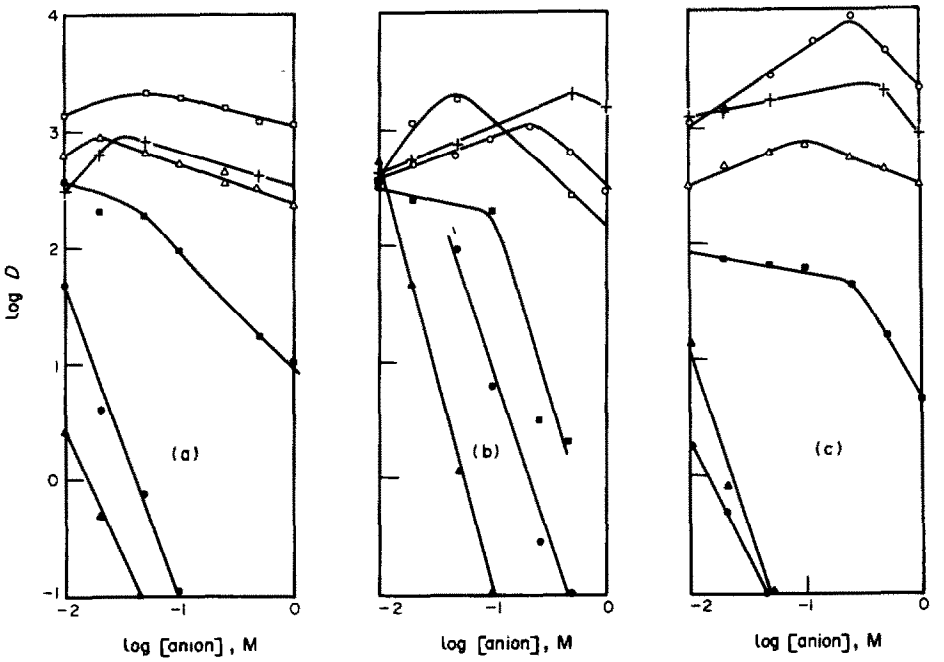


Fig. 5. The effect of the addition of some anions on the extraction of zinc with 0.1*M* PyN solution in benzene.

A. Initial aqueous solutions: $C_{HCl} = 0.01M$, $C_{SCN^-} = 0.1M$.
—□—nitrate,—△—sulphate,—+—ascorbate,—■—acetate,—●—oxalate,—▲—citrate

B. Initial aqueous solutions: $C_{H_2SO_4} = 0.01M$, $C_{SCN^-} = 0.1M$.
—○—chloride,—●—oxalate,—■—acetate,—+—ascorbate,—□—nitrate,—▲—citrate

C. Initial aqueous solutions: $C_{HNO_3} = 0.01M$, $C_{SCN^-} = 0.1M$.
—△—sulphate,—○—chloride,—+—ascorbate,—▲—citrate,—●—oxalate,—■—acetate

base metal ions, were tested for extraction under these conditions. Table 1 shows that the separation factors for most of the test elements are greater than 10^3 and zinc can be separated from a large number of metal ions in a single extraction, followed by 4 or 5 scrub stages which will barely affect the recovery of zinc, whilst eliminating the impurities from organic phase. Mercury and copper are, however, quantitatively co-extracted and the method can be employed for the preconcentration of these metals in water pollution studies.

REFERENCES

1. M. Iqbal, M. Ejaz, S. A. Chaudhry and R. Ahmed, *Sepn. Sci.*, 1976, **11**, 255, and references therein.
2. M. Iqbal and M. Ejaz, *J. Radioanal. Chem.*, 1978, **42**, 335.
3. J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1958, **1**, 249.
4. G. H. Ayres and S. S. Baird, *ibid.*, 1961, **7**, 237.
5. A. L. Kirika, V. I. Fadeeva and I. P. Alimarin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1969, **7**, 1427.
6. M. Iqbal and M. Ejaz, *Talanta*, 1975, **22**, 143.
7. M. Ejaz, *Sepn. Sci.*, 1975, **10**, 425.
8. M. Y. Mirza, M. Ejaz and A. R. Sani, *Anal. Chim. Acta*, 1967, **37**, 402.
9. A. S. Kertes and Y. Marcus, *Ion Exchange and Solvent Extraction of Metal Complexes*, p. 748. Interscience-Wiley, New York, 1969.
10. S. A. Chaudhry, R. Ahmed and M. Ejaz, *J. Radioanal. Chem.*, 1977, **35**, 235.

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RECENT ANALYTICAL DEVELOPMENTS USING CHEMILUMINESCENCE IN SOLUTION

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Summary—The rapid growth of analytical methods which utilize chemiluminescent techniques reflects their many advantages relative to conventional procedures. Measurement of light emission is simple and rapid and extremely high sensitivities may be achieved with inexpensive instrumentation and without resort to preconcentration. As a consequence, attention is now being directed towards expanding the scope of chemiluminescent analyses, both by study of previously unexploited light-emitting processes and by modification to determine specific analytes of interest. This review describes the requirements and methodology, presents newer applications of established procedures and considers the potential of some new systems for chemiluminescent analysis.

Chemiluminescence (CL) or "cold light" is the light-emission produced by a chemical reaction without any associated generation of heat.[1–3] Chemical light-producing systems also occur in, or are derived from, living systems and the term bioluminescence (BL) is used for such emissions.[4] Whereas the study of CL has mainly been confined to this century, BL has fascinated man since antiquity, and a wide range of BL species has been identified.[5]

In recent years extremely sensitive analytical techniques, based on CL and BL reactions and possessing unique advantages compared with conventional methods, have been applied to chemical analysis.[3,6–8] They are now used in air pollution studies, forensic investigations, measurement of bacterial concentrations and selective analyses for trace metals in water supplies. Recent comprehensive reviews covering analyses by gas phase CL[9,10] and also BL procedures[6,11] are available. In this survey attention is therefore focused on newer advances in CL analysis in solution and the scope and potential of such techniques are emphasised.

THE PHYSICAL BASIS OF CL

Besides the intrinsic fascination, interest in CL has been stimulated by its mechanistic challenge and the desire to develop the light-output to practical levels. In contrast with BL processes, however, the light-yields of CL reactions are poor. Luminol, which for many years was recognized as the most efficient CL material, has a quantum yield of only 0.01, whereas that of firefly luciferin is nearly unity.[1,4] The reasons for the poor efficiencies in CL become evident on consideration of the criteria necessary for light-emission. These are a chemical reaction which provides considerable free energy, and an energy transfer to a fluorescent acceptor which becomes excited to its first singlet electronic level. CL then occurs by emission of a photon as the excited molecule relaxes.

Unlike many other light-producing processes, CL does not involve the intermediate formation of heat or electric power. Therefore the necessary free-energy change of the reaction in kcal/mole (ΔG) is given by equation (1) where λ_{ex} is the long-wavelength limit in nm for excitation of the emitting molecule. Hence for visible CL emissions ΔG must be at least between 40 and 70 kcal/mole and this requirement is met by many oxidations which involve peroxide intermediates. On decomposition the peroxide transfers excess of energy to a suitable acceptor which may be a reactant, product or selected additive:

$$-\Delta G \geqslant (hc/\lambda_{ex})$$

or

$$[(2.86 \times 10^4)/\lambda_{ex}] \text{ kcal/mole} \qquad (1)$$

where h is Planck's constant, c is the velocity of light, and λ_{ex} is in nm.

The main difference between CL and fluorescence therefore lies in the manner of excitation of the emitting molecule. All effects which limit fluorescence efficiency will therefore also occur with CL, together with the chemical constraints of low yields of peroxide intermediates relative to side-reactions which do not lead to CL.

BENEFITS OF CL ANALYSIS

CL techniques complement existing analytical processes and in many cases provide a more sensitive alternative or an entirely novel approach. The basis of CL analysis is measurement of a change in emission intensity in the presence of the analyte. This may appear as (*a*) enhancement of light-intensity (catalysis) or (*b*) attenuation of the emission (quenching or inhibition). Calibration is necessary and often a linear relationship between intensity and analyte concentration can be established over a wide concentration range.[6,12]

The development of extremely efficient photomultipliers has enabled CL with quantum yields of 10^{-14}–10^{-15} to be detected.[13] As most CL analytical systems use processes with quantum yields of 0.01–1, high sensitivities are achievable. In fact precision is often restricted by reagent purity rather than by instrumental limitations. The accuracy is further assisted by the large intensity changes produced by trace amounts of analyte.

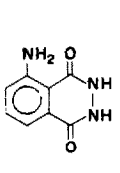
Apart from the high sensitivities possible, CL analysis has other advantages. Equipment is inexpensive and consists of a light-detector, a mixing cell and, if necessary, filters to obtain particular emission wavelengths. In addition, the procedures involve no chemical manipulation and do not interfere with the reacting environment. The measurements can be obtained quickly and hence CL methods are valuable when large numbers of samples need to be assayed, as with fractions from ion-exchange columns, or for determinations at various field locations.[6,12]

LIQUID-PHASE ANALYSIS

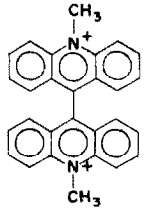
Chemiluminescence systems

For analysis in solution the most frequently used CL reactions are the alkaline oxidations of luminol (I) and lucigenin (II). The blue CL (λ_{em} 425 nm; λ_{em} = wavelength of maximum emission) from luminol was first observed in 1928 and the reaction has subsequently been studied to such a degree that it may be regarded almost as a CL standard. Hydrogen peroxide is the normal oxidant, although sodium hypochlorite, sodium perborate or potassium ferricyanide may also be used. The optimum pH of 10–11 is obtained with alkali metal hydroxides or carbonates. Lucigenin gives a blue-green CL (λ_{em} 470 nm) of similar efficiency to that of luminol when its alkaline solution is oxidized with hydrogen peroxide.[1,2]

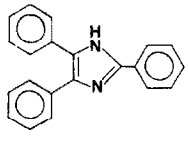
CL reactions involving alkaline oxidations can be used to indicate acid–base or redox titration endpoints either by the appearance or the quenching of CL when excess of titrant is present. The luminol and lucigenin reactions together with the CL oxidations of lophine (III) and siloxene (IV) have been those most frequently used for CL titrations. Basic ethanolic solutions of lophine afford yellow CL (λ_{em} 525 nm) when exposed to air.



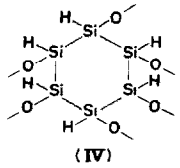
(I)



(II)



(III)



(IV)

Siloxene is a polymeric material obtained from the reaction of hydrochloric acid with calcium silicide suspended in alcohol. In acidic strongly oxidizing media it gives yellow to red CL, the colour depending on the oxidant and degree of oxidation. The advantages and scope of such CL titrations have recently been described in detail.[14]

Trace metal ion determinations

The intensities of luminol and lucigenin CL are often substantially modified by the presence of other materials. Substances which lower the intensity without affecting the total light-output are classed as inhibitors, but if the quantum yield is also suppressed the material is termed a quencher.[15] These substances act by preferentially removing a reactant through chemical interaction or complex formation, or by acting as radical scavengers.

Materials which produce an increase in CL intensity are generally referred to as catalysts despite the fact that they are often irreversibly converted into products of higher oxidation state. Many metal ions are catalysts[6,12] and as all are capable of reacting by one-electron transfers it was originally suggested that their function was to produce hydroxyl radicals from hydrogen peroxide. A recent study of the effect of Co(II) on luminol CL, however, indicated that catalysis occurred through a cobalt(II)–H_2O_2 complex which subsequently oxidized luminol in a rate-determining step.[16]

Advantage can be taken of such intensity changes to determine trace additives. The analyses are possible since in the presence of excess of luminol and hydrogen peroxide the emission intensity is proportional to the concentration of many metal ions over a wide range. The CL method was developed in Kiev by Babko, Lukovskaya and Dubovenko in the early 1960s and this group continues to report prolifically.[23–41] More recently, significant advances in instrumentation and application have emerged from the investigations of Seitz and Hercules[12,17–21] at the University of Georgia. Typical results are shown in Table 1.

The Kiev group determined the light-output by measurement of the optical density of exposed photographic film surrounding a reaction cuvette, and the mean errors of this approach can be quite high. Seitz and Hercules, however, have employed a flow system in conjunction with a photoelectric recording device which gives exceptional sensitivities (as low as 0.001 ppm in favourable cases) and very good reproducibility, and is ideal for rapid determinations of numerous samples.[17,18] Buffered luminol solution and hydrogen peroxide are mixed in the flow system and aliquots of sample are introduced by an injection valve as required. A background solution which simulates the sample minus trace metal catalyst is also circulated. Nitrogen is bubbled through the reaction

Table 1. Trace metal analysis with luminol and lucigenin CL

Metal ion	Oxidant–additive	Detection limit, *M*	Sensitivity, *μg/ml*	Reference
Co(II)	H_2O_2	10^{-10}		12
Cu(II)	H_2O_2	10^{-9}		12
Ni(II)	H_2O_2	10^{-8}		12
Cr(III)	H_2O_2	10^{-9}, 10^{-10}		17, 22
Fe(II)	O_2	10^{-10}		18
Fe(III)	H_2O_2–amine		0.0002	23
Mn(II)	H_2O_2–amine	10^{-8}		12
Hg(II)	H_2O_2		0.2	24
	H_2O_2–Cu^{2+}–CN^-		0.002*	25
Ag(I)	H_2O_2–α,α'-bipyridyl		0.01	26
	H_2O_2–Cu^{2+}–CN^-		0.001*	25
Au(III)	H_2O_2		0.01	26
Os(VI) or (VIII)	H_2O_2		0.0002	26
Os(IV)	H_2O_2		0.002	26
Ru(III) or (IV)	H_2O_2 or KIO_4		0.0004	26
Ru(VI)	H_2O_2 or KIO_4		0.001	26
Rh(III)	KIO_4–HCl		0.04	27
V(IV)	O_2–$P_2O_7^{4-}$		0.002	28
V(V)	H_2O_2–Co complex		0.04	20
Ir(IV)	KIO_4		0.04	27
Ce(IV)	H_2O_2–Cu^{2+}		0.1*	30
Th(IV)	H_2O_2–Cu^{2+}		1.0*	31
Ti(IV)	H_2O_2–Cu^{2+}		0.02*	32
Hf(IV)	H_2O_2–Cu^{2+}		0.01*	32
Lucigenin analyses				
Fe(II)			0.006	33
Fe(III)			0.05	34
Tl(III)			0.4	34
Mn(II)			0.0005	34
Cu(II)			0.0002	34
Cr(III)			0.005	35
Cr(II)			0.003	36
Ag(I)			0.1	37
Os(IV), (V) and (VI)			0.00002	38
Pb(II)			0.5	39
Bi(III)			1.0	40
Co(II)			0.001	41

* Analysis through inhibition of CL.

cell to promote mixing. Detection limits are extremely low and are restricted only by the level of the background light. Rigorous removal of contaminants from reagents in the reference solution would further improve detection limits. The increase in CL intensity due to the sample is recorded and the trace metal concentration is determined from a calibration curve relating ion concentration to CL intensity.

For optimum results the most suitable pH, oxidant and stoichiometry need to be established. It must also be shown that in the concentration range of interest, the ion being determined does not form complexes or an insoluble hydroxide. For analysis by intensity inhibition a catalysed system is generally used and the most appropriate catalyst must also be identified.

Unlike less sensitive analytical procedures which require elaborate preconcentration techniques, the problems of CL analysis are associated with the need to determine specific analytes in a complex sample. Techniques for achieving selectivity depend on differences in the chemistry of the catalysts. The judicious use of complexing agents can suppress such interfering reactions and allow specific determinations to be made. This is illustrated by the case of Cr(III) determination.[17] Cr(III) and other metal ions form strong complexes with EDTA which prevent the ions from acting as catalysts. The Cr(III) complex, however, is kinetically slow to form and if conditions are selected which allow completion of the analysis before significant Cr(III)–EDTA complex formation occurs, Cr(III) alone is determined. Any contribution from remaining interfering ions can be assessed by a second measurement which involves a simple modification. This procedure offers greater sensitivity than other methods for determination of Cr(III) in natural waters[17] and biological samples[19] and only Cr(III), and not total chromium, is measured.

The analysis for Fe(II) exemplifies another approach to selectivity.[18] Provided oxygen is present, Fe(II) is the only common metal ion which catalyses luminol CL in the absence of hydrogen peroxide. Adventitious oxidants are destroyed and all iron converted into Fe(II) by treatment with sulphite. Oxygen is passed through the reaction cell as both oxidant

and mixer. This method has been used for analysis of natural waters. As it provides significantly lower detection limits and requires no pretreatment of samples it should supersede older analytical methods for Fe(II).

Analyses with lucigenin have been investigated to a lesser extent but reveal some interesting differences. For example, Tl(III), Pb(II) and Bi(III) catalyse lucigenin but not luminol CL and hence the two systems may prove to be complementary.

Recent innovations have enabled high-speed high-resolution liquid chromatography to be used for separation of metal ions. A sensitive automatic detection technique for these ions has proved difficult to achieve. Luminol CL detectors should be ideal for this purpose and recent studies have established that they permit rapid and sensitive monitoring of such chromatographic eluents.[42]

A modification of the CL method for the determination of metal ion catalysts and luminescence inhibitors is under development by Pantel and Weisz.[43] This procedure uses a "luminostat" in which addition of hydrogen peroxide to luminol is automatically regulated so as to maintain the luminescence at a preset constant level. It has been shown that the rate of addition is a measure of the metal ion concentration and inhibitors may be determined indirectly. Preliminary results indicate that Cu(II) can be determined in the range 0.5–5 μg/ml and the inhibitor L-histidine in the range 2.5–20 μg/ml.

Analyses of other materials

The system based on luminol with catalysis by metal ions may be adapted to analyse for oxidants such as H_2O_2, OCl^-, Br_2, I_2, $Fe(CN)_6^{3-}$ and MnO_4^-. In the absence of peroxide, background levels are reduced a hundredfold and hence detection limits of 10^{-9}–$10^{-10}M$ are possible even though CL intensities are lower than for metal ion catalysis.[7,12,44]

Various organic compounds modify the intensities of liquid-phase CL[9]. Many of these materials are of significance in forensic chemistry and methods have been developed to determine cyanide,[25,45] organophosphorus agents[46] and cannabis[47] through the inhibition of luminol CL. Blood may be detected at dilutions of 1 in 10^7 and procedures exist for distinguishing between foetal and adult haemoglobin.[48] The catalytic effect of haemoglobin on luminol CL also forms the basis of detectors for bacteria and micro-organisms.[49]

There has been a recent trend to extend the scope of conventional CL analytical systems to cover analytes of specific interest. For example, specific sensitive analyses for glucose have been reported which employ luminol CL to monitor peroxide generation from the enzyme-catalysed oxidation of glucose [equation (2)]. The method is considered valuable for the rapid determination of small quantities of glucose in biological tissues:[20,50]

$$\text{glucose} + O_2 + H_2O \xrightarrow[\text{oxidase}]{\text{glucose}} \text{gluconic acid} + H_2O_2 \quad (2)$$

Vitamin B_{12}[51] and biotin[52] are other important biological substances for which CL analyses using luminol have been devised. The biotin assay is particularly elegant and involves monitoring competitive protein-binding reactions by using a CL label. It has advantages over other techniques in that it does not require involved separation procedures and the inconvenience of handling radioactive materials is avoided.

Liquid-phase analyses using other CL systems

With the growing awareness of the versatility and advantages of CL analyses, increasing attention has been focused on the potential of other liquid-phase CL systems. These methods are, in general, at an early stage of evaluation, but sufficient information is available to predict that many will be developed to practical application. The following examples are typical of these recent studies.

The most efficient CL known is that from the peroxyoxalates and involves the oxidation of a diaryl oxalate by hydrogen peroxide in the presence of a fluorescent compound [equation (3)].[3,53] The fluorescent material may be selected to provide the optimum compromise between emission wavelength, chemical stability and quantum yield. Seitz and his co-workers have recently commenced an assessment of the analytical possibilities of this system. It was shown to be superior to luminol for the determination of enzyme-generated peroxide from glucose in urine, since the peroxyoxalate method gave less background signal and enabled a lower detection limit to be achieved.[21] A further application is the use of an

$$\text{ArOCOCOOAr} + H_2O_2 \rightarrow 2\text{ArOH} + \left[\begin{array}{c}O\\ \|\\ C\\ |\\ C\\ \|\\ O\end{array}\right]\!\!\left[\begin{array}{c}O\\ \|\\ C\\ |\\ C\\ \|\\ O\end{array}\right] \xrightarrow{\text{fluorescer}} 2CO_2 + \text{fluorescer}^* \longrightarrow \text{fluorescer} + h\nu \quad (3)$$

automated peroxyoxalate system to determine the reduced form of nicotinamide adenine dinucleotide (NADH) which is important in biochemical analysis, since many enzyme or substrate assays are coupled to its production or consumption. The viability of the procedure has been demonstrated in the determination of lactate dehydrogenase (LDH) activity in serum. At high pH, NADH is produced [equation (4)] which in the presence of Methylene Blue reduces oxygen to hydrogen peroxide [equations (5) and (6)]. The peroxide is monitored by CL analysis using bis (2,4,6-trichlorophenyl) oxalate (2,4,6-TCPO) and perylene.[54]

$$NAD^+ + \text{lactate} \overset{\text{LDH}}{\rightleftharpoons} \text{NADH} + H^+ + \text{pyruvate} \quad (4)$$

$$H^+ + NADH + \text{Methylene Blue}_{oxidized} \rightarrow NAD^+ + \text{Methylene Blue}_{reduced} \quad (5)$$

$$\text{Methylene Blue}_{reduced} + O_2 \rightarrow \text{Methylene Blue}_{oxidized} + H_2O_2 \quad (6)$$

Peroxyoxalate CL is subject to catalysis by weak bases (*e.g.*, amines) and inhibition by organic acids, but the analytical possibilities provided by this behaviour have yet to be exploited. One limitation of the peroxyoxalate system is the susceptibility of diaryl oxalates to hydrolysis. This applies both in synthesis and storage and even slight hydrolysis can have a substantial effect on the light-emission characteristics. 2,4,6-TCPO is one of the most stable oxalates, however, and Seitz and co-workers did not encounter significant stability problems in its use.

There are few satisfactory means for determining formaldehyde, which is an important pollutant of both water and the urban atmosphere. Recently the orange CL from gallic acid, formaldehyde and alkaline peroxide has been shown to provide a particularly sensitive analytical procedure[55] for formaldehyde in water, with detection (if a flow system is used) down to 1 μg/l. and a determination range of 10^{-7}–$10^{-2}M$.

A somewhat older procedure is available for the liquid-phase determination of ozone. Rhodamine B and gallic acid in ethanol produce CL with ozone down to concentrations of 0.0003% (v/v).[56] Gas-phase analyses for ozone have also been developed.[9,10]

Another new area which has exciting possibilities is the use of the weak CL from autoxidation of hydrocarbons. This emission has been detected by Nathan and Mendenhall of Battelle Institute, using very sensitive equipment. One of several analytical applications of this study involves the prediction of the service life of aircraft fuels. This may be achieved with far greater accuracy than by accelerated tests since analysis is carried out under actual-use conditions.[57]

An interesting new procedure has recently been reported by Klockow and Teckentrup[58] who have shown that the low-intensity CL from the sulphide-catalysed reaction of iodine or bromine with azide is dependent on the halogen and sulphide concentrations and is not influenced by the azide concentration. Optimum CL intensity is achieved at pH > 8 with Methylene Blue as sensitizer and, under these conditions, $10^{-6}M$ sulphide may readily be determined with a flow spectrometer. A reliable and practical means for determination of trace quantities of the atmospheric pollutant, hydrogen sulphide, is desirable and further developments of this CL procedure will be of considerable interest.

REFERENCES

1. F. McCapra, *Quart. Rev.*, 1966, **20**, 485; *Pure Appl. Chem.*, 1970, **24**, 611; *Prog. Org. Chem.*, 1973; **8**, 231.
2. K. D. Gundermann, *Angew. Chem. Intern. Ed.*, 1965, **4**, 566.
3. M. J. Cormier, D. M. Hercules and J. Lee, (eds.), *Chemiluminescence and Bioluminescence*, Plenum, New York, 1973.
4. F. McCapra, *Endeavour*, 1973, **32**, 139.
5. W. D. McElroy and H. H. Seliger, *Sci. Am.*, 1962, **207**, (12), 76.
6. W. R. Seitz and M. P. Neary, *Anal. Chem.*, 1974, **46**, 188A.
7. U. Isaacson and G. Wettermark, *Anal. Chim. Acta*, 1974, **68**, 339.
8. L. S. Bark and P. R. Wood, *Selected Annual Rev. Anal. Sci.*, 1971, **1**, 41.
9. A. Fontijn, D. Golomb and J. A. Hodgeson, in M. J. Cormier, D. M. Hercules and J. Lee, (eds), *Chemiluminescence and Bioluminescence*, p. 393, Plenum, New York, 1973.
10. J. H. Glover, *Analyst*, 1975, **100**, 449.
11. W. R. Seitz and M. P. Neary, *Methods Biochem. Anal.*, 1976, **23**, 161.
12. W. R. Seitz, in M. J. Cormier, D. M. Hercules and J. Lee (eds.), *Chemiluminescence and Bioluminescence*, p. 427. Plenum, New York, 1973.
13. H. H. Seliger, in M. J. Cormier, D. M. Hercules and J. Lee (eds.), *Chemiluminescence and Bioluminescence*, p. 461. Plenum, New York, 1973.
14. L. Erdey, in E. Bishop (ed.), *Indicators*, p. 709. Pergamon, Oxford, 1972.
15. A. T. Pilipenko and N. M. Lukovskaya, *J. Anal. Chem. USSR*, 1970, **25**, 1784.
16. T. G. Burdo and W. R. Seitz, *Anal. Chem.*, 1975, **47**, 1639.
17. W. R. Seitz, W. W. Suydam and D. M. Hercules, *ibid.*, 1972, **44**, 957.
18. W. R. Seitz and D. M. Hercules, *ibid.*, 1972, **44**, 2143.
19. R. T. Li and D. M. Hercules, *ibid.*, 1974, **46**, 916.
20. D. T. Bostick and D. M. Hercules, *ibid.*, 1975, **47**, 447.
21. D. C. Williams, G. F. Huff and W. R. Seitz, *ibid.*, 1976, **48**, 1003.
22. V. I. Rigin and A. S. Bakhmurov, *Zh. Analit. Khim.*, 1976, **31**, 93; *Chem. Abstr.*, 1975, **82**, 80014.
23. I. E. Kalinichenko and O. M. Grischchenko, *Ukr. Khim. Zh.*, 1970, **36**, 610; *Chem. Abstr.*, 1970, **73**, 105171.
24. L. I. Dubovenko and T. A. Bogoslovskaya, *ibid.*, 1971, **37**, 1057; *Chem. Abstr.*, 1972, **76**, 67862.
25. A. T. Pilipenko, G. V. Angelova and I. E. Kalinichenko, *ibid.*, 1974, **40**, 1302; *Chem. Abstr.*, 1975, **82**, 164439.
26. N. M. Lukovskaya, A. V. Terletskaya and T. A. Bogoslovskaya, *Zh. Analit. Khim.*, 1974, **29**, 2268; *Chem. Abstr.*, 1975, **82**, 132556.
27. N. M. Lukovskaya, L. V. Markova and N. F. Evtushenko, *ibid.*, 1974, **29**, 767; *Chem. Abstr.*, 1974, **81**, 44896.
28. A. T. Pilipenko, E. V. Mitropolitska and N. M. Lukovskaya, *Ukr. Khim. Zh.*, 1975, **41**, 1196; *Chem. Abstr.*, 1976, **85**, 13327.
29. A. K. Babko and N. M. Lukovskaya, *Zh. Analit. Khim.*, 1965, **20**, 110; *Chem. Abstr.*, 1966, **64**, 5751.
30. L. I. Dubovenko and Chan Ti Huu, *Ukr. Khim. Zh.*, 1969, **35**, 637; *Chem. Abstr.*, 1969, **71**, 54723.
31. *Idem, ibid.*, 1969, **35**, 957; *Chem. Abstr.*, 1970, **72**, 36224.
32. L. I. Dubovenko and V. A. Bilochenko, *ibid.*, 1974, **40**, 423; *Chem. Abstr.*, 1974, **81**, 32896.
33. L. I. Dubovenko and A. Yu. Nazarenko, *ibid.*, 1975, **41**, 1205; *Chem. Abstr.*, 1976, **85**, 13306.
34. A. P. Tovmasyan, *Materialg. Konf. Molodykh Uchenykh. Akad. Nauk. Arm. SSR*, 1972, 188; *Chem. Abstr.*, 1975, **83**, 187824.
35. L. I. Dubovenko and A. M. Guta, *Izv. Vysshykh. Uchebn. Zavedenii. Khim. i Khim. Tekhnol.*, 1975, **18**, 1211; *Chem. Abstr.*, 1976, **84**, 38257.

36. L. I. Dubovenko, A. M. Guta and D. M. Kryzhanovskaya, *Visn. L'uiv. Univ., Ser. Khim.*, 1972, **30**, 90; *Chem. Abstr.*, 1973, **79**, 61217.
37. A. K. Babko, A. V. Terletskaya and L. I. Dubovenko, *J. Anal. Chem. USSR*, 1968, **23**, 809.
38. A. T. Pilipenko and A. V. Terletskaya, *Zh. Analit. Khim.*, 1972, **27**, 1570; *Chem. Abstr.*, 1972, **77**, 172304.
39. L. I. Dubovenko and L. D. Guz, *Ukr. Khim. Zh.*, 1970, **36**, 1264; *Chem. Abstr.*, 1971, **74**, 134595.
40. L. I. Dubovenko and E. Ya. Khotinets, *Zh. Analit. Khim.*, 1971, **26**, 784; *Chem. Abstr.*, 1971, **75**, 14640.
41. L. I. Dubovenko and N. V. Beloshitskii, *ibid.*, 1974, **29**, 111; *Chem. Abstr.*, 1974, **80**, 140814.
42. R. Delumyea and A. V. Hartkopf, *Anal. Chem.*, 1976, **48**, 1402.
43. S. Pantel and H. Weisz, *Anal. Chim. Acta*, 1975, **74**, 275.
44. J. Kubal, *Chem. Listy*, 1968, **62**, 1478.
45. M. Busljeta and K. Weber, *Acta Pharm. Jugoslav.*, 1975, **25**, 247.
46. K. Weber and J. Matkovic, *Arch. Toxicol.*, 1965, **21**, 38; K. Weber, J. Matkovic and M. Busljeta, *Acta Pharm. Jugoslav.*, 1969, **19**, 47.
47. J. Monforte, K. Weber and L. Grlic, *Acta Pharm. Jugoslav.*, 1972, **22**, 27.
48. K. Weber, *Deut. Z. Ges. Gerichtl. Med.*, 1966, **57**, 410.
49. S. Witz and W. H. Hartung, *U.S. Pat.* 3959081, 1976; *Chem. Abstr.*, 1976, **85**, 30563; H. Tribble, R. Shaffer, M. Shepel, W. Kraybill and A. Pital, Edgewood Arsenal, Aberdeen Proving Ground, 1976, *Natl. Tech. Inform. Service Rept.* AD-A026 162/8SL.
50. J. P. Auses, S. L. Cook and J. T. Maloy, *Anal. Chem.*, 1975, **47**, 244.
51. T. L. Sheehan and D. M. Hercules, *ibid.*, 1977, **49**, 446.
52. H. R. Schroeder, P. O. Vogelhut, R. J. Carrico, R. C. Boguslaski and R. T. Buckler, *ibid.*, 1976, **48**, 1933
53. M. M. Rauhut, *Accounts Chem. Research*, 1969, **2**, 80.
54. D. C. Williams and W. R. Seitz, *Anal. Chem.*, 1976, **48**, 1478.
55. D. Slawinski and J. Slawinski, *ibid.*, 1975, **47**, 2101.
56. D. Bersis and E. Vassiliou, *Analyst*, 1966, **91**, 499.
57. R. A. Nathan and G. D. Mendenhall, described by W. Worthy in *Chem. Eng. News*, p. 30, 24 Nov., 1975; R. J. Jakobsen, R. A. Clarke, R. A. Markle and G. D. Mendenhall, Battelle Columbus, 1976, *Natl. Tech. Inform. Service Rept.* AD-A028 782/1SL; R. A. Nathan, G. D. Mendenhall, J. A. Hassell and J. D. Wallace, *Ind. Res.*, 1975, **17**, 62.
58. D. Klockow and J. Teckentrup, *Talanta*, 1976, **23**, 889.

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DESORPTION OF OXYGEN AND NITROGEN FROM IRON SURFACES

APPLICATION OF X-RAY PHOTOELECTRON SPECTROSCOPY TO SURFACE ANALYSIS

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Summary—The patterns of desorption of oxygen and nitrogen from metal surfaces were examined and applied in the determination of gaseous elements in metal samples. The abundance of gaseous elements on metal surfaces is controlled by thermal desorption and diffusion to or from the surface. A heat treatment suitable for the separation of adsorbed gases from those in the bulk sample is discussed. Preheating of the metal samples at *ca.* 300° in a vacuum reduces the residual adsorbates to a minimum and retards the diffusion of the gaseous elements from the bulk to the surface.

In the quantitative determination of oxygen and nitrogen in metals, adsorbed surface layers are responsible for appreciable errors, especially in the case of granular or finely powdered samples.[1] Determination of oxygen in fine particles may be meaningless owing to the amount of adsorbed oxygen[2] and the determination of nitrogen is also affected by the surface layers of nitrogen. A pretreatment is required to eliminate the adsorbate species while retaining the gaseous elements in the bulk. In the search for such a procedure, observations of the surface oxygen and nitrogen have been made by X-ray photoelectron spectroscopy while the samples were heated in vacuum.

Experimental results obtained in studies of the adsorption of gases on metals at high pressures[3,4] can be applied in the identification of the chemical species of nitrogen and oxygen adsorbed on the polished surface of metals in air. The chemical species which are desorbed from the heated metals in vacuum and the diffusion of gaseous elements from the bulk metal to the surface are discussed in this report. The thermal desorption of each species and the desorption rate from the surface may be used to estimate the amounts on metal surfaces relative to the bulk content.

EXPERIMENTAL

Spectra were recorded with an AEI-ES 200 spectrometer with achromatic Mg $K\alpha$ radiation, as described previously.[3] A metal plate (15 mm long, 6 mm wide and 2 mm thick) was used as the substrate for gas-adsorption experiments. Granular or powdered metal supports gave unsatisfactory photoelectron spectrum measurements. Polycrystalline iron specimens (purified by repeated electron-beam fusion and zone-melting), Fe–Si3% and Fe–Cr3% alloys were prepared for this work.

The adsorption experiments were carried out at ambient temperature and pressure and required that a clean metal surface be exposed to a given atmosphere. Experimental difficulties prevented the cleaning of the metal surface in a given atmosphere, so the metal surface was cleaned by heating in the spectrometer as reported previously.[5] At high pressure, the substrate reacts with atmospheric gas molecules to form static adsorbates in equilibrium with the atmospheric gases. Adsorbed species of lower desorption energies and physisorbed species become predominant at high pressure. In this work, adsorption atmospheres at pressures up to 200 mmHg were used, the system being evacuated to 2×10^{-9} mmHg prior to the measurements.

RESULTS AND DISCUSSION

Oxygen

The X-ray photoelectron spectrum of the O(1*s*) level observed on an iron surface cleaned with a fine file in the ambient atmosphere is shown in Fig. 1*a*. The substrate was then heated stepwise from room temperature to 400° in a vacuum. The Fe(2*p*) line profile changes [corresponding to the O(1*s*) reduction] with increasing temperature, from the oxidized state (709.5 eV) to the reduced metallic state (706.3 eV), Fig. 1*b*. The relative intensity values shown in Fig. 1 give the count-rate normalized to the Fe(2*p*) intensity from the substrate, making possible the comparison of the O(1*s*) intensity at different stages of heating. For example, a relative intensity of 0.5 means that the intensity of the emission line from the heated substrate is equal to half that from the same surface at normal temperature (curve 1 in Fig. 1).

The O(1*s*) line profile due to the oxygen on the iron surface filed in the ambient atmosphere, consists of the peaks at 533.0 and 529.8 eV, which have been assigned[6,7] to the physisorbed (or loosely chemisorbed) oxygen and the oxide form of oxygen, respectively. The chemisorbed state may be present, its 531.5-eV peak remaining unresolved between these two peaks. Each oxygen species is desorbed in turn on heating in a vacuum, the physisorbed oxygen at below 200°, and the chemisorbed oxygen and oxide oxygen at 300° or higher. The physisorbed oxygen (even that with the highest binding energy) decreases by thermal desorption at below 200°. In the next

stage, slow reduction of the oxide and chemisorbed oxygen is produced probably by reaction with atmospheric carbon monoxide or other reductants in the residual gases.[8] At each heating step, a spectrum was recorded after the metal had been kept for 30 min at that temperature. In the first 10 min of heating, most of the gases desorbable at that temperature were evolved, as indicated on a pressure gauge. The relative intensity value (defined above) is lowered to 0.16 at 300° and on increase of the substrate temperature to 400° is further reduced (to 0.13). On the other hand, when the sample was kept at 300° for a long time, the oxide oxygen intensity increased gradually, reaching 1.4 times its initial value after 42 hr at this temperature. These results suggest that the amount of oxygen observed on the iron surface will be affected by competing thermal desorption and diffusion from the bulk to the surface. The diffusion rate of oxygen in iron crystals at 300–400° becomes significant[9,10] and cannot be disregarded in measurements of the surface abundances of gaseous components in this temperature range.

The rate of reduction of the amount of oxygen was affected by the oxidizing conditions. The oxidized iron surface (due to filing in the ambient atmosphere) could be reduced readily by heating, but when the surface cleaned by heating in a vacuum was exposed to air or oxygen at normal temperature, additional heating to the same temperature in the spectrometer could not reduce the surface oxide any further, even after 15 hr at 400°. Figure 2 shows the oxygen and iron core lines from the surface heated again at 400° in a vacuum after the cleaned iron had been exposed to dry air. There was little difference in the profiles shown in Figs. 1*b* (1) and 2.

The factors affecting the reduction rate are now considered.

The apparent reduction rate of the surface oxygen by the residual gases in the vacuum chamber may be affected by the surface population of oxygen or the thickness of the oxide film. The bonding force between the adsorbed gas molecules and the surface is known to change with increasing surface coverage.[11,12] In the present case, the oxygen on the surface [Fig. 1*a* (1)] consists of adsorbed oxygen with

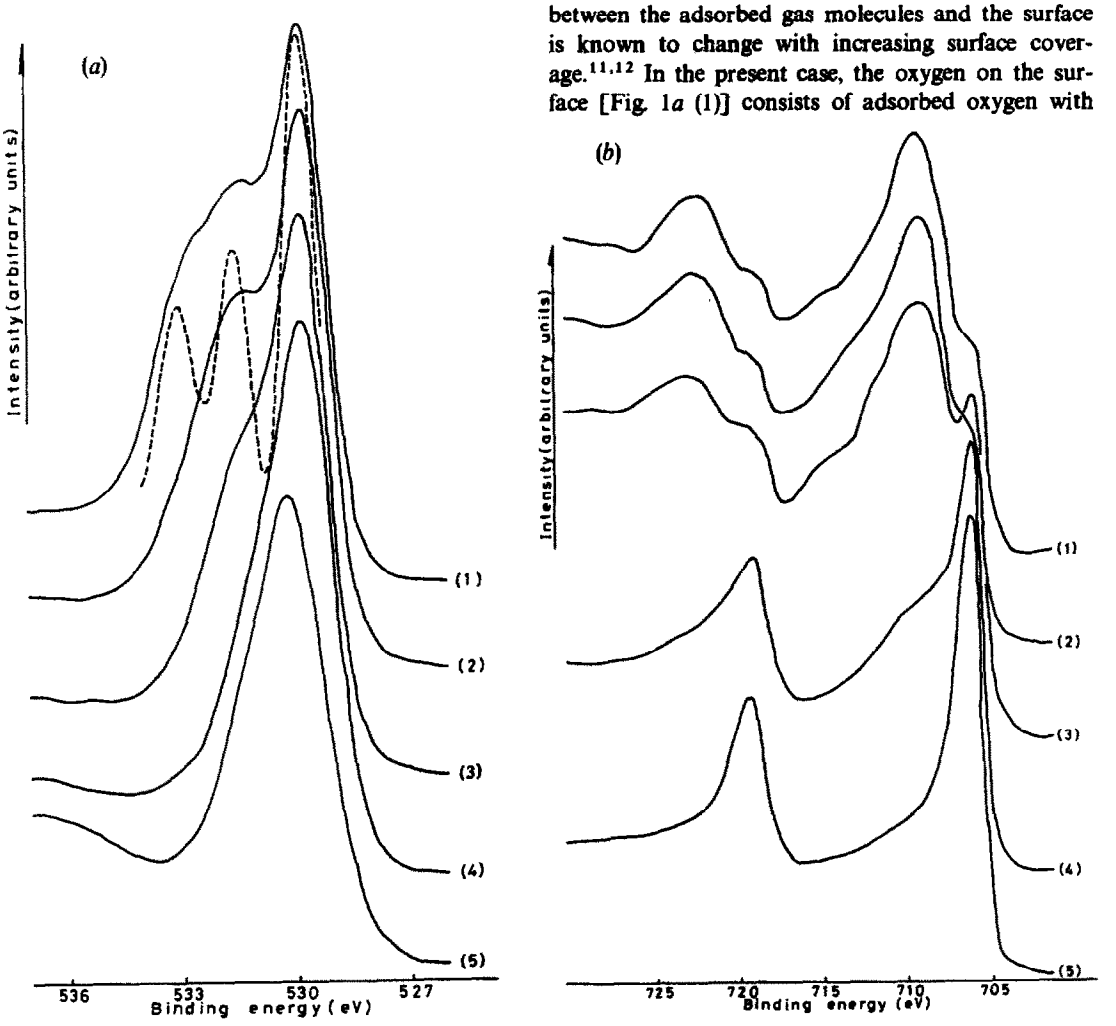


Fig. 1. (*a*) The O(1*s*) line profiles for a filed iron surface heated in a vacuum between 50° and 400°. The relative intensity values are at: (1) normal temperature (*ca.* 50°), 1.00, (2) 100°, 0.78, (3) 200°, 0.67, (4) 300°, 0.16, (5) 400°, 0.13. The broken line represents the theoretical curve calculated for curve (1), assuming that the three component peaks have the same half-width (1.6 eV). (*b*) The Fe(2*p*) line profiles, corresponding to the O(1*s*) lines shown in Fig. 1*a*.

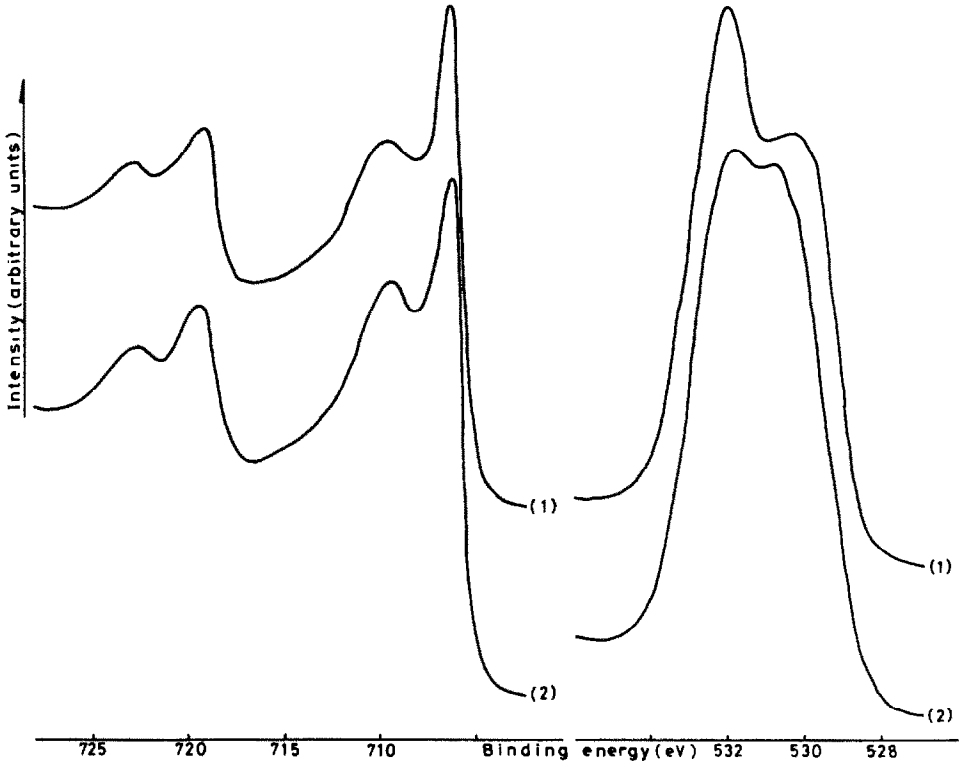


Fig. 2. (1) The Fe(2*p*) and O(1*s*) line profiles for an iron surface exposed to air at normal temperature. Prior to exposure, the iron substrate was heated in a vacuum for 10 hr at 400°. (2) Fe(2*p*) and O(1*s*) line profiles obtained by reheating the iron surface at 400° in a vacuum after its exposure to air.

a comparable amount of oxide oxygen. The surfaces for which the spectra are shown in Fig. 2, [(1) and (2)], are both saturated with adsorbed gas molecules on the active sites (on exposure at atmospheric pressure) because further exposure does not increase the O(1*s*) line intensity. Therefore, the extent of coverage must have little effect on the observed reduction pattern. The energy shift of the O(1*s*) line is not significant as compared with the instrumental resolution and it is probable that changes among the oxidized states cannot be distinguished from the core line spectra. No further information was available on excitation with the Mg K_α source because of the negligible influence of the outer shell electrons on the spectrum. An iron specimen which had been highly oxidized by heating to incandescence in the atmosphere was heated at 400° in a vacuum for up to 10 hr but no evidence of the metallic state was observed in the core line spectra. This result suggests that some other state of oxygen with a higher bonding force occurs on the cleaned surface on re-exposure to air and oxygen. This state could not be identified from the photoelectron core line profiles but its existence was revealed by the possibility of its reduction by the residual gases in the vacuum chamber.

Another possible reason for the differences in reduction rate is that the heated iron surface forms a more stable oxide film with oxygen than does the disordered substrate prepared by filing the metal surface. The filed surfaces and the annealed surfaces should not be equivalent in numbers of lattice vacancies and active sites available to adsorb gas molecules. The present work gave no indications of any difference in the chemical nature of the oxygen adsorbed upon the two surfaces, but it is assumed that the oxygen adsorbed upon the disordered surface is loosely bound and can be reduced by prolonged heating in a vacuum.

It has been calculated from thermodynamic data that the oxides formed on the polished surfaces of titanium and zirconium are too stable to be reduced by reducing agents in the residual gases.[8] It has been observed that the amount of oxidized titanium on the surface appears to be reduced. The oxide form of oxygen on these metal surfaces also decreases remarkably on prolonged heating at 400°. In this case, the surface reduction is less likely to be due to atmospheric reducing agents than to the diffusion of oxygen from the surface to the inner layers. This is because the solubility of oxygen in titanium and zirconium is so high that there is no restriction on loss of oxygen from the surface to the bulk by this. It is suggested that a similar dissolution process occurs with the iron surface.

Heating at 300° in a vacuum is sufficient to reduce the amount of oxygen and the oxygen-containing molecules adsorbed on the mechanically regenerated iron surface. About 85% of the oxygen adsorbed on the surface can be eliminated. Above this temperature, the diffusion of oxygen atoms appears to have a sig-

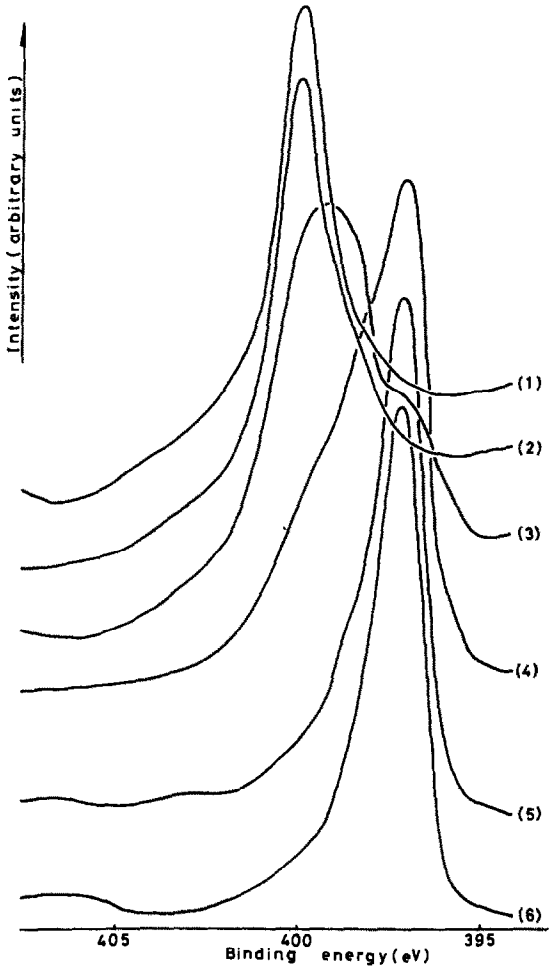


Fig. 3. The N(1*s*) line profiles for a filed iron surface heated in a vacuum. The temperatures and relative intensity values are: (1) normal temperature (*ca.* 50°), 1.00, (2) 100°, 0.81, (3) 200°, 0.46, (4) 300°, 0.18, (5) after 7 hr heating at 400°, 1.01, (6) after 20 hr heating at 400°, 1.06.

nificant effect on the loss of oxygen from the bulk by the surface reduction.

Nitrogen

Figure 3 shows the N(1*s*) line profiles for the surface used for the oxygen work. Desorption of nitrogen from the heated substrate and diffusion of nitrogen atoms from the lower layers to the surface could also be observed. From the line profiles obtained from nitrogen, on the polished surface (in the atmosphere at normal temperature), it can be seen that the nitrogen exists in the –NO form, as shown by the 400.0-eV peak in Fig. 3 (1). With increase in temperature the peak shifts to a position of lower binding energy. At 200°, the transient profile of nitrogen around 398–399 eV appeared [Fig. 3 (3)]. The energy value is close to that of nitrogen in the –CN form (398.5 eV), but the chemically bound –CN is very stable so the observed transient species must be different. At 300°, a peak of high intensity with an energy value of 397.2 eV, close to that of nitride, is observed. The relative intensities of peaks obtained from some irons and iron-base alloys are shown in Fig. 4. It was noted that the relative abundance of nitrogen on the surface decreased to a minimum at around 300°. This suggests that the desorption of adsorbed NO occurs without dissociation into –N, and almost all of the NO-form nitrogen is desorbed before the total nitrogen intensity falls to a minimum. A sharp increase of the N(1*s*) intensity at 400° is due to diffusion from the deeper layers to the surface. Below 200° desorption predominates, as shown by the decreasing intensity due to the NO-form nitrogen. Above 300° there is an increased rate of diffusion to the surface. The nitrogen concentration in the bulk affects the segregation rate of nitrogen[13] on heating. The iron with low nitrogen content (19 ppm) reached a lower surface abundance of nitrogen than the other iron specimens with higher nitrogen content (120 ppm), as shown in Fig. 4. Calculation of enrichment factors on these surfaces indicates that the nitrogen atoms accumulate strongly on the surface.[14]

On iron-base alloys with 3% of silicon or chromium, the surface segregation could not be observed, although the nitrogen contents of these alloys were 120 and 220 ppm, respectively. In these alloys, nitrogen atoms form stable chemical species such as nitrides and diffusion of the atoms through the iron lattice is inhibited, so surface enrichment of nitrogen does not occur on heating. It is noted that the limit of solubility of nitrogen in iron at 400° is 200 ppm, far higher than the concentration determined in the bulk metal. Nitrogen at concentrations far lower than the saturation limit is driven to the surface, because the high energy released by the segregation lowers the surface potential.

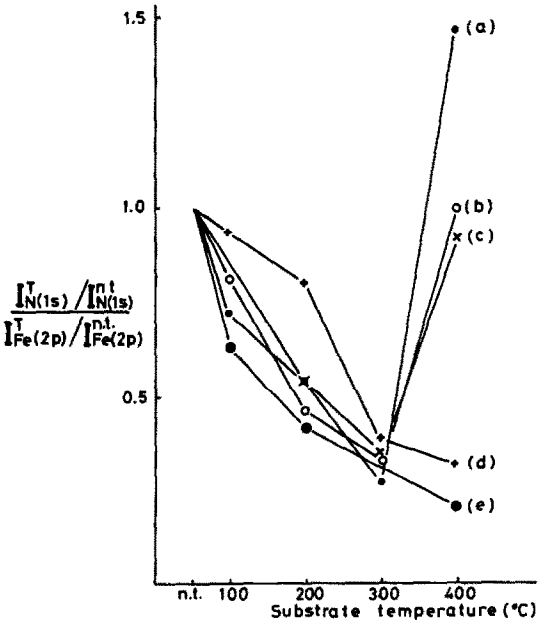


Fig. 4. Relative intensity values of the N(1*s*) lines obtained from filed surfaces of various irons: (*a*) 35 ppm N, (*b*) 19 ppm N, (*c*) 17 ppm N, (*d*) 3% Cr and 220 ppm N, (*e*) 3% Si and 120 ppm N.

On the silicon- and chromium-containing iron surfaces, the intensity of the N(1*s*) line from nitride decreases slightly on raising the temperature from 300° to 400°, as shown by curves (*c*) and (*d*) in Fig. 4. This suggests that when diffusion through the substrate lattice is inhibited, a sluggish desorption from the surface can be observed on prolonged heating above 300°, and that the competitive effects of desorption and diffusion from the bulk to the surface define the surface abundances of oxygen and nitrogen.

CONCLUSIONS

The species containing oxygen and nitrogen adsorbed on a mechanically regenerated iron surface are effectively desorbed by heating in a vacuum. The temperature at which the concentration of adsorbed species falls to a minimum is around 300°. At this temperature the diffusion of nitrogen and oxygen from the lower layers of the sample to the surface is unimportant. If the iron specimen is preheated at 300° in a vacuum, about 85% of the oxygen and 80% of the nitrogen on a polished iron surface can be desorbed. On heating at higher temperatures there is a possibility of loss of gaseous components from the bulk metal. From the desorption rate–temperature curves, the preferential desorption of each chemical species can be used for the determination of surface oxygen and nitrogen.

REFERENCES

1. N. P. Sinyaeva, A. M. Vasserman, L. L. Kunin, V. M. Khokhrin, and Yu. G. Olesov, *Zh. Analit. Khim.*, 1975, **30**, 1143.
2. H. Goto and M. Hosoya, *Sci. Rept. Res. Inst. Tohoku Univ., A*, 1970, **22**, 116.
3. F. Honda and K. Hirokawa, *J. Electron Spectrosc.*, 1977, **10**, 125.
4. *Idem*, *ibid.*, in the press.
5. K. Hirokawa, F. Honda and M. Oku, *ibid.*, 1975, **6**, 333.
6. P. R. Norton, R. L. Tapping and J. W. Goodale, *Surface Sci.*, 1977, **65**, 13.
7. C. R. Brundle, T. J. Chuang and D. W. Rice, *ibid.*, 1976, **60**, 286.
8. K. Hirokawa and F. Honda, *J. Appl. Phys. (Japan), Suppl. 2, Pt. 2*, 1974, 783.
9. J. H. Swisher and E. T. Turkdogan, *Trans. AIME*, 1967, **239**, 426.
10. M. T. Hepworth, R. P. Smith and E. T. Turkdogan, *ibid.*, 1966, **236**, 1278.
11. J. C. Fuggle and D. Menzel, *Surface Sci.*, 1975, **53**, 21.
12. H. D. Hagstrum, *ibid.*, 1976, **54**, 197.
13. H. J. Grabke, W. Paulitschke, G. Tauber and H. Viefhaus, *ibid.*, 1977, **63**, 377.
14. K. Hirokawa, M. Honda and F. Honda, *Z. Anal Chem.*, in the press.

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A NEW CATALYTIC REACTION OF RHENIUM AND ITS ANALYTICAL APPLICATION

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Summary—Small amounts of perrhenate in fairly concentrated sulphuric acid media and in the presence of tin(II) chloride are found to catalyse the acid hydrolysis of α-furildioxime, with production of a new absorption peak at 320 nm, due to the di-α-furildiketone produced. The catalytically active species is a sulphate complex of rhenium(IV). The catalytic action of rhenium is promoted by citric acid. Rhenium can be determined in the range 0.0005–0.5 μg/ml. Interferences are eliminated by a preliminary extraction. The method has been applied to the determination of rhenium in copper concentrates of low rhenium content, copper ores and rocks. On the basis of the inhibitory effect of molybdenum the reaction can be used for determination of this element as well.

Kinetic methods are amongst the most sensitive for rhenium determination. They are based on the catalytic action of rhenium in the reduction of tellurates[1] and selenates[2] in the presence of tin(II) chloride. The absorbance of the sol of elemental tellurium or selenium is proportional to the rate of the corresponding catalytic reaction and is used as a quantitative measure of the rhenium content in solution. Rhenium also catalyses the interaction of iodide and chlorate[3] but a preliminary reduction of rhenium with zinc amalgam is required, which complicates the analytical determination.

The reaction of rhenium with α-furildioxime is widely applied as a spectrophotometric method for its determination.[4,5] In this paper a new catalytic reaction of rhenium is described which occurs in the presence of α-furildioxime, sulphuric acid, and tin(II) chloride as reducing agent.

EXPERIMENTAL

Procedure

The optimal conditions for microdetermination of rhenium by the new catalytic reaction are: temperature 20°; 0.25 ml of rhenium(VII) solution, 0.10 ml of 1*M* citric acid, 0.25 ml of 25*N* sulphuric acid, 0.25 ml of 0.40% solution of α-furildioxime in ethanol, 0.15 ml of 0.03*M* tin(II) chloride in 15*N* sulphuric acid, added in the order given.

Calibration curves obtained for different concentration ranges by the fixed-time method are linear. The absorbance is measured at 400 nm against a blank in 1-cm cells 120 hr after the preparation of the solution for 0.0005–0.01 μg of Re, after 6 hr for 0.005–0.05 μg and after 20 min for 0.05–0.5 μg. Statistical treatment of the data used to plot the calibration curves (each point being the average from 7 experiments) shows the apparent molar absorptivities to be:

0.5 μg of Re/ml ($2.7 \times 10^{-6}M$) – 2.8×10^5 l.mole^{-1}.cm^{-1}

0.05 μg of Re/ml ($2.7 \times 10^{-7}M$) – 3.7×10^6 l.mole^{-1}.cm^{-1}

0.0005 μg of Re/ml ($2.7 \times 10^{-9}M$) – 1.3×10^7 l.mole^{-1}.cm^{-1}

RESULTS AND DISCUSSION

Because α-furildioxime has low solubility in water, solutions in organic solvents are usually used. In acid media oximes are known[6] to be unstable and to hydrolyse to hydroxylamine and the corresponding ketone. We have studied the changes in the absorption spectrum of alcoholic solutions of α-furildioxime on dilution with sulphuric acid of various concentrations.

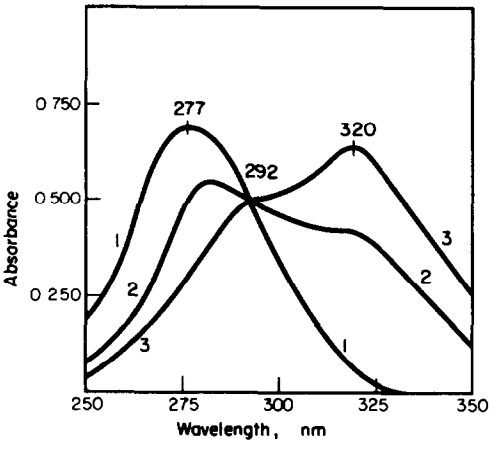


Fig. 1. Absorption spectra of alcoholic solution of α-furildioxime in 1*N* (curve 1), 8.5*N* (curve 2) and 18*N* H_2SO_4 (curve 3).

It is seen from Fig. 1 that the spectrum of α-furildioxime changes with change in sulphuric acid concentration, a new maximum being observed at 320 nm. We have established that this is due to the hydrolytic formation and subsequent solvation of di-α-furildiketone in this medium.

Over a wide range of sulphuric acid concentration and in the presence of tin(II) chloride as reducing

agent, microamounts of rhenium catalyse the acid hydrolysis of α-furildioxime. It is seen from Fig. 2 that with increasing sulphuric acid concentration up to 9–10*N* in the presence of the reduced Re species (curve 2) the absorbance at 320 nm increases more rapidly than that of the blank solution (curve 1). The spectrum

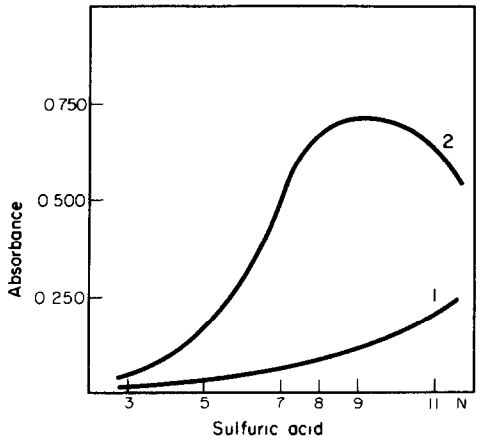


Fig. 2. Changes in the light absorption of α-furildioxime solutions at 400 nm as a function of the concentration of H_2SO_4. Curve 1—in the absence of rhenium, curve 2—in the presence of 0.3 μg of rhenium.

is not affected. The indicator reaction, which is catalysed to different extents by the hydroxonium ion and by rhenium, proceeds by the reaction:

$$\alpha\text{-furildioxime} + 2H_2O \xrightleftharpoons{H_3O^+,\ Re(IV)\ sulphate} \text{di-}\alpha\text{-furildiketone} + 2NH_2OH$$

The catalytic action is maximal in the range 8–10*N* sulphuric acid. On further increase of the acid concentration the effect becomes smaller because of the appearance of another interaction which affects the state of the catalytically active rhenium species. All further experiments were done at an acidity of 8.5*N* sulphuric acid with the absorbance measured at 400 nm. The sensitivity at this wavelength is lower but interference from high concentrations of α-furildioxime is avoided.

The hydrolysis of α-furildioxime also occurs in hydrochloric or phosphoric acid medium but the catalytic action of rhenium appears only in sulphuric acid medium, so the catalytically active rhenium species is presumably a sulphate complex of rhenium(IV). The catalytic reaction does not take place in the absence of a reducing agent. Neither rhenium(V) in the form of $ReOCl_5^{2-}$, prepared according to Jakob and Jezowska,[7] nor rhenium(IV) in the form of $ReCl_6^{2-}$ has any catalytic action.

The influence of various reaction conditions on the rate of the reaction was studied. α-Furildioxime can exist in three isomeric forms, the most reactive being the anti-form. The quality of the reagent depends on the content of anti-form.

Solvent effect

The most favourable conditions are achieved with an alcohol solution of the reagent. The catalytic effect increases with increasing solvent polarity ($CH_3OH > C_2H_5OH > CH_3COCH_3 >$ dioxan). All further experiments were carried out with ethanol because of its lower toxicity and ready availability.

Influence of α-furildioxime

The absorbance of the solution as a function of the concentration of the reaction substrate in the presence (curve 2) and absence (curve 1) of rhenium is shown in Fig. 3. The blank was measured against water, and the test solution against the blank. The absorption of the

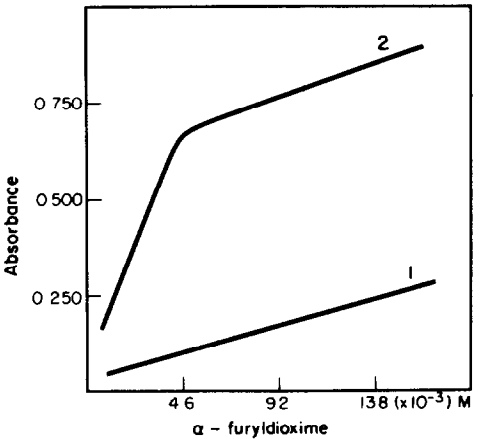


Fig. 3. The dependence of the light absorption on the concentration of α-furildioxime. Curve 1—blank, curve 2—in the presence of 0.3 μg of rhenium.

blank is a linear function of the α-furildioxime concentration over the entire concentration range investigated. When rhenium is present the absorption curve changes its slope at an α-furildioxime concentration higher than $4.54 \times 10^{-3} M$. This can be explained in terms of another interaction between rhenium and the organic reagent. The concentration of the substrate that corresponds to the point at which the slope of the curve changes was taken as the optimal.

Influence of tin(II) chloride

The concentration of the reducing agent is also of importance (Fig. 4). The maximal concentration of the catalytically active rhenium species is obtained in the presence of $4 \times 10^{-3} - 8 \times 10^{-3} M$ tin(II) chloride; at higher concentrations the catalytic activity of rhenium decreases.

Temperature effect

The slope of the calibration curve increases considerably as the temperature is raised; the absorbance of the blank also increases, which is why it is preferable to carry out the reaction at 20°.

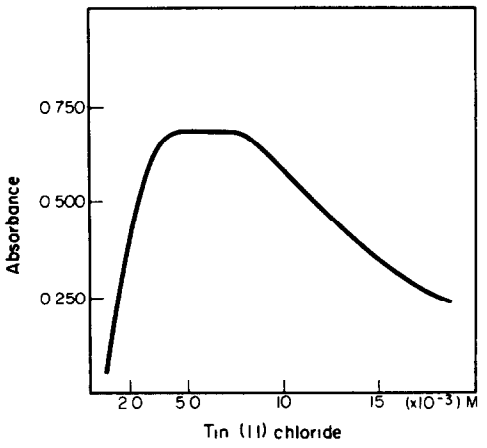


Fig. 4. The dependence of the light absorption on the concentration of tin(II) chloride. Re = $1.6 \times 10^{-6}M$; α-furildioxime = $4.6 \times 10^{-3}M$; time—30 min.

Influence of activators

It was established that several hydroxycarboxylic acids activate the catalytic action of rhenium. Citric acid is much more efficient than tartaric acid. Increasing the concentration of tartaric or citric acid above $0.07M$ does not further enhance the catalytic effect. Of the activators investigated, citric acid is the best, giving enhancement of the absorbance by a factor of 4.

Interferences

Interferences were studied; they were inhibitory in nature. The tolerance limits are shown in Table 1. The interferences can be eliminated by liquid–liquid extraction or ion-exchange.

Determination of rhenium in industrial and natural samples

The method was applied to the determination of rhenium in copper concentrates, ores and rocks. The sample was decomposed at 700° with sodium peroxide in a sintered corundum crucible. The crucible was cooled, 5 ml of water were added and the crucible was put in a boiling water-bath for 30 min. These decomposition conditions give the hydroxides of iron and other elements that co-precipitate molybdenum and other interfering elements. The contents of the crucible were transferred to a centrifuge tube fitted with a ground-in stopper, 10 ml of pyridine saturated with $5M$ sodium hydroxide were added and the mixture was extracted as described earlier.[8] The organic layer was transferred quantitatively to a 50-ml beaker by syringe and evaporated to dryness on a hot water-bath. The residue was dissolved in water and the solution passed through a column of Dowex 50W × 8 (H^+-form) to reduce the salt content of the solution. The eluate and washings were combined and made ammoniacal, and the resulting solution was concentrated in a conical Teflon crucible under an infrared lamp, to about 0.15 ml. The conditions described provided a complete separation of rhenium from the interfering elements. Then the catalytic reaction was carried out. The rhenium content was read from a calibration curve prepared with the same fixed time.

The results were treated statistically and compared with those obtained by the thiocyanate and α-furildioxime method.[9] When rhenium is determined in ores and rocks, a double extraction with 30–40 ml of pyridine is necessary. The results are presented in Table 2. As seen, the precision of the catalytic method is good. The results obtained are in agreement with those from other methods.

The proposed method is highly selective. It may be used to determine rhenium in various samples, with a relatively simple procedure and equipment.

Application to the indirect determination of molybdenum

The inhibition of the rhenium reaction by molybdenum can be used for the indirect catalytic determination of microamounts of molybdenum. The absorbance decreases linearly with concentration of the inhibitor over a wide range of molybdenum concentration. The absorbance is measured at a time interval chosen according to the molybdenum content: 24 hr after preparation of the solution (0.040 μg of Re, 0.02–0.20 μg of Mo); 3 hr (0.20 μg of Re; 0.10–1.00 μg of Mo); 30 min (0.80 μg of Re; 0.40–4.00 μg of Mo). The calibration curves were constructed by statistical evaluation of 7 determinations for each point. The apparent molar absorptivities in the determination of 0.40 μg of Mo ($2.08 \times 10^{-6}M$), 0.10 μg ($5.2 \times 10^{-7}M$) and 0.020 μg ($1.04 \times 10^{-7}M$) were 4.09×10^5, 1.44×10^6 and 7.36×10^7 $l.mole^{-1}.cm^{-1}$ respectively.

For practical use preliminary elimination of the interfering ions is required. Molybdenum is isolated from the major interfering ions by extraction in acidic medium ($0.01–2M$ hydrochloric acid) with α-benzoinoxime solution in chloroform.[11] Under these

Table 1. Interferences

Interferent (E)	Tolerance ratio Re:E	Interferent (E)	Tolerance ratio Re:E
Mo(VI)	1:0.2	Cr(VI), W(VI)	1:100
Bi(III)	1:4	V(V), Cu(II)	
Pb(II), Ni(II)	1:5	Cd(II), Mn(II)	
Fe(III)	1:10	Na(I), Al(III)	
Ca(II), Mg(II), Zn(II) Ti(IV), Co(II)	1:20		

Table 2. Practical applications to determinations of Re

Sample	No. of detns.	Re, *g/ton*	*S*, *g/ton*	Method
Copper concentrate	7	2.11	0.05	catalytic
	7	2.10	0.13	micro-variant of thiocyanate method[9]
Copper concentrate	7	0.67	0.015	catalytic
	7	0.68	0.043	micro-variant of the method with α-furildioxime[9]
Copper ore	5	0.029	0.0022	catalytic
	5	0.028	0.0023	catalytic with a standard addition
	2	0.025		neutron-activation method[10]
Andesite	5	0.0056	0.00049	catalytic

S = standard deviation.

Table 3. Practical applications to determination of Mo

Sample	No. of detns.	Mo, μg/g	*S*, μg/g	Method
Maize	5	0.56	0.045	catalytic
	5	0.55	0.046	standard addition technique
Cotton	5	0.41	0.030	catalytic
		0.4		spectral*
Mineral water, Sofia	5	5.3	0.40	catalytic
	5	5.2	0.42	standard addition technique
Mineral water, Merichleri	16	117	0.1	catalytic
		80		spectral[12]

S = standard deviation.
* O.R.S.T.O.M., Laboratoire de Spectrographie, Bondy, France.

conditions vanadium and tungsten are also extracted but their interference is negligible.

The method has been applied to the determination of molybdenum in plant materials and mineral water. A sample of 0.5–1 g of the plant material is preliminarily dried at 105° in a porcelain crucible, 0.5 ml of ethyl alcohol is added to the residue and the solution is set on fire. When the burning has ceased, the sample is placed in a cold muffle and gradually heated to 500° with free access of air, then kept at this temperature for 10–15 min. After cooling, the ash is wetted with 1*M* potassium nitrate, dried on a water-bath and ignited again in a muffle at 500° to provide complete combustion. Then 2.5 ml of 6*M* hydrochloric acid are added to the cooled residue and the crucible is placed on a boiling water-bath for 30 min. The contents of the crucible are then transferred to a separatory funnel (wetted with chloroform) with 7–8 ml of water and extracted with two 5-ml portions of 0.1% α-benzoinoxime solution in chloroform (3 min shaking). The extracts are collected in a 50-ml beaker and evaporated to dryness on a water-bath; 2 ml of conc. sulphuric acid are added to the dry residue and the beaker is heated on a sand-bath until fuming. After cooling, 0.5 ml of 30% hydrogen peroxide solution is added and the beaker is heated again on the sand-bath until the evolution of fumes ceases. The salts are dissolved in a small quantity of water, and the solution is transferred into a conical Teflon crucible and evaporated to 0.20 ml by infrared heating. Then the catalytic reaction of a known amount of Re with α-furildioxime is performed in the presence of this solution. The molybdenum content is read from a calibration curve obtained with the same amount of rhenium and the same measurement time.

For water samples the analysis begins with the extraction of molybdenum with 0.1% α-benzoinoxime solution in chloroform. The further procedure is as described above. If the molybdenum content is less than 2 μg/l. a preliminary concentration of the sample is necessary.

The method has been applied to the determination of the molybdenum content of plant samples and mineral water. The results obtained are presented in Table 3 and are in good agreement with those obtained by other methods.

REFERENCES

1. N. S. Poluektov, *Zh. Prikl. Khim. SSSR*, 1936, **9**, 2312.
2. D. I. Ryabchikov, V. I. Lazareva and A. I. Lazarev, *Zh. Analit. Khim.*, 1965, **20**, 960.

3. V. K. Pavlova and K. B. Yatsimirskii, *ibid.*, 1965, **20**, 1106.
4. O. G. Koch and G. A. Koch-Dedic, Handbuch der Spurenanalyse, Teil 2, Springer-Verlag, Berlin, 1974.
5. V. M. Peshkova and Chon Un Am, *Vestn. Mosk. Univ. Ser. Khim.*, 1960, No. 4, 59.
6. Houben-Weyl, *Methoden der organischen Chemie*, Vol. 10/4, p. 269. Thieme Verlag, Stuttgart, 1968.
7. W. F. Jakob and B. Jezowska, *Z. Anorg. Allgem. Chem.*, 1934, **220**, 16.
8. N. Jordanov, M. Pavlova and D. Bojkova, *Talanta*, 1976, **23**, 463.
9. S. Stefanov, N. Jordanov and M. Pavlova, *Mikrochim. Acta*, 1976 II, 449.
10. M. Pavlova, N. Jordanov, M. Michailov and S. Gabrovska, unpublished results.
11. G. Charlot, *Les Méthodes de la Chimie Analytique—Analyse Quantitative Minérale*, 4th Ed. Masson, Paris, 1961.
12. E. Pencheva, *Ph.D. Thesis*, Inst. Gen. Inorg. Chem., Bulg. Acad. Sci., Sofia, 1968.

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SHORT COMMUNICATIONS

SOLVENT EXTRACTION SEPARATION OF HAFNIUM WITH 4-METHYL-3-PENTENE-2-ONE

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Summary—A new method for the extractive separation of hafnium from zirconium is presented. Zirconium is extracted with pure mesityl oxide from 4*M* nitric acid/4*M* sodium nitrate medium, followed by extraction of hafnium with mesityl oxide from 0.4*M* hydrochloric acid/2*M* ammonium thiocyanate medium. It is possible to accomplish clean separations of Hf from Zr in ratios from 1:20 to 1:200. The separation of hafnium from commonly associated elements such as scandium, yttrium, uranium, thorium, alkali and alkaline earth metals in 500:1 weight ratio to hafnium is also possible.

A large number of extractants have been used for the solvent extraction of hafnium, but very few of them are capable of separating zirconium from hafnium. The commonly used extractants are 2-thenoyltrifluoroacetone,[1] 3-thianaphthenoyltrifluoroacetone,[2] 8-hydroxyquinoline,[3] *N*-benzoyl-*N*-phenylhydroxylamine,[4] bis(2-ethylhexyl)phosphoric acid[5] and diantipyrinylmethane.[6] However, these reagents are not satisfactory, as either the extraction is incomplete or zirconium is invariably co-extracted. In a few cases, it is essential to use very high acid concentrations to accomplish quantitative extraction. Amongst oxygenated solvents, tributyl phosphate,[7,8] trioctylphosphine oxide,[9] isobutyl methyl ketone,[10] dioctyl sulphoxide[11] and trioctylamine[12] are used as extractants, but these extractions are also not useful, as polymerization may occur or multistage countercurrent extraction may be necessary. The other reagents used for the solvent extraction of hafnium are summarized in recent monographs.[13,14]

This paper presents systematic investigations relating to the solvent extraction separation of hafnium from zirconium and other elements with 4-methyl-3-pentene-2-one (mesityl oxide). It is possible to extract hafnium quantitatively from 0.4*M* hydrochloric acid containing ammonium thiocyanate (at 2*M* concentration) as auxiliary complexing agent. The metal is stripped from the organic phase with 0.3*M* perchloric acid and determined photometrically at 540 nm with Xylenol Orange. The proposed method is simple, rapid, selective and applicable at microgram levels.

EXPERIMENTAL

Reagents

Stock solution of hafnium. Prepared by dissolving 0.5 g of hafnium oxide in 10 ml of a mixture of concentrated hydrofluoric acid and sulphuric acid (9:1). After digestion, it was evaporated nearly to dryness, then the residue was leached with dilute sulphuric acid and made up to 100 ml with distilled water, to give an acid concentration of 0.4*M*. It was standardized gravimetrically with mandelic acid.[13] The solution was found to contain 4.0 mg of hafnium per ml. A solution containing 20 μg of hafnium per ml was prepared by suitable dilution.

Xylenol Orange. A 0.05% solution in 0.3*M* perchloric acid containing 30% ethanol.

General procedure

An aliquot of solution containing about 20 μg of hafnium is taken. Enough hydrochloric acid and ammonium thiocyanate are added to make their concentrations 0.4 and 2.0*M*, respectively, in a total volume of 25 ml. The solution is shaken with 10 ml of mesityl oxide for 30 sec and the layers are allowed to settle and separate. Hafnium is stripped by shaking the organic phase with two 10-ml portions of 0.3*M* perchloric acid. To the combined back-extract 3 ml of 0.05% Xylenol Orange solution are added and the volume is made up to 25 ml. The absorbance of the violet red complex is measured[15] photometrically at 540 nm against a reagent blank similarly prepared.

RESULTS AND DISCUSSION

Effect of acidity and mesityl oxide concentration

The concentration of hydrochloric acid was varied from 0.1 to 1.0*M* and that of mesityl oxide from 25 to 100% (2.01–8.07*M*). Benzene was used as the diluent. All the extractions were done from 2*M* ammonium thiocyanate medium and the distribution ratio was calculated as usual. The extraction was not quantitative with diluted mesityl oxide (Table 1), but complete with 100% mesityl oxide from 0.2–1.0*M* hydrochloric acid/2*M* ammonium thiocyanate. At higher acidity, there was decrease in extraction owing to competitive equilibria with the excess of chloride ion. It was possible to strip the complex into the aqueous phase by equilibrating the organic phase twice with 10-ml portions of 0.3*M* perchloric acid. All the extractions were done at room temperature (25°).

An attempt was made to ascertain the composition of the extractable species. Hafnium was extracted at fixed acidity with varying concentrations of mesityl oxide (with benzene as the diluent). The concentration of thiocyanate was also varied at a fixed concentration of mesityl oxide and hydrochloric acid. A plot of log of distribution ratio *vs.* log of mesityl oxide concentration had a slope of 1.96. Similarly the plot of log of distribution ratio *vs.* log of thiocyanate ion concentration had a slope of 4. This shows that the probable nature of the extractable species is $Hf(SCN)_4 \cdot 2MeO$ where MeO means mesityl oxide. Hence hafnium is extracted as a disolvated species in the presence of thiocyanate as auxiliary complexing agent.

Effect of thiocyanate concentration

The concentration of thiocyanate was varied from 0.2 to 5.0*M* with the hydrochloric acid concentration constant at 0.4*M*. Pure mesityl oxide was used as the extractant. The results are shown in Fig. 1, and indicate that the extraction is quantitative when the ammonium thiocyanate concentration is at least 2*M*.

Table 1. Effect of acidity and mesityl oxide concentration (Hf = 20 μg; [NH_4SCN] = 2*M*)

Mesityl oxide concentration	Hydrochloric acid, *M*	Extraction, %	Distribution ratio, *D*
25% (2.01*M*)	0.1	4.6	0.12
	0.2	5.1	0.13
	0.4	8.0	0.21
	0.6	12.1	0.34
	0.8–1.0	8.7	0.23
40% (3.22*M*)	0.1	7.0	0.18
	0.2	7.0	0.18
	0.4	16.3	0.48
	0.6	18.1	0.55
	0.8–1.0	9.3	0.25
50% (4.02*M*)	0.1	11.6	0.32
	0.2	11.6	0.32
	0.4	24.4	0.80
	0.6	27.2	0.93
	0.8	15.8	0.46
	1.0	11.6	0.32
60% (4.85*M*)	0.1	15.8	0.46
	0.2	19.7	0.61
	0.4–0.6	33.7	1.27
	0.8	34.4	1.31
	1.0	29.7	1.05
75% (6.03*M*)	0.1	35.3	1.36
	0.2	48.8	2.38
	0.4	62.8	4.22
	0.6	64.2	4.48
	0.8	66.9	5.05
	1.0	57.7	3.41
90% (7.63*M*)	0.1	63.3	4.31
	0.2	72.7	6.65
	0.4	83.7	12.83
	0.6	86.5	16.01
	0.8	97.8	111.1
	1.0	95.3	50.69
100% (8.07*M*)	0.1	86.0	15.35
	0.2–1.0	100.0	∞

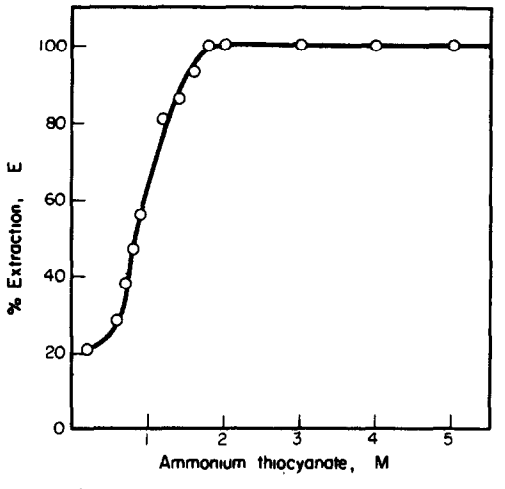


Fig. 1. Effect of thiocyanate concentration. Hf(IV) = 20 μg; HCl = 0.4*M*; mesityl oxide = 100%.

Periods of extraction

The period of equilibration was varied from 5 to 30 sec in 5-sec steps and the extraction was quantitative if the shaking period was at least 25 sec. All earlier methods need a much longer period of shaking for complete extraction.[13]

Effect of diverse ions

The effect of diverse ions on the extraction of hafnium (20 μg) from 0.4*M* hydrochloric acid/2*M* ammonium thiocyanate with pure mesityl oxide was studied. The tolerance limit was calculated as described earlier.[16] The results are shown in Table 2. Most ions are tolerated in weight ratios (to hafnium) of over 100:1. Citrate, tartrate, oxalate, fluoride and EDTA show strong interference.

Separation of zirconium, hafnium and other elements

The conditions for the solvent extraction of zirconium and hafnium with mesityl oxide are not identical and it is possible to exploit this difference for their separation from one another and other elements. Thus a mixture of zirconium, hafnium and other elements in varying proportion was taken. To the aqueous phase sodium nitrate and nitric acid were added so that the concentration of each was 4*M* in a total volume of 25 ml. The aqueous phase was then extracted with 10 ml of pure mesityl oxide. Hafnium remained in the aqueous phase. From the organic layer zirconium was stripped with water and determined photometrically with Alizarin S.[17] The aqueous phase from the initial separation was evaporated to dryness, and the residue was leached with water. Hydrochloric acid and ammonium thiocyanate were added so that their concentrations were 0.4 and 2*M* respectively in a total volume of 25 ml. The hafnium was then extracted with 10 ml of mesityl oxide, leaving all other elements in the aqueous phase. Hafnium was stripped from the organic phase with 0.3*M* perchloric acid and determined photometrically as

Table 2. Effect of diverse ions (Hf = 20 μg; 0.4*M* HCl; 2*M* NH_4SCN; 100% mesityl oxide)

Tolerance limit, *mg*	Ions added
50	Li^+, K^+, Mg^{2+}, CH_3COO^-, SO_4^{2-}
25	Ca^{2+}, Ba^{2+}, Sr^{2+}, Cr^{3+}
15	Al^{3+}, AsO_2^-, thiourea, malonate^{2-}
10	Rb^+, Cs^+, Rh^{3+}, Ir^{3+}, Sc^{3+}, Y^{3+}, Tl^{3+}, Ge^{4+}, Be^{2+}, Fe^{2+}, Cu^{2+}, Br^-, I^-, ascorbate$^-$
5	Pt^{4+}, Zn^{2+}, Cd^{2+}, Os^{3+}, Hg^{2+}, Ga^{3+}, In^{3+}, Mn^{2+}, Th^{4+}, Zr^{4+}, Sb^{3+}, VO_3^-, SeO_3^{2-}, TeO_3^{2-}
2	Ru^{3+}, Pd^{2+}, UO_2^{2+}, Au^{3+}, WO_4^{2-}, $Cr_2O_7^{2-}$, $Mo_7O_{24}^{6-}$
None	cit^{3-}, $tart^{3-}$, $C_2O_4^{2-}$, F^-, $EDTA^{4-}$

Table 3. Separation of hafnium from zirconium (100% mesityl oxide)

Ratio: Hf:Zr	Taken		Found	
	Hafnium, μg	Zirconium, *mg*	Hafnium, μg	Zirconium, *mg*
1:20	100	2.00	98.0	2.02
1:30	100	3.00	98.2	3.02
1:40	50	2.00	48.8	2.00
1:50	20	1.00	19.1	1.00
1:80	50	4.00	47.8	4.00
1:100	20	2.00	19.5	1.99
1:150	20	3.00	19.5	3.01
1:200	20	4.00	20.0	4.01

described above. It was thus possible to separate hafnium from 20–200 times as much zirconium. The results are shown in Table 3.

This separation of hafnium from zirconium is very rapid and hence important. So also, it is possible to separate hafnium from alkali and alkaline earths, platinum group metals, and elements which are usually associated with it, such as scandium, yttrium, beryllium, uranium and thorium.

From ten experiments the average recovery of hafnium was 20 ±0.2 μg. The relative standard deviation was ±1.9%.

REFERENCES

1. E. H. Huffman and L. J. Beaufait, *J. Am. Chem. Soc.*, 1949, **71**, 3179.
2. J. R. Johnston, W. J. Holland and H. Gerard, *Mikrochim. Acta*, 1972, 608.
3. D. Dyrssen and V. Dahlberg, *Acta Chem. Scand.*, 1953, **1**, 1186.
4. A. D. Shendrikar, *Talanta*, 1969, **16**, 51.
5. E. A. Pepelyaera, N. A. Shostenko, I. B. Onisimova and T. I. Ionova, *Nauch. Trudy Nauchno-issled. Proekt. Inst. Radkomet. Prom.*, 1972, **44**, 116.
6. A. I. Busev, V. P. Zhivopistsev and B. I. Petrov, *Talanta*, 1972, **19**, 173.
7. E. N. Lebedeva, S. S. Korovin and A. M. Rozen, *Zh. Neorgan. Khim.*, 1964, **9**, 1744.
8. J. Hure, M. Rastoix and J. R. Saint, *Anal. Chim. Acta*, 1961, **25**, 118.
9. D. F. Wood and J. T. Jones, *Analyst*, 1965, **90**, 125.
10. W. Fischer, H. P. Pohlmann and K. Adam, *Z. Anorg. Allgem. Chem.*, 1964, **328**, 252.
11. Anon., *Chem. Bull.*, 30 (1976).
12. E. Cerrai and C. Testa, *Energia Nucl.*, 1959, **6**, 707.
13. A. K Mukherji, *Analytical Chemistry of Zirconium and Hafnium*. Pergamon, Oxford, 1970.
14. A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*. Van Nostrand-Reinhold, London, 1970.
15. K. L. Cheng, *Talanta*, 1959, **3**, 81.
16. S. Kalyanaraman and S. M. Khopkar, *Anal. Chem.*, 1977, **49**, 1192.
17. S. C. Dhara and S. M. Khopkar, *ibid.*, 1965, **37**, 1158.

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NITROGEN DETERMINATION IN COAL AND COKE WITH AN AMMONIA ELECTRODE

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Summary—The selective-electrode procedure described for determining 0.2–2.5% of nitrogen in coal and coke offers significant advantages over Kjeldahl distillation and titration. The Kjeldahl digest is diluted, neutralized, cooled, diluted to volume, adjusted to a standard temperature and rendered alkaline prior to measurement with an ammonia-selective electrode. Accuracy and precision of 1% relative are demonstrated by comparative analyses of a range of samples. Important experimental aspects discussed include the role as neutralization indicator played by vanadium derived from the catalyst, precision of the mV-meter, the influence of solution temperature and concentration, the repeatability of the readings, and interferences.

The quantitative determination of 0.2–2.5% nitrogen is required for ultimate analysis and characterization of coal and coke. Standard methods specify semimicro[1] or macro[2] Kjeldahl digestions for conversion of organic nitrogen into ammonium compounds. The addition of sodium hydroxide liberates ammonia, which is distilled, absorbed in boric acid, and titrated. A primary source of error in this procedure is the distillation step, since experimental conditions (including rate of steam flow, vigour of distillation, and volume of solution) must be correctly balanced to ensure efficient removal of ammonia without any carry-over of alkaline spray.

Ammonia-selective electrodes offer an alternative means of measuring the ammonium content of sample digests, and have been used for the determination of nitrogen after a Kjeldahl digestion of plant,[3] water,[4,5] soil,[6] brewing[7] and agricultural materials,[8] but these methods can be time-consuming because of the use of aliquots from the digest, or the use of standard additions to overcome possible interference effects. The results achieved are comparable with those from the distillation procedure, and the concomitant advantages are speed, simplicity and safety. However, earlier investigations with coal and coke in this laboratory (in 1972) could not achieve comparable precision, and work was abandoned until improved electrodes became available. The method now proposed is comparable with and has now replaced Kjeldahl distillation procedures for the semimicro determination of nitrogen in coal and coke.

EXPERIMENTAL

Reagents

Catalyst. K_2SO_4 (anhydrous), V_2O_5 and Se were finely ground and mixed in 93:5:2 weight ratio.

Electrode internal filling solution. 0.01*M* $(NH_4)_2SO_4$/0.50*M* KCl.

Other reagents. Distilled and demineralized water; nitrogen standard solution 100 μg/ml; 40% sodium hydroxide solution; conc. sulphuric acid, low in nitrogen; sucrose.

Apparatus

Neutralization funnel. A 25-ml dropping funnel, with vented adapter for connection to a Kjeldahl flask.

Polyethylene jars for alkaline digest. Capacity 300 ml, approximately 90 mm tall with wide (45 mm diameter) mouth; caps tightly fitting, with polyethylene inserts to prevent evaporation. The jars are selected so that their weights differ from each other by less than 1 g.

Measurement lids. A screw cap (without insert) for polyethylene jars, containing a 21-mm diameter hole for insertion of the electrode and a pinhole for equilibration of pressure with the atmosphere.

Ammonia-selective electrode. Orion Research Model 95–10, with an integral reference element within the electrode body. An O-ring (15 mm i.d., 21 mm o.d.) is positioned around the electrode body, to suspend the electrode securely from the lid, with the membrane approximately 40 mm above the base of the jar; this arrangement permits convenient transfer of the electrode between jars and allows the electrode to rest at an angle to the vertical during measurements.

Millivolt meter. Beckman 4500 digital, or Beckman analogue expanded-scale pH-meter.

Temperature-controlled water-bath. An integral thermostat/water-pump assembly controls the bath temperature at 2° (±0.1°) above room temperature. The outflow from the pump powers a submerged water-propelled magnetic stirrer.

Stirrer bars. Teflon-coated, length 25 mm.

Sampling

All samples were ground to pass a 76-μm sieve and equilibrated with the laboratory atmosphere prior to analysis.

Procedure

Determination. Weigh 100 mg of sample into a 50 ml Kjeldahl flask and add 2.0 g of catalyst. Homogenize the mixture by gently shaking, add 4.0 (±0.2) ml of conc. sulphuric acid, insert a loose-fitting stopper, and heat at boiling point on a digestion stand. When the contents have become clear and no carbonaceous material is visible, continue heating for a further 20 min. Cool for 10 min and add 25 ml of water. Connect the neutralization funnel and adapter to the flask, place approximately 15 ml of 40% sodium hydroxide solution in the funnel, and slowly (with constant swirling) neutralize the acid until one drop of alkali causes the solution to change to a deep green colour. Cool to ambient temperature in a cold water-bath.

Transfer the neutralized digest to a plastic jar, rinse with water, and add more to bring the net weight of the contents to 250 (±0.5) g (use a top-loading balance). Add 4.0 (±0.2) ml of 40% sodium hydroxide solution and immediately secure

the cap on the jar. Homogenize the solution by gently swirling, place the jar in the temperature-controlled water-bath and allow 30 min for temperature equilibration before measurement.

Place a stirrer bar in the jar and secure a "measurement lid" on the jar. Rinse the electrode, wipe off excess of liquid, place the jar on the magnetic stirrer, immediately insert the electrode into the sample solution, and read the emf to the nearest 0.1 mV when stability is reached.

Calibration. Three samples of sucrose are weighed to provide a matrix for the reference solutions containing 500, 1500 and 2500 μg of nitrogen. If high accuracy and precision are required an accurate calibration function is necessary. A simple linear regression routine with a programmable calculator has been found most satisfactory for this purpose.

The electrode is tested before sample measurements by adding 2.5 and 25 ml of standard "nitrogen" solution successively to an alkaline sucrose digest prepared as described above, and the stabilized emf is read after each addition. A difference of 52–54 mV between the two potentials indicates that the electrode is functioning correctly. This deviation from the theoretical Nernstian slope of 59 mV is due to the high concentrations of the sample and electrode internal filling solutions.

RESULTS AND DISCUSSION

Application to a range of coals and allied materials was evaluated after development of the procedure. Table 1 compares the nitrogen contents found for typical samples analysed by the electrode and standard distillation methods. A maximum difference of 0.03% N was observed at 2% N, and the correlation coefficient between the two methods was 0.9998.

Table 1. Comparison of electrode and Kjeldahl distillation methods

Sample	% N, dry basis		
	Electrode	Distillation	Difference
Tar	0.25	0.24	+0.01
Tar	0.35	0.34	+0.01
Coal	0.85	0.84	+0.01
Coke	1.24	1.25	−0.01
Coal	1.51	1.50	+0.01
Coal	1.79	1.78	+0.01
Coal	2.05	2.08	−0.03
Pitch	2.41	2.39	+0.02

Table 2. Comparative statistics of analyses of reference coal BHP–CRL SC114 for nitrogen

Procedure	Mean N%	Std. devn.	Data points
Distillation	1.499	0.010	55
Electrode	1.506	0.012	25

Standard reference coal or coke samples have not been given certificate values for nitrogen, and accordingly accuracy and precision were evaluated through a statistical analysis of the results obtained from a reference bituminous coal sample (BHP–CRL SC114–Wongawilli Seam) which is used within the authors' laboratory. Table 2 gives the statistics of the control graphs for the distillation and electrode procedures; there was no significant difference at the 99.5% confidence level.

Role of vanadium during neutralization

The vanadium in the catalyst mixture provided an integral pH-indicator because of the distinct colour variations with pH of the species in solution; partial reduction of V_2O_5 to V(IV) occurs in boiling sulphuric acid.[9] Under the experimental conditions, a predominant blue colour in the diluted digest solution, due to the VO^{2+} ion, changed to a deep green with the formation of other vanadium species at approximately pH 4. A perceptible brownish colour occurs at approximately pH 7, and liberation of ammonia is insignificant below pH 7.5.[10] Taking proper heed of the solution colour during the neutralization of the sample digest ensures that residual acid is completely removed without loss of ammonia.

Other catalyst mixtures are also effective for the conversion of organic nitrogen into ammonium compounds. For example, mercuric sulphate may replace the vanadium pentoxide, or both the pentoxide and the selenium, in accordance with standard methods.[1,2] However, the use of such catalysts would necessitate an auxiliary means of end-point detection in the neutralization of the digest solution.

Precision of the mV-meter

The emf measurements reported in this work were made with a digital instrument capable of direct reading to ±0.1 mV. An appraisal of the calibration functions obtained showed that correlation coefficients better than 0.9995 were regularly attained, and an inaccuracy of ±0.1 mV in the emf reading would represent a relative error of 0.4% in the nitrogen concentration over the whole range of interest. This implies that an analogue meter without scale expansion and precise to only ± 1 mV is incapable of determining nitrogen to better than 4% relative. However, an expanded-scale analogue meter, calibrated at 1 mV intervals on the expanded scale, was tested with interpolation by eye and found to return statistical results insignificantly different from those obtained with the digital instrument.

Temperature control

The accuracy and precision statistics shown in Table 2 can only be obtained if the solution and electrode temperatures are identical within 0.1° at the time the emf is read. Dilution and neutralization of the acid sample digest yields a temperature exceeding 50° (approximately 45 ml volume), but this can be lowered rapidly in a cold water-bath. The addition of the excess of alkali causes only a slight temperature increase of 0.2°, predominantly due to heat of dilution. If no temperature control was used, electrically powered magnetic stirrers were found to generate enough heat to result in unstable readings even if insulation was inserted between stirrer and jar.

A series of measurements over the temperature range 15–40° revealed that the absolute value of the electrode potential varied directly with temperature by 0.5 mV/deg. The relative values also change with temperature, since the electrode sensitivity changes by 0.2 mV/deg.[10]

It is essential, therefore, to maintain the electrode and sample solution at constant temperature. The most reliable means of doing this within ±0.1°, over the time period required for measurement of a batch of sample and reference solutions, is through the use of a thermostatically controlled water-bath, operated at 2° above ambient temperature, in conjunction with an immersible or water-propelled magnetic stirring device.

Solution concentration and electrode response

The addition of the final 4 ml of alkali increased the solution pH to 12.2 (±0.1), and gave the equivalent of a 0.5*M* sodium sulphate solution. An electrode internal filling solution with a composition compatible with this molarity was used instead of the solution supplied with the electrode, and

potential drifts arising from dilution by diffusion of water through the membrane were minimized.

The working volume of the diluted sample solution was chosen to achieve the minimal concentration compatible with linear electrode response, an adequate ammonia concentration for rapid equilibration of emf, and to avoid excessively large sample volumes or the need to take aliquots. Reduced quantities of catalyst and sulphuric acid,[5] or aliquots[2,3,6,8] have been chosen previously to minimize the molarity of the final solution. A nitrogen concentration of 4 μg/ml is produced from a sample containing 1.0% organic nitrogen, which is relatively large in comparison with the lower limit of linear electrode response of 0.1 μg/ml.[10] Over the range of nitrogen contents covered, the emf became stable within 3–4 min of insertion of the electrode into the sample solution, and samples could be dealt with every 4–5 min.

A working volume smaller than 250 ml would increase the effective nitrogen concentration as well as the overall molarity of the solution, but the ammonia activity would not be increased proportionately. Experiments on working volumes as low as 60 ml revealed that the high background electrolyte concentrations were detrimental to the accuracy and precision of results because of the disparate osmolar strengths on either side of the membrane. In contrast, increasing the volume even to 500ml did not affect the results.

Repeatability of solution emf

A further advantage of the working volumes used is the low rate of ammonia loss through volatilization. The final portion of alkali may be added some time prior to measurement, since the tightly fitting caps on the jars ensure that negligible volatilization can occur. It was found that the emf values obtained for a series of sample and reference solutions showed insignificant differences on standing for up to four days. The possibility of thus checking readings is a feature of the proposed method. The use of the special "measurement lid" when making readings results in the solution being open to the atmosphere for minimal time.

Reference compound

There are few organic compounds with nitrogen contents similar to the range usually found in coals, and these are not of suitable quality for use as analytical standards. High-purity ammonium sulphate was chosen as the reference material, and for convenience was added in solution form after the digestion and neutralization steps rather than in solid form prior to digestion. No significant differences occurred between the recoveries of nitrogen whether the ammonium sulphate was added before or after the digestion of the sucrose used as matrix for the standards.

Interferences

The method is free from interferences by mineral constituents usually present in coals. Investigations into the possible adsorption of ammonia onto precipitated metal hydroxides revealed no significant interference from the presence of up to 70% of iron or manganese.

The proposed method has proved accurate, precise, rapid and safe for the determination of nitrogen in coal and coke. Although absolute electrode potentials depend upon such factors as temperature and solution molarity, control of these ensures that the method is essentially accurate.

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REFERENCES

1. *Coal and Coke—Determination of nitrogen—Semimicro Kjeldahl method*, ISO Standard 333, 1975.
2. *Coal—Determination of nitrogen by the macro Kjeldahl method*, ISO Standard 332, 1974.
3. E. F. Eastin, *Commun. Soil. Sci. Plant Anal.*, 1976, **7**, 477.
4. A. R. Deschreider and R. Meaux, *Rev. Ferment. Ind. Aliment*, 1973, **28**, 238.
5. J. Mertens, P. van den Winkel and D. L. Massart, *Intern. J. Environ. Anal. Chem.*, 1975, **4**, 25.
6. J. M. Bremner and M. A. Tabatabai, *Commun. Soil. Sci. Plant Anal.*, 1972, **3**, 159.
7. G. K. Buckee, *J. Inst. Brew.*, 1974, **80**, 291.
8. A. R. Deschreider and R. Meaux, *Analusis*, 1973, **2**, 442.
9. H. Remy, *Treatise on Inorganic Chemistry*, Vol. II. Elsevier, Amsterdam, 1959.
10. *Ammonia Electrode* 95–10 *Instruction Manual*, Orion Research, Massachusetts, 1976.

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IODOMETRIC MICRODETERMINATION OF CERTAIN ORGANIC ACIDS

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Summary—A rapid and accurate method for the determination of certain organic acids is described. The acid sample solution is treated with suitable quantities of solid potassium iodate and potassium iodide followed by the titration of the liberated iodine with thiosulphate after 3–5 min. The results are accurate to within 0.3%.

Since most organic acids are intermediate or weak in strength, the methods for determining mineral acids are not always applicable to organic acids. Strong acids can be easily titrated with a standard alkali solution but in titration of a weak acid the pH–neutralization curve has to be considered in order to select the proper solvent, titrant and indicator. As the concentrations of the acid and alkali are reduced, the change in pH at the end-point becomes less and less sharp and there is a limit to the dilution at which an acid–base titration is useful.

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6. J. M. Bremner and M. A. Tabatabai, *Commun. Soil. Sci. Plant Anal.*, 1972, **3**, 159.
7. G. K. Buckee, *J. Inst. Brew.*, 1974, **80**, 291.
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The reaction

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

can also be utilized for determining acids;[1] this is used as an alternative, often more accurate, to alkalimetry.[2] The reaction is practically instantaneous with strong acids but becomes slower when the hydrogen-ion concentration is small. The iodometric method, therefore, gives excellent results with strong acids[3] but the determination of weak acids is not practicable owing to decreased reaction velocity.[3,4] The reaction cannot be accelerated by heating, because of the volatility of iodine. Attempts to adopt the iodometric method for the determination of organic acids have met with only partial success and have limited applicability. Bruhns[5] suggests the addition of a calcium or magnesium salt to the reaction mixture to enhance the reaction rate. His procedure requires about 30 min and is not applicable to those organic acids which do not contain a hydroxyl group. Another modification, proposed by Kolthoff,[6] involves the addition of excess of thiosulphate to the acid solution containing iodide and iodate, and back-titration of the residual thiosulphate. The time allowed for the reaction is 15–30 min for 0.1*N* acid solution and may be much longer for dilute solutions. This modified procedure has been adopted by several workers[7–9] for estimating the acid content in various products by allowing 2–24 hr for the reaction to go to completion. Apart from the long reaction period there is also a possibility of the thiosulphate reacting with the acid.

In order to devise a rapid iodometric method for the microdetermination of certain organic acids, we have studied their reaction with iodide and iodate and reached the following conclusions.

(*a*) Even with a large excess of iodide and iodate solution added to the acid sample the stoichiometric liberation of iodine cannot be achieved within a reasonable period of time.

(*b*) The reaction velocity decreases sharply with increase in the volume of the reaction mixture.

(*c*) If the iodide and iodate are added as an aqueous solution, as was done by earlier workers, the overall volume of the reaction mixture is increased, which decreases the reaction rate. By addition of iodide and iodate in the solid form, however, their amounts can be greatly increased without causing increase in the volume of the reaction mixture, and the reaction goes to completion in 3–5 min at room temperature (30°) even with dilute solutions of these acids.

(*d*) There is wide latitude in the amounts of iodide and iodate to be added, and the presence of undissolved potassium iodate does not affect the results.

EXPERIMENTAL

Reagents

Sodium thiosulphate, 0.1*M*. Standardized with iodate. A 0.01*M* solution was prepared by diluting the 0.1*M* solution with conductivity water.

Organic acids. Solutions were prepared and standardized by alkalimetry, and diluted as required to prepare the test solutions.

Starch, 1% *aqueous solution*.

Procedure

Pipette 5 or 10 ml of a solution containing 0.03–0.1 meq of acid into an iodine flask. Add 2 g of solid potassium iodate and stir the contents of the flask for about 3 min with a magnetic stirrer. Add 3 g of solid potassium iodide and wait for 3–5 min, swirling the flask frequently during this period. Titrate the liberated iodine with 0.01*M* thiosulphate from a microburette, using starch as indicator.

RESULTS AND DISCUSSION

The proposed method was applied to a number of organic acids of varied nature and the results presented in Table 1 show that 0.03–0.1 meq of these acids can be determined with an error of about 0.3%.

In titrating a dilute solution of a weak acid with 0.01*M* alkali, it is not easy to observe the colour change of phenolphthalein at the end-point, since the pink colour fades rapidly.[10] In the iodometric method suggested here, however, detection of the end-point is not difficult when 0.01*M* (or more dilute) thiosulphate is used as the titrant. Also, certain natural products are slightly coloured and the colour change at the end-point of an acid–base titration may be interfered with. In such cases iodometric determination of the acid content can advantageously be adopted. For substances containing another component capable of reacting with alkali, titration with alkali cannot yield correct results. For example, in the determination of carboxylic acids in lac, the alkalimetric method cannot be reliable since the lac resin is readily saponified by alkali [11] The iodometric method is to be preferred in such cases.

Table 1. Iodometric determination of certain organic acids

Compound	Amount taken, *mg*	Amount found, *mg*	Difference, %
Phthalic acid*	8.31	8.29	0.2
	2.49	2.48	0.3
Benzoic acid	9.77	9.75	0.2
	3.66	3.65	0.3
Phenylacetic acid	9.53	9.52	0.1
	4.08	4.07	0.3
Mandelic acid	9.13	9.11	0.1
	4.56	4.55	0.3
o-Chlorobenzoic acid	9.39	9.36	0.1
	4.70	4.68	0.3
Sulphamic acid	9.71	9.70	0.1
	2.91	2.90	0.3
Camphoric acid	9.01	8.99	0.2
	6.01	5.99	0.3
Furoic acid	8.97	8.96	0.1
	3.36	3.35	0.3

* Both protons give the reaction.

The proposed method is rapid and accurate, gives a sharp end-point and hence is suitable for the quantitative analysis of dilute solutions of the organic acids tested. Carbon dioxide does not interfere.

Acknowledgement—The authors thank the University of Jabalpur, Jabalpur, for the award of a research fellowship to one of them (S.N.N.).

REFERENCES

1. I. M. Kolthoff, R. Belcher, V. A. Stenger and G. Matsuyama, Volumetric Analysis, Vol. III, p. 276. Interscience, New York, 1957.
2. M. R. F. Ashworth, *Titrimetric Organic Analysis*, Part II, p. 477. Interscience, New York, 1965.
3. I. M. Kolthoff, *Pharm. Weekblad*, 1920, **57**, 63.
4. M. Groger, *Z. Angew. Chem.*, 1890, **3**, 353.
5. G. Bruhns, *Z. Anal. Chem.*, 1916, **55**, 45.
6. I. M. Kolthoff, *Chem. Weekblad*, 1926, **23**, 260.
7. H. P. Kaufmann, *Allgem. Oel Fett-Ztg.*, 1931, **28**, 225.
8. P. Vieles, *Bull. Soc. Chim. France*, 1939, 1127.
9. G. M. Nabar and C. V. Padmanabhan, *Proc. Indian Acad. Sci.*, 1950, **31A**, 371.
10. N. D. Cheronis and T. S. Ma, *Organic Functional Group Analysis*, p. 485. Wiley, New York, 1964.
11. N. R. Kamath and V. B. Mainker, *Anal. Chem.*, 1950, **22**, 724.

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ELECTROCHEMICAL STUDIES OF *p*-NITROANILINE–FORMALDEHYDE POLYMER

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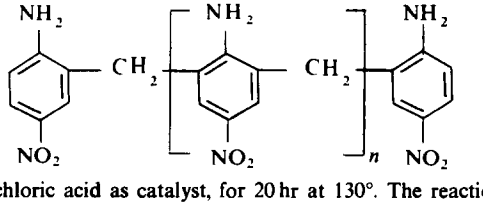
Summary—*p*-Nitroaniline–formaldehyde polymer has been prepared and separated into three fractions by fractional precipitation. The fractions and the conglomerate have been titrated in non-aqueous medium both potentiometrically and conductometrically. The inflections and breaks in the titration curves have been correlated with the degree of polymerization and the structure of the polymer.

Polymers containing weak acidic and basic groups have been titrated to locate the possible existence of hydrogen-bonding between neighbouring NH_2 or OH groups.[1-5] Intramolecular O—H...O bond formation in polynuclear phenolic compounds of *o,o'*-dihydroxydiphenylmethane type has been deduced from simple titrations in non-aqueous solvents[1,2,6] and also from infrared spectra.[7] The present studies deal with the potentiometric and conductometric titration curves of *p*-nitroaniline–formaldehyde condensation polymer and the fractions separated from it. A large number of breaks and inflections occur in the titration curves before the complete neutralization of the NH_2 groups. An attempt has been made to correlate these observations with the degree of polymerization (DP), basic character and hydrogen-bonding in the polymer molecule.

EXPERIMENTAL

Polymer and fractions

p-Nitroaniline–formaldehyde polymer (**I**) was prepared by refluxing 55.2 g (0.4 mole) of *p*-nitroaniline and 30 ml of 40% formaldehyde (0.4 mole) in presence of 2 ml of 10*N* hydrochloric acid as catalyst, for 20 hr at 130°. The reaction product was poured into ice-cold water and washed several times with water. The polymer obtained was quite brittle and could be powdered. About 2.1 g of the powdered material was dissolved in 20 ml of methanol by refluxing for 4 hr. The polymer solution was fractionated by addition of 5% aqueous sodium hydroxide solution as non-solvent. The precipitated fractions were then washed thoroughly to remove the alkali. The amounts of material separated at three consecutive stages of precipitation were 0.200, 0.375 and 0.475 g.



For the potentiometric work, glass electrodes, saturated calomel electrodes and a Beckman pH-meter (model H2) were employed. A Pt–Ir bridge was used in conjunction with a Muirhead audiofrequency oscillator as the source of alternating emf for conductometric titrations. Analytical-grade solvents were used without further purification. The concentration of the polymer solutions ranged between 0.8 and 1.0 g/l. The titrations were performed at room temperature and in a closed cell with a constant flow of nitrogen through it. About 2 min were found to be sufficient for readings to reach equilibrium. The precision of the emf and conductance measurements respectively were ± 3 mV and 1×10^{-6} ohm^{-1}.

RESULTS AND DISCUSSION

The potentiometric titration curves of the polymer and its three fractions are shown in Fig. 1. The titrations were done in a mixture of glacial acetic acid and formic acid with perchloric acid as the titrant. From the formula weight (150) of the repeat unit, 100 g of the polymer should contain 666 meq of NH_2 groups. All the titration curves show a fairly sharp final inflection corresponding to consumption of an amount of

The proposed method is rapid and accurate, gives a sharp end-point and hence is suitable for the quantitative analysis of dilute solutions of the organic acids tested. Carbon dioxide does not interfere.

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REFERENCES

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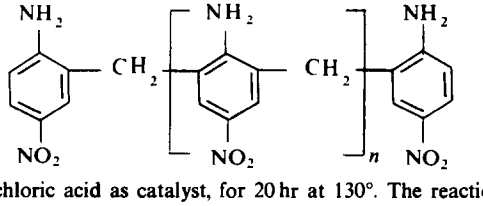
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EXPERIMENTAL

Polymer and fractions

p-Nitroaniline–formaldehyde polymer (**I**) was prepared by refluxing 55.2 g (0.4 mole) of *p*-nitroaniline and 30 ml of 40% formaldehyde (0.4 mole) in presence of 2 ml of 10*N* hydrochloric acid as catalyst, for 20 hr at 130°. The reaction product was poured into ice-cold water and washed several times with water. The polymer obtained was quite brittle and could be powdered. About 2.1 g of the powdered material was dissolved in 20 ml of methanol by refluxing for 4 hr. The polymer solution was fractionated by addition of 5% aqueous sodium hydroxide solution as non-solvent. The precipitated fractions were then washed thoroughly to remove the alkali. The amounts of material separated at three consecutive stages of precipitation were 0.200, 0.375 and 0.475 g.



For the potentiometric work, glass electrodes, saturated calomel electrodes and a Beckman pH-meter (model H2) were employed. A Pt–Ir bridge was used in conjunction with a Muirhead audiofrequency oscillator as the source of alternating emf for conductometric titrations. Analytical-grade solvents were used without further purification. The concentration of the polymer solutions ranged between 0.8 and 1.0 g/l. The titrations were performed at room temperature and in a closed cell with a constant flow of nitrogen through it. About 2 min were found to be sufficient for readings to reach equilibrium. The precision of the emf and conductance measurements respectively were ± 3 mV and 1×10^{-6} ohm^{-1}.

RESULTS AND DISCUSSION

The potentiometric titration curves of the polymer and its three fractions are shown in Fig. 1. The titrations were done in a mixture of glacial acetic acid and formic acid with perchloric acid as the titrant. From the formula weight (150) of the repeat unit, 100 g of the polymer should contain 666 meq of NH_2 groups. All the titration curves show a fairly sharp final inflection corresponding to consumption of an amount of

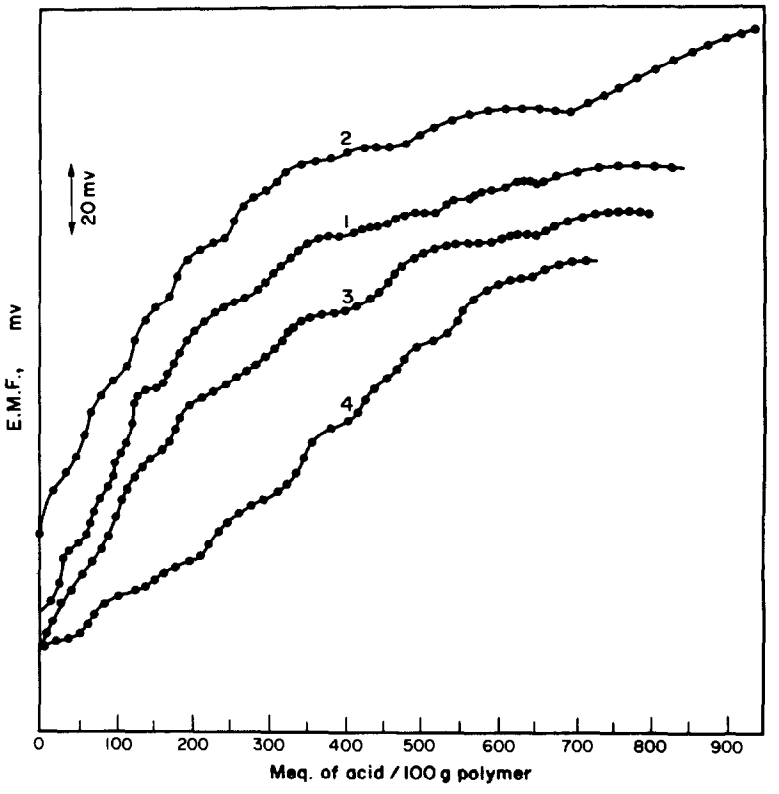


Fig. 1. Potentiometric titration curves of polymer: 1, fraction 1; 2, fraction 2; 3, fraction 3; 4, conglomerate.

Table 1. Observed amounts of basic groups in the three fractions and the condensate

Inflection (Fig. 1)	Fraction 1, *meq*/100 *g*	Fraction 2, *meq*/100 *g*	Fraction 3, *meq*/100 *g*	Condensate, *meq*/100 *g*
1st	33	60	80	65
2nd	70	120	160	130
3rd	100	170	225	205
4th	125	245	315	325
5th	160	300	470	400
6th	295	365	570	460
7th	400	470	655	530
8th	450	675	—	645
9th	525	—	—	—
10th	565	—	—	—
11th	615	—	—	—
12th	665	—	—	—
Break (Fig. 2)				
1st	35	60	80	65
2nd	70	125	325	460
3rd	365	365	400	—
4th	425	420	565	—
5th	480	480	650	—
6th	675	540	—	—
7th	—	675	—	—
Smallest interval	33	60	80	65
Average DP	20.0	11.0	8.3	10.2
Average MW	3000	1665	1245	1530

titrant equivalent to this. However, each shows several additional inflections. Though the intrinsic protonation constants of the various amino groups in the polymer chain should be identical if the groups are in a similar structural environment, some of them are more basic than others. This may be attributed to the formation of intramolecular hydrogen bond between adjacent amino groups. The N—H···N bond is of relatively low energy compared to the O—H···O bond formed in the polynuclear phenolic compounds of *o,o'*-dihydroxydiphenylmethane type.[1,2,6] Presence of NH_2 groups in the same plane, favourable bond angles and appropriate distances between adjacent NH_2 groups are the factors which induce N—H···N bond-formation. Hydrogen-bonds may also be formed between the nitro and amino groups in neighbouring chains, as suggested in *o*-nitroaniline.[8] There may be competition for hydrogen-

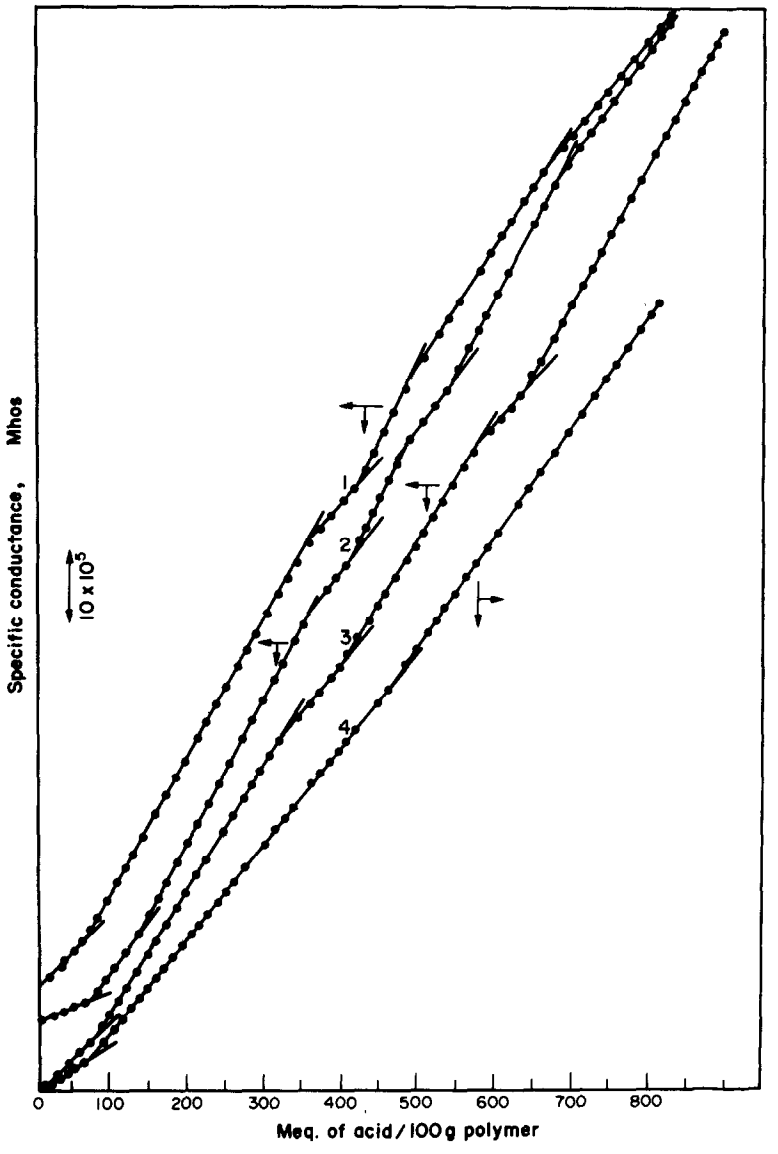


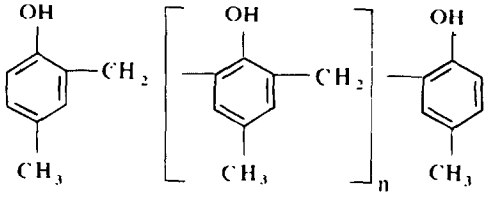
Fig. 2. Conductometric titration curves of polymer: 1, fraction 1; 2, fraction 2; 3, fraction 3; 4, conglomerate.

bonding between the solvent and the solute and also within the solute molecules. There may be a simple van der Waals force instead of hydrogen-bonding. It is also likely that the hydrogen atoms available are not all used for hydrogen-bond formation. Whatever may be the structural reasons, the experimental results indicate a distinct difference in the basic character of various NH_2 groups in the polymer molecule. Another important feature of the titration curves is the fact that they show breaks at more or less regular intervals which are simple multiples of the smallest interval (meq of acid per 100 g of polymer) for a particular fraction or conglomerate. It can be seen (Table 1) that the smallest intervals between any two successive inflections for fractions 1, 2, 3 and the conglomerate are in the neighbourhood of 33, 60, 80 and 65 meq/100 g respectively. The three fractions and the conglomerate were also titrated conductometrically under similar conditions. The curves are shown in Fig. 2. They did not show as many breaks as the number of inflections in the corresponding potentiometric curves but coincidence was observed (Table 1) at certain stages of neutralization. Besides this, the smallest interval obtained from the conductometric titration curve for a particular fraction was found to be in excellent agreement with the corresponding interval in the potentiometric curve.

An important aspect of these studies is that it provides an apparently simple method of calculating the degree of polymerization (DP) of various fractions. Assuming that the smallest interval would be one in which each chain contributes only one NH_2 group, the average DP can be calculated by dividing the total quantity of the titrant (in meq/100 g of polymer) at the final inflection by the amount added at the smallest interval. The average DP of fraction 1, for instance, should be $660/33 = 20$. The product of average DP and the formula weight (150) of the repeat unit should give the average molecular weight of the condensate. The average molecular weight referred to is likely to be a number-average value, because the number of polymer chains in a given weight of the polymer will matter in such calculations, and not their weight. Table 1 shows the amounts of titrant, smallest interval between successive inflections or breaks for the various fractions and the average DP and molecular weights. The assumption on which the DP is calculated

would be invalid, first, if some of the chains did not contribute any NH_2 group for the shortest interval, and secondly if some chains were to contribute more than one NH_2 group for this interval. However, the validity of the titrimetric method has been checked by studying polynuclear compounds of known molecular weight. Some oligomeric compounds of type **II** have been prepared by a stepwise synthesis which gives a homogeneous system of known molecular weight. These molecular weights have been compared by titrimetric methods and found to be in excellent agreement.[1,2]

Thus non-aqueous titrations may be used for the resolution of a polyelectrolyte and also for calculating the DP of the various fractions separated from a condensation polymer.



(II)
$n = 4, 5, 6, 7$

REFERENCES

1. S. K. Chatterjee, *Can. J. Chem.*, 1969, **12**, 2323.
2. *Idem, Indian J. Chem.*, 1969, **6**, 605.
3. *Idem, J. Polymer Sci.*, 1970, **8**, 1299.
4. S. K. Chatterjee and V. B. Agrawal, *ibid.*, 1971, **9**, 3225.
5. S. K. Chatterjee and N. D. Gupta, *J. Macromol. Sci.*, 1974, **A8**, 451.
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7. N. D. Coggeshall, *ibid.*, 1950, **72**, 1836.
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DOSAGE DE QUELQUES DERIVES ORGANOMERCURIELS PAR LA CYSTEINE

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(*Reçu le* 1 *décembre* 1977. *Accepté le* 10 *janvier* 1978)

Résumé—La réaction bien connue entre les thiols et les sels mercuriques permet le dosage potentiométrique des premiers. Ce type de dosage a été étendu à un certain nombre de dérivés organiques du mercure. Il permet d'évaluer quantitativement à l'aide d'une solution titrée de cystéine, un certain nombre de composés hydroxymercuriarylés. La présence d'un atome de chlore ou de soufre lié au métal rend inapplicable cette méthode.

La formation de mercaptides, dûe à la grande affinité des thiols et des ions mercuriques est un phénomène bien connu[1]. La réaction conduit à la formation de sels, ou de complexes très stables. Mais il n'est pas nécessaire que le mercure(II) se trouve à l'état ionisé pour réagir. En effet, lorsqu'il existe à l'état organométallique, il ne met en jeu que deux liaisons: l'une avec un atome de carbone et l'autre avec un hétéroatome; or en raison de sa tétracoordinance il est encore susceptible de participer à d'autres liaisons. Ceci explique qu'il est possible d'observer une réaction entre les thiols et ces dérivés organomercuriels avec formation de mercaptides.

A titre d'exemples, les sels de sodium des acides hydroxymercurbenzoïque, *p*-chloromercuribenzoïque,[2] *p*-hydroxybenzène-azo-phénylmercuriacétique,[3] salyrganique,[4] donnent des réactions avec les thiols que se prêtent à des dosages spectrophotométriques, ampérométriques ou polarographiques.[5–7]

En outre, certains auteurs ont proposé un dosage en retour de thiols par une volumétrie classique, dosant l'excès d'organomercuriel n'ayant pas réagi, par la cystéine[8] ou l'acide thioglycolique.[9]

Pour notre part nous avons réalisé le dosage inverse, de certains organomercuriels d'intérêt pharmaceutique, à l'aide de la cystéine.

L'originalité de la méthode que nous proposons provient de l'emploi d'une indication potentiométrique. Nous avons pu montrer en effet, que l'on observe au point d'équivalence une variation tout à fait satisfaisante du potentiel d'un système comportant une électrode de goutte de mercure et une électrode de référence au sulfate mercureux.

Cette réactivité des organo-mercuriels vis à vis d'une électrode de mercure n'était pas nécessairement prévisible. En effet, en raison de l'insertion du mercure dans la molécule organique par des liaisons covalentes mercure–carbone, le comportement de cet élément pouvait être totalement différent de celui d'ions mercuriques libres.

PARTIE EXPERIMENTALE

Réactifs

Solution titrée de cystéine à 0,05M. Cystéine base 6,06 g, eau distillée qsp 1000 ml.

Solution aqueuse d'acétate de sodium à 10%.

Electrodes

Le système d'électrodes utilisé est le même que celui qui a été proposé pour le dosage des dérivés soufrés par l'acétate mercurique.[10] Il comporte une électrode à goutte de mercure et une électrode de référence au sulfate mercureux. Il est également possible d'utiliser une électrode combinée de platine.

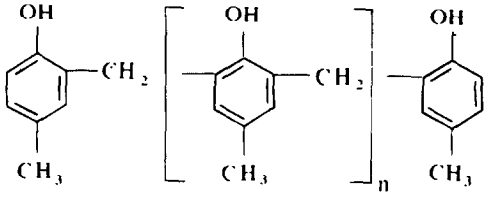
Etalonnage de la solution de cystéine

Il peut se pratiquer de deux façons:
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—soit par une solution titrée d'iode.[11]

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La solution de cystéine doit être préparée extemporanément, elle est en effet de conservation difficile.

Technique proposée

Peser exactement une prise d'essai *p* de dérivé organomercuriel de l'ordre de 0,10 mmole et la dissoudre selon les modalités suivantes.

(1) Pour l'hydrargyrophényle sodique (Hermophenyl®), on utilise simplement une quantité suffisante d'eau distillée pour permettre l'immersion des électrodes.

(2) Pour la merbromine, il est préférable d'ajouter, après dissolution, 20 ml de solution d'acétate de sodium à 10%.

(3) Pour le borate de phénylmercure et le nitromersol, la dissolution est effectuée dans 5 ml d'acide acétique pur, puis le volume est complété avec de l'eau distillée.

Titrer ensuite à l'aide de la solution de cystéine (R_1) en suivant la variation de potentiel à l'aide de l'un des deux systèmes d'électrodes précités. La fin du dosage est indiquée par une brusque élévation du potentiel. Une mole de cystéine correspond à une mole d'organomercuriel.

Choix des conditions opératoires

Elles sont différentes selon la nature des dérivés organomercuriels envisagés.

Nous avons étudié le comportement de quatre dérivés hydroxymercuriques antiseptiques utilisés en pharmacie ou en cosmétologie: la merbromine (**I**), l'hydrargyrophényle sodique (Hermophenyl®) (**II**), le borate de phénylmercure (**III**) et le nitromersol (**IV**), qui présente la particularité d'inclure le mercure dans un cycle.

Si trois d'entre eux sont relativement bien définis chimiquement, il n'en est pas de même pour l'hydrargyrophényle sodique qui est un mélange complexe contenant principalement soit le composé **IIa**[12] soit le composé **IIb**[13] (Tableau 1).

Choix du solvant

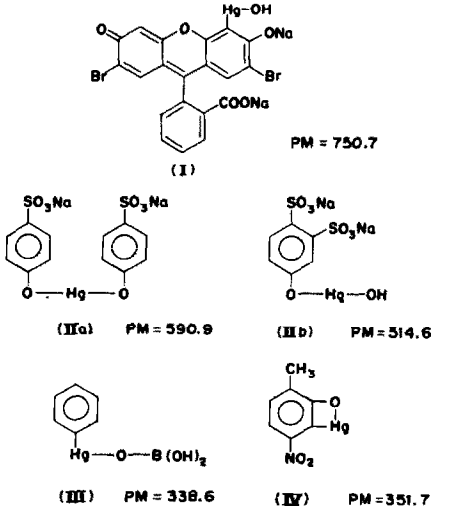
Si la merbromine et l'hydrargyrophényle, sels de sodium, sont solubles dans l'eau, il n'en est pas de même pour le borate de phénylmercure et le nitromersol. Pour les dissoudre, il est nécessaire d'utiliser l'acide acétique pur. Mais il est possible de réaliser une dilution aqueuse de la solution ainsi obtenue sans entrainer de précipitation.

Influence du pH

Elle est surtout importante dans le cas de la mercurescéine qui est le sel d'un acide carboxylique. Tout abaissement du pH risque donc d'entrainer la précipitation de l'acide correspondant et donc d'entraver le dosage. Or nous avons constaté que l'addition d'une solution de cystéine à une solution aqueuse de merbromine entraine un abaissement du pH. Mais dans les conditions de concentration proposées, ceci n'entraine pas de précipitation de l'acide, sans doute en raison de l'association de la cystéine et de l'organomercuriel. Cependant, cette éjection de proton lors de la réaction montre qu'il y a compétition entre ce dernier et le mercure organique. L'alcalinisation du milieu réactionnel, en éliminant les protons doit donc permettre une réaction plus facile; l'acidification, même compatible avec l'absence de précipitation (pH 6,5) a par contre un effet négatif. La figure 1 montre ainsi que la variation de potentiel est plus rapide si le pH initial est de 8,4 (solution d'acétate de sodium) que si le milieu est initialement tamponné à pH 6,5. Par contre, une alcalinisation plus importante (pH 10) diminue l'importance de la variation de potentiel. Dans ce cas de l'hydrargyrophényle sodique, sel d'acide sulfonique, le pH n'intervient pratiquement pas. En effet, la force des acides sulfoniques est suffisamment grande pour qu'il n'y ait pas de recul d'ionisation significatif même en milieu légèrement acide.

C'est la raison pour laquelle nous avons préconisé dans le seul cas de la merbromine l'alcalinisation du milieu réactionnel par l'acétate de sodium. D'autres sels susceptibles de tamponner, comme le phosphate disodique, conduisant à des moindres valeurs de variation de potentiel, ont donc été écartés.

Tableau 1.



RESULTATS OBTENUS

Influence de la nature de l'hétéroatome lié au mercure

Les quatre dérivés indiqués ci-dessus présentent tous une liaison entre le mercure et un oxygène. Ils permettent d'obtenir des courbes de titrage satisfaisantes.

Par contre, les composés mercuriels où le métal est lié à un atome de soufre (thiomersal) ou de chlore (mercurobutol; tert-butyl-chloromercuri-2-phénol) ne donnent aucune réaction décelable. Ce fait est assez logique puisque l'on connait la force des liaisons formées entre le mercure et ces deux éléments.

Dans le cas des dérivés hydroxymercuriques, il ne s'agit cependant pas d'une réaction de substitution de l'anion hydroxyle par le reste sulfuré de la cystéine. En effet, s'il en était ainsi on n'observerait aucune variation de pH.

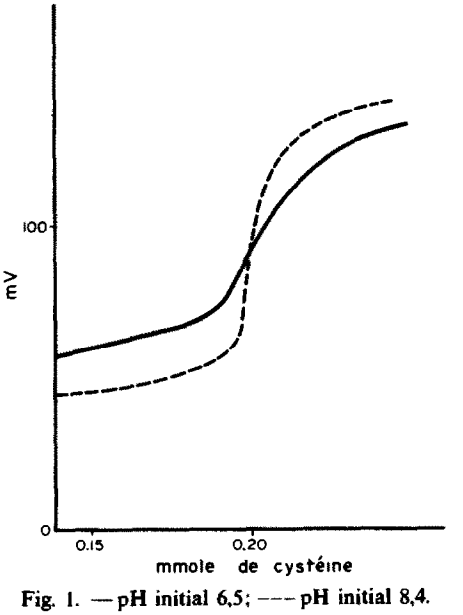


Fig. 1. — pH initial 6,5; --- pH initial 8,4.

Tableau 2.

	Spectrométrie absorption atomique, %	Potentiométrie ± écart type (8 dosages), %
Merbromine	90 ± 5	91,7 ± 0,6
Hydrargyrophényle sodique* (Hermophenyl®)	82 ± 5	78,3 ± 2,6
Borate de phénylmercure	100 ± 5	100 ± 3
Nitromersol	100 ± 5	96,4 ± 2,8

* Résultats calculés en fonction de la formule IIb.

Or dans le cas de la mercurescéine notamment, l'addition de cystéine entraine une acidification.

Precision de la methode

Les dosages réalisés nous ont paru initialement donner des valeurs faibles. Aussi, sachant que les dérivés organomercuriels fournis commercialement sont fréquemment des mélanges de pureté plus ou moins grande, nous avons confirmé les résultats obtenus en réalisant parallèlement un dosage du mercure par spectrométrie d'absorption atomique, après minéralisation sulfo-permanganique.

Le tableau 1 montre que les résultats des deux méthodes se recoupent d'une façon satisfaisante et que la précision de la méthode proposée est très bonne, notamment dans le cas de la merbromine puisque le dosage est réalisé à moins de 1% près.

Conclusion

Le dosage des dérivés organiques hydroxymercuriels est grandement facilité par la méthode potentiométrique que nous proposons et qui met en jeu une réaction stoechiométrique avec la cystéine.

Ce dosage est d'une précision supérieure à la méthode de dosage du mercure de la Pharmacopée Française. Il est, d'autre part, beaucoup plus simple et rapide que les méthodes utilisant soit l'absorption atomique soit l'extraction d'un chélate de la dinaphtyl thiocarbazone. Ces méthodes nécessitent en effet une minéralisation préalable.

BIBLIOGRAPHIE

1. J. M. Karchmer, *The Analytical Chemistry of Sulfur and its Compounds*, Wiley-Interscience, New York, 1970.
2. I. Fridovich et P. Handler, *Anal. Chem.*, 1957, **29**, 1219.
3. R. Zak, W. M. Curry et R. M. Powben, *Anal. Biochem.*, 1964, **10**, 135.
4. I. M. Klotz et B. R. Carver, *Arch. Biochem. Biophys.*, 1961, **95**, 54.
5. A. C. Allison et R. Cecil, *Biochem. J.*, 1958, **69**, 27.
6. R. Benesch et R. E. Benesch, *Methods Biochem. Anal.*, 1962, **10**, 43.
7. S. J. Leach, *Austr. J. Chem.*, 1960, **13**, 520.
8. F. P. Chinard et L. Hellermann, *Methods Biochem. Anal.*, 1954, **1**, 1.
9. M. Wroński, *Z. Anal. Chem.*, 1964, **206**, 352.
10. A. Billabert, M. Callanquin et M. Hamon, *Analusis*, 1975, **3**, 258.
11. *Pharmacopée Française*, IXe, Ed., 1972.
12. *Merck Index*, 9e Ed., Merck, Rahway, New York.
13. *Index nominum 1975/1976*, Société Suisse de Pharmacie, Zurich.

Summary—The well-known reaction between thiols and mercuric salts can be used for determination of the former. The method has been extended to determination of several organomercurials. Cysteine is used for titration of hydroxyaryl mercury compounds. The presence of a chloride or sulphur atom bound to the metal makes the method inapplicable, however.

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INTERACTIONS OF TETRATHIONATE WITH SULPHITE AND SULPHIDE

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Summary—Tetrathionate is converted into thiosulphate in the presence of sulphite, sulphide and their mixtures. These reactions can be applied to analysis for any of these sulphur compounds by determination of the amount of thiosulphate formed. The chemical interactions may also be involved in the regulation of the oxidative sulphur pathways in micro-organisms and be employed to prepare colloidal sulphur particles.

Colorimetric methods based on cyanolysis[1,2] and sulphitolysis[3] have been described for determining tetrathionate and other polythionates. Coulometry has also been successfully applied to the determination of polythionates.[4] In addition an ion-selective electrode can be sensitively used to monitor tetrathionate concentrations.[5] The interactions of tetrathionate with sulphite and sulphide produce thiosulphate[4,6] which can be determined by various titrimetric methods. In this paper the chemical interactions are appraised with a view to determining tetrathionate iodometrically, and suggesting their involvement in the inorganic sulphur metabolism of autotrophic bacteria.

EXPERIMENTAL

Potassium tetrathionate was obtained from K & K Laboratories; other chemicals of analytical grade were from B.D.H. Ltd. Fresh standard stock solutions were prepared daily. Portions (1–5 ml) of the reaction mixtures were diluted with doubly-distilled water to 90 ml and titrated with 0.0025*N* iodine, 0.5 ml of 0.8% starch solution being used as indicator; 5 ml of 35% w/v formaldehyde solution were used to mask sulphite. Preliminary experiments showed that the chemical reactions yielding thiosulphate took place instantaneously upon the mixing of the reagents. In the following experiments the time between mixing and titration varied from 10 to 30 min; the order of preparations and titrations was chosen by use of random number tables.

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RESULTS AND DISCUSSION

The conversion of tetrathionate into thiosulphate is based on the following reactions:

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-} \quad (1)$$

$$S_4O_6^{2-} + S^{2-} \rightarrow 2S_2O_3^{2-} + S \quad (2)$$

$$S_4O_6^{2-} + S^{2-} + SO_3^{2-} \rightarrow 3S_2O_3^{2-} \quad (3)$$

$$S_4O_6^{2-} + 3CN^- + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + SCN^- + 2HCN \quad (4)$$

Tetrathionate alone does not react with iodine. Thiosulphate is oxidized to tetrathionate during the iodine titration:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (5)$$

Trithionate is stable under the conditions of the titrimetric assay. Sulphite is oxidized to sulphate by iodine but this can be prevented by masking the sulphite with formaldehyde:

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2HI \quad (6)$$

$$SO_3^{2-} + HCHO + H^+ \rightarrow CH_2OHSO_3^- \quad (7)$$

Table 1 shows that the tetrathionate determination based on sulphitolysis prior to the iodometric assay is quantitative if about 30–100% excess of sulphite is used.

The reduction of tetrathionate to thiosulphate by sulphide [equation (2)] was found to give a recovery of 89–100% (Table 2); the variation probably resulted from the instability of the sulphide solution. Conversely, this reaction can successfully be applied to the determination of sulphide. In mixtures of sulphide and sulphite [equation

Table 1. Conversion of tetrathionate into thiosulphate in the presence of sulphite

Addition, *μmole*		I_2 titration, *μmole*		Found, *μmole*		
$S_4O_6^{2-}$	SO_3^{2-}	−HCHO	+HCHO	$S_2O_3^{2-}$	SO_3^{2-}	Recovery of $S_2O_3^{2-}$, %
50	100	74.5	25.5	51.0	49.0	102
50	66.7	39.5	24.8	49.6	14.7	99.2
50	50.0	24.3	24.1	48.2	0.2	96.4
50	33.3	15.6	15.9	31.8	0	95.5
50	16.7	7.6	7.9	15.8	0	94.6
50	0	0	0	0	0	—
0	66.7	59.3	0	0	59.3	—

Table 2. Conversion of tetrathionate into thiosulphate in the presence of sulphide

Addition, μmole $S_4O_6^{2-}$	Addition, μmole S^{2-}	I_2 titration, μmole	Found, μmole $S_2O_3^{2-}$	Recovery of $S_2O_3^{2-}$, %
28.5	0	0	0	—
28.5	7.1	6.6	13.2	93.6
28.5	10.7	9.5	19.0	88.8
28.5	14.3	13.8	27.6	96.5
28.5	17.8	17.8	35.6	100
28.5	21.4	21.1	42.2	98.5

Table 3. Conversion of tetrathionate into thiosulphate in the presence of sulphite and sulphide

Addition, μmole $S_4O_6^{2-}$	Addition, μmole SO_3^{2-}	Addition, μmole S^{2-}	I_2 titration, μmole	Found, μmole $S_2O_3^{2-}$	Recovery of $S_2O_3^{2-}$, %
26.7	0	0	0	0	—
26.7	10.7	0	5.7	11.4	106
26.7	0	10.7	10.6	21.2	99.1
26.7	10.7	10.7	15.3	30.6	95.3
26.7	7.1	14.3	18.1	36.2	101
26.7	14.3	7.1	14.1	28.2	98.9

(3)], tetrathionate was converted into thiosulphate with a recovery of 95–100% of the stoichiometric values (Table 3).

ionate was converted into thiosulphate with a recovery of 95–100% of the stoichiometric values (Table 3).

The cyanolysis of tetrathionate [equation (4)] was tested for its suitability for the iodometric titration. The resulting thiocyanate, however, also reacts with iodine, though at a slower rate than thiosulphate, and therefore the titration procedure based on this reaction sequence was found to give inconsistent results.

The following reductants did not catalyse the conversion of tetrathionate into thiosulphate: AsO_2^-, NO_2^-, SeO_3^{2-}, Zn, ZnS.

Once converted into thiosulphate, tetrathionate can be determined by methods such as colorimetry,[1–3] coulometry,[4] and titration procedures using a number of different indicators.[6–14] The sensitivity of the iodometric titration can be greatly increased by additional alkaline treatment preceding the amplification reaction[11] and this feature can also be included in the procedure described for tetrathionate in the present work. The chemical reactions of tetrathionate with sulphite and sulphide can, of course, be applied to the analysis for any of these sulphur compounds by determination of the amount of thiosulphate formed.

These reactions offer a quick iodometric method for monitoring residual tetrathionate in bacterial cultures growing on this substrate. Moreover, the reaction between tetrathionate and sulphide can be conveniently employed to produce colloidal sulphur particles which can be used, for example, to prepare sulphur–agar media for the isolation of sulphur-oxidizing micro-organisms. These chemical interactions may also be important in the intermediary sulphur metabolism of autotrophic bacteria which utilize thiosulphate for energy either through its initial cleavage to sulphite and sulphide or by its initial oxidation to tetrathionate. Enzymes utilizing both routes have been detected in many sulphur-oxidizing bacteria, suggesting that the interplay of the pathways may be partly dependent on the chemical interactions of the sulphur-intermediates.

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REFERENCES

1. D. P. Kelly, L. A. Chambers and P. A. Trudinger, *Anal. Chem.*, 1969, **41**, 898.
2. T. Koh and K. Taniguchi, *ibid.*, 1973, **45**, 2018.
3. *Idem, ibid.*, 1974, **46**, 1679.
4. E. Blasius and J. Münch, *Z. Anal. Chem.*, 1972, **261**, 198.
5. O. H. Tuovinen and D. J. D. Nicholas, *Appl. Environ. Microbiol.*, 1977, **33**, 477.
6. L. Szekeres, *Talanta*, 1974, **21**, 1.
7. E. Blasius and K. Ziegler, *Arch. Eisenh.*, 1973, **44**, 669.
8. J. P. Danehy and C. W. Zubritsky, *Anal. Chem.*, 1974, **46**, 391.
9. P. D. Sharma and Y. K. Gupta, *Talanta*, 1974, **21**, 168.
10. H. Wiele, *Z. Anal. Chem.*, 1975, **273**, 15.
11. R. Belcher, S. S.-T. Liao and A. Townshend, *Talanta*, 1976, **23**, 541.
12. M. Hanif, M. Saleem, Z. Sheikh and J. Zýka, *Microchim. Acta*, 1976, **II**, 625.
13. S. Ikeda and H. Satake, *Bunseki Kagaku*, 1976, **25**, 544.
14. M. Sarwar, *Z. Anal. Chem.*, 1977, **284**, 43.

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SOLVENT EXTRACTION OF METALS WITH HYDROXAMIC ACIDS

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Summary—Solvent extraction with hydroxamic acids has been investigated, with comparison of aliphatic and aromatic reagents for the extraction of iron, copper, cobalt and nickel. Caprylohydroxamic acid has been evaluated for use in extraction systems for titanium, vanadium, chromium, molybdenum and uranium, both in terms of acidity of aqueous phase and oxidation state of the metal. It has been established that caprylohydroxamic acid in 1-hexanol is a suitable extractant for the removal of titanium(IV), vanadium(V), chromium(VI), molybdenum(VI) and uranium(VI) from 6*M* hydrochloric acid.

Although a considerable amount of solvent extraction work has been done with benzohydroxamic acid as the chelating ligand,[1–4] very little work has been done on extraction with aliphatic hydroxamic acids. Two probable reasons for the neglect of these reagents are that because of the lack of conjugation they do not give the coloured complexes obtained with benzohydroxamic acid, and that the aliphatic systems tend to be water-soluble whereas aromatic hydroxamic acids are preferentially soluble in polar organic solvents such as alcohols.[5] The electronegativity of the group to which the hydroxamic acid grouping is attached will have a large effect on the acidity of the reagent. Consequently aromatic and aliphatic hydroxamic acids could be expected to display quite different chelate-forming properties. The hydrophilic nature of the aliphatic reagents could be suppressed by increasing the size of the alkyl group in order to confer on them preferential solubility in organic solvents.

The investigation described in this paper is in two parts. Initially, the problem of solubility in water was overcome by using stearohydroxamic acid. A solution of this reagent in amyl alcohol was used to study the solvent extraction behaviour of iron(III), copper, cobalt and nickel as a function of pH. For comparison, the extraction study included benzohydroxamic acid and a phenoxyacetohydroxamic acid which was assumed to be intermediate in properties, containing an electronegative grouping which was isolated from the acid group by one methylene group. In the second part of the work, stearohydroxamic acid was discarded because of its very low solubility and replaced by caprylohydroxamic acid. This reagent (in 1-hexanol) was used to study the extraction behaviour of elements of higher oxidation states (IV, V and VI), as a function of solution acidity. In the case of vanadium and molybdenum, the effect of varying the oxidation state of the metal was also studied.

EXPERIMENTAL

Preparation of hydroxamic acids

Benzo-, stearo-, and caprylohydroxamic acids were prepared by the action of hydroxylamine on ethyl benzoate, stearate and caprylate respectively, by the method of Blatt.[6] *p*-Cresol was reacted with sodium chloroacetate, and the *p*-cresoxyacetic acid obtained upon acidification was esterified to give the ethyl ester. This was converted into *p*-cresoxyacetohydroxamic acid by reaction with hydroxylamine.

As the solubility of stearohydroxamic acid in amyl alcohol was only 3 g/l., the first series of extractions, involving iron, copper, cobalt and nickel, was done with 0.3% w/v solutions of the three hydroxamic acids in amyl alcohol. Extractions of titanium, vanadium, chromium, molybdenum and uranium were done with a 0.5% w/v solution of caprylohydroxamic acid in 1-hexanol. In all cases, equal volumes of aqueous and organic phase were used. The initial concentration of each metal in the solutions extracted was 10 ppm.

Iron, copper, cobalt and nickel were determined by atomic-absorption spectrophotometry. Other elements were determined colorimetrically, titanium with acid and hydrogen peroxide, vanadium with *N*-benzoylphenylhydroxamic acid, chromium with diphenylcarbazide, molybdenum with thiocyanate and stannous chloride, and uranium with PAR.

RESULTS AND DISCUSSION

The solvent extraction behaviour of iron(III), copper, cobalt and nickel with the three hydroxamic acids is shown as distribution *vs.* pH curves in Fig. 1. All the hydroxamic acids will separate iron and copper from cobalt and nickel, which have very low distribution coefficients. Benzohydroxamic acid gives the most effective iron–copper separations, virtually complete from an aqueous phase at pH 2. From Fig. 1, the $pH_{\frac{1}{2}}$ values for iron(III) and copper with the three reagents are found to be 1.8/3.9, 2.3/4.7 and 2.6/4.6 for benzo-, *p*-cresoxyaceto- and stearohydroxamic acid respectively. Thus *p*-cresoxyacetohydroxamic acid is seen to be similar to the aliphatic rather than the aromatic hydroxamic acids in its behaviour towards these two metals. The solvent extraction of a simulated copper-leach liquor containing iron, nickel and cobalt, was studied at or near pH 2 with the three reagents. Two extractions of the aqueous phase were performed with equal volumes of organic extractant, and the organic extracts were successively washed with an equal volume of pH 2 solution. The fractions of each of the four metals extracted by this technique are shown in Table 1; the results are seen to be in agreement with extraction curve data. The iron is selectively extracted with each reagent but the 91% extraction of iron with benzohydroxamic acid is superior to the 75 and 73% obtained with *p*-cresoxyaceto- and stearohydroxamic acids respectively. Christian and co-workers[1] postulated the existence of a 1:1 (violet) complex of iron(III) with benzohydroxamic acid at low pH and a 1:2 (red) complex at higher pH values in the presence of excess of

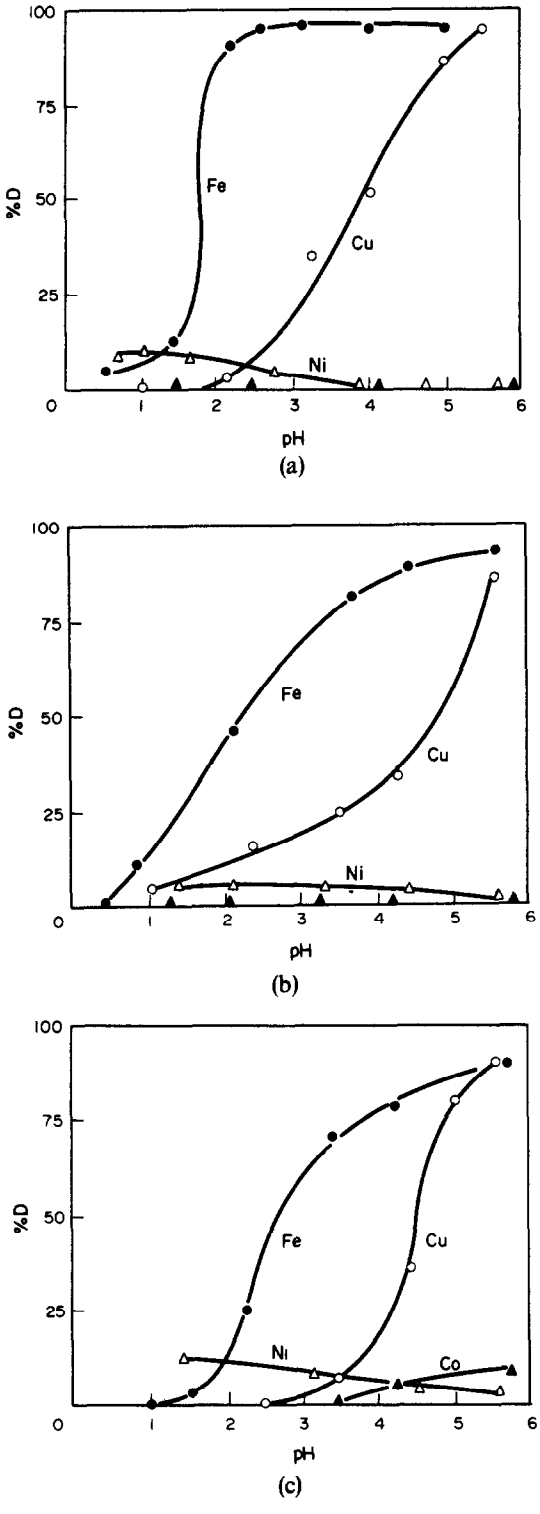


Fig. 1. Extraction curves showing distribution of iron, copper, cobalt and nickel as a function of pH for (a) benzo-, (b) *p*-cresoxyaceto and (c) stearohydroxamic acids (0.3% w/v solutions in amyl alcohol).

reagent. They also claimed that at pH values above 3 a 1:3 complex is formed. The solvent extraction curve does not indicate which species is extracted but it seems likely that it is the 1:3 complex which can be 90% extracted at pH 2.0.

The low solubility of stearohydroxamic acid in amyl alcohol and the poor solubility of its metal complexes caused problems which were eliminated by the use of caprylohydroxamic acid as the reagent. The chain of 8 carbon atoms gives a high enough partition coefficient between alcohols and water for extractions to be carried

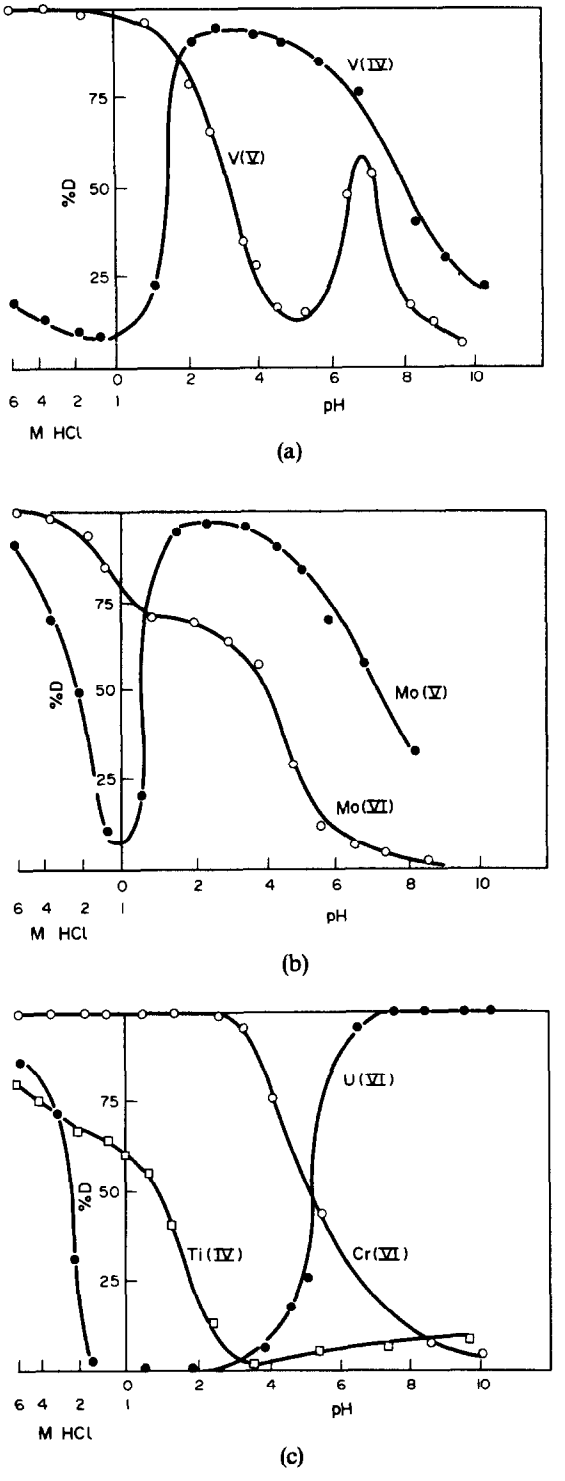


Fig. 2. Extraction curves showing distribution as a function of acidity for caprylohydroxamic acid (0.5 w/v in 1-hexanol) as extractant (a) for vanadium(IV) and (V), (b) for molybdenum(V) and (VI), and (c) for titanium(IV), chromium(VI) and uranium(VI).

Table 1. Iron, copper, cobalt and nickel extracted by hydroxamic acids from a simulated copper-leach liquor at pH 2

Ligand	Extracted, %			
	Fe	Cu	Ni	Co
Benzohydroxamic acid	91	8	5.5	3
Stearohydroxamic acid	73	4.3	4.8	4.5
p-Cresoxyacetohydroxamic acid	75	7.5	5.5	2.5

out with these solvents. Wise and Brandt[2] have studied the effect of solvent on the extraction of vanadium with benzohydroxamic acid and concluded that C_5–C_{10} alcohols gave complete extraction. To reduce mutual solubility effects further, 1-hexanol was chosen as the working solvent for the caprylohydroxamic acid.

Figure 2(a) shows the extraction data for vanadium(IV) and (V). Complete extraction of vanadium(V) with the aliphatic hydroxamic acid is found only in the range 2–6*M* hydrochloric acid. Above pH 2 the extraction of vanadium(V) falls off rapidly and above this value the extraction is poor except in the pH range 6–8 where it would appear that a different type of complex is formed (at an optimal pH value of 7.0). The behaviour of vanadium(V) with caprylohydroxamic acid is quite different from its behaviour with benzohydroxamic acid[2] where the optimum pH range for extraction was found to be 1.2–5.5. The authors reported that at pH 0.2 the extraction was reduced to 84%; with caprylohydroxamic acid vanadium is 97% extracted at pH 0.2. With the reduced state, vanadium(IV), quite different extraction behaviour is found, with low extraction from solutions more acidic than pH 1 and an optimal pH range of 2–5 over which the metal is 90% extracted. Figure 2(b) shows the behaviour of molybdenum with caprylohydroxamic acid. In this case the metal in both the (V) and (VI) oxidation states is efficiently extracted from 6*M* hydrochloric acid. Whereas the molybdenum(VI) extraction falls only gradually as the acidity is reduced, molybdenum(V) extraction falls sharply so that very little is extracted from 1*M* hydrochloric acid. In this case however, there is an optimal range for extraction at higher pH, molybdenum(V) being 90% extracted at pH 1.5–4.

Kuehn and co-workers,[4] in a paper on the spectrophotometric determination of vanadium and molybdenum, used benzohydroxamic acid as the extractant and varied the oxidation states of the metals to obtain separation. Vanadium and molybdenum were oxidized by dichromate and extracted as the benzohydroxamic acid complexes from an aqueous solution at pH 2. From Figs. 2(a) and (b) it is seen that if caprylohydroxamic acid replaces benzohydroxamic acid, efficient extraction of the elements in their higher oxidation states would be achieved fron 2–6*M* acid solution. Furthermore, the chromium(VI) present in excess would also be extracted. Kuehn and co-workers destroyed the complexes after vanadium measurement by reduction with iron(II) in sulphuric acid before determining molybdenum as the molybdenum(V) thiocyanato complex. Figure 2 reveals that reduction of vanadium to the quadrivalent state will prevent its extraction into the organic phase but the prevention of extraction of a molybdenum(V)—benzohydroxamic complex depends upon close control of the acidity within the range 0.5–2*M*.

Figure 2(c) reveals that chromium(VI) is efficiently extracted from an aqueous medium from pH < 3 to 6*M* hydrochloric acid. Uranium(VI) may be extracted efficiently at pH above 6, in agreement with the findings of Meloan and co-workers[3] who obtained an optimal pH of 6.2 for the extraction of uranium(VI) with benzohydroxamic acid. Uranium is also capable of being efficiently extracted by caprylohydroxamic acid from 6*M* hydrochloric acid. Titanium(IV) is not extracted appreciably at any pH higher than 2. Extraction of this element improves as the acidity is increased, with 80% extraction achieved from 6*M* acid.

It is apparent that the aliphatic hydroxamic acids could play an important role in the solvent extraction of metals both for analytical separation and in the hydrometallurgical field. The data presented indicate the usefulness of these reagents for extraction of the higher oxidation states of vanadium, chromium, molybdenum and uranium from acidic liquors. They are not as efficient as benzohydroxamic acid for iron–copper separations, however.

REFERENCES

1. R. V. Christian, I. D. Leffler and J. S. Dahler, *Anal. Chem.*, 1954, **26**, 1666.
2. W. M. Wise and W. W. Brandt, *ibid.*, 1955, **27**, 1392.
3. C. E. Meloan, P. Holkeboer and W. W. Brandt, *ibid.*, 1960, **32**, 791.
4. P. R. Kuehn, O. H. Howard and C. W. Weber, *ibid.*, 1961, **33**, 740.
5. W. W. Brandt, *Rec. Chem. Prog.*, 1960, **21**, 159.
6. A. H. Blatt, *Organic Synthesis*, Vol. 11, 2nd Ed. p. 67. Wiley, New York, 1947.

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DETERMINATION OF SILVER IN IRONS AND STEELS BY ATOMIC-ABSORPTION SPECTROMETRY WITH AN INDUCTION FURNACE: DIRECT ANALYSIS OF SOLID SAMPLES

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Summary—The silver contents of 17 irons and steels have been determined by dropping 0.5–20 mg of millings or turnings of the metals into an induction furnace situated within an atomic-absorption spectrophotometer. The limit of detection was 0.005 μg/g and the relative standard deviations were 12% or better for silver contents of not less than 0.05 μg/g. Samples are added to the furnace at 4–5 min intervals.

Metals or metalloids of low melting-point such as thallium, tin, lead, arsenic, antimony, bismuth, selenium, tellurium and silver are known to have detrimental effects on the properties of certain steels and of nickel-base alloys when present in very low concentrations, often less than 10 μg/g. Of these, silver is stated to impair the hot workability of stainless steels when present at trace levels[1] and, according to a General Electric Co. specification covering wrought and cast nickel-cobalt-base alloys,[2] the concentration of silver should not exceed 5 μg/g. Actually steels seldom contain silver in concentrations in excess of 1 μg/g unless the element has been deliberately added.

Golden and Atwell[3] have determined silver in ingot irons by d.c. arc emission spectrography after preconcentration of silver as sulphide, with molybdenum as a carrier. With a triple exposure the limit of detection for iron samples was reported to be 0.2 μg/g. Hofton[4] has determined silver in steels by atomic-absorption spectrometry after a straightforward dissolution procedure. The calculated detection limit was 1.1 μg/g but Hofton quoted results only for the determination of silver in prepared steels containing 90–200 μg of silver per g. Burke[5] has determined silver in aluminium-, iron- and nickel-base alloys by atomic-absorption spectrometry after extraction as an ion-association complex from hydrochloric acid solution containing ascorbic acid and potassium iodide, into a solution of trioctylphosphine oxide in 4-methylpentan-2-one, with a limit of detection of 0.05 μg/g. Dulski and Bixler[6] have applied the method of Burke[5] and a method based on dissolution in nitric acid followed by atomic-absorption spectrometry with a heated graphite atomizer for the determination of silver in four irons and steels. With the heated graphite atomizer, the limit of detection was ≤0.02 μg/g of silver.

However, spectrographic methods following preconcentration, and methods involving dissolution followed by atomic-absorption spectrometry, are relatively slow and, therefore, we have applied atomic-absorption spectroscopy with an induction furnace to the direct determination of silver in solid samples of irons and steels. The method is similar to that already described for the determination of trace levels of bismuth in steels and cast irons.[7]

EXPERIMENTAL

Materials and reagents

Standard irons and steels. British Chemical Standards, National Bureau of Standards alloys, and alloys from the Institutet för Metallforskning, Sweden.

Silver nitrate, Engelhard photographic quality.

Standard silver nitrate solution A (500 μg/ml silver concentration). Dissolve 0.787 g of silver nitrate in 50 ml of distilled water and dilute to 1 litre with 0.16*M* nitric acid.

Standard silver nitrate solution B (silver 0.1 μg/ml). Prepare freshly each day by a series of appropriate dilutions of solution A with 0.16*M* nitric acid.

Apparatus and method for obtaining absorbances for a series of solid samples

These were identical to those previously described[7] except that the graphite core and side-arms were made from AGTS grade graphite (British Acheson Electrodes), which had been previously baked for about 10 hr under vacuum at 2200°. The resonance line at 328.1 nm from a silver hollow-cathode lamp (Activion Glass Ltd.) was used with a band-width of 0.2 nm on the Perkin Elmer 300 S atomic-absorption spectrophotometer. The experimental conditions for the determination of silver are shown in Table 1. The temperature of the furnace core should be approximately 2270°.

Table 1. Experimental conditions for the determination of silver

Concentration range μg/g	Mass range of sample, mg	Damping position	Scale expansion
0.2–5	0.5–10	4	None
0.05–1	2–10	1	None
<0.05	5–20	1	×5

Calibration graphs

For the determination of silver in steels containing 0.2–5 μg/g, calibration graphs of peak absorbance *vs.* amount of silver are obtained by dropping increasing amounts of NBS standard steel SRM 361, which can be taken to have a silver content of 4.0 μg/g, into the graphite core under conditions capable of producing absorbances up to 1.0. The silver contents of steels containing < 1 μg/g may be determined by employing the standardized steel JK 2C in a similar way to obtain the calibration graph.

Calibration graphs can also be obtained for 0.5–3 ng of silver in aqueous solution by using a core temperature of approximately 2270°. Suitable volumes of standard silver nitrate solution B are dispensed from glass microlitre pipettes onto carbon discs (3 mm thick × 6.5 mm diameter) cut from "Specpure" carbon rod, these discs having been previously baked under vacuum at 2200°. The discs are dried under an infrared lamp for 30 sec and then dropped into the graphite core.

Analysis of irons and steels for silver

When a series of irons and steels is being analysed, suitable amounts are dropped into the graphite core over a period of 2–3 hr and, during the same run, various masses of SRM 361 or JK 2C are also added for the purpose of constructing a calibration graph, generally at the beginning of the run. When the run is completed, the calibration graph is drawn and the mass of silver in each sample is obtained from the graph. The concentrations of silver in the samples are then calculated.

RESULTS AND DISCUSSION

The method of direct analysis of solid samples is very sensitive and calibration graphs must be constructed with damped absorbances for standards containing more than 1 μg of silver per g, if the apparent absorbances towards the upper end of the calibration graph are to be less than 1.0. Because of the damping, the calibration graph is then a curve, as it is when constructed from different masses of SRM 361 corresponding to 2–10 ng of silver. However, calibration graphs for 0.2–3 ng of silver, constructed with JK 2C (silver 0.36 μg/g) without damping, are straight lines through the origin, the amount of silver giving 1% absorption being approximately 18 pg. A calibration graph for 0.5–3 ng of silver produced from a standard aqueous silver nitrate solution was also a straight line through the origin. The nitric acid used (0.16*M*) containing no added silver nitrate, was shown to contain 7.5 ng of silver per ml by addition of 10 μl to a carbon disc, drying the disc and dropping it into the furnace at 2300°. The calibration graph for silver from solutions was corrected for the silver in the nitric acid.

A series of irons and steels was analysed for silver contents by dropping 2–20 mg samples (degreased with a suitable solvent, dried, weighed to the nearest 10 μg, and transferred with forceps) into the furnace at approximately 2270°. The results are shown in Table 2.

The standard deviations for materials SRM 365, BCS 260/3, 260/4 and 456, and JK 1C are 0.002–0.003 μg/g and hence the limit of detection of the method is 0.005 μg/g.

Before it was decided to standardize JK 2C for the calibration graphs for the analysis of irons and steels containing < 0.2 μg of silver per g, a few materials containing 0.1–0.2 μg of silver per g were analysed with use of a calibration graph constructed with SRM 361. The silver contents found for SRM 364 and BCS 451, 452 and 453 were 0.10, 0.10, 0.19 and 0.13 μg/g respectively with relative standard deviations (eight replicates) of 5, 9, 9 and 9% respectively.

SRM 1261 (which is SRM 361 in rod form) is certified to contain 4 μg of silver per g and thus SRM 361 is a suitable standard and can be assumed to have the same silver content as SRM 1261. The silver content of SRM 361 or 1261 has been determined as 3.6 and 4.0 μg/g by Paulsen *et al.*,[8] 4 μg/g by Burke,[5] 3.4 μg/g by Kirk *et al.*,[9] and 4.4 and 4.6 μg/g by Dulski *et al.*[6] An average value of 4.0 μg/g was chosen for the silver content of SRM 361.

The precision of our method is considered to be satisfactory. The most commonly occurring element existing at appreciable concentrations in steels and volatile at 2270° is manganese (b.p. 2150°). For certain steels a relatively high concentration of manganese atoms would be produced in the light-path of the furnace. To check that no light in the region of the 328.1 nm line from the silver hollow-cathode lamp would be scattered by manganese atoms, 4.6–7.1-mg samples of "Specpure" manganese were dropped into the furnace while light of wavelengths 323.2,

Table 2. Results for the determination of silver in irons and steels

Iron or steel	Type	No. of samples analysed	Average result, μg/g	Relative standard deviation, %
SRM 361	AISI 4340 steel	—	4.0*	—
364	High-C steel (modified)	6	0.13	7
365	Electrolytic iron	10	0.015	17
BCS 149/3	High purity iron	5	0.030	27
260/3	,,	9	0.006	45
260/4	,,	14	0.005	38
451	Mild steel	5	0.10	7
452	,,	6	0.19	12
453	,,	5	0.15	5
454	,,	6	0.12	6
455	,,	6	0.11	4
456	,,	5	0.020	12
457	,,	6	0.18	10
458	,,	6	0.31	6
459	,,	6	0.10	6
460	,,	6	0.052	10
JK 1C	Iron	5	0.014	14
2C	0.2%C steel	12	0.36	5

* Assumed to be same as certified value for SRM 1261 (the rod form of this standard).

Table 3. Results for the determination of silver in irons and steels containing < 1 μg/g.

Iron or steel	Certificate value* μg/g	Results reported by		
		Burke[5] μg/g	Dulski *et al.*,[6] μg/g	This study, μg/g
SRM 364	0.5 and 0.2†			0.13
365	~0.02‡	0.08	0.02	0.015
BCS 149/3		0.05		0.030
260/3		<0.05		0.006
JK 1C	<0.1			0.014

* Single determination.
† SRM 1264.
‡ SRM 1265.

323.9, 326.7, 331.7, 332.2 and 334.4 nm successively, from non-resonance antimony lines, passed through the furnace. In no case was any absorbance recorded. To test for possible molecular absorption from any volatile non-metallic elements that might be released from steels at 2270°, the silver hollow-cathode lamp was replaced with a deuterium lamp, and six samples of steel JK 2C (known to contain sulphur, phosphorus, arsenic and antimony) were dropped into the furnace with instrumental settings of 328.1 nm and band-width 0.2 nm. In all cases the absorbances were zero, showing that there was no molecular absorption.

These observations lead us to believe that the silver contents reported in Table 2 are of good accuracy. Our confidence is reinforced by the fact that the furnace has also been used in a similar way to determine the lead contents of sixteen irons and steels, which are standards for lead, with good agreement between the concentrations of lead as determined by us and as reported on the certificates.[10] Unfortunately there are no irons or steels with silver contents less than 1 μg/g that are standards for that element. The silver contents of a few of the alloys used in this study have been reported by other investigators and a comparison of our results with theirs is shown in Table 3.

As far as it is possible to make a comparison, our results are in reasonable agreement with those of others. The results for SRM 364 and BCS 451, 452 and 453 obtained by using a calibration graph prepared from SRM 361 are less accurate than those shown in Table 2 because the small peak absorbances are outside the recommended range for more accurate results. However the agreement between both sets of results is still quite good.

The method is fairly fast, with weighed turnings or millings of an iron or steel being added to the furnace at intervals of 4–5 min. Calibration graphs for silver obtained from steel JK 2C and from aqueous solution, produced from absorbances obtained in the same run at 2260°, were not identical, the absorbance peak being 16% larger for the same amount of silver obtained from solution than from the steel (possibly release of silver from the globule of molten steel is slower than that from silver nitrate). However in the absence of a suitable steel standard for silver, it should be possible to obtain semiquantitative results by constructing a calibration graph by use of suitable volumes of standard silver nitrate solution.

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REFERENCES

1. D. W. P. Lynch, *Proc. Electric Furnace Conf., Am. Inst. Min. Met. Pet. Engrs.*, 1961, **19**, 220.
2. W. F. Simmons, *MCIC Newsletter*, Dec. 1974.
3. G. S. Golden and M. G. Atwell, *Appl. Spectry.*, 1970, **24**, 514.
4. M. E. Hofton, *British Steel Corporation Open Report*, GS/TECH/558/1/74/C.
5. K. E. Burke, *Talanta*, 1974, **21**, 417.
6. T. R. Dulski and R. R. Bixler, *Anal. Chim. Acta*, 1977, **91**, 199.
7. D. G. Andrews and J. B. Headridge, *Analyst*, 1977, **102**, 436.
8. P. J. Paulsen, R. Alvarez and C. W. Mueller, *Appl. Spectry.*, 1976, **30**, 42.
9. M. Kirk, E. G. Perry and J. M. Arnitt, *Anal. Chim. Acta*, 1975, **80**, 163.
10. D. G. Andrews, A. M. Aziz-Alrahman and J. B. Headridge, *Analyst*, in press.

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RAPID SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM WITH TRIFLUOPERAZINE DIHYDROCHLORIDE

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Summary—Trifluoperazine dihydrochloride reacts with platinum(IV) in sodium acetate–hydrochloric acid buffer containing copper(II) catalyst to form a bluish-green 1:1 complex with absorbance maximum at 504 nm. A 50-fold ratio of reagent to metal ion is necessary for complete complexation. Beer's law is valid over the concentration range 0.5–8 ppm of platinum(IV) with optimum concentration range 1–7 ppm. The molar absorptivity is 6.50×10^3 l.mole^{-1}.cm^{-1}. The effects of pH, time, temperature, concentration of reagent and copper, order of addition of reagents, and the interferences from various ions are reported.

Most of the reagents proposed for the spectrophotometric determination of platinum are unsatisfactory for one reason or another. Many reagents require either heating or a long time for maximum colour development. For example, acetylacetone[1] requires heating for 5 hr, acenaphthenequinone monoxide[2] for 2 hr, sodium 4-(mercaptoacetamido)benzene sulphonate[3] and *o*-hydroxythiobenzhydrazide[4] for 15–20 min. In the present paper we have investigated the reaction of platinum(IV) with trifluoperazine dihydrochloride (TFP), 10-[3-(4-methyl-1-piperazinyl)propyl]-2-trifluoromethane phenothiazine dihydrochloride and propose TFP for the rapid spectrophotometric determination of platinum(IV). The method offers the advantages of simplicity, rapidity, reasonable selectivity and determination at room temperature without the need for heating or extraction.

EXPERIMENTAL

Reagents

TFP solution. A 1% aqueous solution of TFP was prepared and stored in an amber bottle in a refrigerator.

Platinum solution. A stock solution of platinum was prepared by dissolving a known weight of platinum wire (99.99% pure) in hot *aqua regia* and the solution was evaporated almost to dryness. The residue was treated with 5 ml of conc. hydrochloric acid and evaporated to a small volume. This treatment was repeated five times in order to destroy any nitroso complexes formed. The residue from the final evaporation was then dissolved and diluted to 1 litre with 1*M* hydrochloric acid. The stock solution was further diluted as needed.

Buffer solutions. Walpole buffer solutions in the pH range 0.65–5.2 were prepared from 1*M* sodium acetate and 1*M* hydrochloric acid.

All other reagents were analytical grade and were used without further purification.

Procedure

Transfer the sample solution containing 12.5–200 μg of platinum to a calibrated 25-ml standard flask. Add 5 ml of sodium acetate–hydrochloric acid buffer, 1.5 ml of 0.1*M* copper(II) sulphate solution and 5 ml of 1% TFP solution. Dilute the solution to the mark with doubly distilled water. Mix the solution thoroughly and after 13 min measure the absorbance at 504 nm against a reagent blank prepared under similar conditions. Calculate the platinum concentration of the sample by reference to a previously prepared calibration curve.

RESULTS AND DISCUSSION

TFP is highly soluble in water. It forms a bluish-green complex with platinum(IV) in sodium acetate–hydrochloric acid buffer containing copper(II) catalyst at room temperature (27°). The complete complexation takes place in 13 min. The absorbance remains constant for 4 hr and then gradually decreases. The absorption spectra of the platinum–TFP complex, reagent blank and platinum(IV) are shown in Fig. 1. The complex gives maximum absorption at 504 nm where TFP, copper(II) and platinum(IV) have little absorption.

The effect of pH on the colour reaction was studied with a solution containing 125 μg of platinum and 3 ml of 1% TFP in 25-ml standard flasks. The maximum absor-

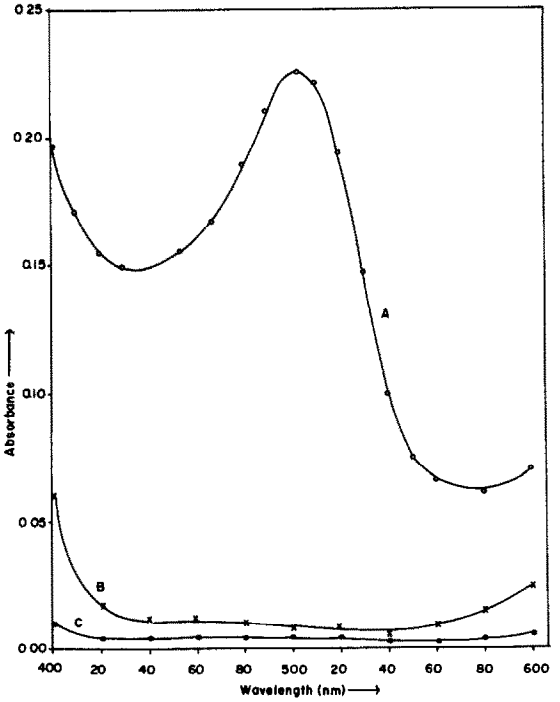


Fig. 1. Absorption spectra of platinum–TFP complex, reagent blank and platinum.

(A) Platinum(IV)–TFP complex in sodium acetate–hydrochloric acid buffer, pH 2.3, containing 1500 ppm of Cu(II) (concentration of platinum = 5 ppm).

(B) Reagent blank in sodium acetate–hydrochloric acid buffer, pH 2.3 containing 1500 ppm of Cu(II) (concentration of TFP = $1.7 \times 10^{-3}M$).

(C) Platinum(IV) in sodium acetate–hydrochloric acid buffer, pH 2.3.

Table 1. Effect of diverse ions on the determination of platinum. Amount of Pt(IV) taken: 5 ppm.

Ion added	Tolerance limit, *ppm*	Ion added	Tolerance limit, *ppm*
Fluoride	2.4×10^3	Au(III)	0.5
Chloride	7.0×10^3	Pd(II)	1
Bromide	1.5×10^3	Pd(II)	4*
Iodide	4	Rh(III)	60
Nitrate	8.0×10^3	Ir(III)	60
Phosphate	1.0×10^3	Ru(III)	1
Sulphate	1.2×10^4	Ru(III)	3†
Acetate	1.0×10^3	Os(VIII)	123
Oxalate	80	Fe(III)	1
Citrate	2.0×10^3	Fe(III)	5§
Tartrate	2.0×10^3	Pb(II)	110
DMG	100	Co(II)	450
EDTA	2.0×10^3	Ni(II)	250
		Ag(I)	2
		Zn(II)	3.2×10^3
		Cd(II)	1.0×10^4
		Al(III)	1.3×10^3
		Cr(III)	80
		Se(IV)	2.1×10^3
		Te(IV)	103
		Ti(IV)	240

* In the presence of 100 ppm of dimethylglyoxime.
† In the presence of 2000 ppm of EDTA.
§ In the presence of 2000 ppm of citrate or tartrate.

bance of the complex remained constant over the pH range 1.65–3.4. At pH values greater than 3.4, the maximum absorbance of the complex decreased and a buffer medium of pH 2.3 was therefore selected for all measurements.

The effect of reagent concentration was examined by measuring the absorbance of solutions containing 5 ppm of platinum and various amounts of TFP. A 50-fold ratio of reagent to metal ion was necessary for complete complex formation. The order of addition of reagents was not critical. The absorbance values remained constant over the temperature range 6–50°, but decreased with rise in temperature above 50°.

Effect of copper(II) concentration

The complex is formed only in the presence of copper(II), which does not react with TFP but catalyses its reaction with platinum(IV). The optimum concentration of copper(II) is 1500–3500 ppm. With less than 1500 ppm more time is required for the development of the maximum colour. With more than 3500 ppm, the absorbance slightly increases. A concentration of 1500 ppm of copper(II) is chosen.

The complex obeys Beer's law over the range 0.5–8 ppm of platinum. The optimum range (Ringbom plot[5,6]) is 1–7 ppm. The molar absorptivity is 6.50×10^3 l.mole^{-1}.cm^{-1}. The absorbance of ten solutions containing 5 ppm of platinum had a maximum relative error of 0.5% and a relative standard deviation of 0.3%.

Table 2. Determination of platinum in synthetic mixtures corresponding to platinum–rhodium thermocouple composition

Pt(IV) taken, *ppm*	Rh(III) added, *ppm*	Pt(IV) found*, *ppm*
1.5	0.20	1.49
3.0	0.40	3.0
5.0	0.66	5.00
7.0	0.93	7.10

* Average of ten determinations.

The effect of diverse ions which often accompany platinum was studied with 5 ppm of platinum. An error of 2% in the absorbance was considered tolerable. The results presented in Table 1 show that platinum can be selectively determined in the presence of a large excess of many anions and cations, but gold, palladium, ruthenium, silver, iron(III) and iodide interfere seriously.

The continuous variation, mole-ratio and slope-ratio methods indicate the formation of a 1:1 complex between the metal and the reagent. The apparent stability constant of the complex as evaluated by the mole-ratio method has the value log $K = 5.17 \pm 0.1$ at 27°. Ion-exchange studies show the complex is cationic.

Determination of platinum in Pt–Rh mixtures

Synthetic mixtures corresponding to platinum–rhodium thermocouple compositions were prepared and the platinum content was determined by following the procedures. The results are given in Table 2.

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REFERENCES

1. E. E. Rakovskii and B. S. Rabinovich, *Izv. Sib. Otdel. Akad. Nauk SSSR, 1970* (9), *Ser. Khim. Nauk* (4), *98*; *Ref. Zh. Khim., 1971*, (5) *19GD Abstr. No. 5G28.*
2. S. K. Sandhwani and P. R. Singh, *Talanta*, 1973, **20**, 248.
3. C. S. Bhandari, M. R. Bhandari and N. C. Sogani, *J. Inst. Chem., India*, 1969, **41**, 254.
4. P. K. Gangopadhyay, H. R. Das and S. C. Shome, *Anal. Chim. Acta*, 1973, **66**, 460.
5. A. Ringbom, *Z. Anal. Chem.*, 1938, **115**, 332.
6. G. H. Ayres, *Anal. Chem.*, 1949, **21**, 652.

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4-AMINO-3-METHYL-5-MERCAPTO-1,2,4-TRIAZOLE AS A GRAVIMETRIC REAGENT FOR DETERMINATION OF SILVER IN SILVER COMPOUNDS, ALLOYS AND COMPLEXES

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Summary—A simple, convenient and accurate gravimetric method for the determination of silver is presented. 4-Amino-3-methyl-5-mercapto-1,2,4-triazole precipitates silver quantitatively from ammoniacal tartrate medium. The complex is weighed as $AgC_3H_5N_4S$ after drying at 120–30°. Separation of silver from a large number of cations is described. Application of the method for quantitative analysis of alloys and complexes of silver is reported. The average relative error for the range 20–70 mg of silver is ± 0.25% and the relative standard deviation at the 40-mg level is 0.2%.

We have reported the analytical use of 4-amino-3-methyl-5-mercapto-1,2,4-triazole for gravimetric determination of copper in ores, alloys and complexes.[1] We have also reported a systematic study of the structure of some metal complexes of this reagent.[2] We are now reporting further application of the ligand as a reagent for the gravimetric determination of silver in compounds, alloys and complexes. Silver is generally estimated by the conventional halide methods, but the products are photosensitive, and if chloride is used, undue excess must be avoided or formation of $AgCl_2^-$ may lead to negative errors. The conversion factors are also rather poor in terms of sensitivity. The present method is convenient, simple, accurate and free from some of the drawbacks of the chloride method.

The method is based on the quantitative precipitation of silver as a cream complex with 4-amino-3-mercapto-1,2,4-triazole in ammoniacal medium. Unlike the reagent, the silver complex is insoluble in dilute ammonia and hot water. Hence excess of the reagent and other ions are readily removed by washing with hot water. Electrolytes such as ammonium nitrate and tartaric acid coagulate the complex readily.

EXPERIMENTAL

Reagents

The chemicals used were all of analytical-reagent or chemically pure grade. The reagent was prepared by the method given in the literature.[3,4] Its probable structure is given in Fig. 1. A twice recrystallized sample was used for preparing aqueous solutions of the reagent.

The stock solution of silver was prepared by dissolving a known amount of silver nitrate in doubly distilled water containing a few ml of conc. nitric acid and making up to known volume. The stock solution was standardized by the chloride method.[5] Aliquots of this solution were used for estimation.

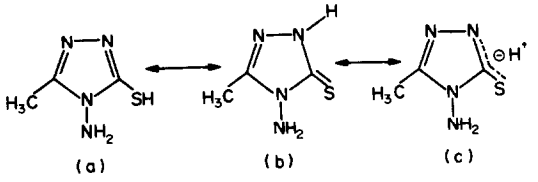


Fig. 1.

Solutions of various metal ions were prepared by dissolving the nitrates or sulphates to give concentrations of 4–5 mg/ml in water containing a few drops of the appropriate acid.

Various alloys of silver with standard compositions were prepared by melting the desired amounts of the constituent metals in an electric furnace and stirring well for homogeneity. The cooled alloys were well polished, washed with water and air-dried.

Procedure

In a 250-ml beaker, an aliquot of the stock solution containing 20–30 mg of silver was diluted to about 100 ml, followed by the addition of 2 g of tartaric acid and then ammonia solution (1 + 1) till the solution became clear and distinctly ammoniacal. The solution was then heated to 80° and a hot 1% solution of the reagent was added in slight excess. A cream coloured precipitate was formed. It was digested on a water-bath for about 40 min, filtered off on a previously weighed porosity-4 sintered-glass crucible, washed repeatedly with hot water and dried at 120–130° to constant weight.

Effect of diverse ions

Various metal ions were added to study their potential interference in the quantitative precipitation of silver. To a solution containing 20.00 mg of silver were added solutions containing different foreign ions, followed by 2–3 g of tartaric acid and then silver was estimated as described above. In the case of Cu(II) and Cd, EDTA was used as masking agent. The results are given in Table 1.

Application to silver alloys and complexes

The method described is suitable for the analysis of silver alloys and silver complexes. The results are reproducible and accurate and compare well with those for the chloride method.

Procedure for silver alloys. A known amount of the alloys in the form of turnings was dissolved in nitric acid (1 + 1) and made up to known volume. Aliquots of these solutions were used for standardization by the chloride method and

Table 1. Determination of silver in presence of various metal ions (silver present in solution = 23.48 mg)*

Foreign ion	Quantity of foreign ion added, mg	Silver found, mg	Error, %
Pb(II)	50	23.40	−0.3
	100	23.40	−0.3
Bi(III)	50	23.53	+0.2
	100	23.57	+0.4
Cd(II)†	50	23.44	−0.2
	100	23.40	−0.3
Cu(II)†	50	23.40	−0.3
	100	23.40	−0.3
Hg(II)	50	23.40	−0.3
	100	23.49	0.0
Al(III)	50	23.44	−0.2
	100	23.40	−0.3
Fe(III)	50	23.49	0.0
	100	23.49	0.0
Zn(II)	50	23.44	−0.2
	100	23.44	−0.2
Ni(II)	50	23.44	−0.2
	100	23.49	0.0
Co(II)	50	23.40	−0.3
	100	23.40	−0.3
Mn(II)	50	23.44	−0.1
	100	23.44	−0.1
Mg(II)	50	23.49	+0.0
	100	23.57	+0.4

* Found by chloride method.
† Disodium salt of EDTA was added as masking agent.

Table 2. Determination of silver in alloys and complexes

Sample	Ag present, %	Ag found, %
Silver rich alloy (Ag–Cu)	71.80*	71.5
Silver rich alloy (Ag–Cu)	89.50*	89.6
Copper rich alloy (Ag–Cu)	9.99*	10.1
Silver brazing alloy (Ag–Cu–Zn)	48.85*	48.8
$Ag(C_3H_5N_4S)$†	45.55	45.4
$Ag(C_2H_3N_4S_2)$§	42.35	42.0
$Ag(C_5H_9N_4S)$‡	40.74	40.6
$Ag(C_2H N_2S_3)$¶	42.00	41.7

* Found by chloride method.
† Silver complex of 4-amino-3-methyl-5-mercapto-1,2,4-triazole.
§ Silver complex of 4-amino-3,5-dimercapto-1,2,4-triazole.
‡ Silver complex of 4-amino-3-propyl-5-mercapto-1,2,4-triazole.
¶ Silver complex of 2,5-dimercapto-1,3,4-thiadiazole.

Table 3. Analysis of the reagent and its silver complex

		C, %	H, %	N, %	S, %	Ag, %
$C_3H_6N_4S$	Calcd.	27.69	4.62	43.08	24.62	—
	Found	27.8	3.9	42.8	24.5	—
$Ag(C_3H_5N_4S)$	Calcd.	15.20	2.11	23.64	13.51	45.51
	Found	15.2	2.1	23.0	13.3	45.4

Table 4. The positions (cm^{-1}) and assignments of major infrared bands in the spectra of the ligand and the silver complex

Ligand	Ag(I) complex	Assignment
3100–3200 mg (multiple bands)	3100 mg 3070–95 (two bands)	ν(N–H)
2540 sh	—	ν(S–H)
1632 sld	1610–20 S	Thioamide band(I)*
1610 sld		
1580 S		
1322 S	1360 S	Thioamide band II†
1044 S	1010 S	Thioamide band III§
1027 sld		
750 S	670 S	Thioamide band IV‡
—	405 sh	ν(Ag–N)
—	350 m	ν(Ag–S)

* Due to S(N–H) (major contribution + ν(C=N) (minor contribution).
† Due to ν(C=N) (major contribution) + ν(C–N) (minor contribution).
§ Due to ν(C–N) (major contribution) + ν(C=S) (minor contribution).
‡ Due to ν(C=S).
S = strong, sh = sharp, sld = shoulder, m = medium, and b = broad.

for estimation by the method described. The results are given in Table 2.

Procedure for silver complexes. A known weight of the complex was decomposed by repeated heating with conc. nitric acid, then the solution was evaporated to dryness and the residue taken up in dilute nitric acid and the silver estimated as described. The results are given in Table 2.

Analysis of the reagent and complex

The reagent and the complex were analysed for C, H and N by micro methods and the sulphur content was estimated by the sulphate method[5] after fusion with alkali. The silver was determined by the chloride method after decomposition of the complex with conc. nitric acid. The results are given in Table 3.

RESULTS AND DISCUSSION

Accuracy and precision

In five determinations over the range 20–70 mg of silver from pure silver solution, there was an average bias of −0.2%, and the relative standard deviation at the 40-mg level was 0.2%.

Effect of other ions

The determination of silver in ammoniacal tartrate medium is possible in the presence of Pb(II), Hg(II), Bi, Fe(III), Al, Ni, Mn(II), Co(II), Zn, and Mg. The interference of Cu(II) and Cd can be overcome by the addition of 1 g of the disodium salt of EDTA as masking agent.

Characteristics of the complex

The complex decomposes sharply at 235°. The weight of the complex remains constant up to at least 170°. Hence the complex can conveniently be dried at 120–130°.

The analytical data given in Table 3 show that a 1:1 complex is formed. The conversion factor is 0.4551.

Comparison of the infrared spectrum (KBr disc, Beckman IR-12 instrument) with that of the ligand showed that the band due to ν(S–H) at about 2500 cm^{-1} in the spectrum of the ligand was totally absent in the spectrum of the complex, thus indicating that the thiol group was deprotonated, as required for charge balance. This might suggest bonding of silver with the thiol sulphur of the ligand. This bonding scheme is reasonable because Ag^+ and RS^- are a *b*-class acid and base respectively and such bonding is in conformity with the hard and soft acid and base theory.[6–9] Further evidence for the type of bonding came from shifts in the positions of the major bands, particularly the thioamide bands I, and II, III and IV.[2] The bonding scheme is given in Fig. 2.

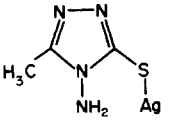


Fig. 2.

The insolubility of the complex in water suggests that the complex is polymeric as indicated in Fig. 3. An alternative is a linear polymer.

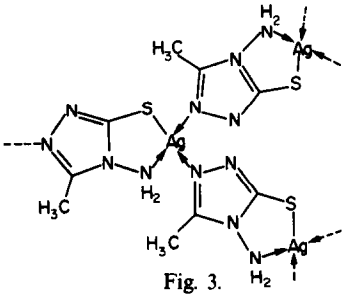


Fig. 3.

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REFERENCES

1. R. V. Gadag and M. R. Gajendragad, *J. Indian. Chem. Soc.*, in the press.
2. *Idem, Indian J. Chem.*, in the press.
3. L. F. Audrieth, E. S. Scott, P. S. Kipper, *J. Org. Chem.*, 1954, **19**, 733.
4. K. S. Dhaka, J. Mohan, V. K. Chadha and H. K. Pujari, *Indian J. Chem.*, 1974, **12**, 288.
5. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 2nd Ed., pp. 462, 486. Longmans, London, 1951.
6. S. Ahrland, J. Chatt and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.
7. R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.
8. *Idem, Chem. Eng. News*, 1965, **43**, 90.
9. *Idem, Chem. Brit.*, 1967, **3**, 103.

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ANALYTICAL DATA

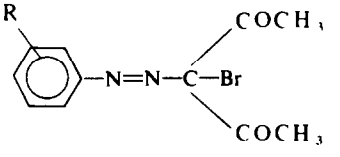
POLAROGRAPHY OF SOME 3-ARYLAZO-3-BROMOPENTANE-2,4-DIONES

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Summary—The polarographic reduction of 3-arylazo-3-bromopentane-2,4-diones has been studied at different concentrations and pH. These compounds give a single 2-electron transfer and well-defined diffusion-controlled irreversible waves. The effect of fourteen substituents (electron-donating and electron-withdrawing) has been determined. A correlation between half-wave potential and Hammett substituent-constant has been established.

The polarographic investigation of aromatic azo-compounds has been a subject of much interest[1,2] owing to their use in medicine and dyeing of textile fibres, and as powerful chelating agents. It has been reported[3,4] that highly sensitive methods for the estimation of iron, lanthanides and some other metal ions can be based on polarography using azo-compounds. A literature survey reveals that in spite of the importance of 3-arylazo-3-bromopentane-2,4-diones (*A*) as precursors of potential antidiabetic compounds,[5] no systematic polarographic studies have so far been made on them.



(*A*)

In the present paper we report our results on their polarographic behaviour, with emphasis on (*i*) the reaction path involved in the reduction at the dropping mercury electrode and (*ii*) the effect of substituents on the ease of reduction and the correlation of $E_{1/2}$ with the Hammett substituent-constant (σ).

EXPERIMENTAL

Reagents

3-Phenylazo-3-bromopentane-2,4-dione and its 2′-methyl, 3′-methyl, 4′-methyl, 2′-methoxy, 3′-methoxy, 4′-methoxy, 2′-ethoxy, 4′-ethoxy, 2′-chloro, 3′-chloro, 4′-chloro, 2′-bromo and 4′-bromo derivatives were synthesized[5] in the laboratory. All the compounds were recrystallized from ethanol and their purity was checked by TLC. Stock solutions ($1 \times 10^{-3} M$) of the compounds were prepared in methanol. Britton–Robinson buffers in the pH range 2.0–11.0 were prepared.

Apparatus

A Cambridge pen-recording polarograph was used, at 30 $\pm 0.2°$. The capillary characteristics were $1.215\,mg^{2/3} \cdot sec^{1/2}$. A saturated calomel electrode was used as reference.

Procedure

The concentration of depolarizer in the solutions to be polarographed was $2.0 \times 10^{-4} M$. For this purpose 4.5 ml of buffer, 2 ml of methanol (the minimum amount required to keep the compounds in solution), 1.0 ml of 1*M* potassium chloride and 2 ml of stock solution of the test compound were mixed by passage of a slow stream of hydrogen. Freshly prepared gelatin solution (0.005%) was used as the maximum suppressor. Polarograms were recorded after the hydrogen had been passed for about 10 min. To determine the number of electrons involved in the reduction, the waves for the $2.0 \times 10^{-4} M$ solutions of 3-phenylazo-3-bromopentane-2,4-diones were compared with those for azobenzene in Britton–Robinson buffer of pH 2.60, by the method of DeVries and Kroon,[6] using a mercury pool cathode. The temperature coefficient was calculated by Nejedly's method.[7]

RESULTS AND DISCUSSION

All the compounds are reduced in a single 2-electron step. The height of the wave is limited by diffusion, as was shown by its linear dependence on the square-root of the height of the mercury column and on concentration. The wave-height remains practically constant in the pH range 2.0–11.0 and the temperature coefficient is in the range 1.0–1.4%/deg, which further indicates the diffusion-controlled nature of the waves. The half-wave potential is linearly dependent on pH and shifts towards more negative potential with increase in pH. Values of half-wave potentials, $dE_{1/2}/dpH$ and diffusion-current constants are given in Table 1.

The course of reduction was found to be irreversible when tested by means of logarithmic plots.[8] The irreversibility was further proved by the shift in half-wave potential towards more negative potential with increasing concentration of depolarizer. At pH 2.60 a shift of 20–30 mV was observed when the concentration was changed from $1.0 \times 10^{-4} M$ to $1.5 \times 10^{-4} M$. Hillson[9] and others[10] have reported that reduction of azo-compounds at the d.m.e. takes place in a 2-electron wave, at the azo-group, giving hydrazo derivatives, unless an activating group such as $-NH_2$ or $-OH$ is present at the *p*-position in the benzene ring.[11]

The values of αn_a (product of transfer coefficient and number of electrons involved per molecule of reactant in the rate-determining step of the electrode process) and *P* (number of protons involved per molecule of reactant in the rate-determining step) were determined by using the following expressions.[12]

$$E_{1/4} - E_{3/4} = \frac{0.0517}{\alpha n_a}$$

$$\frac{dE_{1/2}}{dpH} = -\frac{0.5915}{\alpha n_a} P$$

The values of *P* are summarized in Table 1.

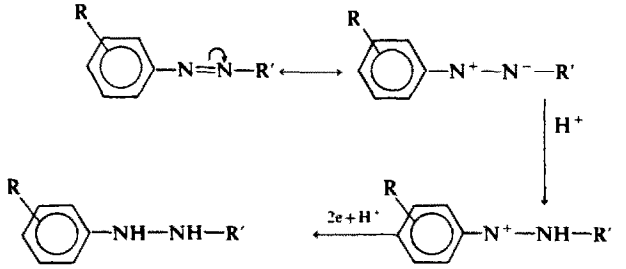
Since two electrons and one proton were found to be involved in the reduction, the following scheme—similar to

Table 1. Polarographic characteristics of 3-arylazo-3-bromopentane-2, 4-diones at pH 2.60, $C = 2.0 \times 10^{-4} M$

R	$-E_{1/2}$, V	i_d, μA	$\frac{dE_{1/2}}{dpH}$, mV/pH	αn	$\Delta E_{1/2}$, V	I*	P
H	0.69	1.57	48	0.74	0.00	6.09	0.75
2'-CH_3	0.64	1.80	52	0.80	0.05	7.44	0.75
3'-CH_3	0.69	1.87	48	0.80	0.00	7.81	0.83
4'-CH_3	0.71	1.87	52	0.74	−0.02	7.81	0.83
2'-OCH_3	0.67	1.50	48	0.72	0.02	6.00	0.83
3'-OCH_3	0.64	1.50	48	0.80	0.05	6.00	0.75
4'-OCH_3	0.71	1.65	52	0.80	−0.02	6.83	0.75
2'-OC_2H_5	0.68	1.50	52	0.74	0.01	6.00	0.75
4'-OC_2H_5	0.71	1.80	50	0.74	−0.02	7.44	0.75
2'-Cl	0.66	1.80	52	0.80	0.03	7.44	0.83
3'-Cl	0.65	1.50	52	0.80	0.04	6.00	0.75
4'-Cl	0.68	1.65	48	0.80	0.01	6.83	0.75
2'-Br	0.65	1.65	52	0.74	0.04	6.83	0.83
4'-Br	0.68	1.80	48	0.80	0.01	7.44	0.83

* $I = id/Cm^{2/3}t^{1/6}$.

that for other azo-compounds—can be proposed for the reduction:



This mechanism finds support from the increase in $E_{1/2}$ with pH, as protons are consumed in the reduction.

Effect of substituents

It is apparent from Table 1 that the values of the transfer coefficient (αn) and $dE_{1/2}/dpH$ are reasonably constant for these compounds. The conditions for applying the Hammett equation are thus fulfilled.[13] The half-wave potentials were plotted against the Hammett substituent-constants (σ). The values of σ_{o-x} used were those for the corresponding o-benzoic acids.[14] A linear relationship was found between the half-wave potentials, of the m- and p-derivatives, and the Hammett substituent-constants, and the value of the specific reaction constant is 0.10 V. The half-wave potentials for o-derivatives were corrected for the steric effect, by use of the expressions

$$\Delta E_{1/2} = \delta_{\pi,R}(E_s)_{o-x} + \rho_{\pi,R}\sigma_{o-x}$$

$$(E_{1/2})_{corrected} = [E_{1/2} - \delta_{\pi,R}(E_s)_{o-x}]$$

Values of steric substituent-constants $(E_s)_{o-x}$ were taken from the literature (cf. ref. 13). These corrected half-wave potentials for o-derivatives when combined with those for the m- and p-derivatives, gave a single regression time for the plot *vs.* σ (except for the 3'-OCH_3 derivative). The value of the specific reaction constant obtained from this plot was 0.088 V. Florence[16] and other workers[13,14] have reported similar values of specific reaction constants for azobenzene and other azo-compounds. The positive values of ρ further suggest a nucleophilic mechanism for the electrode process (electron-uptake as the potential-determining step).

Zuman[17] has reported that comparison of the half-wave potentials of o- and p-substituted derivatives gives the magnitude of the polarographic *ortho*-shift (Δ_o). The values for the methyl, methoxy, ethoxy, chloro and bromo groups in this series of compounds are all small and positive, as can be seen from Table 1.

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REFERENCES

1. T. M. Florence and Y. J. Farrer, *Aust. J. Chem.*, 1964, **17**, 1085.
2. W. U. Malik, V. K. Mahesh and R. N. Goyal, *J. Electroanal. Chem.*, 1974, **54**, 411.
3. H. Zollinger, *Azo and Diazo Chemistry*, Interscience, New York, 1961.
4. G. W. Latimer, *Talanta*, 1968, **15**, 1.
5. H. G. Garg and C. Prakash, *J. Org. Chem.*, 1970, **35**, 1056.
6. T. De Vries and J. L. Kroon, *J. Am. Chem. Soc.*, 1953, **75**, 2484.
7. V. Nejedly, *Collection Czech. Chem. Commun.*, 1922, **1**, 319.
8. L. Meites, *Polarographic Techniques*, 2nd Ed., Interscience, New York, 1965.
9. P. J. Hillson and P. P. Birnbaum, *Trans. Faraday Soc.*, 1952, **48**, 478.
10. C. R. Castor and H. J. Saylor, *J. Am. Chem. Soc.*, 1953, **75**, 1427.
11. T. M. Florence, *J. Electroanal. Chem.*, 1974, **52**, 115.
12. B. Janik and P. J. Elving, *J. Am. Chem. Soc.*, 1970, **92**, 235.
13. P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, New York, 1967.
14. H. H. Jaffe, Chem. Rev., 1953, **53**, 191.
15. M. Charton and B. I. Charton, *J. Org. Chem.*, 1971, **36**, 260.
16. T. M. Florence, *Aust. J. Chem.*, 1965, **18**, 609.
17. B. Fleet and P. Zuman, *Collection Czech. Chem. Commun.*, 1966, **32**, 2066.

NOVEL COLOUR REACTIONS FOR AMMONIUM ION IN ACIDIC SOLUTION

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During an investigation of the stability of aqueous solutions of the aldoxime HS-6, 3-carbamoyl-2'-hydroxyliminomethyl-bis(1-pyridiniomethyl) ether dichloride, a green colour and increased acidity were observed after several months of storage at ambient temperature. Among the decomposition products[1] were found 2-pyridinecarboxaldehyde, formaldehyde, and ammonium ion. In an attempt to reproduce the colour, various concentrations of these compounds were heated in mildly acidic (pH 3 phosphate buffer) solution. Although the green colour could not be obtained (blue or purple hues being produced instead), the reaction became the possible basis for an assay method for ammonium ion. The presence of ammonium ion appears to be essential, as no colour was given with various aliphatic primary, secondary or tertiary amines, quaternary salts or glycine. Substitution of 3- or 4-pyridinecarboxaldehyde for the 2-isomer yielded negative results, but 2-acetylpyridine gave a blue colour and an intense blue fluorescence.

Investigations are in progress regarding the mechanisms of these reactions and their application to trace analysis for ammonium ion. Though ammonia in aqueous medium combines with 2-pyridinecarboxaldehyde[2] to give the stable yellow trimer $(C_6H_6N_2)_3$, we found that in moderately acidic solution (pH 3) the aldehyde and ammonium ion gave a yellow solution and precipitate that gradually turned green and then blue on standing in air. The material formed in acidic solution yielded an empirical formula of $C_{30}H_{21}N_7$ and an experiment with $^{15}NH_4Cl$ indicated that the product incorporated two nitrogen atoms derived from the ammonium chloride.

When formaldehyde was heated with 2-pyridinecarboxaldehyde and ammonium ion, a deep blue colour rather than a yellow precipitate resulted. It is suspected that the ammonium ion initially condenses with formaldehyde to give Werner's[3] postulated methyleneimine $CH_2{=}NH$, which then combines with the pyridine compound.

These reactions are of considerable analytical interest as the two most widely used colorimetric methods for the determination of ammonia (Nessler and indophenol) are run in basic solution where such ammonia-producing compounds as oximes and amides are most labile. Preliminary results indicate that the colour of ammonium ion and formaldehyde with 2-pyridinecarboxaldehyde (550 nm) or the fluorescence with 2-acetylpyridine (excitation 340 nm, emission 440 nm) are comparable in sensitivity to the aforementioned methods. The sensitivity appears to be optimum at a pH of 3, with heating for about 20 min at 100° and formaldehyde and pyridine compound concentrations of 0.5M and 0.005M, respectively.

Also under study are various substituted pyridine, quinoline or other aza-aromatic aldehydes and ketones, not only for enhancing sensitivity, but for obtaining a clearer picture of the mechanisms involved.

REFERENCES

1. I. Christenson, Acta Pharm. Suecica, 1972, 9, 323.
2. G.H. Lenart, Ann. der Chemie, 1915, 410, 101.
3. E.A. Werner, J. Chem. Soc., 1917, 111, 846.

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SPECTROSCOPIC STUDIES OF THE METAL COMPLEXES OF ETHYLENEDIAMINETETRA-ACETIC ACID IN AQUEOUS SOLUTION

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Summary—Aqueous solutions of the metal complexes of ethylenediaminetetra-acetic acid (EDTA) are widely used in analysis; though X-ray diffraction methods cannot be directly used for structural determination in solution, ultraviolet–visible region, vibrational and NMR spectroscopy studies demonstrate that the species in solution adopt a similar range of stereochemistries to those determined for the solid state. Thus a review of the spectroscopic properties of the solutions suggests that chelates are formed in which the denticity of EDTA varies from one to six and the co-ordination number about the metal from four to nine.

In a previous article we discussed the structural properties of a representative series of the metal complexes formed by ethylenediaminetetra-acetic acid (EDTA, H_4Y).[1] It was observed that X-ray diffraction structural determinations had demonstrated the existence of stereochemistries in which the denticity of EDTA varied from two to ten, and in which the metal-ion co-ordination number ranged from four to ten. In this second article we wish to relate some of the structural features which have been established for the solid state to the stereochemistries adopted by EDTA and its complexes in aqueous solution. In recent years the spectroscopic methods characteristic of modern chemistry have been extensively applied to the study of these solutions; corresponding emphasis will be placed on the results obtained from ultraviolet–visible, infrared, Raman and NMR spectroscopy studies. It must, however, be pointed out that despite the sophisticated techniques, such as C-13 and O-17 NMR, which have been applied, for example to Ni(II)/EDTA solutions, there remains considerable discordance in the interpretation of results.

In the previous article it was noted that there was a very extensive interest in the chemistry and applications of EDTA. There has been no decline in this interest: recent reviews have examined the use of EDTA in soil analysis,[2] and also its use as a chromogenic agent in solution analysis.[3] A review of the conformational possibilities for the EDTA ion has been presented by the eminent Russian crystallographer Porai-Koshits and his colleagues.[4] There is evidence also of continued interest in the synthesis of novel complexes of EDTA. Thus a number of Co(III) complexes of the type $[Co(H_2Y)(NH_3)_5]ClO_4$ have been prepared, and there is good evidence that they contain unidentate EDTA.[5] The hydrothermal syntheses of the first EDTA complexes of osmium have also been reported.[6]

EDTA AND COMPLEX FORMATION IN SOLUTION

In aqueous solution EDTA reacts immediately with the majority of metal ions to form complexes which exist in equilibrium with the component ions:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(4-n)-} \quad (1)$$

The stability constant for complex formation can be expressed as:

$$\beta = \frac{[MY^{(4-n)-}]}{[M^{n+}][Y^{4-}]}. \quad (2)$$

For most metal ions this equilibrium lies far to the right. Tabulations of the stability constants of EDTA complexes are available[7] and clearly demonstrate why EDTA is so widely used as a complexing agent.

The simplest type of structure found for EDTA metal complexes in the solid state has sexidentate EDTA and the metal ion six-co-ordinate.[1] Structural deviations from this configuration are determined by a variety of factors including ligand geometry and ionic radius. Similar considerations apply in solution, where the complexes may incorporate solvent water molecules into the co-ordination sphere of the metal ion. There is a very extensive discussion in the literature concerning two distinct possibilities, namely the existence of seven-co-ordinate species in which EDTA remains sexidentate with the seventh site occupied by water, and the alternative six-co-ordinate species in which a water molecule displaces one metal–carboxylate bond. Schwarzenbach[8] ascribed the presence of titratable hydrogen ions in solutions containing Cr(III) and EDTA to the existence of $Cr(H_2O)Y^-$ species. He also suggested[9] that since many EDTA–metal complexes could be protonated at about the same pH (~3), it appeared that in these complexes one carboxylate group was free and the EDTA quinquedentate, with a water molecule occupying the sixth co-ordination position. Thus the presence of a free

carboxylate group in all these solutions led to protonation at about the same pH.

There is evidence for the formation of hydroxyl complexes at high pH:

$$MY^{(4-n)-} + OH^- \rightleftharpoons M(OH)Y^{(5-n)-}$$

This process is most evident for Co(III) and other tervalent ions which readily form hydroxy complexes; these have been extensively studied in solution, and also isolated as solids.[10] This class of non-labile complex affords the maximum opportunity for the detection of hydroxy-species and their presence has also been inferred in studies of Co(II) and Ni(II)/EDTA solutions.[11] The same lability can occur in the mixed-ligand complexes formed with other anions: Co(III)–EDTA complexes containing Cl^-, Br^- and NO_2^- as ligands have been isolated from solution;[12] Schwarzenbach[9] has also reported the presence of species such as $NiY(SCN)^{3-}$ in aqueous solution, but their isolation as complexes has proved more difficult. Similarly species containing neutral ligands, *e.g.*, $NiY(NH_3)^{2-}$, have been detected in solution. This particular group of complexes is less frequently observed (or possibly studied!); it is however well-established that Hg(II)/EDTA solutions react with ammonia, and that the equilibrium

$$HgY^{2-} + NH_3 \rightleftharpoons HgY(NH_3)^{2-}$$

favours complex formation.[13] Hg(II)/EDTA solutions appear to have somewhat special properties which will be discussed later.

All metal–EDTA complexes undergo reaction with protons at low pH. Stability constants for the addition of one proton:

$$MY^{(4-n)-} + H^+ \rightleftharpoons MHY^{(3-n)-}$$

have been extensively determined.[7] Study of the addition of a second proton is difficult because of the low solubility of the products. The materials which crystallize from metal–EDTA solutions at low pH demonstrate that there are two possibilities: for systems with high stability constants, species such as $H_2CuEDTA$[1] separate from solution. For complexes with lower stability constants dissociation takes place. Thus under the appropriate conditions products containing uncomplexed H_2Y^{2-} separate from solutions containing alkali metal ions or Mg^{2+} and EDTA. It appears however that the slightly stronger Ca^{2+}–EDTA complex does not dissociate, and that solid $CaH_2Y.3H_2O$ contains H_2Y^{2-} in complexed form.[14]

The stability constants for alkali-metal/EDTA solutions have been determined[7] and indicate that in aqueous solution the species are almost wholly dissociated; in view, however, of the extensive use which is made of these solutions in analysis, considerable interest attaches to the conformation of the ions present at various pH-values.

Although most metal EDTA complexes involve discrete metal ions, other metal-containing species are known to form complexes. Particularly notable are the oxo-species such as VO_2^+, MoO_2^+ and MoO_3 which undergo the reactions:[1]

$$VO_2^+ + Y^{4-} \rightleftharpoons VO_2Y^{3-}$$

$$2MoO_3 + Y^{4-} \rightleftharpoons (MoO_3)_2Y^{4-}$$

The formation of binuclear complexes is not unique to MoO_3 and a number of more or less complex species of this type have been postulated to exist in solution. Thus it has recently been suggested that mixed binuclear species containing complexed zirconium and neodymium ions are formed in EDTA solution.[15] In contrast, Schwarzenbach[9] has demonstrated that displacement reactions such as:

$$MgY^{2-} + Co^{2+} \rightleftharpoons CoY^{2-} + Mg^{2+}$$

are governed by the relative stabilities of the complexes concerned.

A great many papers have been devoted to gaining an understanding of the various solution species outlined above. Systems such as Pd(II)/EDTA[16] and Ni(II)/EDTA[17] have attracted the attention of numerous authors, who have used a wide variety of techniques. However, spectroscopic methods afford particular advantages in that they provide the most direct insight into the nature of EDTA/metal species; in turn a brief examination of the peculiar advantages of these techniques provides a necessary background to their application in the study of EDTA complexes in solution.

SPECTROSCOPIC METHODS FOR THE STUDY OF EDTA/METAL SOLUTIONS

Ultraviolet–visible region spectroscopy

This was the first spectroscopic method to be used for the study of EDTA complexes in aqueous solution. Bhat and Krishnamurthy[11] briefly surveyed some of the earlier observations, in the introduction to their paper which reported the ultraviolet–visible region spectra of the EDTA complexes of Co(II), Ni(II) and Cu(II) at various pH-values. The method has considerable value for the identification of new species in solution on the basis of change of absorbance and wavelength of absorption, particularly for bands arising from *d–d* or charge-transfer transitions. The interpretation of the spectra has been widely discussed.[18] The method is restricted by the nature of the origin of the electronic transitions involved, and the structure of the species cannot usually be derived directly from the spectrum alone. The spectra may, however, demonstrate that a complex of known crystal structure persists in solution. In addition the spectra can be used to obtain stability constants or kinetic data which in turn may be used to infer probable structures. The derivation of the results can involve complex arguments and require extensive study of the complexes formed by aminocarboxylic acids related to EDTA; the method is typified by the work of Higginson and Samuel.[19] More recently Kloosterboer[20]

has correlated data from ultraviolet–visible, infrared and NMR spectroscopy studies of a group of complexes in aqueous solution. This approach is likely to be more fruitful, since in the past notably different conclusions have been drawn from separate studies of one species by different techniques.

Vibrational spectroscopy

Full analysis of the vibrational spectra of EDTA and its complexes is made difficult by their structural complexity; however, from the study of various characteristic group frequencies, structural information can be inferred. Both infrared and Raman spectroscopy have been used; the former offers the advantage of simplicity of application for the solid complexes, but is limited for H_2O solutions because of the strong absorption by the solvent. For D_2O solutions the existence of an infrared transmission "window" in the 1700–1600 cm^{-1} region allows study of the important ν_{as} carboxyl(ate) vibrations of the complexes in solution. The method requires that thin films of concentrated solution be mounted between CaF_2 windows.[21] Raman spectroscopy allows detailed study of the vibrational spectra of solids and of solutions in both H_2O and D_2O. Normally, the ν_{as} vibration of the carboxyl(ate) groups is weakly Raman-active and for H_2O solutions coincides with a Raman-active vibration of water; however, other regions of the spectra provide useful correlations.

Characteristic spectral regions. The various regions of vibrational absorption which are observed may be discussed in terms of the origin of the vibrational mode, and in order of decreasing transition energy. In the following brief survey consideration is given to data obtained from both the solid species and their aqueous solutions.

ν_{C-H} *stretching frequencies (3050–2800 cm^{-1}).* The ν_{C-H} vibration of the methylene and ethylene groups of free and complexed EDTA species are weakly infrared-active but strongly Raman-active. Sawyer[22] suggests that the presence of infrared-active ν_{C-H} bands close to 3000 cm^{-1} is characteristic of uncomplexed EDTA species which are *N*-protonated, and that complete deprotonation results in the appearance of new bands near to 2800 cm^{-1}, together with the corresponding disappearance of absorption at wavenumbers above 3000 cm^{-1}. A study of the Raman spectra of aqueous solutions of the sodium salts of EDTA[23] confirms these wavenumber shifts. For complexed EDTA species ν_{C-H} occurs between 2900 and 3000 cm^{-1} and there is a general decrease in frequency with increasing ionic radius of the metal.[24]

Carboxyl(ate) asymmetric stretching frequencies (1750–1550 cm^{-1}). The asymmetric stretching vibrations (ν_{as}) of the various types of carboxyl(ate) group found in EDTA complexes have been observed to vary systematically with the nature of the group:[21,25]

(*i*) ν_{as} CO_2H, above 1700 cm^{-1}: free carboxyl
(*ii*) ν_{as} CO_2H, 1690–1660 cm^{-1}: co-ordinated carboxyl
(*iii*) ν_{as} CO_2^-, 1660–1620 cm^{-1}: covalently bonded carboxylate
(*iv*) ν_{as} CO_2^-, 1620–1580 cm^{-1}: ionic carboxylate, either free or ionically bonded
(*v*) ν_{as} CO_2^-, 1590–1560 cm^{-1}: bridging bidentate carboxylate

As is usually the case for group-frequency assignments, exceptions to these correlations may be found.

For both the solid complexes and for their solutions in D_2O it is often possible to observe bands due to more than one type of carboxyl(ate); the infrared bands observed for some Co(III) and Pd(II) complexes of EDTA, listed in Table 1, provide typical results.

Carboxyl(ate) symmetric stretching frequency (1400 cm^{-1}). ν_{sym} of carboxyl(ate) groups is typically at about 1400 cm^{-1}, but proves to be far less sensitive to group character than ν_{as}. However, Sawyer[24] has suggested that the wavenumber separation of ν_s and ν_{as} provides an index of the covalence of the $M-O_2C$ bond.

ν_{C-C} *stretching frequencies (950–850 cm^{-1}).* For acetic acid ν_{C-C} is at 886 cm^{-1}, and for the acetate anion it is observed at 926 cm^{-1}.[26] Correspondingly, in EDTA and its complexes ν_{C-C} values in this region have been assigned to various types of acetate group. It has also been observed that there is a general correlation between ν_{as} for the carboxyl(ate) and this frequency. Thus in PdH_4YCl_2, with four free carboxyls, ν_{as} for CO_2H is at 1730 and 1707 cm^{-1}, and ν_{C-C} at 890 cm^{-1}. For Na_4EDTA with four ionic carboxylates ν_{as} for CO_2^- is at 1582 cm^{-1}, and ν_{C-C} at 932 cm^{-1}.[27] This inverse relationship has been observed for several groups of compounds but is complicated by solid-state splittings, particularly for ν_{C-C}.

Metal–ligand frequencies (600–200 cm^{-1}). There have been several studies of characteristic metal–ligand frequencies which provide a useful background to the interpretation of those of EDTA complexes.[28]

Table 1. ν_{as} for carboxyl(ate) for solid Co(III) and Pd(II) complexes (cm^{-1})

Complex	$\nu_{as}CO_2H$	$\nu_{as}CO_2M$	$\nu_{as}CO_2^-$	Ref.
$Na[CoHYCl].\frac{1}{2}H_2O$	1750	1650	—	12
$Na_2[CoYCl]$	—	1648	1600	12
$PdH_2Y \cdot 3H_2O$	1740	1625	—	16
$PdH_4YCl_2 \cdot 5H_2O$	1730, 1707	—	—	16

For the latter, by analogy with those formed by ethylenediamine, Raman-active metal–nitrogen vibrations were assigned in the 450–500 cm^{-1} region.[26] In studies of Pb(II) and Sn(II) complexes of EDTA in aqueous solution[29] metal–carboxylate vibrations were assigned in the 530–368 cm^{-1} region.

NMR spectroscopy

Numerous NMR studies of aminopolycarboxylic acids and their complexes have been reported in the literature, and the subject has been reviewed by Kostromina.[30] The detailed arguments involved in the interpretation of the NMR spectra of EDTA and its complexes are frequently complex, particularly for temperature-dependent studies, or for those involving the more exotic magnetic nuclei. In this section we discuss the more obvious factors relating to PMR studies, and when discussing individual complexes or groups of complexes draw attention to the use of C-13 or O-17 NMR where these methods have provided useful results.

PMR spectroscopy. PMR data have been reported for EDTA in aqueous solutions containing non-complexed counter-ions, and also for diamagnetic and paramagnetic complexes. The first two categories were initially studied by Kula *et al.*[31] who observed that for free EDTA ions the spectra are simple, comprising two proton resonances, with an intensity ratio of 2:1, which can be attributed to the methylene protons of the acetate groups and to the ethylene protons respectively. Separate resonances due to the "acid" protons are not observed, even at low pH, since as a result of rapid exchange their signals merge with that of H_2O in aqueous solutions, or with HOD in D_2O solution.

The simplest spectra are observed for labile diamagnetic complexes and closely resemble those of the uncomplexed EDTA ions, but for non-labile complexes the spectra may be of considerable complexity. The origins of these differences can be discussed on the basis of criteria proposed by Day and Reilley,[32] who considered the lability of the complexes relative to the time scale of NMR observation, and proposed three categories.

(*i*) Complexes in which both M–N and M–O bonds are labile.

(*ii*) Complexes in which M–N bonds are non-labile, but M–O bonds are labile.

(*iii*) Complexes in which both types of bond are non-labile.

For complexes of the first type, exchange is so rapid that the methylene protons remain equivalent, as do the ethylene protons. However, at low pH the proton signals shift with protonation of the EDTA moiety, a process which may be followed by plotting chemical shift *vs.* pH. As protonation is competitive with complexation by the metal it is then possible to derive stability constants from the data. Despite the rapid exchange which is evident, for example, in the PMR spectra of Pb(II)/EDTA solutions,[32] coupling between the magnetic metal isotopes and the EDTA protons is observed: hence the 21% of ^{207}Pb present in natural lead splits 21% of the proton signals into doublets.

For complexes of the second category decreased lability of the metal–nitrogen bonds reduces the symmetry of the ligand; and though the labile metal–oxygen bonds allow the carboxylate groups to interchange between co-ordination positions in the ethylene-ring plane, and those at right angles to it, the two methylene protons of each of the carboxylate groups become non-equivalent. As a result the two sets of acetate protons generate an AB splitting pattern. The ethylene protons remain equivalent however.

For the final category of complex, and for one in which EDTA is sexidentate, there are two types of carboxylate (corresponding to the G- and R- rings); in addition, in each type of ring the methylene protons are non-equivalent. The resulting methylene proton spectrum is typically composed of two AB patterns. These features are found in the PMR spectra of Co(III)/EDTA solutions, and in addition the ethylene resonances are also highly split.[32]

EDTA complexes with paramagnetic metal ions. The PMR spectra of EDTA–metal complexes are strongly influenced by the presence of free electron spins on the metal ion, and the proton resonance signals are shifted markedly. The spectra of several of the complexes formed between aminocarboxylic acids and Ni(II) have been studied by Pratt and Smith.[33] In turn their data have been applied to Ni(II)/EDTA solutions at varying pH and temperature.[34] Selective deuteration of the acetate methylene groups demonstrates that proton conformation is an important factor in determining the extent of the shifts. These shifts are caused both by contact interaction due to bonding and also by pseudo-contact (anisotropic) interaction. As a result, for Ni(II)/EDTA solutions the resonances due to axial and equatorial ethylene protons are widely split, and separate resonances are also observed for methylene protons with different conformations.

THE RESULTS OF SPECTROSCOPIC STUDY

Group I: Li^+, Na^+, K^+

A comparison of the PMR spectra[31] of Li^+, Na^+ and K^+/EDTA solutions with those of solutions containing the non-complexing $(CH_3)_4N^+$ ion demonstrates that both Li^+ and Na^+ inhibit protonation, since for these ions the inflection points of the PMR resonance shift (δ) *vs.* pH curves occur at lower pH than those observed for the $(CH_3)_4N^+$ solutions. The PMR data have also been interpreted as indicating initial *N*-protonation of the Y^{4-} ion (as opposed to carboxylate protonation), with both nitrogen atoms being equally protonated in HY^{3-}.[35] In contrast, infrared studies[36] on solutions in D_2O have been interpreted as indicating the deuteration of only one

nitrogen atom in DY^{3-}. Thus it was reported that at high pD where Y^{4-} is the only EDTA species present in solution, ν_{as} for the carboxylate is at 1585 cm^{-1}, and that as the solution becomes more acid a new band appears at 1620 cm^{-1}. At the pD at which titration indicates DY^{3-} attains maximum concentration both bands are observed, but for D_2Y^{2-} only the higher-frequency band remains. The 1620 cm^{-1} band was therefore attributed to the carboxylate groups adjacent to the protonated nitrogen (subsequent vibrational studies suggest, however, that this particular wavenumber region is also characteristic of a strongly hydrogen-bonded carboxylate group). It was observed that after further acidification a weak shoulder appears at 1700 cm^{-1}, characteristic of carboxylate protonation.

The ^{23}Na NMR spectra of Na^+/EDTA solutions show that resonance-shifts for the sodium accompany the monoprotonation of Y^{4-}, but that virtually no further shift occurs as the second proton is added.[37] It appears therefore that interaction between Y^{4-} and Na^+ is essentially through the nitrogen atoms and that monoprotonation minimizes chelation. The initial Raman study of these solutions was also interpreted as indicating protonation of the nitrogen atoms;[26] a subsequent study[38] supports this conclusion and also suggests that monoprotonation is symmetrical at both nitrogen atoms. Thus it was observed that the conversion of Y^{4-} into HY^{3-} in H_2O solution is accompanied by a shift of the ν_{C-H} bands, which suggests that all the methylene groups are equally affected. It appears that the HY^{3-} ion in solution has a folded configuration in solution similar to that of H_2Y^{2-} in solid K_2H_2Y,[1] with the single proton situated in a "four-co-ordinate" site. Addition of the second proton causes little change in the ν_{C-H} value, but is accompanied by splitting of the single ν_{C-C} band observed for HY^{3-}-containing solutions into two components. It appears that this splitting can be attributed to the involvement of the second pair of carboxylate groups in the formation of hydrogen bonds to the protonated nitrogen atoms. The formation of a folded configuration of this type has been suggested for the ion $HDCTA^{3-}$ (DCTA = 1,2-cyclohexanediaminetetra-acetic acid) on the basis of NMR evidence,[39] thus supporting the proposed structures of the related HY^{3-} and H_2Y^{2-} ions. It may be noted that the Raman spectra suggest that the species present in D_2O are not identical to those in H_2O solution.[26]

Group (II)A: Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}

Infrared and PMR studies of alkaline earth metal EDTA complexes in aqueous solution have been reported.[21,30,31] In D_2O the asymmetric carboxylate frequencies follow a very similar pattern to those observed for uncomplexed EDTA, indicating that in acid *N*-protonation takes place; however, complexation inhibits this process to an extent which can be related to the stability constants of the complexes. For the Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}EDTA solutions the areas of the ν_{as} peaks at 1620 cm^{-1} for CO_2^- are equal to those at 1580 cm^{-1}, at pD 4.9, 4.1, 5.1 and 5.8 respectively.[21] Thus it appears that the inhibition of *N*-protonation is maximal for Ca^{2+} solutions. The PMR spectra[31] suggest a similar conclusion: for Ca^{2+}, Sr^{2+} and Ba^{2+}/EDTA solutions single breaks are observed in the δ *vs.* pH curves, corresponding to the addition of two protons over a narrow pH range, again pointing to the inhibition of protonation by complexation. For Mg^{2+} solutions, however, no break in the δ *vs.* pH curve was observed before solid separated from the solution. The PMR spectra of this group of complexes comprise solely the two resonances typical of complexes in which both M–N and M–O bonds are highly labile. Line-broadening of these resonances in the presence of excess of ligand has been interpreted as evidence for stronger bonding between Mg^{2+} and EDTA than between Ca^{2+} and EDTA. For the former, separate resonances due to ligand and complex are reported, but for the latter rapid exchange is evident since at pH above 9.5 the resonances of ligand and complex coalesce, owing to ligand exchange.

Raman spectroscopy has confirmed that the protonation which takes place at low pH causes the Ca^{2+} complex to dissociate:[14,26] the spectrum at pH 3.8 is similar to that of the free H_2Y^{2-} ion. However, as the pH of the solution increases, a new band appears at 445 cm^{-1} which can be assigned to the vibrations of the metal–nitrogen or metal–oxygen bonds of the complex. In contrast to this evidence for dissociation in the acid solution, the solid which separates at low pH from concentrated Ca^{2+}/EDTA solutions has a vibrational spectrum which suggests that it is a complex.[14] This difference in the solid and solution species may, however, simply reflect the greater insolubility of the acid complex compared with that of the dissociation products. The species present in the Ca^{2+} and Sr^{2+} solutions in which the overall metal:ligand ratio is 3:1 have been investigated by 100-MHz PMR spectroscopy.[40] Evidence is presented for the presence in solution of binuclear calcium and strontium species involving bridging EDTA; it is suggested that each metal ion is bonded to two oxygen atoms and a single nitrogen atom, with one or more OH^- ions included in the co-ordination spheres of the metal ions.

Group (II)B: Zn(II), Cd(II), and Hg(II)

The EDTA complexes of Zn(II) and Cd(II) have infrared spectra in D_2O solution which are very similar to those of complexes with other bivalent cations, including Co(II) and Ni(II).[21] Thus for all these chelate solutions in the mid pD range, ν_{as} for CO_2^- is about 1600 cm^{-1}, indicative of complex formation. The Raman spectra of the solutions (~pH 7) in H_2O are virtually identical, suggesting that similar species are present in all the solutions.[14] The solids which can be isolated from these solutions have the stoichi-

ometry $Na_2MY.xH_2O$, and a preliminary comparison of the Raman spectra of both solids and solutions suggest that similar species are present.[14]

Acidification of the D_2O solutions of the Group (II)B chelates brings about marked changes in the spectral region corresponding to $\nu_{as.}$ CO_2^-. In Zn(II)/EDTA solutions at pD 2.2 a band at 1720 cm^{-1} is evident and has been observed to increase in intensity as pD is decreased to 0.9.[21] It thus appears that the process of protonation in this solution follows a different pattern from that observed for the Group (II)A metal/EDTA solutions. Apparently the higher stability of the Zn(II)/EDTA complex reduces the pD at which protonation is initiated, so carboxylate rather than nitrogen-atom protonation takes place. It may be envisaged that the process of protonation progressively reduces the denticity of the EDTA with increasing acidity.

The bands in the 1700–1600 cm^{-1} region of the spectrum of Cd(II)/EDTA solution demonstrate a similar pattern of protonation to that proposed for Zn(II), but for Hg(II)/EDTA in acidic D_2O solutions bands are observed at 1710, 1615 and 1595 cm^{-1}. This different vibrational pattern of the Hg(II)/EDTA complex has also been observed for Raman spectra of the alkaline H_2O solutions, which show significant deviations from the general pattern of vibrational spectra observed for Zn(II) and Cd(II), and which have been interpreted as indicating the formation of a hydroxy complex at about pH 7.[26]

In the mid-pH range the PMR spectra of the Zn(II) and Hg(II) chelate solutions resemble those observed for the Group (II)A metals. The lability of the Cd(II) complex, however, is decreased so much that the complex falls into the category of non-labile M–N bonded complexes.[32] The acetate region of the spectrum shows an AB pattern, with a superimposed ABX pattern due to the 25% of Cd isotopes with $I = \frac{1}{2}$. More recently C-13 NMR studies of this group of complexes have confirmed that rapid exchange takes place in solution (pH 6–10), since only averaged methylene-carbon peaks were observed, and only one carboxylate-carbon peak was detected.[41] A more detailed examination of the PMR spectrum of Zn(II)/EDTA solution has been reported by Kula.[42] He observed that from pH 11 to pH 13 the proton peaks show a shift with the addition of one equivalent of OH^-. It appears that this corresponds to the formation of a hydroxy complex in which the OH^- group displaces an R-ring carboxylate group. Above pH 13 rapid exchange between free EDTA species and the complex becomes evident and Kula suggests that this is due to the presence of $Zn(OH)_3^-$ species.

There is apparently a marked tendency for Hg(II)/EDTA species to form ternary systems with anions. A study of the PMR spectra of Group (II)B complexes with polyaminocarboxylic acids established that the Hg(II) complex of ethylene glycolbis(β-aminoethyl ether)tetra-acetic acid is extremely sensitive to the presence of both halide and thiocyanate ions.[43] Experimental difficulties prevented extension of these observations to EDTA complexes, but it was noted that the complexes of 1,2-cyclohexanediaminetetra-acetic acid (DCTA) were similarly sensitive. An indication of the possible types of species involved is provided by the results of potentiometric studies[44] which suggest ionic formulations such as $[HgYCl.HgCl_3]^{4-}$ for the species present in solutions containing $HgCl_4^{2-}$ and Hg(II)/EDTA; it is suggested that a chloride ion displaces an equatorial carboxylate group, and that the $HgCl_3^-$ moiety is bonded to the free carboxylate group.

Group (III): Al(III), Ga(III), In(III) and Tl(III)

Saito and Terry[45] have reported the synthesis of Group (III) EDTA complexes of the types $NaMY.4H_2O$ and MHY; they suggest that the sodium salts, which are readily soluble in water, incorporate one co-ordinated water molecule, and that this stoichiometry is retained in solution. The ready separation of $Na_2InYBr.4H_2O$ from aqueous solution suggests that other mixed-ligand complexes may also exist; investigation of possible aqueous species has, however, been restricted to studies of Al(III)/EDTA solutions.

Both the infrared and PMR spectra of Al(III)/EDTA solutions are atypical[21,31] and can probably be explained on the basis of quinquedentate complexation by EDTA, coupled with the formation of an OH^--containing ternary species; this could have a similar stereochemistry to that observed for H_2OFeHY.[1] However, other interpretations cannot be excluded, because the data are inconclusive: the possibilities have been reviewed by Howarth *et al.*[41]

Group (IV): Sn(II) and Pb(II)

The asymmetric-vibration frequencies for carboxyl(ate) and the PMR spectra of the EDTA complexes of Sn(II) and Pb(II) in aqueous solution follow the pattern reported for Zn(II).[29] Interest attaches to the stereochemical requirement of the non-bonding *s*-electrons, and their possible influence on the stereochemistry of the complexes both as solids and in solution. It has been observed that there are considerable similarities in the Raman spectra of both solids and solutions, and that these spectra may be interpreted on the basis of a $C_2v\psi$ seven-co-ordinate arrangement about the metal, with EDTA sexidentate.[29]

First row transition metals

Bivalent ions: Mn(II), Co(II), Ni(II) and Cu(II). The ultraviolet–visible region spectra of this group of EDTA complexes have been widely studied because of their utility for analytical purposes.[3] It has been observed that the spectra provide evidence for the existence of "normal" species in the mid-pH region, and for the presence of protonated forms in acid solution. There is adequate evidence also for the formation of ternary hydroxy species, and for complex formation with other anions. Somewhat surprisingly,

though the application of additional spectroscopic techniques has yielded confirmatory data for the ternary and protonated species, the precise denticity of EDTA in the mid-pH range species remains in some doubt.

The infrared spectra of the solutions follow the pattern observed for Zn(II)/EDTA; that similar carboxylate protonation is involved has been confirmed by Raman study of acidic Ni(II) and Cu(II)/EDTA solutions.[46] Though the Raman spectra of the Mn(II), Ni(II) and Cu(II) solutions have been reported[14,26] they provide no conclusive evidence for the presence or absence of co-ordinated water, or for the denticity of EDTA.

An O-17 NMR study of the rate of exchange of ^{17}O-labelled H_2O in Mn(II)/EDTA solutions[47] leads to the conclusion that a seven-co-ordinate species is present in which EDTA is sexidentate and that the stereochemistry is similar to that of Mn(II) in $Mn_3(HY)_2.1OH_2O$.[1] However, for Ni(II)/EDTA solutions, which have attracted most attention, the denticity of EDTA is described as either quinquedentate or sexidentate, depending on the method of study. Recently, Everhart and Evila[17] have concluded on the basis of temperature-dependent PMR studies that EDTA is substantially quinquedentate in Ni(II) solutions. A comparison[48] of the PMR spectra of Co(II)/EDTA solutions (~pH 7) with those containing the ions $(CoYOH)^{3-}$ and $(CoYCN)^{3-}$ similarly leads to the conclusion that the solution species present is $(CoYH_2O)^{2-}$. On balance it seems very probable that a water molecule is involved in the metal co-ordination sphere in these solutions; in addition it is not unexpected that Mn(II) should adopt a higher co-ordination number than do Ni(II) and Co(II).[1]

Tervalent ions: Cr(III), Fe(III) and Co(III). A preliminary study of the infrared spectra of Cr(III) and Fe(III)/EDTA in D_2O solution was interpreted as indicating a pH-dependent equilibrium

$$HFeY \rightleftharpoons FeY^- \rightleftharpoons [FeYOH]^{2-}$$

Subsequently, however, it was established that μ-oxo-bridged dimers are readily formed in alkaline Fe(III)/EDTA solutions;[50] the structures of the complexes present in these EDTA-containing solutions have not definitely been established, though it appears that the dimer is formed from monomeric hydrated ions. Fe(III)/HEDTA (HEDTA = *N*-hydroxyethylethylenediaminetriacetic acid) solutions are similarly dimeric, and a complex has been isolated which has been shown to have two iron moieties, each of which has quinquedentate HEDTA, linked by a μ-oxo-bridge.[50] Fe(III)/EDTA/O_2^{2-} solutions have also been studied,[51] and it is reported that they have useful oxidizing properties, particularly for organic molecules; however, no structural data are available.

A rather unstable Mn(III) complex ($KMnYH_2O \cdot 1.5H_2O$) has been isolated, and in solution has been reported to have properties analogous to those of Fe(III)/EDTA species.[52] The formation of a complex between Cr(III) and EDTA in solution is an extremely slow process[53] and the complex which is formed is non-labile. Thorneley and Sykes[54] were able to isolate $CrH_3YCl_2H_2O \cdot 3H_2O$ which appears to be stable in concentrated hydrochloric acid. The authors suggest that EDTA is terdentate in the compound and that there are also two chloride ions and a water molecule in the co-ordination sphere.

Co(III)/EDTA solutions have been extensively studied. CoY^- in aqueous solution adopts the same sexidentate six-co-ordinate conformation established for the solid RbCoY.[1] Thus the C-13 NMR spectrum[41] shows NMR shifts corresponding to distinct equatorial and axial carboxylate and methylene carbons, in addition to ethylene carbon signals. The high stability of the complexes facilitates NMR observation and in this same study detachment of a carboxylate group induced both by protonation and by excess of OH^- was demonstrated. It appears that H_2O, OH^- and Cl^- exclusively displace an equatorial carboxylate group; for Br^-, however, two isomers were detected, which probably correspond to equatorial and axial substitution.

The stability of Co(III) complexes has allowed the isolation of a complex in which EDTA is unidentate[5] and also a complex in which EDTA apparently bridges two $[Co(NH_3)_5]^{3+}$ moieties. From the reported ultraviolet–visible region spectra it appears that these species persist in aqueous solution.

Transition metal oxo species: VO_2^+ and MoO_3. The EDTA complexes of the VO_2^+ ion have been shown to have solid-state structures in which EDTA is quadridentate.[1] Earlier infrared studies[55] of the species present in D_2O indicate that similar configurations are retained in solution: for Na_3VO_2Y, the ν_{as} values for carboxyl(ate) are 1625 and 1595 cm^{-1}; for $NaVO_2HY$ they are 1711, 1626 and 1593 cm^{-1}, and for $NaVO_2H_2Y$ 1717 and 1632 cm^{-1}. Thus in solution the first complex has bands characteristic of free and complexed carboxylate groups, the second of free and complexed carboxylate and free carboxyl groups, and the third of complexed carboxylate and free carboxyl groups.

Studies of Mo(VI)/EDTA solutions show that the combining ratio of metal:ligand is 2:1, in contrast to most EDTA complexes. The PMR spectra[56] of solutions containing this ratio of Mo(VI) (in the form of molybdic acid) to EDTA have single ethylene resonances and a methylene AB quartet characteristic of stable sexidentate EDTA complexation. The solution species are probably ethylenediamine-bridged, corresponding to the structure observed for the solid complex $Na_4(MoO_3)_2Y \cdot 8H_2O$.[1]

Second and third row transition metals

Zr(IV) and Hf(IV). The complexes formed between Zr(IV), Hf(IV) and EDTA have similar stabilities to those of aqueous Co(III)/EDTA complexes and so might be expected to have similarly detailed PMR

spectra. Sawyer and Aochi[57] have observed, however, that the PMR spectra are pH-dependent and show evidence of two species in equilibrium. For both solutions at pH 3.5 a single methylene AB quartet is observed; as the pH is increased the spectra increase in complexity, but may be assigned to an equilibrium involving a second species also characterized by a methylene AB quartet. Since the complexes present are expected to be non-labile, the first quartet may be interpreted in terms of an eight-co-ordinate stereochemistry with two water molecules in the co-ordination sphere. The expansion of the co-ordination number would remove the non-equivalence of the equatorial and axial carboxylate groups, and hence the structure of the simple chelate in solution at low pH is thought to be similar to that observed for the solid EDTA–zirconium complex.[1] At higher pH it is known that hydrolysis and polymerization take place, and the nature of the species present is not clear.

Rh(III). Ezerskaya and Filiminova[58] have discussed the species present in Rh(III)/EDTA/Cl^- solutions in terms of the equilibria

$$[RhYH_2O]^- \underset{HCl}{\overset{2N}{\rightleftharpoons}} [RhHYCl]^- \underset{HCl}{\overset{6N}{\rightleftharpoons}} [RhH_2YCl_2]^-$$
(*i*) (*ii*) (*iii*)

and

$$[RhYH_2O]^- \overset{OH^-}{\rightleftharpoons} [RhYOH]^{2-}$$
(*iv*)

Their assignments of stereochemistry made on the basis of the ultraviolet–visible region spectra and other physical measurements have been confirmed by examination of infrared spectra in D_2O solutions[59] and by the PMR studies.[60]

The PMR spectrum indicates the presence of four different acetate groups—a result to be expected for a stable quinquedentate EDTA complex. However, as the pH is increased, the spectrum changes to a pattern similar to that observed for sexidentate EDTA in Co(III) solutions and it thus appears that RhY^- is formed; then, as the pH is further increased, there is evidence for the formation of (*iv*). The PMR spectrum of (*ii*) is similar to that observed for (*i*), while that of the strongly acid solutions containing (*iii*) provides evidence for the two different sets of methylene protons characteristic of a terdentate EDTA complex in which there are two bonded carboxylate and two non-bonded carboxyl groups.

Pd(II) and Pt(II). There have been several studies of the quadridentate and bidentate EDTA complexes of Pd(II).[16] It appears that in PdH_2Y EDTA is quadridentate, and it is known that in PdH_4YCl_2 it is bidentate, but there has been considerable disagreement in the literature about the interconversion of the two stereochemistries in solution. A combination of Raman, NMR, and infrared spectroscopy[16] demonstrates, however, that PdH_4YCl_2 hydrolyses in solution to a bidentate hydrate. The process of hydrolysis may be followed by Raman spectroscopy: the solid, and its solution in acetone, have Pd–Cl bands at 320 cm^{-1}, but these are not observed for aqueous solutions. The PMR spectra of acid (~pH 3) and acetone solutions are composed of similar methylene AB quartets and single ethylene resonances, and it appears that the species present are similarly characteristic of bidentate structures. In the mid-pH range the aqueous spectrum collapses to two single resonances and then at pH 11 the methylene quartet reappears. It seems probable that these changes are associated with the deprotonation of the carboxyl groups followed by the formation of a stable hydroxy species $PdY(OH)_2^{4-}$ and that at no stage is a quadridentate complex present in the solutions. The PMR spectra of PdH_2Y solutions are more complex than those of the bidentate species and are characterized by the presence of a widely split AB quartet probably associated with the co-ordinated carboxylate groups. The two sets of spectra (bidentate and quadridentate) show no evidence of equilibria and it appears that the two forms do not interconvert in solution.

The PMR spectra of the equivalent Pt(II) complexes are complex.[61] However, the spectrum of PtH_4YCl_2 in 6*M* hydrochloric acid is similar to that of PdH_4YCl_2 in acetone, and the Raman spectrum of the hydrochloric acid solution shows that the complex is present in the chloride form. At higher pH hydrolysis and deprotonation occur and the spectra cannot be satisfactorily interpreted.

The lanthanides

La(III), Lu(III) and Y(III). A simple sexidentate, six-co-ordinate EDTA complex is sterically implausible for even the smallest lanthanide ion[62] and a simple EDTA complex in aqueous solution must incorporate co-ordinated water molecules. There is evidence, however, that more complex species may also be present. Ultraviolet–visible region spectroscopic studies have suggested the existence of mixed species involving, for example, Nd(III)/Zr(IV)/EDTA dimers;[15] and ultraviolet–visible region spectra of Nd(III) and Er(III)/EDTA 1:2 complexes have been reported, in which shifts due to the displacement of water molecules by a second EDTA moiety were observed.[63]

The PMR spectra[63] of the La(III) and Y(III)/EDTA systems when excess of ligand is present have been similarly interpreted. Up to pH 7 the spectrum of the La(III)/EDTA system is composed of separate signals due to the complex LaY^- and free EDTA; however, in more alkaline solutions displacements of the proton resonances are observed, indicative of the attachment of an HY^- ion bonding through an iminodiacetate group. Similar features were observed for Y(III), but for the smallest lanthanide ion, Lu(III), there was no evidence of interaction with a second EDTA ion.

Stereochemistry in solution

The diversity of structures which have been

detected for EDTA complexes in solution are mostly explicable on the same bases as the solid state structures, though with some salient exceptions. The relationship which is apparent between many of the stereochemistries of the compounds in solution and the crystalline state must be a reflection of the same considerations of ligand geometry and ionic radius which are applicable to the solid-state complexes: a good example of the effect of increasing ionic radius is provided by the degree of hydration of the Mn(II), Zr(IV) and La(III)/EDTA complexes. It is also evident that the strain inherent in the fully sexidentate configuration of the EDTA ligand in solution is reflected by the relative ease with which one carboxylate bond is displaced. These two considerations lead therefore to a "normal" pattern of complexation in which the EDTA is intermediate (owing to rapid exchange) between quinquedentate and sexidentate, and with a variable number of co-ordinated water molecules, dependent on the ability of EDTA to "encompass" the metal ion. As in the solid state, this preferred arrangement can be modified by the spatial requirements of other species present as, for example, in VO_2^+ and MoO_3 complexes. It is interesting to note that structures were postulated for the EDTA complexes of these species in solution before those for the solid state were established; subsequent comparison has demonstrated the similarity of solid and solution species and the accuracy of prediction of the nature of the solution species. A more marginal case is provided by the complexes of Pd(II), an ion which has a well-established tendency to square planar four-co-ordinate geometry; it is a tendency which apparently dominates both solid and solution geometries of its EDTA complexes.

For complexes with stereochemistries which deviate from "normal", two different factors operate: thus the relative insolubility of solid protonated or anionic complexes allows isolation, but it is apparent that their separation is not an indication that they are the only species, or even the major species, in solution. Some care is required, therefore, before the assumption is made that solid-state stereochemistry also applies for solutions. The detection of novel species in solution is of course greatly facilitated if the complex is non-labile, and so is determination of the stereochemistry. High stability is also of importance for the synthesis of unusual stereochemistries in solution; indeed it appears that the synthesis of novel Cr(III) and Co(III) complexes is solely limited by the ingenuity of the synthesizer. Such complexes apart, it must be borne in mind that the interaction times of various spectroscopic methods may be comparable with the rate of bond breaking and making in solution; as a result "averaged" species are often detected by NMR methods.

There are few instances where solid-state complexes do not have their equivalents in solution, and *vice versa*; so much is this the case that there is little need to rehearse once again the gamut of possible solution stereochemistries. There is perhaps one notable exception to this generalization: it does appear that there is adequate evidence for the formation of several different EDTA-bridged species in solution in the presence of excess of metal ions. Though the structures of similarly bonded crystalline complexes are known, there are as yet insufficient data to confirm fully the solution stereochemistries which have been proposed.

REFERENCES

1. R. H. Nuttall and D. M. Stalker, *Talanta*, 1977, **24**, 355.
2. O. K. Borggaard, *Acta. Agric. Scand.*, 1976, **26**, 144.
3. F. Bermejo-Martínez, in *Chelates in Analytical Chemistry*, A. J. Barnard, Jr. and H. Flaschka (eds.) *Vol. 5*, Chap. 1. Dekker, New York, 1976.
4. M. A. Porai-Koshits, A. I. Pozhidaev and T. N. Polynova, *Zh. Strukt. Khim.*, 1974, **15**, 1117.
5. H. Ogino, K. Tsukahara and N. Tanaka, *Inorg. Chem.*, 1977, **16**, 1215.
6. M. Saito, T. Uehiro and Y. Yoshino, *Chem. Letters*, 1977, **7**, 809.
7. L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes, Supplement*, Chemical Society, London, 1971.
8. G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, 1948, **31**, 459.
9. G. Schwarzenbach, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 257.
10. I. A. W. Shimi and W. C. Higginson, *J. Chem. Soc.*, 1958, 260.
11. T. R. Bhat and N. Krishnamurthy, *J. Inorg. Nucl. Chem.*, 1963, **25**, 1147.
12. M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, 1956, **78**, 5178.
13. L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, The Chemical Society, London, 1964.
14. D. M. Stalker, *Ph.D. Thesis*, University of Strathclyde, 1976.
15. T. V. Ternovaya, V. P. Shelest, N. A. Kostromina and Ts. B. Konunova, *Russ. J. Inorg. Chem.*, 1975, **20**, 1779.
16. A. A. McConnell and R. H. Nuttall, *Inorg. Chim. Acta*, 1976, **19**, 253 and references therein.
17. D. S. Everhart and R. F. Evila, *Inorg. Chem.*, 1975, **14**, 2755 and references therein.
18. For example see F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd Ed., Interscience, London, 1972.
19. W. C. Higginson and B. Samuel, *J. Chem. Soc. A*, 1970, 1579.
20. J. G. Kloosterboer, *Inorg. Chem.*, 1975, **14**, 536.
21. D. T. Sawyer and J. E. Tackett, *J. Am. Chem. Soc.*, 1963, **85**, 314, 2390.
22. D. T. Sawyer and P. J. Paulsen, *J. Am. Chem. Soc.*, 1958, **80**, 1597.
23. R. H. Nuttall and D. M. Stalker, *J. Chem. Soc. Dalton*, 1977, 1884.
24. D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, 1960, 82, 4191. D. T. Sawyer and P. J. Paulsen, *ibid.*, 1959, **81**, 816.
25. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.
26. K. Krishnan and R. A. Plane, *J. Am. Chem. Soc.*, 1968, **90**, 3195.
27. A. A. McConnell, *M.Sc. Thesis*, University of Strathclyde, 1974.
28. D. M. Adams, *Metal-Ligand and Related Vibrations*, Arnold, London, 1967.

29. A. A. McConnell and R. H. Nuttall, *Spectrochim. Acta*, 1977, **33A**, 459.
30. N. A. Kostromina, *Russ. Chem. Rev.*, 1973, **42**, 261.
31. R. J. Kula, D. T. Sawyer, S. I. Chan and C. M. Finley, *J. Am. Chem. Soc.*, 1963, **85**, 2930.
32. R. J. Day and C. N. Reilley, *Anal. Chem.*, 1964, **36**, 1073.
33. L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, 1969, **65**, 915.
34. L. E. Erickson, D. C. Young, F. F. L. Ho, S. R. Watkins, J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, 1971, **10**, 441.
35. J. L. Sudmeier and C. N. Reilley, *Anal. Chem.*, 1964, **36**, 1698.
36. K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, 1963, **85**, 309.
37. T. L. James and J. H. Noggle, *ibid.*, 1969, **91**, 3424.
38. Ref. 23 and R. H. Nuttall and I. Thom, unpublished observations.
39. Y. Fujiwara and C. N. Reilley, *Anal. Chem.*, 1968, **40**, 890.
40. D. E. Leyden and J. F. Whidby, *Anal. Chim. Acta*, 1968, **42**, 271.
41. O. W. Howarth, P. Moore and N. Winterton, *J. Chem. Soc. Dalton*, 1974, 2271.
42. R. J. Kula, *Anal. Chem.*, 1965, **37**, 989.
43. G. H. Reed and R. J. Kula, *Inorg. Chem.*, 1971, **10**, 2050.
44. E. V. Shemyakina, A. Y. Fridman and M. N. Dyatlova, *Russ. J. Inorg. Chem.*, 1976, **21**, 497.
45. K. Saito and H. Terry, *J. Chem. Soc.*, 1956, 4701.
46. R. H. Nuttall and D. M. Stalker, *Inorg. Nucl. Chem. Letters*, 1976, **12**, 639.
47. M. S. Zetter, M. W. Grant, E. J. Wood, H. W. Dodgen and J. P. Hunt, *Inorg. Chem.*, 1972, **11**, 2701.
48. D. S. Everhart and R. F. Evila, *ibid.*, 1977, **16**, 120.
49. G. McLendon, R. J. Motekaitis and A. E. Martell, *ibid.*, 1976, **15**, 2306.
50. S. J. Leppard, H. Schugar and C. Walling, *ibid.*, 1967, **6**, 1825.
51. C. Walling, M. Kurz and H. J. Schugar, *ibid.*, 1970, **9**, 931.
52. Y. Yoshina, A. Ouchi, Y. Sunoda and M. Kojima, *Can. J. Chem.*, 1962, **40**, 775.
53. P. Anderson, T. Berg and J. Jacobsen, *Acta Chem. Scand.*, 1977, **A31**, 219.
54. R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc. A*, 1969, 742.
55. P. Petráš, J. Podlohová and J. Podlaha, *Collection Czech. Chem. Commun.*, 1967, **32**, 1802.
56. S. I. Chan, R. J. Kula and D. T. Sawyer, *J. Am. Chem. Soc.*, 1964, **86**, 377.
57. Y. O. Aochi and D. T. Sawyer, *Inorg. Chem.*, 1966, **5**, 2085.
58. N. A. Ezerskaya and V. N. Filiminova, *Russ. J. Inorg. Chem.*, 1963, **8**, 424.
59. R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1963, 4271.
60. B. B. Smith and D. T. Sawyer, *Inorg. Chem.*, 1968, **7**, 2020.
61. L. E. Erickson, J. W. MacDonald, J. K. Howie and R. D. Clow, *J. Am. Chem. Soc.*, 1968, **90**, 6371.
62. J. L. Hoard, B. Lee and M. D. Lind, *ibid.*, 1965, **87**, 1612.
63. N. A. Kostromina and T. V. Ternovaya, *Russ. J. Inorg. Chem.*, 1972, **17**, 825.

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APPLICATIONS OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—VI*

A COMPARISON OF SOME EXPERIMENTAL AND THEORETICAL DETECTION LIMITS

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Summary—Design details are given for a high-sensitivity Zeeman-modulated spectrometer using commercial hollow-cathode lamp sources. Experimental detection limits are given for 6 elements, and the values compared with theoretical values calculated on the basis of signals limited only by photon noise. Some conclusions are drawn regarding the sensitivity limits accessible to atomic-absorption spectroscopy with present technology.

In recent years Zeeman modulation (ZM) has been examined extensively as a means of background correction for atomic-absorption spectroscopy (AAS), and in this regard it has proved itself to be remarkably effective.[1–7] However, there is an additional aspect of the ZM technique that is of potential interest to the analytical spectroscopist but has not yet received attention, namely, its inherent ability to offer an elegant means of approaching the highest level of sensitivity which AAS, in its present form, is capable of achieving. The design and performance of a ZM spectrometer capable of reaching its theoretical sensitivity limit, and the comparison between the experimental and theoretical sensitivity of the instrument, is the subject of the present paper.

THEORY

Three major reasons have been found for the inherent sensitivity of the ZM technique.

(1) For reasons apparent in previous papers[1–7] the signal to noise (S:N) ratio of a correctly designed ZM spectrometer should be limited only by photon noise [due to cancellation of absorption noise, source noise *etc.*; see also equation (1) below]. Furthermore, the equality of the integrated total π-component and total σ-component intensities automatically ensures that photon noise is minimized; a situation which is difficult or impossible to attain with a double-beam instrument with a deuterium background-corrector.

(2) Owing to the inherent stability of a ZM spectrometer, long-term integration can be readily carried out with high accuracy, correspondingly improving the signal:noise ratio of a signal limited by photon noise.

(3) In practical terms it becomes realistic to employ, for instance, a flame atomizer in conjunction with nebulizers capable of approaching 100% efficiency of sample-delivery at high solution-uptake rates (a particular advantage in circumstances where a large volume of an analyte solution of low concentration is available). A number of such nebulizers have been described,[8–14] including apparatus capable of handling high salt concentrations.[8,12–14] However, in such cases the high matrix concentration itself imposes limitations for practical samples unless correspondingly effective background correction, such as that given by ZM, is also available.

Conditions for obtaining a signal limited only by photon noise

The calculation below is specifically applicable to the spectrometer design given by the experimental section. That is, it will be assumed that the transverse Zeeman effect is to be observed, that a birefringent modulator is to be used to rotate linearly polarized radiation by 0–90° at a frequency f, and that the spectrometer responds to radiation of a fixed linear polarization.

Let N = the number of atoms in the absorption beam, I = the intensity, k = the Beer's law absorption coefficient and S = electrical signal associated with I. On summation of the intensities for a multiplet with i π-components and j σ-components, the total π and σ intensities are given by

$$I_\pi = \sum_{l=1}^{i} {}^{0}_{\pi}I_l \exp\left[-({}^{a}_{\pi}k_l N + {}^{b}_{\pi}k_l)\right]$$

$$I_\sigma = \sum_{l=1}^{j} {}^{0}_{\sigma}I_l \exp\left[-({}^{a}_{\sigma}k_l N + {}^{b}_{\sigma}k_l)\right]$$

where ${}^{a}k$ is the atomic-absorption coefficient, and ${}^{b}k$ is the background-absorption coefficient summed over all contributing sections of the optical path; ${}^{0}I_l$ is the

* Part V—G. F. Murphy and R. Stephens, *Talanta*, 1978, **25**, 223.

intensity of the i-th component of the incident radiation.

Since

$$\sum_1^i {}^0_\pi I_l = \sum_1^j {}^0_\sigma I_l$$

then

$${}^0_\pi I_l \Big/ \sum_1^i {}^0_\pi I_l = \alpha_l = \text{constant}$$

and

$${}^0_\sigma I_l \Big/ \sum_1^j {}^0_\sigma I_l = \beta_l = \text{constant}.$$

Assuming ${}^bk$ remains constant over the multiplet,

$$I_\pi/I_\sigma = \sum_1^i \alpha_l \exp[-{}^a_\pi k_l N] \Big/ \sum_1^j \beta_l \exp[-{}^a_\sigma k_l N] \quad (1)$$

$$= f(N), \text{ where } f \to 1 \text{ as } N \to 0.$$

Owing to the use of a birefringent modulator the total intensity received is given by Malus's law, *i.e.*,

$$I_{\text{total}} = I_\pi \sin^2 2\pi ft + I_\sigma \cos^2 2\pi ft$$

$$= \tfrac{1}{2}(I_\sigma + I_\pi) + \tfrac{1}{2}(I_\sigma - I_\pi)\cos 4\pi ft. \quad (2)$$

The two terms on the right-hand side of (2) correspond respectively to a d.c. and an a.c. electrical signal (S_{DC} and S_{AC} below), and hence may be separated by suitable circuitry.

Therefore provided equal amplification is applied to both signals,

$$(S_{DC} - S_{AC})/(S_{DC} + S_{AC}) = I_\pi/I_\sigma = f(N) \quad (3)$$

Equation (3) thus represents the required condition of an analytical signal dependent on N as the only unknown variable.

It should be noted, however, that although equation (3) requires the division $(S_{DC} - S_{AC}/(S_{DC} + S_{AC})$, and the present instrument was designed around this mode of operation, the alternative approach of applying automatic gain control to the photomultiplier or preamplifier to maintain for example a constant value of the d.c. component of I_{total} is equally valid. Thus for a variable gain G,

$$G(I_\sigma + I_\pi) = c = \text{constant}$$

therefore

$$G(I_\sigma - I_\pi) = S_{AC}$$

$$= \frac{c\left\{\left(\sum_1^j {}^0_\sigma I_l \exp[-{}^a_\sigma k_l N]\right) - \left(\sum_1^i {}^0_\pi I_l \exp[-{}^a_\pi k_l N]\right)\right\}}{\left\{\left(\sum_1^j {}^0_\sigma I_l \exp[-{}^a_\sigma k_l N]\right) + \left(\sum_1^i {}^0_\pi I_l \exp[-{}^a_\pi k_l N]\right)\right\}} \quad (4)$$

$$= g(N) \text{ where } g \to 0 \text{ as } N \to 0.$$

Conditions for validity of equation (3)

Experimentally, equation (3) [or equation (4)] has been found to represent spectrometer noise cancellation down to the photon-noise level provided the following conditions are fulfilled.

(1) Radiation observed by the spectrometer must be of a fixed linear polarization, to avoid Schlieren noise due to random polarization caused by (variable) thermal gradients around the atomizer.

(2) Self-absorption noise within the source must either be negligible or else compensated for, since equation (3) does not distinguish between analyte atomic absorption and atomic absorption within the source.

(3) Source radiation must be modulated, to permit S_{DC} to be distinguished from the background emission of the atomizer.

EXPERIMENTAL

Spectrometer design—adherence to theory

The spectrometer, shown in Fig. 1, was designed around equation (3) and its associated conditions. A flame atom-reservoir was used, in conjunction with a high delivery-rate nebulizer and integration times up to 100 sec (described in more detail below) to maximize the ZM advantages already mentioned. The spectrometer design features permitting the conditions (1)–(3) associated with equation (3) to be satisfied are discussed below.

Condition (1). This is satisfied provided that (*a*) when a transverse magnetic field is used, the source and not the atomizer is Zeeman-modulated (a layout which also permits greater flexibility in the choice of atomizer); (*b*) a birefringent modulator is placed between the source and atomizer, to induce periodic polarization rotation, and a fixed linear polarizer (P_2, Fig. 1) is used to isolate one particular plane for observation by the spectrometer. This ensures that the π and σ components (sampled alternately at the modulation frequency) are affected equally by any frequency-independent but polarization-dependent optical transmission characteristics of the atomizer, provided the modulation frequency is high compared to any variations in such transmission characteristics. A fixed frequency of 100 kHz was used here: this was found to be sufficiently high for the purpose.

Condition (2). Self-absorption appeared to be ubiquitous for all the sources examined, and no satisfactory instrumental technique for its correction has been found. A brief summary of the techniques that were tried is given in Appendix 2. The method finally adopted was to insert a single 1-in. diameter quartz disc as a transmission polarizer in front of the source (P_1, Fig. 1), adjust the angle for zero instrumental output [*i.e.*, so that the net source polarization caused by excessive self-absorption by the π line(s) was exactly balanced], and rely on the natural stability of the commercial hollow-cathode lamps (HCL), used here as ZM sources, to keep the compensated degree of self-absorption constant. It is perhaps something of a tribute to the performance of modern HCLs that even under the odd conditions to which they were subject, this technique was quite satisfactory for all the elements examined except Zn.

Condition (3). This was met as usual by modulation of the lamp supply, at a modulation frequency of 340 Hz.

Spectrometer construction

Electronics. A block diagram of the electronic elements used to satisfy equation (3) and its associated conditions is given in Fig. 1. The details are not given here since the circuits used were not unusual, except for the division operation required to obtain the π:σ ratio in equation (3), and the necessity of good d.c. output stability combined

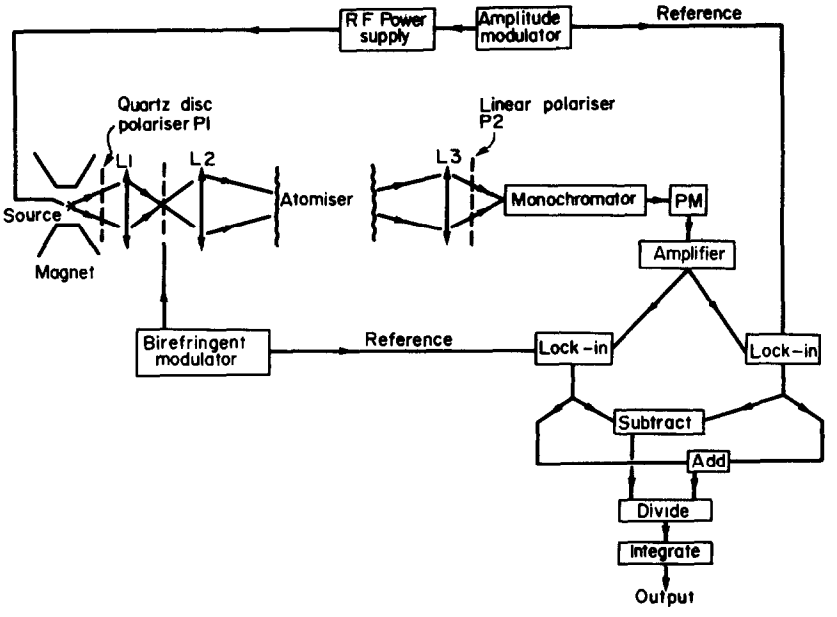


Fig. 1. Block diagram of the spectrometer.

with high amplification. The division was handled by use of a Burr–Brown 4291 K analogue divider, and the stability problem was minimized by use of high-gain a.c.-coupled amplifiers.

Optics. The optical system used is also shown in Fig. 1. Commercial HCLs were used as sources, mounted in a 4-cm magnet gap and driven as described elsewhere.[15] Owing to the necessarily fixed positions of the magnet and monochromator, and the preferably fixed positions of the atomizer and birefringent modulator, the lens L_1 was inserted to compensate for variations in the focal characteristics of the optical system with wavelength. Adjustment of the position of L_1 allowed the system to be optimized for each wavelength used.

The focal lengths of L_1 and L_2 were 5 cm and 10 cm respectively at 3000 Å; L_2 and L_3 were identical. The polarizer P_2 was a stacked reflection polarizer made of five 1-in. square quartz cover slips (Thermal American) mounted at the exit slit of the monochromator at a fixed Brewster angle of 56° in the manner described previously.[3] The monochromator was a McKee–Peterson MP 1018A. The photomultiplier was an RCA 1P28A. The birefringent modulator was a Morvue PEM 3 (Morvue Electronics, Tigard, Oregon) with a $2f$ value of 100 kHz.

Nebulizer. The nebulization system used was similar to that described by Veillon and Margoshes.[10] The version used here consisted of a Perkin–Elmer variable-uptake nebulizer delivering a sample aerosol to the heated spray chamber, with a spiral condenser for desolvation. A small capillary about 1/2 cm long and 100 μm in diameter was inserted between the condenser and burner head. The dead volume between the capillary and burner head was about 40 mL The combination of capillary and dead volume was introduced to lessen the flame perturbation due to the shock wave generated when the aerosol first entered the heating chamber. The apparatus gave about 60% sample delivery to the flame at a solution-uptake rate of 2 ml/min. Desolvation appeared to be essentially complete. Atomization was in air– or nitrous oxide–acetylene flames supported on the appropriate Varian–Techtron burner heads.

The main problem encountered with this nebulizer system was the rather lengthy wash-time required for clean-up,[16] together with an inability to use acid solvents in conjunction with certain elements (*e.g.*, Mg). This was apparently because of the continual acid leaching of these elements from the Pyrex walls of the heating chamber, which gave rise to appreciable blank signals when sub-ppM (parts per milliard; 1 in 10^9) measurements were attempted.

Operation. Optimum usage of the spectrometer was found to require a specific alignment procedure to be followed. It is felt that the procedure developed is probably of some general applicability and interest, and the variables involved and sequence of steps used are therefore given below.

Figure 2 summarizes the interdependence of the main variables involved (excluding standard parameters such as flame stoichiometry, optical alignment, *etc.*). The order of adjusting the variables was: (1) lamp current approximately, (2) burner/nebulizer parameters for optimum signal, then (3) slit-width, (4) magnetic field and (5) lamp current for optimum signal:noise ratio. After about 10 min for the system to stabilize, the angle of the self-absorption compensating polarizer P_1 was set, and the system was realigned from step (1), as necessary. Finally, the desired integration time was selected.

The experimental conditions adopted for each element by means of this procedure are summarized in Table 1.

RESULTS

The detection limits found for various elements are given in Table 1. They were determined by aspirating increasing concentrations of each analyte from 0.1 ppM upwards until a signal of about 10 times the noise level was obtained. The calibration curve was plotted from this signal down to zero, and the concentration corresponding to a signal of twice the standard deviation of the integrator output was measured.

The theoretical detection limits in Table 1 were calculated on the assumption that photon noise was the limiting factor, according to the method given in

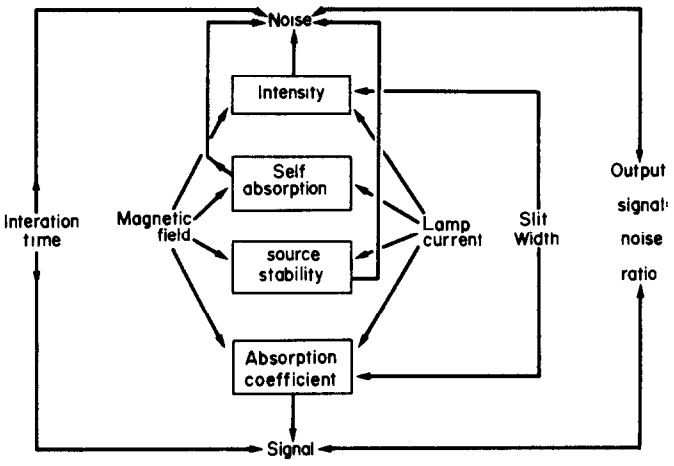


Fig. 2. Interdependence of main variable parameters.

Appendix 1. The order of determination was from the most to the least sensitive elements, as indicated by their 1% absorption values, to minimize possible contamination due to salt build-up in the heating chamber. The heating chamber was newly constructed immediately prior to the detection limit determinations.

DISCUSSION AND CONCLUSION

The comments below are directed towards the present measurements of concentration detection limits for use of flame atomization. These comments can be extended to cover concentration detection limits for non-flame atomizers, since experimental 1% absorption sensitivities have been used for the detection limit calculation in Appendix 1, and there is a considerable amount of published information on non-flame 1% absorption values.[17] It is felt unlikely that this extension will markedly affect the nature of the conclusions given.

The experimental and theoretical detection limits in Table 1 agree within a factor of about two. This is considered sufficiently good to confirm the supposition that photon-noise is the limiting factor, and thus to indicate that the spectrometer did indeed reach its theoretical sensitivity limit. In view of this agreement some further comments will be made concerning the potential analytical sensitivity of ZM instruments, and of the flame AAS technique in general.

The sensitivity found here could be slightly improved by increased integration time, decreased Zeeman factors in certain cases, or increased source intensity (although HCLs appear to have reached a plateau of development, and since the signal:noise ratio is proportional to the square root of the intensity, the large increases in intensity necessary to give useful gains in signal:noise ratio appear unlikely to be feasible). Further increase in sensitivity could also be obtained by increased nebulizer efficiency and uptake rate, but again the extent to which the 1.2 g/min conversion of solution into dry aerosol by the present system could be improved is likely to be limited. [The actual extent of sensitivity enhancements due to such causes may be estimated from equation (4), Appendix 1.] It is therefore felt that at the present performance

Table 1. Experimental conditions and detection limits

Element	Wavelength, Å	Slit-width, μm	Lamp current, mA	Magnetic field,* kG	Flame†	Theoretical detection limit, ppM		Experimental detection limit, ppM	
						t = 2.2 sec	t = 100 sec	t = 2.2 sec	t = 100 sec
Al	3093	20	12	9	N	7	1	6	2
Cu	3248	60	8	6	A	1	0.2	0.5	0.2
Fe	2483	60	14	8	A	5	0.6	10	2
Mg	2852	70	7	6	A	0.06	0.009	0.05	§
Si	2516	200	13	8	N	100	20	200	30
Zn	2139	500	13	7	A	0.3	0.05	0.2	‡

* Measured over a 4 × 4 cm area at centre of pole face.
† N = nitrous oxide–acetylene; A = air–acetylene.
§ Value not determined, owing to inability to obtain a sufficiently low blank signal.
‡ Value not determined, owing to long-term source instability (self-absorption drift).

levels of HCLs, nebulizer systems, *etc.*, major gains in sensitivity over the values found here are unlikely to be made.

It must also be pointed out that the background-correction ability of a ZM spectrometer is finite; at optimum alignment the present instrument could tolerate background to analyte absorption ratios of typically about 100:1 before a spurious absorption became apparent. Although such discrimination was adequate for the present work, the sensitivity of the instrument could not be greatly increased without its background-correction capability becoming suspect. Thus further major sensitivity enhancements, even if they were possible, would be of limited value unless a corresponding improvement of background rejection could also be achieved. This is thought likely to prove a matter of some difficulty, because, for example, of the failure of assumptions such as the invariance of ^{b}k over the multiplet.

The remarks above have been made in regard to ZM instruments. However, the magnitudes of the Zeeman factors, Z, in Table 2 (Appendix 1) are a direct measure of the sensitivity loss caused by use of Zeeman modulation relative to a hypothetical ideal double-beam instrument (the actual loss factor is approximately $Z \cdot \sqrt{2}$, since only one plane of polarization was observed here). In view of the small values of the Zeeman factors it is suggested that these comments on sensitivity limitations need not be confined to the ZM technique.

It is therefore concluded in regard to flame AAS as a general analytical method that the detection limit values in Table 1 approach a sensitivity limit inherent in our present AAS technology. Small improvements in these figures can be foreseen (although probably at the cost of considerable ingenuity), but large improvements appear unlikely without some correspondingly major development in present instrumental techniques.

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APPENDIX 1

Calculation of theoretical detection limits

Let the photon count-rate, r, $= n$ sec^{-1} at the photocathode, integration time used $= t$ sec, photocathode quantum efficiency $= q$, single-stage dynode gain $= g$, total photomultiplier gain $= G$.

From random-walk considerations, for example, the number of photoelectrons leaving the photocathode in time t is nqt with a standard deviation $\sqrt{nqt}$. Since re-emission at the dynode is also statistical, the number of electrons leaving the first stage is:

$$g(nqt \pm \sqrt{nqt}) \pm \sqrt{gnqt} = gnqt \pm (g^2 + g)^{\frac{1}{2}}\sqrt{nqt}$$

(the $\pm$ terms are standard deviations). Similarly, the number of electrons leaving the Nth stage is:

$$g^N nqt \pm (g^{2N} + g^{2N-1} + \ldots + g^N)^{\frac{1}{2}}\sqrt{nqt}$$
$$= Gnqt \pm G[(1 + 1/g + \ldots 1/g^N)nqt]^{\frac{1}{2}}.$$

Analogous formulae have been developed by other workers concerned with similar signal:noise calculations.[18,19]

At the detection limit, $r_\pi \simeq r_\sigma = n/2$ and therefore fluctuations in the difference between I_π and I_σ have a magnitude

$$\pm G[nqt(1 + 1/g + \ldots 1/g^N)]^{\frac{1}{2}}. \quad (1)$$

Let $C_{1\%}$ be the conventional 1% absorption sensitivity. Let $S_{1\%}$ be the corresponding signal. Let k_π, k_σ and k respectively be the atomic-absorption coefficients of the total π and σ intensities at the particular experimental field strength and of the zero-field line.

In a magnetic field H, for the $S_{1\%}$ signal to have the same value as before, $C_{1\%}$ must be multiplied by a Zeeman factor Z, because of the change in absorption coefficient which occurs. That is, for $(S_{1\%})_H = (S_{1\%})_{H=0}$

$$I_\pi/I_\sigma = \exp[-(k_\pi - k_\sigma)ZC_{1\%}] = (I/I_0)_{H=0} = \exp[-kC_{1\%}]$$

therefore

$$Z = k/k_\pi - k_\sigma \quad (2)$$

but

$$(S_{1\%})_H = G(nqt/2)/100 \quad (3)$$

(the factor $n/2$ occurs because only the π line(s) can carry useful atomic absorption information).

Therefore in the ZM mode the signal to standard deviation ratio, R, for $C_{1\%}$ is given by $1/Z$ times the ratio of equation (3) to equation (1), *i.e.*,

$$R = \frac{1}{Z} \times \frac{nqt}{200} \times \frac{1}{[nqt(1 + 1/g + \ldots 1/g^N)]^{1/2}}$$
$$= \frac{1}{200Z}\left(\frac{nqt}{1 + 1/g + \ldots 1/g^N}\right)^{1/2}$$

Therefore the detection limit concentration, C_{DL}, for $R = 2$ is given by

$$C_{DL} = 400ZC_{1\%}\left(\frac{1 + 1/g + \ldots 1/g^N}{nqt}\right)^{1/2}. \quad (4)$$

Table 2. Numerical values of variables used to calculate C_{DL}

Element	Z	$C_{1\%}$ *ppm*	Photomultiplier voltage, V	g	nq, *sec*$^{-1}$
Al	2.7	0.10	410	1.8	1.9×10^8
Cu	2.7	0.015	460	2.0	1.0×10^8
Fe	2.0	0.025	600	2.4	1.4×10^7
Mg	2.4*	0.0024	310	1.6	1.2×10^9
Si	1.9	0.81	510	2.1	3.9×10^7†
Zn	1.2	0.0064	490	2.1	5.9×10^7

* Anomalously high because a low magnetic field was used for optimum lamp stability.

† An extra count of 2.9×10^7 sec^{-1} was included in the calculation of C_{DL} owing to flame emission at the Si wavelength.

Experimentally, k, k_π and k_σ were obtained by a conventional measurement using the π or σ channels of the spectrometer. Values of nq and g were obtained by direct measurement of the photocathode and anode currents at high light-exposure: determination of the relative gain curve of the photomultiplier then permitted nq and g to be determined for variable incident intensities from a knowledge of only the anode current. Values found for ng, g, $C_{1\%}$ and Z are given in Table 2. These values were used to determine the theoretical detection limits in Table 1.

APPENDIX 2

Summary of possible self-absorption correction techniques

All the techniques described below were able to correct for source self-absorption and its associated noise or drift. None of the techniques was felt to be satisfactory, however, for the reasons indicated.

(1) *Sample modulation.* The maximum frequency obtained with a long-path burner was about 3 Hz. At high self-absorption levels this produced modulation noise at low integration times. In addition, the complexity of an already complicated nebulizer system was increased. A signal loss by a factor ≥ 2 is difficult to avoid.

The alternative system of switching the light beam round the atomizer (*e.g.*, by mirrored chopper blades) was not examined.

(2) *Phase-shift measurement.* With a modulated source the self-absorption and analyte signals are slightly phase-shifted owing to the finite sputtering time required to initiate the self-absorption. However, the phase shifts are not constant for all elements, and phase shifts of only a few degrees at best are produced. This requires high amplification to separate a clean analyte signal, with the result that amplification noise and the original self-absorption noise can become comparable. Modulation frequencies up to 5 kHz were examined.

(3) *Dual-beam measurements.* For these to be effective, the focal characteristics of the two optical systems must be closely matched, so that the same region of source emission is observed. The instrumental complexity of the apparatus is considerably increased, and the simplicity of alignment of the original ZM system is lost.

REFERENCES

1. T. J. Hadeishi and R. D. McLaughlin, *Science*, 1971, **174**, 404.
2. T. J. Hadeishi, *Appl. Phys. Lett.*, 1972, **21**, 438.
3. R. Stephens and D. E. Ryan, *Talanta*, 1975, **47**, 659.
4. J. B. Dawson, E. Grassan, D. J. Ellis and M. J. Keir, *Analyst*, 1976, **101**, 315.
5. H. Koizumi and K. Yasuda, *Anal. Chem.*, 1975, **47**, 1679.
6. *Idem, ibid.*, 1976, **48**, 1178.
2. *Idem, Spectrochim. Acta*, 1976, **31B**, 523.
8. A. Venghiattis, *Appl. Opt.*, 1968, **7**, 1313.
9. A. Hell, W. F. Ulrich, N. Shifrin and J. Ramirez-Muñoz, *ibid*, 1968, **7**, 1317.
10. C. Veillon and M. Margoshes, *Spectrochim. Acta*, 1968, **23B**, 553.
11. G. Uny, J. N'Guea Lotton, J. P. Tardiff and J. Spitz, *ibid.*, 1971, **26B**, 151.
12. H. J. Isaaq and L. P. Morgenthaler, *Anal. Chem.*, 1975, **47**, 1661.
13. *Idem, ibid.*, 1975, **47**, 1668.
14. *Idem, ibid.*, 1975, **47**, 1748.
15. References in G. F. Murphy and R. Stephens, *Talanta*, 1978, **25**, 223.
16. G. F. Kirkbright and M. Sargent, *Atomic Absorption and Fluorescence Spectroscopy*, Chap. 8, Academic Press, New York, 1974.
17. G. F. Kirkbright, *Analyst*, 1971, **96**, 609.
18. J. D. Winefordner and T. J. Vickers, *Anal. Chem.*, 1964, **36**, 1947.
19. J. W. McCarthy in *Spectrochemical Methods of Analysis*, J. D. Winefordner ed., Wiley, New York, 1971.

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APPLICATIONS OF THE ZEEMAN EFFECT TO ANALYTICAL ATOMIC SPECTROSCOPY—VII*

LINE INTERFERENCES

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Summary—Equations are developed to describe the response of Zeeman-modulated spectrometers to a line background-absorption interference. The treatment is used to demonstrate that the analyte sensitivity is identical but the line background-responses are different for source-modulated and atomizer-modulated spectrometers. Two correction procedures are developed, the applicability of which depends on the separation of the zero-field source line and the interfering absorption line. Experimental data are shown for the interference of Co in the determination of Hg and of Pt in the determination of Fe.

Previous investigations have shown the technique of Zeeman modulation (ZM) to provide a powerful method of background correction for atomic-absorption spectroscopy (AAS) under circumstances where the background absorption remains invariant over the multiplet.[1–8] However, no work has appeared to date regarding the behaviour of ZM instruments under circumstances where the background absorption is not constant.

Source-modulated ZM spectrometers are invariably sensitive to such interferences, because of the change in the $\pi:\sigma$ intensity ratio caused by a frequency-dependent absorption within the source-emission multiplet. Spectroscopic interferences of this type may arise, for example, from molecular or radical absorption bands, or the overlap of atomic lines. Pairs of lines capable of behaving in this fashion have been tabulated by Norris and West.[9] Owing to the width of a Zeeman multiplet, the probability of observing such overlap interference is higher with a ZM source than with a conventional single-beam measurement (see also Fig. 2 below).

The situation with atomizer-modulated instruments usually differs from that of their source-modulated counterparts. Dawson and co-workers[7] were the first to point out, correctly, that in atomizer-modulated ZM spectrometers background correction is achieved at exactly the same wavelength as that at which the AAS measurement is made. The same statement has been repeated subsequently elsewhere.[8] However, this factor does not necessarily enable ZM corrections to be made when the background absorption is wavelength-dependent, since such an interference can itself show Zeeman structure which will generally alter the $\pi:\sigma$ ratio transmitted through the atomizer. The conditions for observing interference in an atomizer-modulated instrument, and the relations between source-modulated and atomizer-modulated spectrometers, are discussed in more detail later.

The present work has been carried out to determine the extent (in a ZM spectrometer) of some spectroscopic interferences due to atomic line overlap, and to examine some techniques by which the problem can be overcome. Experimental work was carried out on a source-modulated spectrometer, but it is felt likely to be also applicable to atomizer modulation for reasons considered below.

THEORY

Relation between source-modulated and atomizer-modulated instruments

Let emission and absorption line profiles be described by functions $a(\nu)$ and $g(\nu + \nu_{ab})$ respectively, where $a(\nu)$, $g(\nu + \nu_{ab})$ will in general be characteristic of different atomic species. The peak values of $a(\nu)$, $g(\nu + \nu_{ab})$ will be assumed to be separated by some frequency ν_{ab}.

In the derivation below, the term in the bracket following the function a or g denotes the frequency at which the function is located. For example $a(\nu + \nu_j)$ represents a profile identical to $a(\nu)$, but displaced from it by some frequency ν_j. The symbols a_j and g_j will be used to denote the jth component of a Zeeman multiplet, displaced to its appropriate frequency in the multiplet. The profile $a_j(\nu)$ will be treated as proportional to, but of lower amplitude than, the line $a(\nu)$ at zero magnetic field. Thus Lorentz and Doppler broadening will be assumed to be invariant during all the operations carried out below.

In the following discussion the possibility of a simultaneous continuous background absorption has been ignored, since it would serve only to introduce a common proportionality constant into the expressions developed for I_π and I_σ. This does not affect the nature of the arguments used.

* Part VI—R. Stephens, *Talanta*, 1978, **25**, 435.

Let I = intensity
N = number of atoms in the absorption beam
J and K = the numbers of π and σ components respectively in the source-modulated emission multiplet

J' and K' have the equivalent meaning for the atomizer-modulated absorption multiplet. Subscripts π and σ will be used to denote the appropriate transverse Zeeman-effect components.

In general, under zero magnetic-field conditions the intensity relationships are

$$I^0 = \int_0^x a(\nu)\,d\nu, \quad I_\nu = I_\nu^0 \exp[-g(\nu)N]$$

and

$$I = \int_0^\infty a(\nu)(\exp[-g(\nu)N])\,d\nu.$$

Therefore for a source-modulated instrument,

$$I_\pi = \sum_1^J \int_0^\infty a_j(\nu)(\exp[-g(\nu + \nu_{ab})N])\,d\nu.$$

Putting $a_j(\nu) = \alpha_j a(\nu_j)$ and $\nu_j = \nu + \delta\nu_j$ gives

$$I_\pi = \sum_1^J \int \alpha_j a(\nu + \delta\nu_j)(\exp[-g(\nu + \nu_{ab})N])\,d\nu$$

$$\simeq \sum_1^J \int \alpha_j a(\nu + \delta\nu_j)[1 - g(\nu + \nu_{ab})N]\,d\nu \quad (1)$$

for small N. Similarly,

$$I_\sigma \simeq \sum_1^K \int \beta_k a(\nu + \delta\nu_k)[1 - g(\nu + \nu_{ab})N]\,d\nu \quad (2)$$

where α_j, β_k, $\delta\nu_j$, $\delta\nu_k$ are constants at any given magnetic field strength. Similarly, for atomizer modulation,

$$I_\pi = \int_0^\infty a(\nu)\left(\exp[-N]\sum_1^{J'} \alpha_{j'} g[\nu + \nu_{ab} + \delta\nu'_j]\right)d\nu$$

$$\simeq \int a(\nu)\left[1 - N\sum_1^{J'} \alpha_{j'} g(\nu + \nu_{ab} + \delta\nu'_j)\right]d\nu$$

$$= \int\left[a(\nu)\sum_1^{J'} \alpha_{j'} - N\alpha_{j'} g(\nu + \nu_{ab} + \delta\nu_{j'})\right]d\nu \quad (3)$$

on substituting $1 = \Sigma\alpha_{j'}$. (This use of the principle of spectroscopic stability is necessary in order that $\int a(\nu)d\nu$ should remain constant during the following operations.) Then substituting $\nu = \nu' - \delta\nu'$ into (3) gives

$$I_\pi = \sum_1^{J'} \int \alpha_{j'} a(\nu' + \delta\nu_{j'})(1 - g(\nu' + \nu_{ab})N)\,d\nu' \quad (4)$$

since the function a is symmetrical with respect to a change in sign of j, because of the symmetry of a Zeeman multiplet about its zero-field frequency. Similarly,

$$I_\sigma = \sum_1^{K'} \int \beta'_k a(\nu' + \delta\nu'_k)(1 - g(\nu' + \nu_{ab})N)\,d\nu'. \quad (5)$$

Equations (4) and (5) generally differ from equations (1) and (2) except in the special case where $J = J'$ and $K = K'$. Thus source-modulated and atomizer-modulated spectrometers show the same response to the analyte absorption signal at low analyte concentrations. This equality of the two systems has not been deduced previously, and is felt to be worth noting in view of their current parallel development.

From the comparison of equations (1) and (2), and (4) and (5), the relative sensitivity of the two modulation systems to a line interference close to the zero-field AAS line frequency will generally vary with the particular system considered. However, since these equations are all of the same form, the types of correction procedure developed for one method of modulation are likely to be valid for the other. Thus the techniques developed and described below for a source-modulated spectrometer can be expected to be equally applicable to an atomizer-modulated instrument.

Dependence of I_π:I_σ on the magnetic field strength, H

From equation (1), putting $\nu' = \nu + \delta\nu_j$,

$$I_\pi = \int \sum_1^J \alpha_j a(\nu')(1 - g(\nu' + \nu_{ab} - \delta\nu_j)N)d\nu'$$

With an atmospheric atomizer, however, $g(\nu')$ is wider than $a(\nu')$ owing to pressure broadening *etc.* Thus $g(\nu')$ will be treated as constant over the integration of $a(\nu)$ for any particular value of j or k. Hence putting

$$I_\pi^0 = \sum_1^J \int \alpha_j a(\nu')\,d\nu' = I_\sigma^0,$$

and

$$\sum_1^J \alpha_j = \sum_1^K \beta_k = 1$$

gives:

$$\frac{I_\pi}{I_\sigma} = \frac{1 - N\sum_1^J \alpha_j g(\nu' + \nu_{ab} - \delta\nu_j)}{1 - N\sum_1^K \beta_k g(\nu' + \nu_{ab} - \delta\nu_k)}$$

$$= \frac{1 - N\sum_1^J \alpha_j \cdot g_j}{1 - N\sum_1^K \beta_k \cdot g_k}. \quad (6)$$

The qualitative behaviour of equation (6) as H changes can be predicted with quite general applicability to any source-multiplet/absorption-profile combination, since the only assumption that needs to be made is that the σ components of the multiplet separate faster than the π components as H increases.

Figure 1 will be used as a simplified diagrammatic representation of equation (6). Hence it is apparent that for large values of ν_{ab} the term $\Sigma_1^K \beta_k g_k$ will increase to a maximum with H as $K/2$ of the σ com-

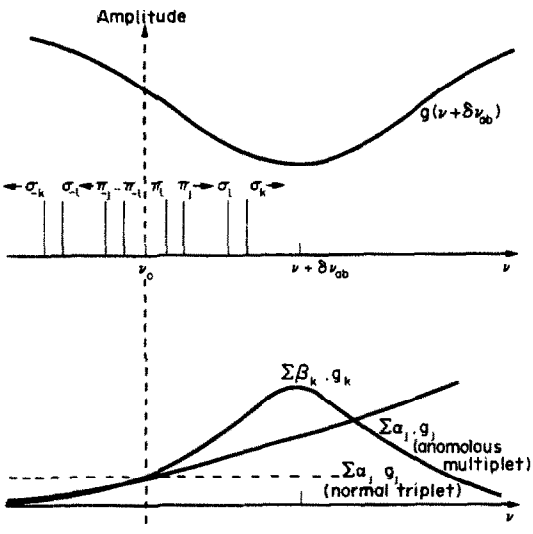


Fig. 1. Diagrammatic representation of equation (6): ν_0 = zero-field emission-line frequency, arrows show direction of displacement with increasing field strength.

ponents are frequency-shifted through the absorption maximum, and will then fall towards zero as H increases further. The term $\Sigma_1^J \alpha_j g_j$ will invariably change more slowly (since $\delta\nu_j < \delta\nu_k$ as mentioned above). Thus as H increases from zero, I_π/I_σ will rise from unity to a maximum, and will fall eventually below unity as H continues to rise. For small values of ν_{ab}, similar arguments can be used to describe the variations of I_π/I_σ with H. Thus I_π/I_σ must remain approximately constant at unity until the σ components have been suitably displaced beyond the absorption maximum, at which point the ratio will begin to fall sharply. Intermediate cases will lie somewhere between these two extremes.

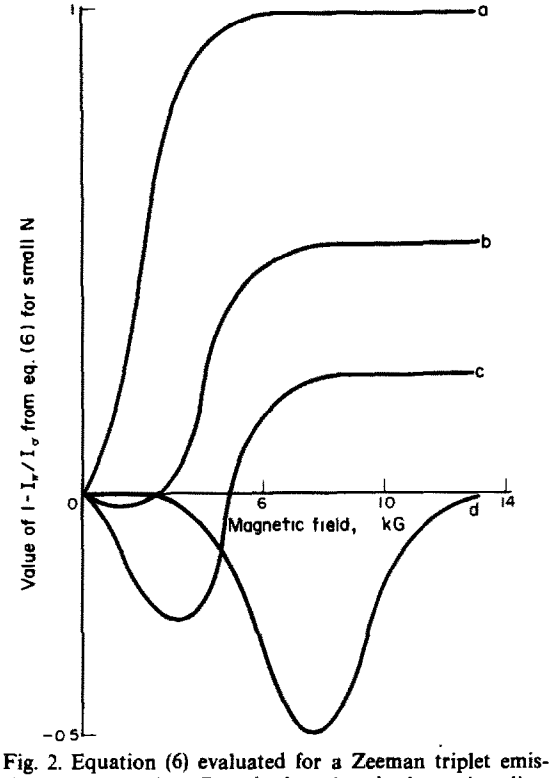


Fig. 2. Equation (6) evaluated for a Zeeman triplet emission source and a Doppler-broadened absorption line. Curves a, b, c, d are for $\delta\nu_{ab}$ values of 0, 0.008, 0.012 and 0.032 Å respectively. The curves also show the greater probability of line overlap with Zeeman modulation (curve d shows a strong interaction at $\delta\nu_{ab}$ equal to twice the half-width of the absorption line).

Some specific examples of this behaviour are shown quantitatively in Fig. 2. In Fig. 2 the function $(1 - I_\pi/I_\sigma)$, which corresponds to the spectrometer output signal, is plotted against H. For calculation purposes, a hypothetical normal Zeeman triplet with a zero-H wavelength of 3000 Å and a Doppler width of 0.016 Å was considered, and the effect of an absorption line displacement of 0–0.032 Å was determined from equation (6). Data available in the work of Mitchell and Zemansky[10] were used for numerical evaluation for g_j and g_k.

Correction of line background absorption

Two correction techniques are apparent from the arguments above.

(*i*) It is evident from equations (1) and (2) that some finite value of H, H_0, will always exist such that $I_\sigma = I_\pi$. From equation (6) it is also evident that H_0 will be independent of N, at least for low atom densities. Finally, it is clear that the trivial solution $H_0 = 0$ only arises when $\nu_{ab} = 0$. (These remarks are immediately obvious in the specific cases calculated in Fig. 2). Thus to achieve background correction it is only necessary to determine H_0 empirically for the particular interfering species, and operate the spectrometer just as usual except that the magnetic field strength must always be set at this predetermined value of H_0.

(*ii*) In practice, the approach just given may not be feasible, owing to an inability to generate a sufficiently high magnetic field strength, or to an unacceptable sensitivity loss associated with a high Zeeman factor[11] at H_0, or to the existence of more than one line interference. Correction can still be achieved under these circumstances, but at the cost of some loss of convenience. Use is made of equations (1) and (2), which show that the absorption of both I_π and I_σ depends on ν_{ab}. There are various ways of utilizing this fact: the following method has been derived for the ZM spectrometer used here, which generates a signal dependent on the ratio I_π/I_σ.[11]

If N_i and N_a are the number of interfering and analyte atoms respectively, equation (1) becomes:

$$I_\pi = \sum_1^J \int \alpha_j a(\nu + \delta\nu_j)\,d\nu - \sum_1^J \int \alpha_j a(\nu + \delta\nu_j)\,[g(\nu + \nu_{ab})N_i + g(\nu)N_a]\,d\nu$$
$$= I_\pi^0 - b_\pi N_i - c_\pi N_a$$

where b_π and c_π are constants dependent on H.

Therefore, using the analogous relation for I_σ,

$$\frac{I_\pi}{I_\sigma} = \frac{I_\sigma^0 - b_\pi N_1 - c_\pi N_a}{I_\sigma^0 - b_\sigma N_1 - c_\sigma N_a} = R$$

Hence, putting $I_\pi^0 = I_\sigma^0 = I^0$,

$$R \simeq 1 - \left(\frac{b_\pi - b_\sigma}{I^0}\right) N_1 - \left(\frac{c_\pi - c_\sigma}{I^0}\right) N_a$$

$$= 1 - dN_1 - eN_a$$

for small N_1 and N_a, d and e being constants dependent on H. This generates a spectrometer signal $S = 1 - R = dN_1 + eN_a$. Therefore if S is measured at two different field strengths H_1 and H_2, $S_{H_1} = d_1N_1 + e_1N_a$ and $S_{H_2} = d_2N_1 + e_2N_a$. Hence

$$\left(S_{H_1} - \frac{d_1}{d_2} S_{H_2}\right) = e_2\left(\frac{e_1}{e_2} - \frac{d_1}{d_2}\right) N_a. \qquad (7)$$

Thus a corrected calibration curve can be obtained by using equation (7). However, the procedure has lost the elegance of the usual Zeeman correction, since it is necessary first to be aware of the existence of an interference of this second type, and then to calibrate the instrument separately for N_1 and N_a in order to determine the constants in equation (7).

Although there is no restriction on the exact values of H_1 and H_2 such as that applied to H_0, in practice these values must be limited to a range giving the maximum discrimination between N_1 and N_a.

Equation (7) is only valid if $e_1/e_2 \neq d_1/d_2$: *i.e.*, it is essential that the absorptions of I_π and of I_σ must vary with ν_{ab}, as indicated by equations (1) and (2).

EXPERIMENTAL

The spectrometer used here has been described previously.[11] The original sample-introduction system was replaced by a conventional pneumatic nebulizer, but the instrument was otherwise unmodified. Since the spectrometer measures I_π/I_σ, the signals measured from the baseline correspond to $1 - I_\pi/I_\sigma$.

Data from two systems each showing an interference due to atomic-line spectral overlap are described here, to illustrate the deductions made above. These are Co at 2563.52 Å and Hg at 2536.49 Å, and Fe at 2719.03 Å at 2719.04 Å. Mercury and iron hollow-cathode lamp sources were used, and the signals due to increasing concentrations of Hg or Co, and of Pt or Fe, were determined at magnetic field strength from 0 to 12.5 kG. Field strengths were measured with a 4-cm^2 search coil centred at the position normally occupied by the lamp cathode.

Very high mercury concentrations were used (Fig. 3), because of the reduction in sensitivity caused by severe self-absorption in the lamp. Self-absorption is immediately apparent with the present equipment from the magnitude of the correction to the π/σ ratio required to restore a base-line value of unity as the magnetic field is increased.[12] This self-absorption was probably caused partly by the extended anode plasma of an RF-excited hollow-cathode lamp,[12] which is presumably capable of vaporizing adsorbed mercury from the lamp walls, and partly by the heating effect of the magnet coils being transmitted to the lamp through the pole pieces.

RESULTS AND DISCUSSION

Figures 3 and 4 show the results obtained for the Hg/Co and Fe/Pt systems. The former combination falls into category (*i*) above: *i.e.*, a field of H_0 (about 7 kG here) exists which is obtainable with the appar-

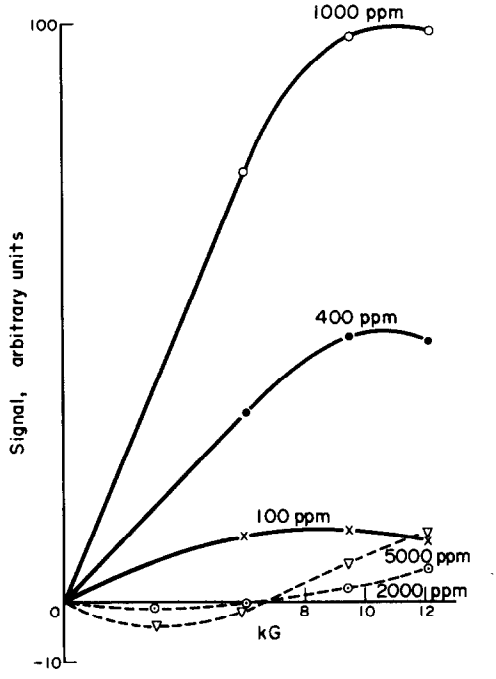


Fig. 3. Signal *vs.* magnetic field strength for Hg and Co. Solid curves are for the Hg response; dashed curves for Co.

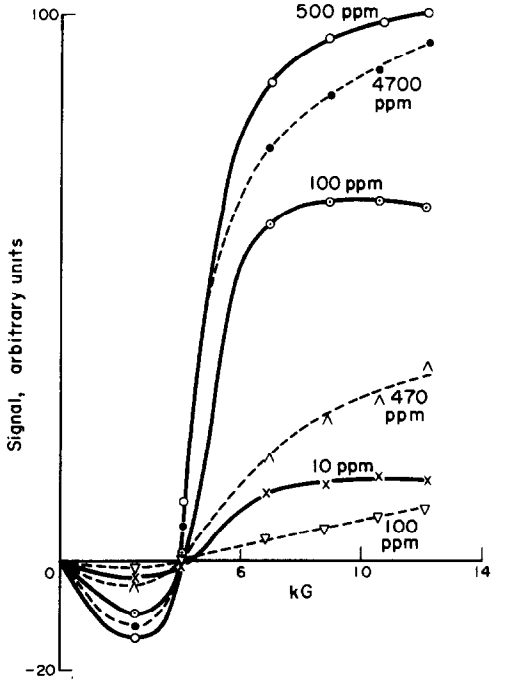


Fig. 4. Signal *vs.* magnetic field strength for Fe and Pt. Solid curves are for the Fe response; dashed curves for Pt.

atus and which does not imply a severe sensitivity loss. Thus conventional Zeeman background correction for the Co interference is available at a specific field strength of 7 kG with no further complication in the experimental operation of the spectrometer.

The Pt/Fe system falls into category (*ii*), because of the close proximity of the lines involved. Although the curves in Fig. 4 show that no useful value of H_0 is available, the differences in the signal *vs.* field-strength curves for Fe and Pt are clearly marked, as predicted above on the basis of equations (1) and (2). Thus equation (7) can be applied to provide a correction for this system, with H_1 and H_2 values of around 7 and 12 kG.

Interestingly, the curves obtained for all four elements compare well with those calculated in Fig. 2. Thus the Hg and Co data in Fig. 3 correspond to curves a and c in Fig. 2, while both the Fe and Pt data in Fig. 4 lie somewhere between curves b and c. The comparison is considered to be good because of the very different conditions involved. All the curves in Fig. 2 assume low atomic concentration, normal Zeeman effect on an infinitely narrow emission line, and an absorption line-width controlled only by natural and Doppler broadening and unaffected by hyperfine splitting. None of the species investigated experimentally satisfies any of these criteria: true, the Hg source line in principle splits to give a normal triplet, but the situation here is undoubtedly less simple owing to a complex hyperfine structure, which is further complicated by severe self-absorption with its associated broadening and structuring[13] of the emission multiplet. Thus the curves in Figs. 2–4 are felt to illustrate well the deductions made above concerning the generally similar dependence of I_π/I_σ on H irrespective of the particular emission-multiplet/absorption-line system actually considered.

CONCLUSIONS

The good qualitative agreement observed between theory and experiment under the present and fairly severe conditions is felt to provide good supportive evidence that the generality of the theoretical treatment is valid. Thus it is considered that one of the two corrective procedures developed here from theoretical considerations can be applied to any form of line background absorption encountered in any type of Zeeman background-corrected measurement, irrespective of whether or not a simultaneous continuum background also exists.

The ability of the ZM spectrometer to compensate for a line background absorption rests upon the spectroscopic equivalence of the π and σ line profiles combined with an ability to control the frequency shift of the σ "reference" relative to the π "sample" lines. Conventional continuum-source background-correctors cannot provide such flexibility. Thus the high efficiency of the ZM technique in comparison with such conventional counterparts, already noted for the special case of an invariant background, is also apparent in the present circumstances.

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REFERENCES

1. T. J. Hadeishi and R. D. McLaughlin, *Science*, 1971, 174, 404.
2. T. J. Hadeishi, *Appl. Phys. Lett.*, 1972, **21**, 438.
3. R. Stephens and D. E. Ryan, *Talanta*, 1975, **22**, 659.
4. H. Koizumi and K. Yasuda, *Anal. Chem.*, 1975, **47**, 1679.
5. *Idem, ibid.*, 1976, **48**, 1178.
6. *Idem, Spectrochim. Acta*, 1976, **31B**, 237.
7. J. B. Dawson, E. Grassan, D. J. Ellis and M. J. Keir, *Analyst*, 1976, **101**, 315.
8. H. Koizumi and K. Yasuda, *Spectrochim. Acta*, 1977, **31B**, 523.
9. J. D. Norris and T. S. West, *Anal. Chem.*, 1974, **46**, 1423.
10. A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Ch. III, Table XI. Cambridge University Press, Cambridge, 1934.
11. R. Stephens, *Talanta*, 1978, **25**, 435.
12. G. F. Murphy and R. Stephens, *ibid.*, 1978, **25**, 223.
13. N. Ioli, P. Minguzzi and F. Strumia, *J. Opt. Soc. Am.*, 1970, **60**, 1192.

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SOME LIMITING FACTORS OF THE ION-EXCHANGE EQUILIBRIUM METHOD FOR DETERMINING APPARENT FORMATION CONSTANTS OF MONONUCLEAR COMPLEXES

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Summary—Some limiting analytical conditions of the ion-exchange equilibrium method are discussed. The most reliable apparent formation constants are obtained when the range of the experimental complexant concentration brackets the reciprocal value of the stability constant for ML-type complexes. This working range will ensure significant analytical differences in the total metal remaining in solution for successive experiments with increasing complexant concentrations. For accurate determination of stepwise formation constants for ML_2-type complexes, the intermediate complex species ML^+ must not be exchanged by the resin to any extent. Otherwise Schubert's equations are no longer valid, and the partition ratios of all cationic species present should be taken into account.

Apparent stability constants of numerous organometallic compounds, especially those involved in biochemical reactions, have been determined by using the ion-exchange equilibrium method proposed by Schubert[1] in 1948. Since then, the simplified Schubert equation, wherein the apparent dissociation constant (K) of a complex ML_y is measured as the ratio $[(K_{d_0}/K_d) - 1]/[L]^y$, has been extensively applied.

The ion-exchange equilibrium method was adopted by soil chemists for determining the stabilities of several metallic complexes of soil organic matter, but its use was strongly criticised by Clark and Turner.[2] They stated that such complexes would be more likely to be of the type M_nL than ML_n, because of the polyfunctional nature of soil organic macromolecules. Later Zunino *et al.*[3] pointed out that an examination of Schubert's original work revealed that to derive the general ion-exchange equation he implicitly made two assumptions which are not valid. The invalidity of these assumptions had been overlooked for a long time, and even today there are some authors who still make use of these assumptions to describe the method.[4]

At present there is renewed interest in studying the stability constants of organometallic complexes, because of the increase in heavy metal pollution of soils and natural waters throughout the world.[5] Since the ion-exchange equilibrium method has been frequently applied and is simple and rapid, it might be attractive for use by environmental chemists. Hence a study to establish the experimental limitations of this method (to complement the theoretical ones already offered) is useful.

In this paper the analytical boundary conditions of the ion-exchange equilibrium method are discussed. An equation relating the complexant concentrations used, stability of the complexes involved and accuracy of the measurements is deduced. This equation shows that only if a suitable concentration range of complexant is chosen will the method render analytically reliable data for calculating stability constants. The effect of the cation-exchange behaviour of intermediate cationic complexes on the validity of Schubert's equations, used to calculate constants for ML_2-type complexes, is also discussed.

Scope of the ion-exchange equilibrium method

The ion-exchange equilibrium method is based on the fact that the partition of a metal between a solution and a cation-exchanger, expressed in terms of the analytical distribution coefficient (K_d), is altered when water-soluble complexes are formed by addition of co-ordinating agents. If the complex is not exchanged by the resin, a decrease in the sorption of the metal is produced, compared with that in the absence of the complexing anion. As a consequence, the experimental K_d values will be reduced; this reduction is a function of the stability of the complex formed and of the complexant concentration present in the aqueous phase.

To calculate the apparent dissociation constant (K) of a general complex M_xL_y, Schubert[1] performed two experiments: one in the absence and the other in the presence of the complexant L. The concentration of the metal must be negligible compared to that of the complexant and also must be low enough to ensure a constant distribution ratio. The following general equation was deduced:

$$K = \frac{(a)^x(L)^y}{\lambda_0^x(s - a/K_{\lambda_0})} \qquad (1)$$

where a = fraction of total metal bound to the exchanger at equilibrium when complexing agent L is present; a_0 = the fraction in the absence of L; s =

fraction of total metal remaining in solution at equilibrium when complexing agent L is present; s_0 = the fraction in the absence of L;

$$\lambda_0 = a_0/s_0.$$

Later, Schubert *et al.*[6] derived a simplified equation to determine the apparent overall formation constant (K_f) for mononuclear ML_y-type complexes:

$$K_f = \frac{(K_{d_0}/K_d) - 1}{[L]^y} \qquad (2)$$

where K_{d_0} and K_d are the analytical distribution coefficients in absence and presence of complexant L respectively and K_d is defined as

$$K_d = \frac{\text{total amount of metal on the resin}}{\text{total amount of metal in solution}} \times \frac{\text{volume of solution}}{\text{mass of resin}}$$

$$= PV/m$$

where P is the partition ratio (mass ratio of metal on the resin to metal in solution), V is the volume of solution and m the mass of resin. K_f is normally calculated by using the linear form of equation (2), plotting log [L] *vs.* log$[(K_{d_0}/K_d) - 1]$.

As discussed elsewhere,[3] a critical examination of Schubert's treatment[1] shows that in order to obtain equations (1) and (2) by his methods, it is necessary to cancel inequalities related to metal bound to exchanger and to free metal ion in solution. Simultaneous cancellations of these inequalities are algebraically balanced only for mononuclear complexes. Therefore Schubert's equations are applicable only to this type of complex.

Influence of complexant concentration on the accuracy of K_f *measurements*

The ion-exchange equilibrium method has been frequently used to determine apparent stability constants of zero-charge ML- and ML_2-type complexes. However, no attempt has been made to study how the concentration of the complexing agent L, used to obtain the partition ratio data, could influence the accuracy of the measurements.

In a heterogeneous system composed of a cation-exchanger and a solution containing metal ions and complexing species, the distribution of the metal between both phases is a function of the stabilities of the complexes formed and of the complexant concentration. Thus, at equilibrium, the higher the stability and the complexing agent concentration, the less the amount of metal extracted by the exchanger. The method, as outlined by Schubert, requires a very low concentration of total metal compared to that of the complexant. Hence, when very stable complexes are formed, almost all the metal remaining in solution at equilibrium will exist as complex species. Therefore the total amount of metal in solution will increase only slightly when increased concentrations of complexant are successively employed to obtain the experimental P values as a function of complexant concentration. Significant differences in the total amount of metal remaining in solution (for two successive experiments) will be obtained only if low complexant concentrations are used. Correspondingly, for very weak complexes, the method would yield reliable data only if concentrated complexant solutions were used.

For meaningful results to be obtained, the differences in total metal concentration in solution must be larger than the inherent variability of the analytical method used to determine the metal concentration. Therefore the most reliable data for K_f calculations would be obtained by working with the range of complexant concentration that would give the biggest differences in total metal ion concentration in solution. A theoretical approach to definition of this range is now presented, an ML-type complex being considered for simplicity.

From equation (2), for a complex ML, provided that the volume of solution and mass of exchanger are kept constant throughout the experiments,

$$K_f = \frac{1}{[L]}[(P_0/P) - 1],$$

we can define an analytical term A:

$$A = \frac{\text{total mass of metal in solution at equilibrium}}{\text{total mass of metal in both phases at equilibrium}} = \frac{(M_s)}{(M_t)}.$$

Given that M_s = mass of free metal in solution (M_f) plus mass of complexed metal in solution (M_c), and that M_r = mass of metal bound to the resin in the presence of L, then

$$P = M_r/(M_f + M_c)$$

and the following equation can be readily derived:

$$A = \frac{K_f[L] + 1}{P_0 + K_f[L] + 1} \qquad (3)$$

or, taking natural logarithms:

$$A = \exp\{\ln(K_f[L] + 1) - \ln(P_0 + K_f[L] + 1)\} \qquad (4)$$

where P_0 is the value of P in the absence of L.

Equation (4) shows the distribution of A, representing the fraction of the total metal added which remains in solution, as a function of the apparent stability constant K_f and of the concentration of the complexant. The function is depicted in Fig. 1 for several representative values of P_0.

As can be seen from Fig. 1, significant analytical differences among experiments will be obtained around the point of maximum slope. Maximum slope occurs when [L] is equal to $1/K_f$ and, as the product $K_f[L]$ approaches zero or infinity, the differences in

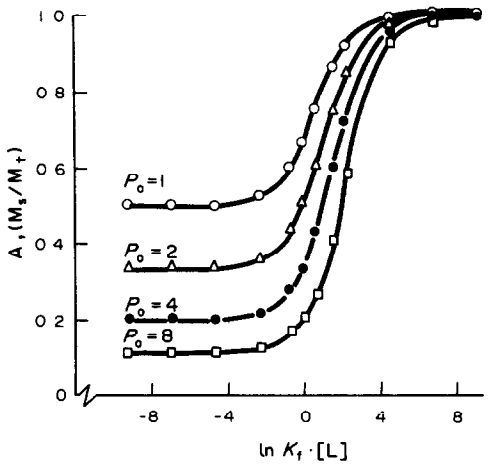


Fig. 1. Effect of the experimental complexant concentration on fraction of metallic species remaining in solution at equilibrium with a cation-exchanger.

the A-values for successive experiments with increasing [L] will approach zero. Therefore, for ML-type complexes, accurate measurements can be made only by working within a complexant concentration range near the value $1/K_f$. As an example, for a given exchanger and metal having a P_0 values of 2, the most accurate K_f calculations will be obtained by selecting complexant concentrations such that the experimental values of A fluctuate between 0.4 and 0.9 (40–90% of the total metal added remains in solution). As P_0 increases, so also does the range of useful A measurements.

Data presented in Table 1 illustrate the usefulness of equation (4) for finding the range of complexant concentration which will ensure significant differences (between experiments) in the metal concentration in solution. The best ranges of [L] for three K_f values representing low, medium and high stabilities have been computed. It can be seen that for stable complexes (log K_f for ML about 14) the ion-exchange method does not seem useful since the optimal complexant concentration range is very low (10^{-15}–$10^{-13}M$) and would demand a working concentration of metal in the range 10^{-17}–$10^{-15}\,M$. Under these conditions the analyst would be compelled to measure concentration differences between excessively dilute metal solutions, which may be difficult or even impossible.

Effect of the cation-exchange behaviour of intermediate species on calculation of K_f *values*

Positively-charged intermediate species may be formed when neutral ML_2-type complexes are formed in solution. In these cases, the overall formation constant K_f represents the product of the stepwise formation constants k_1 and k_2. A brief discussion of interpretation of the experimental data obtained when the ion-exchange method is applied to such complexes seems desirable.

Let us consider the formation of an ML_2 complex. If $k_1 \ll k_2$ a negligible amount of the intermediate species ML^+ is formed and therefore equation (2) can be directly applied. In these cases the following equation can be readily derived to describe the relationship between complexant concentration, stability of the complex and the analytical measurement A:

$$A = \exp\{\ln(K_f[L]^2 + 1) - \ln(P_0 + K_f[L]^2 + 1)\} \quad (5)$$

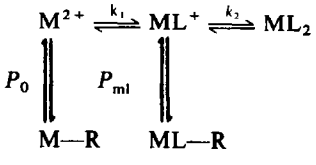
Table 1 also shows the optimal ranges of complexant concentration, calculated by applying equation (5), which should be used for ML_2 complexes of different stabilities.

The stepwise formation constants of some ML_2-type complexes have been determined[7,8] by using the ion-exchange method in conjunction with the equation:

$$P = \frac{P_0}{1 + k_1[L] + k_1k_2[L]^2}. \quad (6)$$

Equation (6) was derived by Li *et al.*[7,8] on the assumption that the intermediate ML^+ species, even though present in the aqueous phase of the system, is not exchanged by the resin. This behaviour has been explicitly reported in certain works, but may not have been checked in others.

It is reasonable to expect that ML^+ species could be exchanged by the cation-exchange resin, provided they are not so large that steric hindrance prevents the exchange. The equilibria can be summarized as:



Therefore an additional partition ratio (P_{ml}) should be introduced in deriving equation (6), giving the

Table 1. Optimal concentrations of complexant for determination of formation constants of some mononuclear complexes

Stability of complexes, log K_f	Limits of recommended complexant concentrations, M	
	ML-type complexes*	ML_2-type complexes†
2.0	3.3×10^{-3}–1.7×10^{-1}	5.8×10^{-2}–4.1×10^{-1}
8.0	3.3×10^{-7}–1.7×10^{-5}	5.8×10^{-5}–4.1×10^{-4}
14.0	3.3×10^{-15}–1.7×10^{-13}	5.8×10^{-8}–4.1×10^{-7}

* Determined by applying equation (4).
† Determined by applying equation (5).

Table 2. Values of K_f, $(k_1 k_2)$, for an ML_2-type complex, calculated by means of equations (2), (6) and (7)

		K_f*		
A, (M_t/M_l)	P $[(1 - A)/A]$	Eq. (2) $(K_{f_2} \times 10^{-5})$	Eq. (6)	Eq. (7)†
0.80	0.25	3.10	$K_{f_2} - 100k_1$	$K_{f_2} + 300k_1$
0.75	0.33	2.30	$K_{f_2} - 100k_1$	$K_{f_2} + 200k_1$
0.67	0.50	1.50	$K_{f_2} - 100k_1$	$K_{f_2} + 100k_1$
0.50	1.00	0.70	$K_{f_2} - 100k_1$	K_{f_2}
0.33	2.00	0.30	$K_{f_2} - 100k_1$	$K_{f_2} - 500k_1$
0.25	3.00	0.17	$K_{f_2} - 100k_1$	$K_{f_2} - 670k_1$
0.20	4.00	0.10	$K_{f_2} - 100k_1$	$K_{f_2} - 750k_1$

* Calculated assuming $P = 8.0$ and $L = 1 \times 10^{-2}$ M
† Calculated assuming $P_{ml} = 1.0$

equation

$$P = \frac{P_0 + P_{ml} k_1 [L]}{1 + k_1[L] + k_1 k_2 [L]^2}. \quad (7)$$

Equation (7) defines the value of P when intermediate charged species are exchanged by the resin; obviously the k values given by this equation will be different from those given by equation (6), for the same experimental P values. The magnitude of these differences is shown in Table 2 where overall K_f values calculated from equations (2), (6) and (7) have been tabulated, with an arbitrary value of 1.0 assumed for P_{ml} in equation (7). It is confirmed that the differences are a function of k_1 (where $k_1 = [ML]/[M][L]$); as k_1 tends to zero, the K_f values tend towards equality.

From this discussion it can be concluded that before equation (6) is applied to calculate stepwise formation constants, it must be verified that intermediate charged species are not exchanged. Alternatively, if the partition ratio for the intermediate cationic species is known, equation (7) can be applied.

REFERENCES

1. J. Schubert, *J. Phys. Coll. Chem.*, 1948, **52**, 340.
2. J. S. Clark and R. C. Turner, *Soil Sci.*, 1969, **107**, 8.
3. H. Zunino, G. Galindo, P. Peirano and M. Aguilera, *ibid.*, 1972, **114**, 229.
4. P. MacCarthy and H. B. Mark, *Proc. 15th Annual Life Sci. Symp. Hanford, Washington*, 1976.
5. A. L. Page, *U.S. Environmental Protection Techn. Series*, Cincinatti, Ohio, 1974.
6. J. Schubert, E. R. Russell and L. S. Myers, *J. Biol. Chem.*, 1950, **185**, 387.
7. N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White and J. Schubert, *J. Am. Chem. Soc.*, 1957, **79**, 5864.
8. N. C. Li, B. E. Doody and J. M. White, *ibid.*, 1957, **79**, 5859.

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PROPERTIES AND CONSTRUCTION OF AZO-DYE REAGENTS FOR INORGANIC PHOTOMETRIC ANALYSIS

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Summary—An approach to constructing new organic reagents (based on azo dyes) for photometric analysis is described. Its essence is the detailed consideration of the electronic structure of the chromophore nuclei of the dyes in the ground and excited states. Knowing the nature of the electron transition, it is possible to construct the organic reagents with optimal properties. The electronic structure of the azo dyes has been analysed in a π-approximation by an MO LCAO SCF method.

Azo dyes have been widely used for creation of organic reagents applied in photometric inorganic analysis, because they are comparatively readily available, can be synthesized in the laboratory as well as in industry, and are generally stable towards light and do not decompose during long-term storage.

Despite the fact that about a hundred reagents based on azo dyes are currently encountered in analytical practice, new reagents are still being created, mainly by empirical variation of the functional group without rigorous consideration of the chromophore system in terms of modern quantum mechanics.

Figure 1 shows the basic types of azo dyes used as the chromophoric nuclei of recently developed organic reagents. Only about ten such structures are used, these giving rise to various reagents by introduction of various functional groups in different positions.

Thus the first problem which arises when constructing organic reagents may be formulated in the following way: to introduce into a dye molecule (chromophore nucleus) those functional groups which ensure the greatest sensitivity, contrast and other optimum properties of a reagent. In other words, it is necessary to find the positions in a molecule where π-donor and π-acceptor substituents should be introduced. The second problem is the systematic synthesis of new chromophore nuclei possessing even more valuable practical properties.

The most general method for solution of these problems is quantum-mechanical analysis of the electronic structure and spectral nature of the dyes. We have determined the electronic structure of the basic types of azo-dye molecules that have found application in practice. The calculation was conducted (in the π-approximation) by use of the MO LCAO SCF method of Pariser, Parr and Pople[1,2], taking account of the configuration interaction with excited states. The interaction of 25 mono-excited configurations covering an energy interval of 10–15 eV was considered. The calculation data provide electron-density distributions for the ground and excited states of the dye molecules. Since the nature of the absorption band with the longest wavelength is of greatest interest, Table 1 lists the data characterizing the electronic structure in the ground state and in two or four excited states. To characterize the band nature of the electronic spectrum of a molecule means to indicate the type of levels between which electron transition

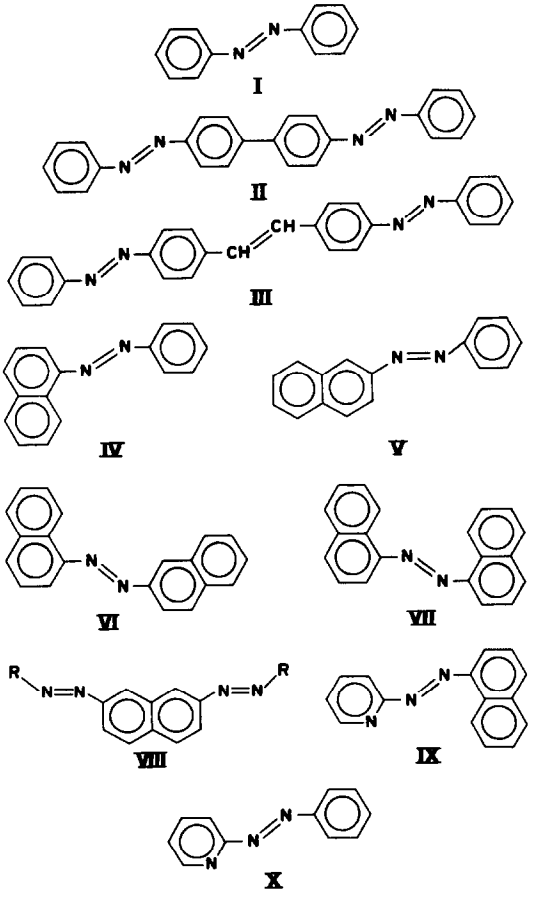
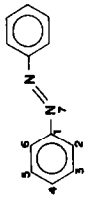


Fig. 1.

Table 1. Distribution of π-electron density in the ground and lowest excited states of certain azo dyes. (Numbering of atoms is shown in formulae in the first column. Δ_{ON} is π-electron charge on the atom in the ground state minus the π-charge in the corresponding excited states. f is the calculated oscillator strengths of the related transitions). The calculations were done with an ALGOL 60 program,[9] a method for coulomb two-centre integrals[10] and empirical values of ionization potentials.[11]

Compound formula	Atom number	Ground state	Excited states			
			Δ 01	Δ 02	Δ 03	Δ 04
	1	0.01	−0.12	0.00	0.00	−0.15
	2	0.01	0.00	−0.05	−0.07	0.01
	3	0.00	−0.02	−0.09	−0.07	−0.04
	4	0.01	−0.07	0.04	0.04	−0.12
	5	0.00	−0.01	−0.08	−0.09	−0.05
	6	0.02	−0.03	−0.05	−0.02	0.03
	7	−0.05	0.25	0.22	0.22	0.31
	f	—	0.99	10^{-8}	0.05	10^{-13}

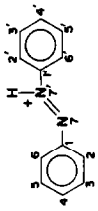
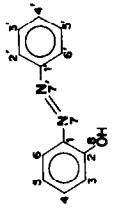
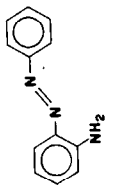
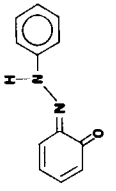
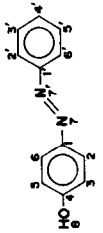
Compound formula	Atom number	Ground state	Excited states			
			Δ01	Δ02	Δ03	Δ04
	1	−0.01	−0.11	0.00	0.01	−0.12
	2	0.05	0.02	−0.17	0.01	0.07
	3	0.03	−0.01	−0.22	−0.01	−0.08
	4	0.12	−0.02	0.07	0.06	−0.12
	6	0.04	−0.02	−0.22	0.01	−0.07
	6	0.08	0.05	−0.19	0.05	0.07
	7	0.01	0.40	0.41	0.42	0.31
	7′	0.58	0.19	0.24	0.24	0.18
	1′	−0.07	−0.19	0.01	−0.01	−0.07
	2′	0.02	−0.10	0.02	−0.15	0.03
	3′	0.03	−0.01	−0.01	−0.27	−0.06
	4′	0.08	−0.12	0.03	0.02	−0.10
	5′	0.04	−0.09	0.00	−0.16	−0.06
	6′	0.02	0.02	0.02	−0.27	0.03
	f	—	0.94	0.025	0.08	0.06

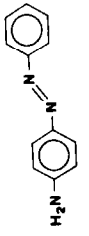
Table 1 (*continued*).

Compound formula	Atom number	Ground state	Excited states Δ01	Excited states Δ02
	1	−0.02	−0.15	−0.02
	2	0.03	−0.11	0.05
	3	−0.05	−0.02	−0.20
	4	0.02	−0.01	0.03
	5	−0.02	−0.11	−0.07
	6	0.02	0.08	−0.19
	7	−0.06	0.28	0.24
	7′	−0.07	0.23	0.26
	1′	0.02	−0.03	−0.04
	2′	0.01	0.01	0.02
	3′	0.00	0.00	−0.01
	4′	0.01	0.00	−0.02
	5′	0.00	0.00	0.00
	6′	0.01	0.01	0.00
	8	0.10	−0.17	−0.03
	f	—	0.70	0.28

Compound formula	Ground state	Excited states Δ01	Excited states Δ02
	−0.03	−0.14	−0.04
	0.03	−0.08	0.07
	−0.05	−0.04	−0.19
	0.02	0.02	0.01
	−0.03	−0.13	−0.05
	0.02	0.08	−0.19
	−0.06	0.29	0.24
	−0.07	0.24	0.26
	0.02	−0.02	−0.06
	0.01	0.02	0.00
	0.00	0.00	−0.01
	0.01	0.01	−0.03
	0.00	0.00	0.00
	0.01	0.02	0.00
	0.12	−0.27	−0.02
	—	0.57	0.38

Compound formula	Ground State	Excited states Δ01	Excited states Δ02
	0.01	0.01	−0.10
	0.19	0.10	0.08
	−0.01	−0.06	−0.13
	0.04	0.03	−0.10
	−0.01	−0.16	0.03
	0.01	−0.11	−0.12
	−0.12	0.28	0.34
	0.45	0.05	0.05
	−0.03	−0.01	−0.06
	−0.01	0.00	−0.02
	0.01	0.00	−0.01
	0.01	−0.01	−0.05
	0.01	0.00	−0.01
	0.00	0.00	−0.01
	−0.54	−0.11	0.13
	—	0.44	0.49

Compound formula	Atom number	Ground state	Excited states Δ01	Excited states Δ02
	1	−0.01	−0.15	−0.02
	2	0.02	0.00	−0.07
	3	−0.04	−0.05	−0.12
	4	0.03	−0.07	0.06
	5	−0.05	−0.04	−0.15
	6	0.02	−0.02	−0.06
	7	−0.05	0.28	0.16
	7′	−0.07	0.22	0.17
	1′	0.02	−0.05	0.00
	2′	0.01	−0.01	0.02
	3′	0.00	−0.01	0.00
	4′	0.01	−0.02	0.02
	5′	0.00	0.00	0.00
	6′	0.02	0.00	0.02
	8	0.10	−0.07	−0.03
	f	—	1.03	0.004

Compound formula	Ground state	Excited states Δ01	Excited states Δ02
	−0.01	−0.15	−0.03
	0.02	0.02	−0.05
	−0.05	−0.07	−0.11
	0.03	−0.06	0.06
	−0.05	−0.05	−0.13
	0.02	−0.01	−0.05
	−0.05	0.29	0.15
	−0.07	0.22	0.15
	0.02	−0.04	0.00
	0.01	−0.01	0.02
	0.00	−0.01	0.00
	0.01	−0.01	0.02
	0.00	0.00	0.00
	0.02	0.01	0.02
	0.11	−0.12	−0.05
	—	1.02	0.001

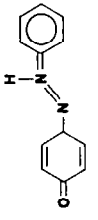
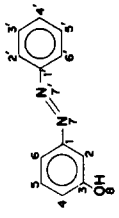
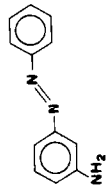
Compound formula	Ground state	Excited states Δ01	Excited states Δ02
	0.02	−0.07	0.06
	0.01	0.06	−0.20
	0.01	−0.01	−0.20
	0.22	0.06	0.08
	0.01	−0.07	−0.17
	0.03	0.04	−0.19
	−0.06	0.24	0.32
	0.38	−0.09	0.13
	−0.03	−0.04	0.00
	−0.01	−0.03	0.02
	0.01	−0.01	0.00
	0.01	−0.04	0.01
	0.01	−0.01	0.00
	−0.02	−0.02	0.02
	−0.49	−0.02	0.11
	—	1.85	0.021

Table 1 (*continued*).

Compound formula	Atom number	Ground state	Excited states Δ01	Δ02
	1	0.02	−0.07	−0.03
	2	−0.03	0.08	−0.23
	3	0.01	−0.13	−0.03
	4	−0.03	−0.07	0.04
	5	0.00	0.00	−0.12
	6	0.02	−0.21	0.06
	7	−0.06	0.27	0.24
	7′	−0.07	0.26	0.26
	1′	0.02	−0.04	−0.05
	2′	0.01	0.02	0.02
	3′	0.00	−0.01	−0.02
	4′	0.01	−0.01	−0.03
	5′	0.00	0.00	0.00
	6′	0.01	0.01	0.00
	8	0.10	−0.09	−0.07
	f	—	0.55	0.47

Compound formula	Ground state	Excited states Δ01	Δ02
	0.02	−0.03	−0.07
	−0.03	0.04	−0.19
	0.01	−0.13	0.00
	−0.04	−0.05	0.00
	0.00	−0.01	−0.10
	−0.01	−0.22	0.08
	−0.05	0.28	0.25
	−0.06	0.27	0.25
	0.02	−0.01	−0.08
	0.01	0.02	0.01
	0.00	0.00	−0.02
	0.01	0.01	−0.05
	0.00	0.00	0.00
	0.02	0.03	−0.01
	0.10	−0.19	−0.06
	—	0.32	0.69

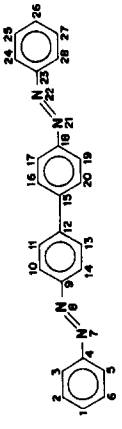
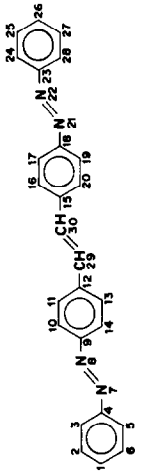
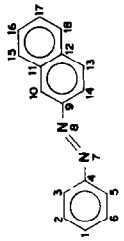
Compound formula	Atom number	Ground state	Excited states Δ01	Δ02	Δ03	Δ04
	1	0.01	−0.01	−0.01	0.03	0.03
	2	0.00	0.00	0.00	−0.12	−0.13
	3	0.02	0.01	0.01	−0.05	−0.06
	4	0.01	−0.03	−0.04	0.00	0.00
	5	0.01	0.00	0.00	−0.10	−0.11
	6	0.00	0.00	0.00	−0.08	−0.09
	7	−0.06	0.10	0.11	0.14	0.14
	8	−0.06	0.10	0.14	0.14	0.15
	9	0.02	−0.06	−0.08	0.01	0.01
	10	0.01	0.00	0.00	0.01	0.02
	11	0.00	−0.03	−0.04	−0.04	0.00
	12	0.01	−0.04	−0.05	0.02	0.02
	13	0.00	−0.03	−0.03	0.00	0.00
	14	0.02	0.00	0.00	0.02	0.02
	15	0.01	−0.04	−0.06	0.02	0.02
	16	0.00	−0.03	−0.03	0.00	0.00
	17	0.02	0.00	0.00	0.02	0.02
	18	0.02	−0.06	−0.08	0.01	0.01
	19	0.01	0.00	0.00	0.01	0.02
	20	0.00	−0.03	0.04	−0.01	0.00
	21	−0.06	0.10	0.14	0.14	0.15
	22	−0.06	0.10	0.14	0.14	0.14
	23	0.01	−0.03	−0.04	0.00	0.00
	24	0.01	0.00	0.00	−0.10	0.11
	25	0.00	0.00	0.00	−0.08	−0.09
	26	0.01	−0.01	−0.01	0.02	0.03
	27	0.00	0.00	0.00	−0.12	−0.13
	28	0.02	0.01	0.01	−0.05	−0.06
	f	—	2.11	10^{-10}	0.20	10^{-6}

Table 1 (*continued*).

Compound formula	Atom number	Ground state	Excited states Δ01	Δ02	Δ03	Δ04
	1	0.01	−0.02	−0.02	0.03	0.03
	2	0.00	0.00	0.00	−0.12	−0.12
	3	0.02	0.00	0.00	−0.08	−0.08
	4	0.02	−0.04	−0.04	0.02	0.02
	5	0.01	0.00	0.00	−0.10	−0.10
	6	0.00	−0.01	−0.11	−0.11	−0.11
	7	−0.06	0.11	0.11	0.14	0.14
	8	−0.06	0.11	0.12	0.15	0.15
	9	0.01	−0.06	−0.07	0.00	0.00
	10	0.01	−0.01	−0.01	0.01	0.02
	11	0.00	−0.01	−0.02	0.00	0.00
	12	0.01	−0.04	−0.04	0.02	0.02
	13	0.00	−0.01	−0.01	0.00	0.00
	14	0.02	0.00	0.00	0.02	0.03
	15	0.01	−0.04	−0.04	0.02	0.02
	16	0.02	0.01	0.01	0.02	0.02
	17	0.02	0.00	0.00	0.02	0.03
	18	0.01	−0.06	−0.07	0.00	0.00
	19	0.01	−0.01	−0.01	0.01	0.02
	20	0.00	−0.01	−0.02	0.00	0.00
	21	−0.06	0.11	0.12	0.15	0.15
	22	−0.06	0.11	0.11	0.14	0.14
	23	0.01	−0.05	−0.05	0.01	0.01
	24	0.01	0.00	0.00	−0.10	−0.10
	25	0.00	−0.01	−0.01	−0.11	−0.11
	26	0.01	−0.02	−0.02	0.03	0.03
	27	0.00	0.00	0.00	−0.12	−0.12
	28	0.02	0.00	0.00	−0.08	−0.08
	29	0.00	−0.01	−0.01	0.00	0.00
	30	0.00	−0.01	−0.01	0.00	0.00
	f	—	2.05	10^{-10}	0.20	10^{-6}

Compound formula	Atom number	Ground state	Excited states Δ01	Δ02
	1	0.01	0.00	−0.06
	2	0.00	0.00	−0.01
	3	0.02	0.02	−0.01
	4	0.01	−0.03	−0.08
	5	0.01	0.02	0.00
	6	0.00	0.00	−0.02
	7	−0.06	0.25	0.20
	8	−0.06	0.25	0.16
	9	0.01	−0.07	−0.03
	10	0.02	−0.14	0.12
	11	0.00	0.01	−0.06
	12	0.01	0.04	−0.05
	13	0.00	−0.15	0.00
	14	0.01	0.02	−0.14
	15	0.00	−0.10	0.03
	16	0.00	−0.02	−0.07
	17	0.00	−0.03	0.00
	18	0.00	−0.08	0.00
	f	—	0.68	0.54

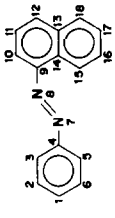
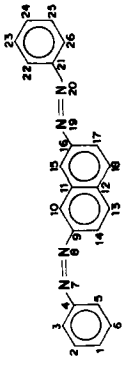
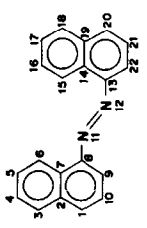
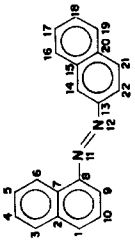
Compound formula	Ground state	Excited states Δ01	Δ02
	0.01	0.00	0.01
	0.00	0.00	0.00
	0.02	0.02	0.02
	0.02	−0.03	0.00
	0.01	0.02	0.01
	0.00	0.00	0.00
	−0.06	0.24	0.13
	−0.06	0.26	0.10
	0.02	−0.12	0.02
	0.02	0.00	−0.02
	0.00	−0.05	−0.06
	0.01	−0.08	0.06
	0.00	0.00	−0.06
	0.01	0.03	−0.09
	0.01	−0.10	0.01
	0.00	−0.05	−0.04
	0.00	−0.03	−0.09
	0.00	−0.10	0.02
	—	0.75	0.02

Table 1 (*continued*).

Compound formula	Atom number	Ground state	Excited states Δ01	Δ02	Δ03
	1	0.01	0.00	0.00	−0.03
	2	0.00	0.00	0.00	0.00
	3	0.02	0.01	0.01	0.00
	4	0.01	−0.02	−0.02	−0.05
	5	0.01	0.01	0.01	0.00
	6	0.00	0.00	0.00	−0.01
	7	−0.06	0.12	0.11	0.10
	8	−0.06	0.13	0.12	0.09
	9	0.01	−0.06	−0.06	−0.05
	10	0.02	−0.13	−0.06	0.07
	11	0.00	0.00	0.00	−0.03
	12	0.01	0.03	−0.01	−0.06
	13	0.00	−0.10	−0.09	−0.02
	14	0.02	0.01	−0.03	−0.06
	15	0.02	−0.13	−0.06	0.07
	16	0.01	−0.06	−0.06	−0.05
	17	0.02	0.01	−0.03	−0.06
	18	0.00	−0.10	−0.09	−0.02
	19	−0.06	0.13	0.12	0.09
	20	−0.06	0.12	0.11	0.10
	21	0.01	−0.02	−0.02	−0.05
	22	0.02	0.01	0.01	0.00
	23	0.00	0.00	0.00	0.00
	24	0.01	0.00	0.00	−0.03
	25	0.00	0.00	0.00	−0.01
	26	0.01	0.01	0.01	0.00
	f	—	1.61	0.002	0.62

Compound formula	Atom number	Ground state	Excited states Δ01	Δ02
	1	0.01	−0.03	−0.01
	2	0.00	0.00	0.00
	3	0.00	−0.04	−0.08
	4	0.00	−0.01	−0.04
	5	0.00	−0.01	−0.01
	6	0.00	−0.04	−0.09
	7	0.01	0.02	0.02
	8	0.02	−0.07	−0.06
	9	0.02	0.01	0.04
	10	0.00	−0.01	−0.02
	11	−0.07	0.22	0.24
	12	−0.07	0.22	0.23
	13	0.02	−0.08	−0.04
	14	0.01	0.02	0.02
	15	0.01	−0.05	−0.10
	16	0.00	−0.02	−0.01
	17	0.00	−0.01	−0.05
	18	0.00	−0.05	−0.09
	19	0.00	0.00	0.00
	20	0.01	−0.05	0.01
	21	0.00	−0.03	−0.02
	22	0.02	0.01	0.06
	f	—	0.92	0.01

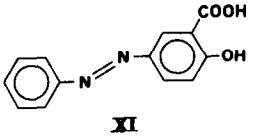
Compound formula	Ground state	Excited states Δ01	Δ02
	0.01	−0.06	0.02
	0.00	0.00	0.00
	0.00	−0.05	−0.04
	0.00	−0.02	−0.02
	0.00	−0.02	0.00
	0.00	−0.06	−0.05
	0.01	0.02	0.02
	0.02	−0.10	−0.01
	0.02	0.00	0.04
	0.00	−0.03	−0.01
	−0.06	0.24	0.22
	−0.06	0.23	0.20
	0.02	−0.05	0.01
	0.02	−0.04	0.00
	0.00	0.00	0.00
	0.00	−0.04	−0.06
	0.00	0.00	−0.08
	0.00	−0.02	0.02
	0.00	−0.03	−0.09
	0.00	0.00	0.01
	0.00	−0.04	−0.09
	0.01	0.03	−0.09
	—	0.94	0.08

occurs and the magnitude and direction of the transition moment, which in turn, is determined by the change in the electron distribution in the molecule during excitation. In other words, the intensity of a band in the spectrum is determined by the magnitude, direction and distance of electronic charge transfer in a molecule, occurring during the absorption of a light quantum by the molecule. To predict and interpret the spectral properties of dyes it seems helpful to use the approach in which the idea of interaction of separate chromophores in molecules of bis-dyes[3,4] is utilized, or general quantum-mechanical analysis of the spectral properties of a system consisting of subsystems that interact only rarely.[5]

Let us consider the conclusions drawn from analysis of the comparison of the electron-density distribution of dye molecules between the ground and excited states (Table 1).

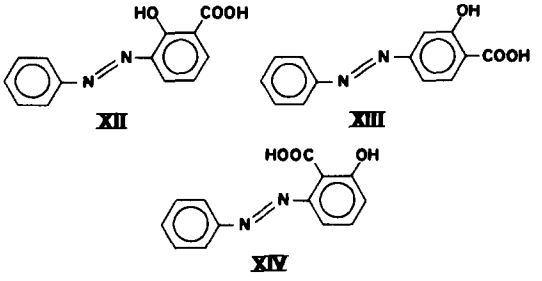
A large number of organic reagents have been synthesized on the basis of azobenzene (Fig. 1). Let us consider the nature of the azobenzene absorption bands. As apparent from the data listed, the nature of the first* band is attributed to the electron-density transfer mainly from the 1-, 4-, 1-′ and 4′-positions of the benzene nuclei to the nitrogen atoms of the azo-group. It is evident from Table 1 that the second band corresponding to the transition forbidden by symmetry has an intrinsically different nature. It is attributed to the electron-density transfer from the *meta*- and *ortho*-positions of the benzene nuclei to the nitrogen atoms of the azo-group. Proceeding from it we may assume that substituents which will maintain the direction and increase the extent of the transfer will increase the intensity of the given band. Substituents which change the direction of the electron-density transfer will decrease the intensity of the given band, but may be conducive to an increase in the intensity of another band for which they maintain the direction of transfer. These assumptions are seen to be valid for the effect of hydroxy and amino groups in different positions on the wavelength and intensity of the bands of hydroxy or amino derivatives of azobenzene. Thus 2-hydroxyazobenzene is characterized by two bands of appreciable intensity (see Table 1). When the π-donor properties of a substituent are improved, *e.g.*, by use of the amino group instead of the hydroxy group, the intensity of the shorter wavelength band increases and the intensity of the longer wavelength band decreases in comparison with those for the hydroxy derivatives.

Another picture is seen in the case of the *p*-hydroxy or *p*-amino derivatives of azobenzene. As in the case of azobenzene itself, electron density is here transferred mainly from the 1- and 4-positions. Transfer from the 4-position coincides in direction with the transfer from the π-donor substituent. Therefore in these derivatives the relative band intensities are as expected, *i.e.*, the long wavelength band is much more intense than the short wavelength band, and a little more intense than that for azobenzene itself. The introduction of π-donor substituents in the *meta*-position sharply changes the electron-density distribution in the ground and excited states of azobenzene, leading to the intensities of the first and second bands becoming closer (see Table 1). From this analysis the following recommendation may be made for synthesis of organic reagents based on azobenzene: π-donor groups should be introduced *para* to the azo-group; constituents possessing weak π-acceptor properties should be introduced into the *meta*-position. Thus functional groups of *o*-hydroxy acid or *o*-hydroxyaldehyde type should be introduced as shown in structure **XI** in order to retain the chromophore structure of azobenzene and thus the intense first band:



XI

and not as in structures **XII–XIV**:



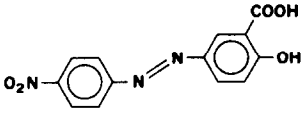
XII **XIII** **XIV**

As follows from the calculation data (Table 1), reagent **XI** must possess the most intense colour. The interaction of this reagent with metal ions, however, will be characterized by only slight colour contrast, as a result of the weak effect of hydroxyl group dissociation in this reagent on the position of the absorption band. The reagents having structures **XII–XIV** possess lower band intensities but the reactions with metals are of sharper colour contrast. This is caused by the fact that the improvement of the π-donor properties of the hydroxy group occurring during dissociation results in increase of the intensity of the shorter wavelength band. Therefore, the reagent of type **XI** and its complexes with metals are more intense in colour but for analytical purposes it will be necessary to separate the excess of reagent from the complex, which is a complicated problem. The reagents of types **XII–XIV** provide stronger colour contrast in their reactions with metal ions, so there is no need for separation of small excesses of the reagents.

A special case is the introduction of strong π-acceptor substituents, such as $-NO_2$, into these chromophoric nuclei. Introduction of a nitro group into the *meta*- or *para*-position considerably changes the electron-density distribution. Along with the nitro-group

* Band numbering starts with the one of longest wavelength.

effect on the original absorption bands of the parent reagent, new bands arise from intramolecular charge-transfer from the oxygen atoms of the nitro group to the nitrogen atoms of the azo group. As an example let us consider reagent XV in which the nitro group is in the *para*-position:



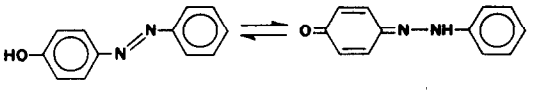
XV

This reagent was originally tested empirically.[6] Its spectrum is characterized by the first (low-intensity) band caused by the intramolecular charge-transfer mentioned above, and the second (intense) band which is analogous in nature to the second band of azobenzene. Therefore, the strong π-acceptor in the *para*-position to the azo-group has the same effect as a π-donor in the *meta*-position. The nitro group fails to improve the contrast properties of this reagent, however, and they remain poor.

The sensitivity of reactions with these reagents can be increased by formation of bis-dyes. In analytical practice, dyes possessing such chromophoric nuclei as bisazobenzene and stilbazo (see formulae II and III in Fig. 1) have already found application. The calculations made (Table 1) reveal that these bis-dyes are analogous in spectral characteristics to azobenzene but the intensities of the bands are doubled. This indicates that in such molecules the chromophoric nuclei behave as two isolated azobenzene molecules. It is curious that the dimethyn group in stilbazo does not influence the spectral properties of the reagent. It is an interesting example of conjugational chain-lengthening not affecting the spectral properties of a dye. In terms of the classical theory of chromophores,[3,4] with a linear arrangement of two interacting chromophores, the position of the absorption maxima of the separate chromophores should not change. The intensity of the bands, however, should either decrease practically to zero or be doubled, depending on the mutual orientation of the separate chromophores. Evidently the band intensities of the separate chromophores are additive in the case cited.

On the basis of the outline above, two rules for directed synthesis of organic reagents on the basis of bis-dyes may be formulated. First, the effect of substituents on the position and intensities of the bands for the bis-dyes should be analogous to the effect of these substituents in separate chromophores. Secondly, the substituents should be introduced into the bis-dye molecules without disalignment of the general symmetry of a molecule. Some of the reagents applied in analytical chemistry and based on bis-dyes are really symmetrical, for instance, phenazo, stilbazogall, stilbazo. They were developed empirically, however, and not by a theoretical approach.

All this holds for azo-dye reagents in which the functional group does not include the azo group and is isolated from it. There are, however, a number of organic reagents based on azobenzene, in which the azo group is a part of the functional grouping. Such reagents usually contain an *o,o'*-dihydroxyazo grouping. As distinct from the phenylazonaphthols considered below, the formation of the quinone–hydrazone form:



is not typical for hydroxy-derivatives of azobenzene. Such derivatives exist in solution only (or mainly) in the azo form. However, when an *o,o'*-dihydroxyazo group is present, complexes with metals can be formed in which the reagent is in the quinone–hydrazone form.[8] The data in Table 1 show that the formation of the quinone–hydrazone form leads to a sharp change in the position and intensity of the absorption bands. The absorption is particularly intense for *p*-quinone–hydrazone formation. Because the quinone–hydrazone structure in azobenzene-based reagents can only arise in complexes, the investigation of the effect of substituents on the spectral properties of such reagents is rather difficult. However, *o,o'*-dihydroxyazo derivatives of azobenzene and its analogues are the most promising organic reagents. Their interaction with metal ions is characterized by sharp contrast and great sensitivity. Because the quinone–hydrazone structure for azobenzene derivatives arises only during complex formation with metals the synthesis of bis-dyes of such a type is not very useful.

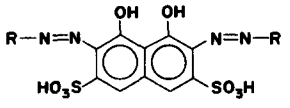
The analysis of theoretical calculations of azo-dye structures containing naphthalene nuclei (Table 1) indicates that irrespective of the position of the azo-group on the naphthalene nucleus, during the excitation which causes the most intense band, electron density is transferred from the 1, 4, 5 and 8-positions of the naphthalene nucleus to the nitrogen atoms of the azo-group. Thus it is recommended that donor groups should be introduced into these positions during synthesis of the azo dyes.

Another peculiarity of azo dyes containing naphthalene or larger cyclic condensed molecules (anthracene, *etc.*) is ease of quinone–hydrazone structure formation.[7] When there are hydroxy groups in the naphthalene nucleus of an azo dye, the reagent exists in solution as two equilibrium forms—the azo and the quinone–hydrazone form. Therefore, the colour contrast in the complexation reaction depends directly on the ratio of the reagent forms in solution.

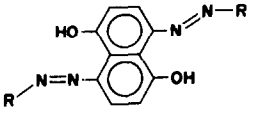
Unlike hydroxyazo dyes possessing benzene nuclei, synthesis of bis-hydroxyazo dyes containing naphthalene nuclei can result in enhancement of the sensitivity of determination, because both parts of bis-dyes can be in quinone–hydrazone form. With selected substituents, a high symmetry of the reagent in the complex (in which the metal is bound only to one chromophoric nucleus) may be achieved.

The data given (Table 1) allow formulation of some

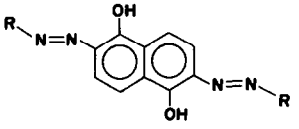
recommendations for the synthesis of bis-dyes possessing naphthalene nuclei. As distinct from the well-known bisazo derivatives of chromotropic acid of the type



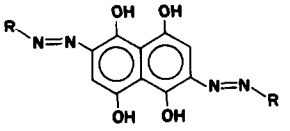
bis-dyes of the types



or



or



should have more intense colours. As can be seen, all the dyes recommended are characterized by having higher symmetry than those applied. This should lead to the greatest sensitivity of reaction.

REFERENCES

1. R. Pariser and R. G. Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.
2. J. A. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.
3. A. I. Kiprianov, *Uspekhi Khim.*, 1971, **40**, 1281.
4. A. I. Kiprianov and G. G. Dyadyusha, *Ukr. Khim. Zh.*, 1969, **35**, 609.
5. J. N. Murrell, *The Theory of the Electronic Spectra of Organic Molecules*, Methuen, London, and Wiley, New York, 1963.
6. Gh. Baiulescu and I. C. Cuirea, *Z. Anal. Chem.*, 1959, **166**, 5.
7. H. Zollinger, *Chemie der Azofarbstoffe*, Birkhauser Verlag, Basel, 1958.
8. A. T. Pilipenko, L. I. Savransky and E. G. Skorokhod, *Zh. Analit. Khim.*, 1972, **27**, 1080.
9. G. I. Kagan, I. N. Fundyler and G. M. Kagan, *Teor. Eksp. Khim.*, 1966, **2**, 589.
10. N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt)*, 1953, **13**, 140.
11. J. Hinze and H. H. Jaffe, *J. Am. Chem. Soc.*, 1962, **84**, 545.

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A POLAROGRAPHIC AND COULOMETRIC STUDY OF THE IRON(III)-SOLOCHROME VIOLET RS SYSTEM

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Summary—Experimental results are presented which clearly illustrate the kinetic character of the polarographic waves/peaks of the iron(III)–Solochrome Violet RS (SVRS) complex formed at pH 4.7. Even in the presence of an excess of iron(III), at the $10^{-3}M$ level of SVRS only half of the azo-dye wave is displaced to more negative potentials. At lower concentrations (*e.g.*, $10^{-6}M$), however, a larger fraction is displaced. The undisplaced wave/peak corresponds to reduction of free dye dissociated from the complex, whereas the displaced wave/peak corresponds to the reduction of the complexed dye directly. The temperature coefficient for the undisplaced peak is 12%/deg at the $10^{-5}M$ level, indicating that the height of this peak is controlled, at least in part, by the rate of dissociation of the iron(III) complex. The rate of increase of the *total* limiting current produced by reduction of the complex and of the free dye dissociated from it, becomes less at higher concentrations and is an indication of adsorption occurring at the dropping mercury electrode. In the controlled-potential coulometric reduction of the complex at a mercury-pool cathode at pH 4.7, the SVRS is reduced completely in a four-electron reaction at a potential only slightly more negative than that for the reduction of the free dye, indicating that the dye is dissociated from the complex and then reduced at this potential; the iron(III) is reduced simultaneously to iron(II). In view of the kinetic nature of the polarographic waves of the SVRS–iron(III) complex, care must be taken in using SVRS as a reagent for the polarographic determination of iron(III).

Chelating azo dyes have been used extensively as reagents in the polarographic determination of metal ions,[1] particularly those such as the aluminium ion which are reduced at high negative potentials. Aluminium can be determined directly by means of its reduction wave at -1.76 V, but is more usually determined[2] by means of its Solochrome Violet RS (SVRS) complex. The complexed azo dye is reduced at a more negative potential than is the excess of free dye, and the height of the wave for the complex is proportional to the concentration of the complex and hence, as excess of reagent is used, to the concentration of aluminium.

This formation of two waves is a kinetic effect and only occurs when the rate of dissociation of the metal complex is slow compared with the rate of the electron-transfer reaction associated with reduction of the free dye. In contrast to the aluminium–SVRS system, the rate of dissociation of the beryllium–SVRS complex must be rapid compared with the electron-transfer reaction associated with the reduction of SVRS as all the dye is reduced at the reduction potential of the free dye, *i.e.*, only a single wave is obtained even in the presence of beryllium. Earlier work in this laboratory[3,4] has shown that in the case of Mordant Red 74 the two metals behave the other way round: the beryllium complex is reduced directly at a more negative potential than is the free dye, whereas the dye in the aluminium complex is reduced (with prior dissociation of the complex) at the reduction potential of the free dye. Potentiometric titrimetry was used in all these cases to confirm that complete complex formation had occurred under the conditions used in polarography.

The addition of excess of aluminium to a Solochrome Violet RS solution at the SVRS level normally used in analysis with conventional d.c. polarography ($10^{-3}M$) causes essentially complete suppression of the wave for the free dye, but addition of excess of iron(III) causes only half of the wave to be displaced to more negative potential.[5] It was considered initially that this effect of iron(III) might be caused by the formation of a stable intermediate, possibly an iron(III)–hydrazo complex, but the present study has shown that the formation of two waves of equal height arises from a coincidental choice of solution conditions and that the effect is kinetic, arising from the similarity in the rate of dissociation of the iron complex and the rate of the electron-transfer reaction associated with the reduction of Solochrome Violet RS.

Rooney and McIver[6] studied the cathode-ray polarographic determination of iron(III) in the range 3×10^{-7}–$5 \times 10^{-5}M$ (with excess of SVRS) in the pH range 4–5. At iron(III) concentrations greater than $7.5 \times 10^{-6}M$ the peak-height was found to be erratic and this they considered might be caused by oxidation of the dye by iron(III). Under similar conditions, using d.c. polarography, Reynolds and coworkers[7,8] found that the slope of the calibration curve decreased when the iron(III) concentration exceeded $4 \times 10^{-5}M$ and that a further change of

slope occurred at $2.5 \times 10^{-4}M$ iron(III). At pH 6.5 the calibration graph was rectilinear up to $1.5 \times 10^{-4}M$ iron(III). Pyburn[5] attempted to use the method of continuous variations polarographically at pH 4.5 to ascertain the stoichiometry of the complex formed, but the results were inconclusive owing to the erratic values of the wave-heights.

As no satisfactory explanations have been given for the observations noted above, it was decided to investigate this system further.

In this communication the limiting current of the first wave (the undisplaced wave) is termed i_{l1} and that of the second wave (the displaced wave), i_{l2}. The heights of the corresponding differential pulse peaks are termed i_{p1} and i_{p2}.

EXPERIMENTAL

Instrumentation

A Princeton Applied Research Corporation PAR174A polarographic analyser was used in the three-electrode mode. All potentials quoted are versus the saturated calomel electrode. Solutions were polarographed in a 50-ml cell kept at 25.0 ± 0.1° unless otherwise stated. Solutions (volume approx. 20 ml) were allowed at least 15 min to reach the required temperature, during which time they were deoxygenated with nitrogen which had been passed over copper wire at 560°.

Differential pulse polarograms were obtained with a pulse amplitude of 50 mV, a forced drop-time of 2 sec and a scanning rate of 1 mV/sec. Potential scans were usually recorded over the range from +0.15 V to −0.90 V. The rate of flow of mercury was 0.46 mg/sec.

Conventional d.c. polarograms were also obtained at a scan-rate of 1 mV/sec, with a low-pass (damping) setting of 3. The natural drop-time was 4.17 ± 0.03 sec at −0.35 V and the mercury flow-rate was 1.65 ± 0.1 mg/sec. These polarograms were used for logarithmic analysis of the wave for the free dye and for obtaining plots of current as a function of height of the mercury reservoir.

Constant-potential coulometry was carried out with a PAR 173/179 coulometric system at a mercury-pool cathode in a 25-ml cell with a platinum anode and a saturated calomel reference electrode contained in individual compartments each separated from the main compartment by means of an anion-exchange membrane.

Reagents

A commercial sample of Solochrome Violet RS was recrystallized four times from 50% v/v aqueous ethanol, dried in a vacuum over at 70° for 48 hr and then stored over silica gel.[9] Potentiometric titration with $0.1M$ sodium hydroxide indicated a purity of 105 ± 2%, assuming the dye was the dihydrate (the end-point is not sharp in this titration). Constant-potential coulometry at −0.70 V with the cell described above indicated a purity of 99 ± 1%. Thin-layer chromatography on silica gel with n-butanol–ethanol–water–concentrated ammonia solution (61:12:26:1 v/v) gave an intense spot for Solochrome Violet RS at $R_f = 0.6$, preceded by a faint pink spot and followed closely by two faint brown spots. Stock standard solutions of (2.00×10^{-3} and 3.00×10^{-3} M) Solochrome Violet RS were prepared.

Iron(III) was added as $0.100M$ ammonium iron(III) sulphate in $0.38M$ perchloric acid.

Acetate buffer (pH 4.68) was 0.11 M in sodium acetate and 0.10 M in acetic acid unless otherwise stated. A universal buffer solution, $2M$ in hydrochloric acid, $1M$ in orthophosphoric acid, $1M$ in glycine and $1M$ in citric acid was also used: 2 ml of this solution were diluted to 50 ml with water and the pH was adjusted to the required value by addition of $10M$ sodium hydroxide. This buffer was only used at pH values >5.8 as the azo-dye complex was not formed at lower pH values in its presence.

Preparation of solutions for polarography

Freshly diluted stock solutions of iron(III) (1 or $2 \times 10^{-3}M$ and 1 or $2 \times 10^{-4}M$) and Solochrome Violet RS (1 or $2 \times 10^{-4}M$) were used. Each solution (50 ml) prepared for polarography contained 25 ml of buffer solution, and the required amount of SVRS and iron(III). No polarographic maxima were observed, but to some solutions 0.5 ml of 0.2% v/v Triton X-100 solution was added in order to study the effect of a maximum suppressor.

Solutions in acetate buffer were heated in a water-bath at 70° for 1 hr and then left overnight before polarography. Solutions of pH > 6 gave reproducible polarograms after standing at room temperature for 1 hr. The pH values of all solutions were measured immediately before polarography and any minor adjustments of pH were made with $6M$ sodium hydroxide or $6M$ perchloric acid.

RESULTS

Differential pulse polarograms were obtained for solutions $2 \times 10^{-5}M$ in SVRS and from 2×10^{-6} to $2 \times 10^{-4}M$ in iron(III) in acetate buffer at pH 4.68, with and without addition of Triton X-100. The results are given in Table 1. In the presence of Triton X-100, the height of the displaced peak, i_{p2}, is proportional to iron(III) concentration up to a ratio of Fe(III) to SVRS of at least 0.67. The total current, $i_{p1} + i_{p2}$, decreases sharply by about 15% at an Fe(III) to SVRS ratio of about 0.2, and again by about 10% at a ratio of 2.0. In the absence of Triton X-100, the height of the displaced peak is proportional to iron(III) initially only up to an Fe(III) to SVRS ratio of about 0.5 and then i_{p2} increases rectilinearly but with lower slope up to a reactant ratio of 1.5. Above this ratio i_{p2} remains constant. It may be significant that the total current, $i_{p1} + i_{p2}$, which otherwise maintains a constant value, is some 15% less within the iron:SVRS ratio range 0.5–1.5, and also that within this range a prewave appears at −0.06 V (see Fig. 1). The change in slope might be attributed to formation of the 1:1 Fe(III):SVRS complex at the expense of the 1:2 complex, but Florence and Belew[9] consider that only the 1:1 complex is formed at pH 4.8.

Pyburn[5] found the ratio of i_{l1} to i_{l2} to be approximately 1 at both pH 4.6 and 6.5 when the concentration of SVRS was $1 \times 10^{-3}M$ and iron(III) was in excess. Florence and Belew,[9] working at pH 4.3 and an SVRS concentration of $2 \times 10^{-5}M$, obtained ratios of i_{l1}/i_{l2} of 0.09 and 0.064 in the presence of tenfold and fiftyfold ratio of iron(III) to SVRS, respectively.

In order to study further the effects of concentration level on the ratio of i_{p1}/i_{p2}, solutions that were from $2 \times 10^{-6}M$ to $1 \times 10^{-3}M$ in SVRS and had a 2:1 ratio of iron(III) to SVRS at pH 4.68 (acetate buffer) and 6.66 (universal buffer) were polarographed. A similar study with a tenfold ratio of iron(III) to SVRS was also made, but hydrolysis of iron(III) was

Table 1. Effect of iron(III) on differential pulse polarograms of SVRS (SVRS concentration = $2 \times 10^{-5}M$; pH = 4.68)

Mole ratio Fe(III):SVRS	$*i_{p1}$, μA	$*i_{p2}$, μA	$i_{p1} + i_{p2}$, μA
At 25°C; 0.002% Triton X-100			
0.00	6.23	0.00	6.23
0.10	5.69	0.57	6.26
0.13	5.72	0.72	6.44
0.20	5.04	1.05	6.09
0.50	2.63	2.60	5.23
0.67	1.81	3.46	5.27
1.00	1.01	4.22	5.23
2.00	1.07	4.24	5.31
3.00	0.94	3.88	4.82
4.00	0.98	3.88	4.86
10.00	0.72	3.54	4.26
At 30°C; no Triton X-100 added			
0.00	6.04	0.00	6.04
0.10	5.58	0.60	6.18
0.20	4.90	1.29	6.19
0.50	2.79	2.80	5.59
0.67	2.44	3.19	5.63
0.75	2.33	3.31	5.64
1.00	1.96	3.83	5.79
1.25	1.27	4.75	6.02
1.50	0.83	5.35	6.18
2.00	0.85	5.31	6.16
3.00	0.84	5.41	6.25
4.00	0.89	5.29	6.18

* i_{p1} = height of the undisplaced peak; i_{p2} = height of the displaced peak.

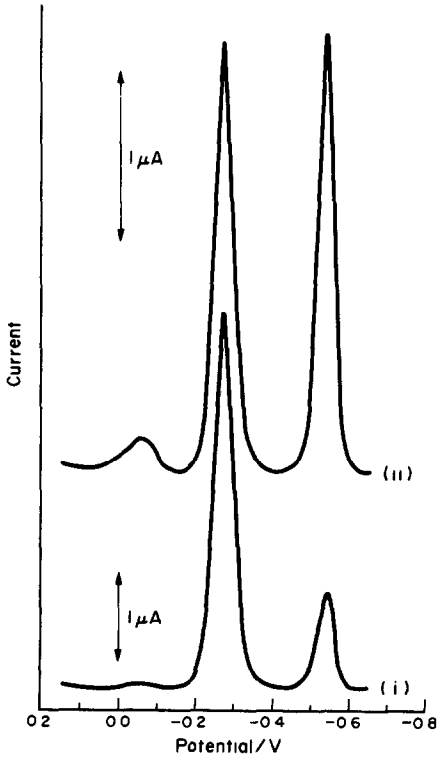


Fig. 1. Differential pulse polarograms showing prepeak at −0.06 V. SVRS concentration = $2 \times 10^{-5}M$, pH = 4.68, 25°C. No Triton X-100 added. Iron(III) concentration, (*i*) $4 \times 10^{-6}M$, (*ii*) $1 \times 10^{-5}M$.

apparent, especially at higher concentrations of iron(III). The results are given in Table 2. The ratio i_{p1}/i_{p2} is clearly highly dependent on the concentration level, pH and the presence or absence of Triton X-100. At pH 4.68 a high proportion of the peak is displaced at the lower concentrations, whereas at high concentrations less than half of the peak is displaced. Conversely, at pH 6.66 slightly greater displacement occurs at the higher concentrations than at lower, but even at high concentrations little more than half of the peak is displaced. At both pH-values the total current, $i_{p1} + i_{p2}$, per unit concentration of SVRS decreases with increasing concentration of SVRS, indicating that adsorption is occurring at the dropping mercury electrode.

A more detailed study of the effect of pH was made next. The effect of pH on the SVRS–iron(III) system has been studied before,[5] but the present study was made with iron(III) in excess. At the $10^{-5}M$ level studied here it is clear (see Table 3) that the individual heights of the undisplaced and displaced peaks remain effectively constant above about pH 6, *i.e.*, for solutions buffered with the universal buffer. At lower pH-values this is not the case; the displaced peak is much larger than the undisplaced peak but i_{p1}/i_{p2} increases to a constant value of about 1.2 as the pH increases to 6. Prewaves, often of appreciable height, were noted at potentials more positive than that for the undisplaced peak and these waves are also listed in Table 3.

Table 2. Comparison of the heights of the undisplaced and displaced peaks at constant Fe(III):SVRS ratio

[SVRS], M	No Triton X-100 (25°C)					0.002% Triton X-100 (30°C)				
	i_{p1}, μA	i_{p2}, μA	i_{p1}/i_{p2}	$i_{p1}+i_{p2}$, μA	$\frac{i_{p1}+i_{p2}}{C_{SVRS}}$, $A.l.mole^{-1}$	i_{p1}, μA	i_{p2}, μA	i_{p1}/i_{p2}	$i_{p1}+i_{p2}$, μA	$\frac{i_{p1}+i_{p2}}{C_{SVRS}}$, $A.l.mole^{-1}$
				pH 4.68, Fe(III):SVRS = 2						
2×10^{-6}	0.12	0.43	0.29	0.55	0.279	0.13	0.38	0.34	0.51	0.253
2×10^{-5}	0.96	4.50	0.21	5.46	0.273	0.50	2.07	0.24	2.57	0.129
1×10^{-4}	10.1	16.5	0.61	26.6	0.266	11.4	9.08	1.26	20.5	0.205
5×10^{-4}	44.9	28.6	1.57	73.5	0.147	34.0	18.8	1.81	52.8	0.106
1×10^{-3}	55.4	46.2	1.20	101.6	0.101	47.5	26.1	1.82	73.6	0.074
				pH 6.66, Fe(III):SVRS = 2						
2×10^{-6}	0.30	0.20	1.50	0.50	0.252	0.41	0.17	2.51	0.58	0.290
2×10^{-5}	2.30	2.19	1.05	4.49	0.225	1.52	1.03	1.48	2.55	0.128
1×10^{-4}	10.2	10.8	0.94	21.0	0.210	8.30	6.60	1.27	14.9	0.149
5×10^{-4}	23.5	29.8	0.79	53.3	0.107	22.5	17.50	1.29	40.0	0.080
1×10^{-3}	32.3	37.0	0.87	69.3	0.069	31.6	29.4	1.07	61.0	0.061
				pH 4.68, Fe(III):SVRS = 10						
2×10^{-6}						0.09	0.42	0.21	0.51	0.252
1×10^{-5}						0.48	1.78	0.27	2.26	0.226
5×10^{-5}						1.55	6.25	0.25	7.80	0.156
1×10^{-4}						3.70	8.94	0.41	12.6	0.126
8×10^{-4}						40.0	14.0	2.86	54.0	0.068

Buffer concentration can affect the height of certain kinetic waves and this effect was studied for the acetate buffer here. The results are shown in Table 4. In view of the other parameters which contribute to the height of these waves and in particular the effect of small changes of pH in this region, the significance of the results is not unequivocal, but it does appear that the height of the displaced peak decreases slightly with increasing buffer concentration.

The temperature coefficient of the limiting current

Table 3. Effect of pH

pH	Undisplaced peak E_p, V	Undisplaced peak i_{p1}, μA	Displaced peak E_p, V	Displaced peak i_{p2}, μA	i_{p1}/i_{p2}	$i_{p1}+i_{p2}$, μA	Prepeaks E_p, V	Prepeaks i_p, μA	Prepeaks E_p, V	Prepeaks i_p, μA
3.94	−0.32	0.73	−0.58	3.92	0.19	4.64			−0.06	0.38
4.68	−0.27	1.07	−0.54	4.23	0.25	5.30	0.00	0.16	−0.08	0.17
5.20	−0.29	1.88	−0.57	3.16	0.60	5.04			−0.02	0.09
6.01	−0.35	2.70	−0.65	2.15	1.25	4.85	−0.08	0.90	−0.16	0.73
6.22	−0.37	2.78	−0.66	2.07	1.34	4.85			−0.16	0.83
6.40	−0.37	2.38	−0.67	2.14	1.11	4.52			−0.17	0.83
7.03	−0.42	2.23	−0.69	2.02	1.10	4.25	−0.05	0.55	−0.22	1.05
7.43	−0.46	2.40	−0.73	2.03	1.18	4.43			−0.25	1.25
7.78	−0.46	2.43	−0.72	1.90	1.28	4.33			−0.26	0.96
8.81	−0.48	2.89	−0.71	2.05	1.41	4.30	0.00	1.00	−0.25	0.45
9.84	−0.43	3.23	−0.66	2.03	1.59	5.26			−0.18	0.30

$C_{SVRS} = 2\times10^{-5}M$, 25°C.
$C_{Fe(III)} = 4\times10^{-5}M$, no Triton X-100 added.

Table 4. Effect of buffer concentration

[Acetate], M	[Acetic acid], M	pH	i_{p1}, μA	i_{p2}, μA	i_{p1}/i_{p2}
0.055	0.05	4.67	1.07	4.23	0.25
0.15	0.16	4.66	0.97	4.50	0.21
0.32	0.33	4.61	0.90	4.45	0.20
0.68	0.89	4.58	1,08	3.72	0.29
0.78	1.88	4.54	1.18	3.38	0.35

$C_{SVRS} = 2\times10^{-5}M$, 25°C.
$C_{Fe(III)} = 4\times10^{-5}M$, no Triton X-100 added.

Table 5. Effect of temperature: no Triton X-100 added except where indicated

C_{SVRS}, M	$C_{Fe(III)}$, M	T, °C	i_{p1}, μA	i_{p2}, μA	i_{tot}, μA	di_{p1}/dT, %	di_{p2}/dT, %	di_{tot}/dT, %	i_{p1}/i_{tot}	$\frac{d\left(\frac{i_{p1} \times 100}{i_{tot}}\right)}{dT}$ %
pH = 4.68										
2×10^{-5}	4×10^{-5}	26.0	1.25	4.30	5.55				0.22	
		35.2	2.60	3.45	6.05	+11.7	−2.2	+1.0	0.43	+2.2
*2×10^{-5}	4×10^{-5}	30.2	0.89	4.40	5.29				0.17	
		39.6	1.95	3.15	5.10	+12.7	−3.0	−0.4	0.38	+2.2
2×10^{-5}	1×10^{-5}	25.0	2.55	2.79	5.34				0.48	
		35.0	3.32	2.75	6.07	+3.0	−0.1	+1.4	0.55	+0.7
pH = 6.66										
2×10^{-5}	4×10^{-5}	25.0	2.30	2.19	4.49				0.51	
		35.0	3.30	2.48	5.78	+4.4	+1.3	+2.9	0.57	+0.7
†*2×10^{-5}	4×10^{-5}	30.2	2.70	1.88	4.58				0.59	
		39.4	3.05	1.08	4.13	+1.4	−4.6	−1.1	0.74	+1.6
2×10^{-5}	1×10^{-5}	25.0	2.55	2.30	4.85				0.56	
		35.0	3.65	2.45	6.10	+4.3	+0.7	+2.6	0.60	+0.4
1×10^{-3}	2×10^{-3}	25.0	32.5	37.0	69.3				0.47	
		35.0	37.5	44.3	81.8	+1.6	+2.0	+1.8	0.46	−0.1
*2×10^{-5}	2×10^{-4}	30.0	2.63	2.05	4.68				0.56	
		40.0	2.94	1.53	4.47	+1.2	−2.5	−0.5	0.66	+1.0

* 0.002% Triton X-100.
† pH 5.96.

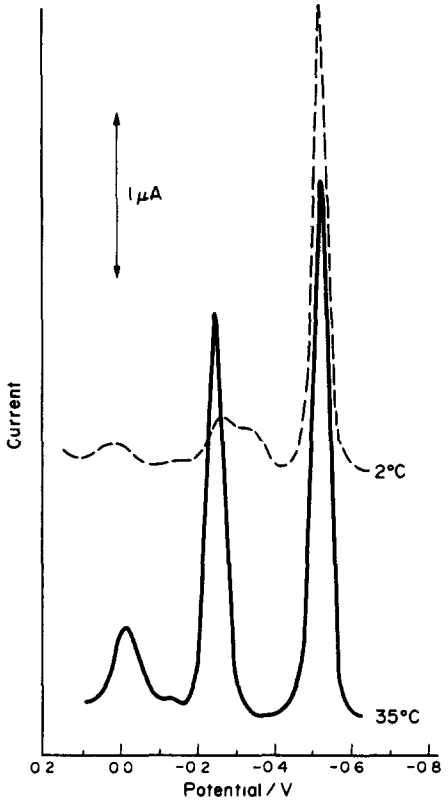


Fig. 2. Effect of temperature on the relative heights of the undisplaced and displaced differential pulse polarographic peaks. Concentration of SVRS = 2×10^{-5}M. Concentration of iron(III) = 4×10^{-5}M. pH = 4.68. No Triton X-100 added.

of a polarographic wave often provides useful information on the nature of the process limiting the current. Diffusion currents increase with temperature, typically by about 1.8%/deg. Some kinetic currents increase by 5–20%/deg, but others behave in a similar manner to diffusion currents. Adsorption waves are not easily recognized by this method as they may increase, decrease, or remain constant as the temperature is increased. In the present study the temperature coefficients of the undisplaced and displaced peaks were studied over a limited temperature range. The results are shown in Table 5.

At pH 4.68 and a 2:1 ratio of iron(III) to SVRS it is clear that the undisplaced and displaced peaks are kinetically controlled, although the total current, $i_{p1} + i_{p2}$, appears to be diffusion-controlled. The temperature coefficient of the undisplaced peak is 12%/deg and this must be caused by the rate of dissociation of the complex increasing rapidly with temperature. This rate of increase of the undisplaced peak at the expense of the displaced peak with increasing temperature is much less marked at pH 6.6, but this would be expected as the extent of displacement is less than at pH 4.68.

One solution was subjected to polarography first at 2° and then at 35°. The polarograms obtained are shown in Fig. 2. The effect of the slower dissociation of the complex at 2° is clearly seen. At this temperature the shoulder of a post-peak can be seen on the undisplaced peak.

Logarithmic analysis of the undisplaced d.c. polarographic wave obtained in the presence of excess of iron(III) (see Table 6) and of the effect of mercury height (h) on the height of this wave (see Table 7)

Table 6. Logarithmic analysis of the undisplaced d.c. polarographic wave

Potential, V	i, μA	$\log(i/i_{l1} - i))$
−0.220	0.0072	−0.965
−0.225	0.0116	−0.728
−0.230	0.0180	−0.490
−0.235	0.0244	−0.305
−0.240	0.0312	−0.133
−0.245	0.0380	0.028
−0.250	0.0460	0.222
−0.255	0.0520	0.382
−0.260	0.0574	0.549
−0.265	0.0624	0.746

$C_{SVRS} = 2 \times 10^{-5} M$, pH = 4.67.
$C_{Fe(III)} = 4 \times 10^{-5} M$, $i_d = 0.0736\ \mu A$.
No Triton X-100 added, 25°C.

indicates a reversible two-electron reduction with a half-wave potential of −0.245 V at pH 4.67. Plots of i *vs.* h and i *vs.* $\sqrt{h}$ are both approximately rectilinear and of finite slope. If the undisplaced wave were solely kinetically controlled, its height would be independent of the height of the mercury reservoir. Complete kinetic control would not be expected here, however, as the value of i_{l1} is about one-quarter the value it would have (*viz.* $i_{l1} + i_{l2}$) if all the dye were reduced at this potential. When the condition $i_k \ll i_d$ does not apply, a contribution from the diffusion of the inactive form (at the particular potential) is to be expected.[10]

The constant-potential coulometry of the SVRS–Fe(III) system was studied at pH 4.7. Coulograms of SVRS and of SVRS–Fe(III) are shown in Fig. 3. Amounts of SVRS and SVRS–Fe(III) solution were added to the coulometric cell by means of a 100-μl syringe after the residual current due to the supporting electrolyte had been backed off. From Fig. 3 it is clear that the iron complex can be reduced completely at the potential for reduction of the free dye; this is to be expected as the complex has adequate time to dissociate at the mercury-pool cathode. Further, it is apparent that the iron(III) is also reduced to iron(II) during this process. A solution of the SVRS–Fe(III) complex, which had been partly reduced in the coulometric cell, was studied polarographically. The polarograms are shown in Fig. 4 and polarographic peaks of a reduction intermediate (unidentified) are evident.

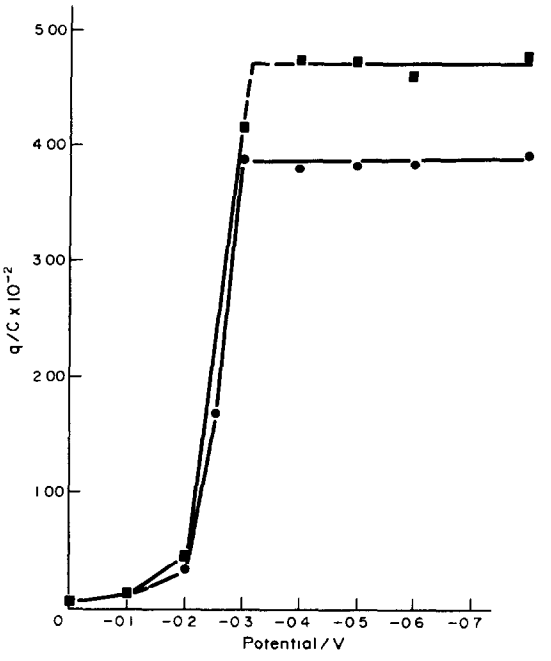


Fig. 3. Coulograms of SVRS (●) and its iron(III) complex (■) at pH 4.7; all potentials relative to the saturated calomel electrode.

Table 7. Effect of mercury height (h) on the height of the undisplaced d.c. polarographic wave

h, cm	$h^{1/2}$, $cm^{1/2}$	i_{l1}, μA
82.4	9.08	0.0690
72.6	8.52	0.0656
62.3	7.89	0.0620
52.3	7.23	0.0554
42.2	6.50	0.0526

$C_{SVRS} = 2 \times 10^{-4} M$, pH = 4.68.
$C_{Fe(III)} = 4 \times 10^{-4} M$, 25°C.

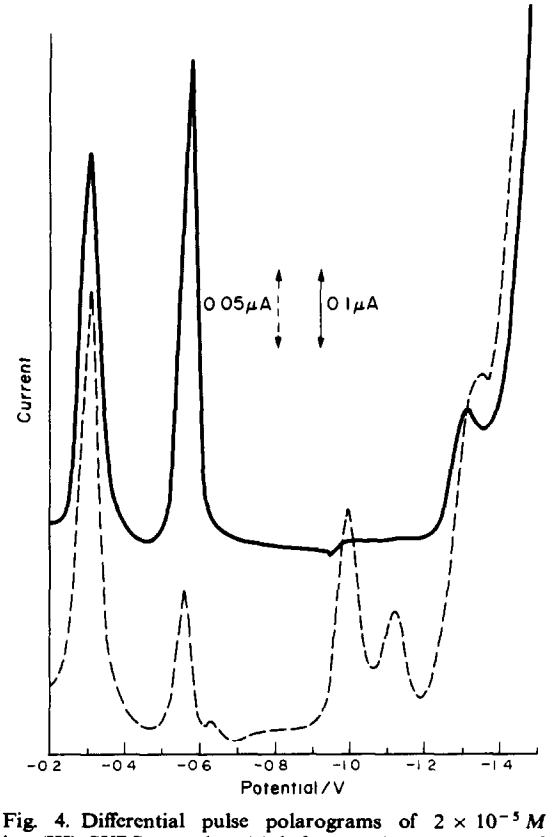


Fig. 4. Differential pulse polarograms of $2 \times 10^{-5} M$ iron(III)–SVRS complex, (*a*) before coulometry (—) and (*b*) after partial reduction at the mercury pool cathode at −0.35 V (– –).

DISCUSSION

The work described in this paper indicates that the SVRS–Fe(III) system is intermediate between the extremes of reaction mechanisms of metal complexes with electroreducible ligands. In the presence of excess of iron(III) the height of the undisplaced peak is clearly governed by the rate of dissociation of the complex, the reduction of the complex proceeding partly through the free dye and in part directly. The non-rectilinear dependence of the total current, $i_{p1} + i_{p2}$, on the total SVRS concentration, over large concentration ranges—the current obtained is disproportionately less at higher concentrations—indicates that adsorption effects are also operative at the DME in these solutions.

Clearly great care must be taken in using the SVRS–iron(III) system for the determination of iron if reproducible results are to be obtained. Rooney and McIver[6] have stressed that calibration curves must be prepared for the particular range of iron(III) that it is required to determine. With the amount of SVRS that they used, the calibration curves were rectilinear up to 0.6 μg/ml (0–1 μg/ml range) and 2 μg/ml (0–3 μg/ml range). Choice of solution conditions can be made by using the tables given in the present paper. Greatest displacement of the wave occurs at the lower pH, *i.e.*, at pH 4.68, and the addition of Triton X-100 is clearly advantageous in producing a rectilinear calibration graph (see Table 1). The temperature should be controlled fairly closely: the temperature coefficient of the height of the displaced wave is frequently negative owing to the increased dissociation of the complex before reduction, but is usually small owing to partial cancellation by the temperature coefficient associated with the diffusion process.

The presence of Triton X-100 has a marked effect on the polarograms obtained and clearly affects the reactions occurring at the surface of the dropping mercury electrode. Surface-active agents are known to have differing effects on polarographic waves, including decreasing wave-heights (or eliminating waves totally), shifting half-wave potentials and splitting waves.[11] Jacobsen and Lindseth have reported recently[12] on the effects of surfactants on differential pulse polarograms.

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REFERENCES

1. G. W. Latimer, Jr., *Talanta*, 1968, **15**, 1.
2. I. Talesnick and J. A. Page, *ibid.*, 1963, **10**, 1055.
3. A. G. Fogg, J. L. Kumar and D. T. Burns, *Analyst*, 1969, **94**, 262.
4. *Idem*, *ibid.*, 1971, **96**, 403.
5. C. M. Pyburn, *Ph.D. Thesis*, Loughborough University of Technology, 1967.
6. R. C. Rooney and P. J. McIver, *Analyst*, 1962, **87**, 895.
7. M. Perkins and G. F. Reynolds, *Anal. Chim. Acta*, 1958, **18**, 616.
8. S. Palmer and G. F. Reynolds, *Z. Anal. Chem.*, 1967, **224**, 252.
9. T. M. Florence and W. L. Belew, *J. Electroanal. Chem.*, 1969, **21**, 157.
10. J. Heyrovský and J. Kůta, *Principles of Polarography*, p. 345. Academic Press, New York, 1966.
11. *Idem*, *op. cit.*, p. 299.
12. E. Jacobsen and H. Lindseth, *Anal. Chim. Acta*, 1976, **86**, 123.

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TITRIMETRIC DETERMINATION OF SOME ORGANIC COMPOUNDS WITH BROMINE CHLORIDE

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Summary—Bromine chloride is used in hydrochloric acid medium as a standard reagent for the rapid and precise determination of organic compounds by direct or indirect titrimetric methods. Hydrazine and its aryl derivative undergo a 4-electron change. Carbonyl compounds are determined by reaction with excess of 2,4-dinitrophenylhydrazine and estimation of the surplus. Sulphanilamide undergoes a substitution reaction in 1:3 molar ratio to bromine chloride. Thiobarbituric acid and thiourea or its alkyl derivatives show an 8-electron change but aryl thioureas also undergo nuclear bromination. Thiosemicarbazide and semicarbazide give a 10- and a 2-electron change respectively. In the direct titration, methionine is oxidized to its sulphoxide whereas cystine and cysteine form cysteic acid. In presence of bromide, glutathione forms the sulphonic acid but in the presence of iodide the product is the disulphide. The analytical results obtained by bromine chloride method are compared favourably with those afforded by established procedures.

Standard solutions of interhalogens have been used extensively as analytical reagents in direct[1,2] and indirect[3] methods of analyses. An aqueous solution of iodine monochloride containing hydrochloric acid was first applied by Heisig[4] and Kubina[5] as an oxidizing agent; it was later used by Kagan *et al.*[6,7] and by Čihalík and Vavrejnová for the titrimetric determination of several organic substances by means of substitution, addition or oxidation reactions. Solutions of iodine bromide have not received much attention. Schulek and Burger[9] found that iodine bromide acts both as an iodinating and brominating agent even in solvents of high dielectric constant, where the compound is supposed to break into iodonium and bromide ions. This behaviour renders iodine bromide unsuitable for use as a halogenating agent in organic preparations. Investigation of the reaction of bromine chloride proved that this reagent acts solely as a brominating agent.

Several aromatic compounds have been determined by bromination with bromine chloride.[10] The bromination period required is appreciably reduced when bromine chloride is used as brominating agent (2 min for salicylic acid) instead of the conventional bromate–bromide mixture (60 min for salicylic acid).[10] The addition and substitution reactions of the interhalogens have been discussed from the theoretical viewpoint.[11,12] A quantitative method for the indirect determination of hydroxylamine with bromine chloride has also been reported.[13] Recently, this reagent has been used for titrating mercaptans.[14]

In the present paper analytical procedures are described which involve use of hydrochloric acid solutions of bromine chloride as a standard reagent for the determination of some organic compounds bearing nitrogen, oxygen or sulphur functional groups.

Hydrazine and its aryl derivatives

The oxidation of hydrazine has been widely used for its measurement. Whereas direct titration of hydrazine with permanganate in alkaline solution does not yield good results, permanganate can be titrated with hydrazine in alkaline solution in the presence of barium ions.[15] The end-point in the chloramine-B method is indistinct, but sharp in the presence of an excess of potassium bromide.[16] Obviously, under these conditions the effective oxidizing agent is bromine. The iodate method has been checked by several workers and found to be unreliable.[17] Ferricyanide[18] has been used to oxidize hydrazine in alkaline solution, nitrogen being formed. However, the conditions are critical, especially the alkali concentration, otherwise oxides of nitrogen are also formed. *N*-Bromosuccinimide[17] is claimed to produce excellent results for hydrazine and its organic derivatives even in dilute solutions, but the reagent solution has to be freshly made. Iodine monochloride[19] and lead tetra-acetate[20] do not suffer from these disadvantages and afford reliable results.

Bromine chloride can be employed for the determination of hydrazine and its organic derivatives. On treatment of the sample with an excess of the reagent the reaction is complete within a minute; the residual reagent is evaluated iodometrically.

Hydrazine reacts according to the equation

$$NH_2NH_2 + 2BrCl \rightarrow N_2 + 2HBr + 2HCl$$

Arylhydrazines also consume 2 moles of bromine chloride per mole of hydrazine. The reaction product can be identified by treating it with alkaline 2-naphthol solution at 0°; phenylhydrazine is found to give 1-phenylazo-2-naphthol. Therefore arylhydrazines presumably react according to

$$ArNHNH_2 + 2BrCl \rightarrow ArN{=}NCl + 2HBr + HCl$$

The diazonium compound may decompose and other products may be formed. However, when phenylhydrazine is reacted with about 200% excess of bromine chloride no precipitate of brominated product is seen even after 10 min at 25°.

Carbonyl compounds

Aldehydes and ketones can be determined by a large number of methods that are based on the reactions of the carbonyl group. The applicability of bromine chloride to evaluate 2,4-dinitrophenylhydrazine led us to develop an indirect method for carbonyl compounds by reacting them in acid medium with excess of 2,4-dinitrophenylhydrazine, filtering off the hydrazone and evaluating the residual reagent with bromine chloride.

Sulphanilamide

The most accurate and widely used procedure for sulphanilamide involves its acidic behaviour in non-aqueous media. Fritz and Keen[21] titrated sulpha drugs in dimethylformamide, using sodium methoxide as standard base and Azo Violet as indicator. In aqueous solution these compounds are determined by diazotization with sodium nitrite in presence of acid, but the titration involves either an external indicator (which makes the end-point troublesome to locate) or an internal indicator such as *p*-dimethylaminobenzaldehyde[22] (which gives a colour change from yellow to colourless which is difficult to perceive). Sulphanilamide cannot be determined by argentometric[23] or by complexometric titration.[24] The reaction of sulphanilamide with bromine chloride was studied to evolve a rapid, precise and convenient method for its determination. The following reaction occurs:

$$H_2N{\cdot}C_6H_4{\cdot}SO_2NH_2 + 3BrCl + H_2O \rightarrow H_2N{\cdot}C_6H_2Br_3 + NH_2SO_3H + 3HCl$$

2,4,6-Tribromoaniline and sulphamic acid are the reaction products. The reaction is complete in a minute.

Thiourea and its alkyl and aryl derivatives

Under mild conditions oxidizing agents convert thiourea and various *N*-substituted thioureas into the corresponding formamidine disulphides. In the case of thiourea itself, Preisler and Burger[25] found the oxidation–reduction potential of the thiourea-formamidine disulphide system to be 0.42 V in dilute hydrochloric acid. On the other hand, the formamidine disulphides are prone to further oxidation, and unless the conditions are carefully chosen, a simple stoichiometry may not be achieved in an oxidation reaction. Singh *et al.* have made successful use of iodine monochloride,[26] iodine monobromide,[27] iodine trichloride[28] and chloramine-T[29] for oxidizing thiourea and various derivatives. Potassium bromate has likewise been used.[30,31] Szebelledy and Mades[32] have titrated solutions of thiocarbamide in the presence of potassium bromide at 40–60° with bromate solution, using auric chloride as catalyst. Gupta[33] also uses bromate–bromide mixture for indirect determinations. A sixfold amplification procedure has been suggested[34] involving the transformation sequence

$$-CSNH_2 \rightarrow NH_3;\ NH_3 + HI \rightarrow NH_4I;$$
$$NH_4I \xrightarrow{\text{oxidation}} HIO_3;\ HIO_3 \xrightarrow{I^-} 3I_2.$$

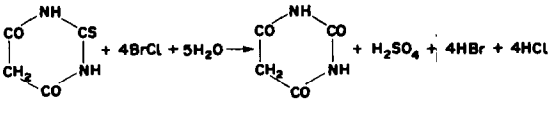
In the present work, thiourea and its alkyl or aryl derivatives are determined by reaction with bromine chloride in acid medium. The principal reaction with thioureas is removal of sulphur as sulphuric acid.

$$RNHCSNHR + 4BrCl + 5H_2O \rightarrow RNHCONHR + H_2SO_4 + 4HBr + 4HCl$$

However, the arylurea formed also undergoes a nuclear bromination reaction and more bromine chloride is consumed.

2-Thiobarbituric acid

Most of the procedures for determining thioamides do not yield quantitative results with 2-thiobarbituric acid. Lead tetra-acetate is suitable for thiosemicarbazide[35,36] and phenylthioureas,[37] hypoiodite for thiourea[38] and cerium(IV) for thiourea and its alkyl derivatives.[39] Iodine is suitable in bicarbonate medium for thiourea and some of its alkyl derivatives.[33] In oxidation of 2-thiobarbituric acid with hypoiodite or iodine in bicarbonate, the reaction is incomplete even after 2 hr, and in reaction with lead tetra-acetate, iodine monochloride or iodine trichloride, more oxidant is consumed than expected. The most widely used procedure involves the acidic behaviour of this compound but the method is very non-selective[4]. The reaction of 2-thiobarbituric acid with bromine chloride is found to be quantitative and rapid. The reaction is:



Thiosemicarbazide and semicarbazide

Suchomelová and Zýka[35] have used an indirect method for the determination of thiosemicarbazide with lead tetra-acetate. However, the reaction is slow (2–10 mg of thiosemicarbazide oxidized in 2–3.5 hr), and is limited to dilute solutions. Recently, the catalytic effect of zinc sulphate has been noted, the reaction being complete within 30 min with 2–60 mg of thiosemicarbazide.[36]

Under the conditions used to determine thioureas, bromine chloride oxidizes thiosemicarbazide according to the equation

$$NH_2CSNHNH_2 + 5BrCl + 4H_2O \rightarrow HCN + N_2 + H_2SO_4 + 5HBr + 5HCl$$

Semicarbazide also reacts with bromine chloride:

$$NH_2CONHNH_2 + BrCl \rightarrow HCN + N_2 + HBr + HCl + H_2O$$

Methionine

Bromate–bromide mixture has attracted much attention as a reagent for the direct and indirect determination of methionine. Thibert and Sarwar[42] titrated methionine with *N*-bromosuccinimide, using Bordeaux Red as indicator; the reagent has to be freshly prepared. Phenyl iodosoacetate reacts quantitatively with methionine but the reaction period is as long as 40 min.[43] Chloramine-T in presence of bromide has been employed for direct titrations; obviously bromine is the effective oxidizing agent.[44] Belcher *et al.*[45] noted that in bromimetric determinations good recoveries are obtained when the sample solution is heated to 50–60° before titration; otherwise excess of reagent must be applied.

Titrations with bromine chloride proceed smoothly even in feebly acidic medium at room temperature, a sharp and stable end-point being obtained. The sulphide group of methionine is oxidized to sulphoxide or to sulphone by an excess of bromine chloride. The sulphide to sulphoxide oxidation is rapid but further oxidation to the sulphone is slow. The reaction can be stopped at the sulphoxide stage if minimal practicable excess of bromine chloride is used. However, the best method is to titrate the sample with bromine chloride to the appearance of the colour of bromine. The following reaction occurs:

$$CH_3SCH_2CH_2CH(NH_2)CO_2H + BrCl + H_2O \rightarrow CH_3SOCH_2CH_2CH(NH_2)CO_2H + HCl + HBr$$

Cystine and its derivatives

Although Siggia and Edsberg[46] stated that an excess of bromate–bromide brings about interfering substitution reactions, Vastagh and Varga[47] determined cystine by reacting it for 10 min at ambient temperature with excess of the reagent. Belcher *et al.*[45] obtained satisfactory results by an indirect procedure.

N-Bromosuccinimide has been used by Thibert and Sarwar[42] and by Schneider *et al.*[48] for the direct titration of cystine, with Bordeaux Red as indicator.

For the reasons mentioned under methionine, bromine chloride is employed for the direct titration of cystine in feebly acidic medium at room temperature, the reaction being

$$[-SCH_2CH(NH_2)CO_2H]_2 + 5BrCl + 6H_2O \rightarrow 2HO_3SCH_2CH(NH_2)CO_2H + 5HBr + 5HCl$$

The same reaction is followed by the derivatives of cystine.

Glutathione

No substance of biological significance has had so many vicissitudes as glutathione. This sulphydryl compound is a tripeptide, γ-glutamylcysteinylglycine, which seems to be present exclusively in the intracellular fluid, mostly in the reduced form and its concentration in different tissues is affected by a variety of conditions. Several analytical reagents have been employed to determine this compound.[49] The iodimetric method of Woodward and Fry[50] is generally acclaimed as suitable, but the sample solution must be acidic, otherwise erratic results are obtained. Chloramine-T in presence of iodide and starch has been used[51] and claimed to be better than iodometry.[52] *o*-Iodosobenzoate[53] and ferricyanide[54] function well in phosphate buffer of pH 7 and have the advantage that most of the concomitant substances do not interfere.

Glutathione can be determined with bromine chloride in acidified solutions containing potassium iodide and starch, the blue of starch-iodine being formed at the end-point. The reactions believed to occur are

$$BrCl + 2KI \rightarrow I_2 + KCl + KBr$$

$$2GSH + I_2 \rightarrow GSSG + 2HI$$

where GSH represents glutathione.

Methionine and cystine do not interfere, but glutathione interferes in the determination of these two compounds by the bromine chloride method, by forming the sulphonic acid:

$$GSH + 3BrCl + 3H_2O \rightarrow GSO_3H + 3HBr + 3HCl.$$

This reaction is also suitable for a direct titration of glutathione.

Cysteine

The iodometric method used for glutathione cannot be applied to cysteine, as variable recoveries are obtained. The reaction is highly sensitive to slight changes in acid, iodide and sample concentration and temperature. These factors are not operative in the mercurimetric titration,[55] based on mercaptide formation. Nevertheless, oxidation with ferricyanide[56] or *o*-iodosobenzoate[57] yields reliable results at pH 7.

Cysteine is often contaminated with amino-acids containing sulphide or disulphide groups which interfere in its determination. It is found that cysteine reacts with bromine chloride in weakly acidic medium, forming cysteic acid:

$$HSCH_2CH(NH_2)CO_2H + 3BrCl + 3H_2O \rightarrow HO_3SCH_2CH(NH_2)CO_2H + 3HBr + 3HCl$$

The reaction is rapid and quantitative and suitable for a direct titrimetric determination. When cysteine and cystine or methionine are present in the same sample, their total can be determined by titration with

bromine chloride. The cysteine content is then found by reaction with *o*-iodosobenzoate.[57] The second amino-acid is obtained by difference.

EXPERIMENTAL

Reagent and samples

Bromine chloride solution, 0.05 *M*. Prepared[58] by dissolving 2.784 g of potassium bromate and 3.967 g of potassium bromide in 400 ml of water, followed by addition of 100 ml of conc. hydrochloric acid in a single lot, and shaking till the colour changes to light yellow, and finally dilution to 1 litre; it is standardized iodometrically and diluted as required.

Hydrazine sulphate and its aryl derivatives, all carbonyl compounds, thiosemicarbazide, 2-thiobarbituric acid, semicarbazide, thiourea and most of its alkyl and aryl derivatives, sulphanilamide, methionine, glutathione, cysteine hydrochloride and cystine were commercially available high-purity chemicals. Substituted phenylthioureas[59] and α-substituted cystines[60,61] were prepared by known methods.

Solutions of these organic compounds were prepared in water, 0.1*M* hydrochloric acid or glacial acetic acid and standardized by established methods (Tables 2 and 3). Less concentrated solutions were made by appropriate dilution. The purity of 2-thiobarbituric acid was determined by non-aqueous alkalimetry,[40] and its solution was prepared by dissolving a known weight of sample in water.

As a check, independent methods were used to determine the purity of thiourea samples. Thiourea was determined by hypoiodite oxidation,[38] methylthiourea by non-aqueous titration with cerium(IV),[39] and other alkyl derivatives by the iodine trichloride reaction.[62] *o*-Tolyl and *o*-chlorophenylthioureas were determined with bromate–bromide mixture,[33] and other phenylthioureas by Pb(IV) titration.[37] *N,N'*-Diphenylthiourea was estimated by non-aqueous alkalimetry[40] and *N*-methyl-*N'*-phenylthiourea by total sulphur analysis by the Carius method.[63]

Procedures

Indirect procedure. A suitable amount of substance (Table 1) is weighed or an equivalent amount of solution taken in a 250-ml flask (fitted with a ground-glass stopper) and dissolved or mixed with 25 ml of water or 0.1*M* hydrochloric acid. Samples may also be dissolved in 5–10 ml of glacial acetic acid and diluted with 20 ml of water at the time of determination. The mixture is then treated with about 50% excess of 0.05*M* bromine chloride and swirled for a specified period (Table 1). The residual reagent is determined by adding 10 ml of 10% potassium iodide solution and titrating the liberated iodine with 0.04*M* thiosulphate. A blank determination on the same volume of bromine chloride is run concurrently.

Direct procedure. A suitable amount of substance (Table 1) is weighed or an equivalent amount of solution taken in a 150-ml Erlenmeyer flask and 10 ml of 0.1*M* hydrochloric acid are added. The solution is diluted to about 30 ml with water and the contents are titrated with 0.025*M* bromine chloride. After each addition of titrant, the colour is viewed against a white background; the end-point is shown by appearance of the yellow colour of free bromine. A blank titration on the same volume of water–hydrochloric mixture containing about 50 mg of potassium bromide is done to find the volume of titrant needed for a discernible end-point; the blank is generally about 0.10 ml.

Procedure for glutathione. The sample, in a 150-ml Erlenmeyer flask, is treated with 0.5 g of potassium iodide, 10 ml of 0.1*M* hydrochloric acid and diluted to about 40 ml. About 1 ml of 0.5% starch solution is added and the contents are titrated with 0.01*M* bromine chloride till a blue colour is obtained.

Procedure for carbonyl compounds. An aqueous solution of the carbonyl compound, in a 150-ml tall beaker, is treated with about 50% excess of 0.05*M* 2,4-dinitrophenylhydrazine in 1*M* hydrochloric acid. The mixture is diluted to about 30 ml with water and stirred magnetically. The hydrazone is filtered off on a Whatman No. 42 paper and washed 3 or 4 times with 5-ml portions of water. The filtrate is collected in a 250-ml flask fitted with a ground-glass stopper. The residual 2,4-dinitrophenylhydrazine in the filtrate is determined by the indirect procedure described above. A blank determination is done on the same volume of hydrazine.

RESULTS AND DISCUSSION

Optimum conditions for the determination of several compounds are given in Table 1. In Tables 2 and 3, results are given for the determination of various compounds. The theoretical and experimental values for the number of equivalents of bromine chloride used in the reaction with several thioureas are summarized in Table 4, along with the identity of the products.

Bromine chloride contains positively-charged bromine but it cannot be regarded as the actual oxidizing

Table 1. Recommended conditions of determination

Compound	Time of reaction at 26°C, *min*	Range of sample, *mmole*
Hydrazine and its derivatives	1	0.1–0.3
Sulphanilamide	1	0.05–0.15
Thiourea and its derivatives	20	0.05–0.12
Thiosemicarbazide	20	0.04–0.1
Thiobarbituric acid	30	0.05–0.12
Semicarbazide	5	0.2–0.6
Methionine	direct titration	0.2–0.5
Cysteine	direct titration	0.05–0.15
Cystine and its derivatives	direct titration	0.03–0.1
Glutathione	direct titration*	0.1–0.4
Glutathione	direct titration†	0.05–0.15
Carbonyl compounds	20§	0.1–0.3

* In the presence of acidified potassium iodide.
† In the presence of potassium bromide.
§ Reaction period for hydrazone formation.

Table 2. Indirect determinations with bromine chloride

Substance	Found, *mg*	Comparison method*	Present method	Relative standard deviation, %	Substance	Found, *mg*	Comparison method*	Present method	Relative standard deviation, %
Hydrazine sulphate	1.85	Ferricyanide[18]	1.83	0.1	2-Thiobarbituric acid	2.03	NaOMe[40]	2.02	0.2
	3.62	NBS[17]	3.64			4.56	NaOMe[40]	4.52	
	5.31	ICl[19]	5.28			5.89	NaOMe[40]	5.93	
	8.54	$KMnO_4$[15]	8.51			7.32	NaOMe[40]	7.29	
	12.63	$KMnO_4$[15]	12.55			10.56	NaOMe[40]	10.62	
Phenylhydrazine	2.32	NBS[17]	2.35	0.3	Semicarbazide	3.48	ICl_3[62]	3.51	0.1
	5.65	LTA[20]	5.68			6.82	KIO_4[65]	6.78	
	12.38	CAT[64]	12.40			9.37	ICl_3[62]	9.43	
	15.21	KIO_4[65]	15.18			13.24	ICl_3[62]	13.12	
						15.51	KIO_4[65]	15.60	
p-Bromophenylhydrazine	3.60	CAT[64]	3.58	0.2	Thiosemicarbazide	2.30	ICl_3[62]	2.32	0.2
	5.04	NBS[17]	4.98			4.82	LTA[36]	4.79	
	9.98	LTA[20]	10.08			6.25	LTA[36]	6.29	
	13.42	KIO_4[65]	13.45			8.39	ICl_3[62]	8.30	
						10.02	ICl_3[62]	10.12	
2,4-Dinitrophenylhydrazine	2.82	CAT[64]	2.85	0.1	Formaldehyde	1.25	NaOI[69]	1.26	0.4
	5.06	NBS[17]	5.10			2.19	NaOI[69]	2.20	
	8.75	CAT[64]	8.68			3.60	NaOI[69]	3.64	
	10.66	CAT[64]	10.73			5.98	NaOI[69]	6.02	
	14.91	CAT[64]	14.85			8.24	NaOI[69]	8.18	
p-Nitrophenylhydrazine	3.52	CAT[64]	3.56	0.1					
	6.86	CAT[64]	6.82						
	9.08	CAT[64]	9.12						
	11.61	NBS[17]	11.56						
	15.73	CAT[64]	15.63						
Isonicotinylhydrazide	3.58	NBS[66]	3.62	0.1	Acetaldehyde	1.58	NaOI[70]	1.56	0.3
	5.92	NBS[66]	5.96			3.26	NaOI[70]	3.29	
	7.25	CAT[64]	7.18			5.67	NH_2OH[71]	5.72	
	8.73	CAT[64]	8.85			8.45	NH_2OH[71]	8.53	
	11.81	NBS[66]	11.72			10.21	NH_2OH[71]	10.32	
	14.34	CAT[64]	14.45						
Sulphanilamide	2.75	$NaNO_2$[67]	2.82	0.2	Acetone	2.68	NaOI[72]	2.64	0.3
	4.24	$NaNO_2$[67]	4.18			4.55	NH_2OH[71]	4.68	
	6.18	NBS[68]	6.23			6.28	NaOI[72]	6.32	
	8.29	$NaNO_2$[67]	8.35			8.67	NH_2OH[71]	8.58	
	12.06	$NaNO_2$[67]	12.15			11.29	NaOI[72]	11.19	

* NBS, *N*-bromosuccinimide; LTA, lead tetra-acetate; CAT, chloramine-T.

species for the conversion of glutathione into its disulphide in the presence of potassium iodide. Oxidation of alkyl and aryl mercaptans by bromine is known to be non-stoichiometric[46] but that of cysteine and glutathione with bromine chloride is found in the present work to proceed smoothly and stoichiometrically. In this connection, the role of iodide and of bromide ions on the rate and extent of oxidation of glutathione by titration with bromine chloride is interesting. When glutathione was titrated with bromine chloride in the presence of a large excess of potassium iodide (100:1 molar ratio), the recoveries were always 3–5% low. Moreover, the sample had to be titrated slowly near the equivalence point as the locally developed iodine-starch colour took considerable time to disappear. On the other hand, a similar titration in the presence of a smaller ratio of potassium iodide (10:1) and a high amount of potassium bromide (100:1 ratio to glutathione) yielded a result about 6% high, but the reproducibility was seriously impaired. When bromide ions were in excess, bromine chloride reacted with them to yield bromine, which then reacted preferentially with the glutathione, leading to high and erroneous recoveries. That positively-charged bromine is not the oxidant in the presence of potassium iodide alone, is confirmed by the non-interference by methionine or cystine. Oxidation of iodide by bromine chloride is then the preferred reaction and the iodine is responsible for oxidation of the glutathione. The role of iodide ions can be explained by assuming the mechanism

$$GSH + I_2 \rightleftharpoons GSI + HI \quad (i)\ I/SH = 2$$

$$GSI + GSH \rightarrow GSSG + HI \quad (ii)\ I/SH = 1$$

In increase in iodide concentration favours the reversal of equation (*i*). If equation (*ii*) is also taken as reversible then the I/SH ratio would be nearer to 2 in presence of excess of iodide, leading to high rather than low recoveries, since the calculation is based on the assumption that I/SH = 1. This view is supported by the observation that when glutathione is titrated

Table 3. Direct determinations with bromine chloride

Substance	Found, *mg*		Present method	Relative standard deviation, %	Substance	Found, *mg*		Present method	Relative standard deviation, %
	Comparison method*					Comparison method*			
Glutathione†	8.45	IB[53]	8.40	0.1	Methionine	6.86	$KBrO_3$[46]	6.89	0.2
	11.69	Ferricyanide[54]	11.58			15.25	PIA[43]	15.20	
	16.23	Iodometry[50]	16.34			20.82	PIA[43]	20.89	
	22.08	IB[53]	22.10			25.07	PIA[43]	24.86	
	26.73	CAT[51]	26.81			30.93	$KBrO_3$[46]	31.15	
	30.44	Ferricyanide[54]	30.41						
	35.82	IB[53]	35.79						
	43.50	Iodometry[50]	43.45						
Cystine	3.86	$KBrO_3$[46]	3.83	0.1	Cysteine§	4.23	Ferricyanide[56]	4.21	0.2
	5.29	TS[63]	5.32			8.56	IB[57]	8.52	
	8.65	$KBrO_3$[46]	8.58			13.48	HMB[55]	13.53	
	13.28	$KBrO_3$[46]	13.35			18.35	HMB[55]	18.46	
	17.34	TS[63]	17.40			22.68	IB[57]	22.75	
Methylcystine	3.21	TS[63]	3.19	0.2	Glutathione§	5.89	IB[53]	5.93	0.2
	6.72	$KBrO_3$[46]	6.78			7.23	Iodometry[50]	7.18	
	10.35	$KBrO_3$[46]	10.42			9.66	Iodometry[50]	9.61	
	15.39	TS[63]	15.28			15.52	IB[53]	15.64	
						21.38	Ferricyanide[54]	21.19	
						28.73	Ferricyanide[54]	28.92	
Isopropyl-cystine	4.22	TS[63]	4.18	0.2	Phenylcystine	5.96	TS[63]	5.90	0.2
	10.78	$KBrO_3$[46]	10.70			8.72	$KBrO_3$[46]	8.79	
	15.20	$KBrO_3$[46]	15.29			15.24	TS[63]	15.12	
	20.86	TS[63]	20.92			25.38	TS[63]	25.29	

* IB, *o*-Iodosobenzoate; PIA, phenyl iodosoacetate; HMB, *o*-hydroxymercuribenzoate; TS, total sulphur.
† Oxidation to disulphide.
§ Oxidation to sulphonic acid.

Table 4. Determination of thioureas with bromine chloride

Compound	Equivalents of BrCl consumed per mole of thiourea		Relative std. devn. %	Product
	Expected	Found		
Thiourea	8	8.0	0.1	Urea
Methylthiourea	8	8.0	0.1	Methylurea
N,N'-Dimethylthiourea	8	8.0	0.1	*N,N'*-Dimethylurea
Allylthiourea	10*	10.0	0.1	3-Bromo-2-chloropropylurea
Amylthiourea	8	8.0	0.1	Amylurea
Phenylthiourea	14	13.6	0.2	2,4,6-Tribromophenylurea
p-Tolylthiourea	12	11.7	0.2	2,6-Dibromo-4-tolylurea
o-Tolylthiourea	12	11.6	0.2	4,6-Dibromo-2-tolylurea
m-Tolylthiourea	14	13.6	0.3	2,4,6-Tribromo-3-tolylurea
o-Chlorophenylthiourea	12	11.8	0.2	2-Chloro-4,6-dibromophenylurea
m-Chlorophenylthiourea	14	13.7	0.1	3-Chloro-2,4,6-tribromophenylurea
m-Anisylthiourea	14	14.0	0.1	2,4,6-Tribromo-3-anisylurea
N,N'-Diphenylthiourea	12	11.8	0.2	4,4'-Dibromo-*N,N'*-diphenylurea
N-Methyl-*N'*-phenylthiourea	14	14.0	0.1	*N*-Methyl-*N'*-(2,4,6-tribromophenyl)urea

* The double bond in allyl group is also attacked by BrCl.

with iodine in the presence of an excess of potassium iodide there is a decrease in the apparent sulphydryl value and the reactions are slow at the end point.

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REFERENCES

1. B. Singh and B. C. Verma, *J. Sci. Ind. Res. India*, 1965, **24**, 536.
2. A. Srivastava and S. Bose, *J. Indian Chem. Soc.*, 1974, **51**, 736.
3. P. N. K. Nambisan and C. G. R. Nair, *Anal. Chim. Acta*, 1970, **52**, 475.
4. G. B. Heisig, *J. Am. Chem. Soc.*, 1928, **50**, 1687.
5. H. Kubina, *Z. Anal. Chem.*, 1929, **76**, 39.

6. Y. A. Fialkov and F. E. Kagan, *Ukr. Khim. Zh.*, 1952, **18**, 55.
7. F. E. Kagan and C. I. Shakh, *ibid.*, 1957, **23**, 537.
8. J. Číhalík and O. Vavrejnová, *Collection Czech. Chem. Commun.*, 1956, **21**, 192.
9. E. Schulek and K. Burger, *Talanta*, 1958, **1**, 147.
10. *Idem, ibid.*, 1958, **1**, 224.
11. *Idem, Acta Chim. Acad. Sci. Hung.*, 1959, **19**, 453.
12. E. Schulek, E. Pungor and K. Burger, *Chem. Zvesti*, 1959, **13**, 669.
13. K. Burger, F. Gaizer and E. Schulek, *Talanta*, 1960, **5**, 97.
14. K. K. Verma, J. Ahmed, M. P. Sahasrabuddhey and S. Bose, *Z. Anal. Chem.*, 1977, **285**, 263.
15. I. M. Issa and R. M. Issa, *Anal. Chim. Acta*, 1956, **14**, 578; *Chemist-Analyst*, 1956, **45**, 40.
16. R. C. Paul and A. Singh, *J. Indian Chem. Soc.*, 1955, **32**, 599.
17. M. Z. Barakat and M. Shaker, *Analyst*, 1963, **88**, 59, and references therein.
18. B. R. Sant, *Anal. Chim. Acta*, 1959, **20**, 371.
19. B. Singh and G. P. Kashyap, *Z. Anal. Chem.*, 1958, **163**, 338.
20. A. Berka, J. Vulterin and J. Zýka, *Newer Redox Titrants*, p. 79. Pergamon, Oxford, 1965.
21. J. S. Fritz and R. T. Keen, *Anal. Chem.*, 1952, **24**, 308.
22. C. E. Fischbach, *Acta Chem. Venezuela*, 1956, **7**, 152.
23. L. Kum-Tatt, *Analyst*, 1957, **82**, 185.
24. H. Abdine and W. S. Abdul Sayed, *J. Pharm. Pharmocol.*, 1962, **14**, 761.
25. P. W. Preisler and L. Berger, *J. Am. Chem. Soc.*, 1947, **69**, 322.
26. B. Singh, B. C. Verma and M. S. Saran, *J. Indian Chem. Soc.*, 1962, **39**, 211.
27. *Idem, Proc. Natl. Acad. Sci. India*, 1963, **A33**, 305.
28. *Idem, J. Indian Chem. Soc.*, 1962, **39**, 490.
29. B. Singh, B. C. Verma and Y. K. Kalia, *ibid.*, 1963, **40**, 697.
30. B. Singh and B. C. Verma, *Z. Anal. Chem.*, 1963, **194**, 112.
31. B. Singh, B. C. Verma and M. S. Saran, *Bull. Chem. Soc. Japan*, 1965, **30**, 43.
32. L. Szebelledy and V. Madis, *Z. Anal. Chem.*, 1938, **114**, 253.
33. P. C. Gupta, *Analyst*, 1963, **88**, 896.
34. R. D. Tiwari, J. P. Sharma and I. C. Shukla, *Talanta*, 1966, **13**, 499.
35. L. Suchomelová and J. Zýka, *J. Electroanal. Chem.*, 1963, **5**, 57.
36. B. T. Gowda and D. S. Mahadevappa, *J. Indian Chem. Soc.*, 1977, **54**, 470.
37. K. K. Verma and S. Bose, *ibid.*, 1973, **50**, 498.
38. S. Škramovský, *Casopis Ceskoslov. Lekarnictva*, 1941, **1**, 21.
39. B. C. Verma and S. Kumar, *Talanta*, 1973, **20**, 916.
40. J. S. Fritz, *Anal. Chem.*, 1952, **24**, 674.
41. M. R. F. Ashworth, *The Determination of Sulphur-Containing Groups*, Vol. III, p. 2. Academic Press, London, 1977.
42. R. J. Thibert and M. Sarwar, *Mikrochim. Acta*, **1969**, 259.
43. K. K. Verma and S. Bose, *J. Indian Chem. Soc.*, 1973, **50**, 542.
44. N. M. M. Gowda and D. S. Mahadevappa, *Talanta*, 1977, **24**, 470.
45. R. Belcher, Y. A. Gawargious and A. M. G. Macdonald, *Mikrochim. Acta*, **1966**, 1115.
46. S. Siggia and R. L. Edsberg, *Anal. Chem.*, 1948, **20**, 938.
48. O. P. Schneider, R. J. Thibert and R. J. Walton, *Mikrochim. Acta*, 1972, 925.
49. J. W. Patterson and A. Lazarow, *Methods of Biochemical Analysis* D. Glick (ed.), Vol. II, p. 263. Interscience, New York, 1961.
50. G. E. Woodward and E. G. Fry, *J. Biol. Chem.*, 1932, **97**, 465.
51. A. Srivastava and S. Bose, *J. Indian Chem. Soc.*, 1975, **52**, 214.
52. D. S. Mahadevappa and N. M. M. Gowda, *Talanta*, 1975, **22**, 771.
53. K. K. Verma and S. Bose, *Analyst*, 1975, **100**, 366.
54. K. K. Verma, J. Ahmed and S. Bose, *Mikrochim. Acta*, **1977**, 161.
55. M. Wrónski, *Analyst*, 1963, **88**, 562.
56. K. K. Verma and S. Bose, *Talanta*, 1975, **22**, 74.
57. *Idem, Anal. Chim. Acta*, 1974, **70**, 227.
58. E. Schulek and K. Berger, *Talanta*, 1958, **1**, 219.
59. G. N. Mahapatra, *J. Indian Chem. Soc.*, 1956, **33**, 923.
60. R. J. Thibert, J. F. C. Diederich and K. G. Rutherford, *Can. J. Chem.*, 1965, **43**, 205.
61. R. J. Thibert, J. F. G. Diederich and G. W. Kosicki, *Can. J. Biochem.*, 1967, **45**, 1595.
62. K. K. Verma, M. P. Sahasrabuddhey and S. Bose, *Talanta*, 1977, **24**, 515.
63. A. Steyermark, *Quantitative Organic Microanalysis*, p. 276. Academic Press, New York, 1961.
64. A. Berka and J. Zýka, *Ceskoslov. Farm*, 1956, **5**, 335.
65. *Idem, Chem. Listy*, 1956, **50**, 314.
66. M. Z. Barakat and M. Shaker, *Analyst*, 1966, **91**, 466.
67. K. Veno and T. Tachikawa, *Bunseki Kagaku*, 1962, **11**, 554.
68. M. Z. Barakat and M. Shaker, *Analyst*, 1964, **89**, 216.
69. S. Bose, *J. Indian Chem. Soc.*, 1957, **34**, 497.
70. S. Bose, *Anal. Chem.*, 1958, **30**, 1526.
71. F. E. Critchfield, *Organic Functional Group Analysis*, p. 61. Pergamon, Oxford, 1963.
72. S. Bose, *Anal. Chem.*, 1958, **30**, 1137.

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SHORT COMMUNICATIONS

INDIRECT POTENTIOMETRIC DETERMINATION OF HYDRAZINE, ISONIAZID, SULPHIDE AND THIOSULPHATE WITH A CHLORAMINE-T ION-SELECTIVE ELECTRODE

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Summary—Indirect potentiometric procedures with chloramine-T (CAT) as the oxidant and a chloramine-T ion-selective electrode are described for the determination of hydrazine and isonicotinic acid hydrazide (isoniazid) in the 1–100 μmole range and of sulphide and thiosulphate in the 0.5–50 μmole range. The reductants react stoichiometrically with a known and excessive volume of added CAT and the unconsumed excess of CAT is measured with the CAT-selective electrode. Aqueous solutions of the reductants were analysed with an error and precision of about 1–2%. Analytical recovery of isoniazid added to tablet diluents was 97–101% (average 98.9%). Results were comparable with those obtained with a titrimetric method for the determination of isoniazid in injection solutions and tablets.

Analytical potentiometry has found a renewal of interest as a result of the recent development of a large number of ion-selective electrodes.[1] Some of these electrodes have been used for the potentiometric determination of ions for which no ion-selective electrodes are available or of reductants which react stoichiometrically with iodine.[2,3] Recently, we reported a new chloramine-T (CAT) ion-selective membrane electrode and its application to potentiometric and kinetic methods of analysis.[4–6] In the present paper an indirect potentiometric method is described for the determination of reductants, based on quantitative oxidation with an excess of chloramine-T, followed by measurement of the unconsumed CAT with a chloramine-T selective electrode.

The proposed method was used for the determination of hydrazine and isonicotinic acid hydrazide (isoniazid) in the 1–100 μmole range (10^{-4}–$10^{-2}M$), and of sulphide and thiosulphate in the 0.5–50 μmole range ($5–500 \times 10^{-5}M$) in aqueous solutions with an error and precision of about 1–2%. The method was applied successfully to the determination of isoniazid in various pharmaceutical preparations.

EXPERIMENTAL

Apparatus

The electrodes and the reaction cell were the same as previously reported.[4] All measurements were taken during constant stirring with a magnetic stirring bar, at such a rate that no bubbles and no vortex were formed, and, in the absence of direct sunlight in order to avoid hydrolysis of the CAT.

Reagents

All solutions were prepared in demineralized distilled water from reagent-grade materials.

Chloramine-T solutions. For a 0.1000*M* stock solution, 28.17 g of chloramine-T trihydrate were dissolved in water, diluted to 1 litre and stored in an amber bottle; it was standardized with standard arsenite solution.[7] This solution is stable for at least one month.

Standard stock solutions of reductants, 0.100*M*. Prepared from the following substances: hydrazine sulphate, $H_2NNH_2 \cdot H_2SO_4$ (primary standard); isonicotinic acid hydrazide, $C_5H_4NCONHNH_2$ (Sigma); sodium sulphide [$Na_2S \cdot 9H_2O$ (Merck)]; sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$. Standardized by conventional methods. Working solutions were prepared fresh daily from the stock solutions by dilution. Hydrazine sulphate solutions must be neutralized before dilution.

Phosphate and citrate buffers, 0.25*M*, pH 6.0. Made by mixing 10 ml of 2.5*M* sodium dihydrogen phosphate or citric acid solution with 80 ml of water, neutralizing with 5*M* sodium hydroxide to pH 6.0 and diluting to 100 ml.

Procedures

Procedure A_1 (for the 1–100 μmole range of hydrazine and isoniazid). Pipette 10.00 ml of $2.50 \times 10^{-3}M$ CAT (25 μmole), 5.00 ml of phosphate buffer (pH 6.0) and 10.00 ml of the sample or standard containing 1–10 μmole of hydrazine or isoniazid into a 50-ml amber narrow-neck reagent bottle. Shake the solution at room temperature continuously for about 15 min. Transfer the solution into the reaction cell kept at 25.0° in a thermostat, start the magnetic stirrer and read the emf when it is stabilized to within ±0.1 mV (in about 20 sec). Include four hydrazine or isoniazid standards in the 1×10^{-4}–$1 \times 10^{-3}M$ range (1–10 μmole). The excess of CAT is found from a plot of *E vs.* log (μmole of CAT in excess), *i.e.*, log (25 − 2 × μmole of reductant).

Procedure A_2, for the 10–10 μmole range of hydrazine and isoniazid. This is similar to procedure A_1, except that 10.00 ml of $2.50 \times 10^{-2}M$ CAT (250 μmole) and standard hydrazine and isoniazid solutions in the 1×10^{-3}–$1 \times 10^{-2}M$ range (10–100 μmole) are used. In this case the abscissa in the calibration curve is log (250 − 2 × μmole of reductant).

Determination of isoniazid in injection solutions. Dilute an exactly measured volume of the injection solution so that 10.00 ml of the dilute solution contain 1–10 or 10–100 μmole of isoniazid and proceed by procedure A_1 or A_2, as appropriate.

Determination of isoniazid in tablets. Weigh at least 20 tablets of the sample and pulverize them with a mortar and pestle. Weigh an appropriate amount of the pulverized sample, dissolve it in water and dilute to 100 ml so that 10.00 ml of the solution contain 1–10 or 10–100 μmole of isoniazid. If a residue remains, filter it off. Proceed by procedure A_1 or A_2. Calculate the mean isoniazid content per tablet. If the tablets contain calcium, substitute 0.25*M* citrate buffer (pH 6.0) for the phosphate buffer to prevent precipitation of calcium phosphate.

Procedure B_1 (for the 0.5–5 μmole range of sulphide and thiosulphate). Pipette 5.00 ml of $5.00 \times 10^{-3}M$ CAT (25 μmole), 5.00 ml of 0.1*M* sodium hydroxide and 10.00 ml of

the sample or standard containing 0.5–5 μmole of sulphide or thiosulphate into a 50-ml amber bottle. Leave the solution in a water-bath at 80° for about 30 min. Cool the solution to room temperature, transfer it into the cell kept at 25.0° in a thermostat, pipette 5.00 ml of 0.1*M* sodium dihydrogen phosphate into it and read the emf when it is stabilized. Include four sulphide or thiosulphate standards in the 5×10^{-5}–$5 \times 10^{-4}M$ range (0.5–5 μmole). In this case the abscissa in the calibration curve is log (25 − 4 × μmole of reductant).

Procedure B_2, for the 5–50 μmole range of sulphide and thiosulphate. This is similar to procedure B_1, except that 5.00 ml of $5.00 \times 10^{-2}M$ CAT (250 μmole) and standard solutions in the 5×10^{-4}–$5 \times 10^{-3}M$ range (5–50 μmole) are used. The abscissa in the calibration curve is log (250 − 4 × μmole of reductant).

RESULTS AND DISCUSSION

Hydrazine and isoniazid determination

A preliminary study of pH in the range 5–8 was carried out to check the quantitativeness of the oxidation of hydrazine and isoniazid with chloramine-T. A known and excessive volume of standard CAT solution was added to the solution and after 15 min the unconsumed CAT was determined by adding excess of iodide and titrating the liberated iodine with standard thiosulphate solution in the presence of starch. Variation of pH in the acidic range had no effect on the oxidation, which was quantitative at pH below 6. Typical results are shown in Table 1. It can be seen that at pH 5–6 two moles (four equivalents) of CAT are consumed per mole of hydrazine or isoniazid, according to the reactions

$$N_2H_4 + 2CH_3C_6H_4SO_2NCl^- \rightarrow N_2 + 2CH_3C_6H_4SO_2NH_2 + 2Cl^-$$

$$C_5H_4NCONHNH_2 + 2CH_3C_6H_4SO_2NCl^- + H_2O \rightarrow C_5H_4NCOOH + N_2 + 2CH_3C_6H_4SO_2NH_2 + 2Cl^-.$$

These results agree with published data.[8] Since the working pH range of the CAT-selective electrode is 5–9, a pH of 6.0 was chosen for the determination. A phosphate buffer of pH 6.0 was found satisfactory.

When the amount of unconsumed chloramine-T was found from a calibration curve obtained with pure aqueous solutions of chloramine-T, negative errors were always observed. There was no systematic negative error when the sum of the unconsumed chloramine-T and *p*-toluenesulphonamide, $CH_3C_6H_4SO_2NH_2$ (one of the reaction products), was the same in all the standards and samples. Therefore, the amount of unconsumed chloramine-T should be obtained from a linear calibration curve constructed by plotting emf *vs.* log (μmole of CAT in excess) for a series of solutions obtained by mixing the same amount of chloramine-T with various standard hydrazine or isoniazid solutions.

The calibration curve should be rechecked every three hours. More accurate results are obtained if standards are included with each series of samples.

By recording the emf for a period of 5–60 min after mixing the reagents, it was found that the reaction is complete in 15 min, for both reductants and both concentration ranges.

Analysis of aqueous hydrazine and isoniazid solutions of known concentration gave the results shown in Table 2. It is seen that amounts of hydrazine in the range 0.06–3 mg and of isoniazid in the range 0.28–14 mg can be determined with an average error and coefficient of variation of about 1–2%.

The proposed method was tested for the determination of isoniazid in pharmaceutical preparations. The values obtained for isoniazid in injection solutions and tablets by the

Table 1. Oxidation of hydrazine and isoniazid with chloramine-T

Sample taken, *mmole*	pH (buffer)	Moles of chloramine-T consumed per mole of sample§
0.1000*	5.2 (acetate)	1.998
0.0988†	5.2 (acetate)	1.996
0.1000*	6.1 (phosphate)	1.997
0.0988†	6.1 (phosphate)	2.004
0.1000*	7.2 (phosphate)	1.635
0.0988†	7.2 (phosphate)	1.628
0.1000*	8.1 (phosphate)	1.423
0.0988†	8.1 (phosphate)	1.419

*Hydrazine.
†Isoniazid.
§Average of two titrations.

Table 2. Results for aqueous hydrazine and isoniazid solutions

Hydrazine in 10-ml sample, *mg*				Isoniazid in 10-ml sample, *mg*			
Taken	Found†	Error, %	S_r, %§	Taken	Found†	Error, %	S_r, %§
Range A_1*				Range A_1*			
0.0641	0.0653	+1.9		0.274	0.294	+7.3	
0.128	0.127	−0.8		0.549	0.527	−4.0	
0.150	0.149	−0.7	0.8 (n = 10)	0.686	0.685	−0.1	1.2 (n = 10)
0.210	0.208	−1.0		0.960	0.969	+0.9	
0.300	0.294	−2.0		1.10	1.10	—	
	Av.	1.3			Av.	2.5	
Range A_2*				Range A_2*			
0.601	0.593	−1.3		4.12	4.18	+1.5	
1.20	1.16	−3.3		5.49	5.52	+0.5	
1.80	1.76	−2.2	0.5 (n = 8)	8.23	8.48	+3.0	1.5 (n = 10)
2.70	2.71	+0.4		11.0	11.1	+0.9	
3.00	3.00	—		13.7	13.5	−1.5	
	Av.	1.4			Av.	1.5	

*Ranges A_1 and A_2 run according to procedures A_1 and A_2, respectively.
†Single measurements.
§S_r = relative standard deviation.

Table 3. Comparison of potentiometric and titrimetric method results for the determination of isoniazid in injection solutions of "Dianicotyl"

Ampoule No.	Isoniazid per 2 ml,* *mg* Potentiometric method	USP iodometric method	Difference, %
1	99.6	98.2	1.4
2	99.3	98.2	1.1
3	98.8	100.0	1.2
4	98.2	98.9	0.7
5	97.5	96.6	0.9
6	97.1	97.5	0.4
7	99.4	99.8	0.4
8	97.5	98.5	1.0
		Av.	0.9

*Single measurement.

Table 4. Comparison of potentiometric and USP iodometric method results for the determination of isoniazid in commercial tablets

Preparation	Isoniazid per tablet, *mg* Present method	USP method	Difference, %
"Dianicotyl" 50 mg (Chropi)	51.6	52.1	1.0
"Dianicotyl" 100 mg (Chropi)	112	108	3.7
"Rimifon" 50 mg (Roche)	54.6	53.0	3.0

potentiometric method are compared with those obtained by the USP standard iodometric method[9] in Tables 3 and 4. In all cases the results indicate no consistent difference between results obtained by the two methods.

To study the interference of some common diluents used in tablet preparation, synthetic tablets containing 200 mg of the diluent and 96 mg of isoniazid were analysed. The results given in Table 5 (recovery from 97.1 to 101.1%, mean 98.9%) show that the diluents examined have no effect on the isoniazid determination.

Analyses of composite tablets containing isoniazid and other drugs reacting with chloramine-T, such as *p*-aminosalicylic acid (PAS) and vitamin B_6 gave large positive errors.

Table 5. Analytical recovery of isoniazid (96 mg) added to 200 mg of various tablet diluents

Diluent	Isoniazid found, *mg*	Recovery, %
Mannitol	94.5	98.4
Starch	93.2	97.1
Sorbitol	95.1	99.1
Sugar	95.1	99.1
NaCl	94.5	98.4
Lactose	97.1	101.1
		Av. 98.9

Table 6. Results for aqueous sulphide and thiosulphate solutions

Sulphide in 10-ml sample, *mg* Taken	Found†	Error, %	S_r, %§	Thiosulphate in 10-ml sample, *mg* Taken	Found†	Error, %	S_r, %§
Range B_1*				Range B_1*			
0.0147	0.0138	−6.1		0.0560	0.0497	−11.2	
0.0588	0.0604	+2.7		0.112	0.110	−1.7	
0.0882	0.0892	+1.1	0.8 ($n = 5$)	0.224	0.226	+0.9	0.4 ($n = 5$)
0.118	0.117	−0.8		0.448	0.445	−0.6	
0.147	0.146	−0.7		0.560	0.558	−0.4	
		Av. 2.3				Av. 3.0	
Range B_2*				Range B_2*			
0.160	0.151	−5.6		1.13	1.18	+4.4	
0.321	0.333	+3.7		2.25	2.33	+3.6	
0.641	0.658	+2.6		3.38	3.29	−2.6	
0.962	0.942	−2.1	0.8 ($n = 5$)	5.07	5.04	−0.6	2.1 ($n = 5$)
1.60	1.59	−0.6		5.63	5.65	+0.3	
		Av. 2.9				Av. 2.3	

*Ranges B_1 and B_2 run according to procedures B_1 and B_2, respectively.
†Single measurements.
§S_r = relative standard deviation.

Sulphide and thiosulphate determination

A high pH favours the oxidation of sulphide and thiosulphate to sulphate by chloramine-T according to the reactions

$$S^{2-} + 4CH_3C_6H_4SO_2NCl^- + 4H_2O \rightarrow SO_4^{2-} + 4CH_3C_6H_4SO_2NH_2 + 4Cl^-$$

$$S_2O_3^{2-} + 4CH_3C_6H_4SO_2NCl^- + 2H_2O \rightarrow 2SO_4^{2-} + 4CH_3C_6H_4SO_2NH_2 + 4Cl^-$$

However, the solution should be nearly neutral during the emf measurement with the CAT selective electrode, to avoid hydroxide interference.[4] Therefore, the redox reaction is carried out in strongly alkaline solutions but the emf is measured after the addition of a buffer of pH 6.0.

Experiments were carried out to ascertain the effect of concentration of reagents, reaction time and temperature on the oxidation of the sulphide and thiosulphate by chloramine-T and to choose the optimum conditions for the analysis. Under the conditions chosen the oxidation is complete in 30 min. The long reaction time required (30 min) and high temperature (80°) are characteristic of all methods using chloramine-T or hypochlorite for sulphide and thiosulphate determination.

Analysis of aqueous sulphide and thiosulphate solutions of known concentrations gave the results shown in Table 6. It is seen that amounts of sulphide in the range 0.01–1.6 mg and of thiosulphate in the range 0.06–5.6 mg can be determined with an average error of about 2–3% and coefficients of variation of about 1%.

In conclusion, the proposed method is sensitive, rapid and accurate, and it offers a simple and convenient alternative to the existing oxidimetric methods for the determination of hydrazine and its derivatives, and of sulphide and thiosulphate. Furthermore, it demonstrates the applicability of the chloramine-T selective electrode to the potentiometric determination of reductants and expands the analytical applications of chloramine-T.

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REFERENCES

1. N. Laksshminarayanaiah, *Membrane Electrodes*, Academic Press, New York, 1976.
2. F. Oehme and L. Dolezalova, *Z. Anal. Chem.*, 1970, **251**, 1.
3. R. Christova, M. Ivanova and M. Novkirishka, *Anal. Chim. Acta*, 1976, **85**, 301.
4. M. A. Koupparis and T. P. Hadjiioannou, *ibid.*, 1977, **94**, 367.
5. *Idem, ibid.*, 1978, **96**, 31.
6. *Idem, Microchim. Acta*, in press.
7. V. J. Jennings, *CRC Crit. Revs. Anal. Chem.*, 1974, **3**, 413.
8. V. R. Nair and C. G. R. Nair, *Anal. Chim. Acta*, 1971, **57**, 429.
9. *U.S. Pharmacopeia XVIII*, p. 327.

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TITRIMETRIC DETERMINATION OF DISSOLVED OXYGEN IN WASTE WATER

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(*Received* 30 *January* 1978. *Accepted* 9 *March* 1978)

Summary—Winkler's procedure for the determination of dissolved oxygen has been modified to cope with substantial amounts of oxidizing or reducing substances in the samples. The manganese(III) is treated with an excess of hydroquinone, the unconsumed part of which is then titrated with standard ceric sulphate solution. A blank determination is also carried out, in which the order of addition of reagents is reversed so that the solution is always acidic, to allow for the interfering substances present. Results obtained by using this modified procedure on clean samples are in good agreement with results obtained by the usual Winkler method.

A number of methods have been reported for the determination of dissolved oxygen in water and waste water, the best known being that of Winkler.[1] Reviews by Young *et al.*,[2] and Potter[3] give a critical account of the subject. Physical methods in which the dissolved gas is extracted from water, though relatively accurate, cannot be applied in routine analysis or for waters containing less than 0.3 ppm of oxygen. Most of the colorimetric methods, including the one recently reported employing tris(4,7-dihydroxy-1,10-phenanthroline) iron(II),[4] are affected by the presence of oxidizable and reducible impurities. A radiochemical method based on the measurement of the activity of released ^{204}Tl is relatively expensive. Electrochemical methods such as polarography, coulometry, galvanic cells and membrane electrodes as well as thermal conductivity methods have been widely employed for the measurement of dissolved oxygen and have been reviewed by Brownman.[5] Though continuous recording instruments have largely replaced the chemical methods for routine work, the instruments must be calibrated by physical or chemical methods. Though there are a number of more modern procedures, Winkler's method in its various modified forms, is still the most common method employed in water pollution laboratories.

In Winkler's method, the presence of oxidizable impurities leads to loss of iodine and hence to apparently low values for the dissolved oxygen. Similarly the presence of reducible impurities gives rise to high results. Azide, permanganate, hypochlorite and ammonium fluoride have therefore been suggested as additives when NO_2^-, Fe^{2+}, SO_3^{2-} and Fe^{3+} respectively are known to be present. The azide modification can be applied to waters containing nitrite in the range 0.05–10 ppm if the azide is added as a combined reagent (even 40 ppm can be tolerated if the azide is added separately) and when there is not more than 1 ppm of ferrous iron.[6,7] If the

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Experiments were carried out to ascertain the effect of concentration of reagents, reaction time and temperature on the oxidation of the sulphide and thiosulphate by chloramine-T and to choose the optimum conditions for the analysis. Under the conditions chosen the oxidation is complete in 30 min. The long reaction time required (30 min) and high temperature (80°) are characteristic of all methods using chloramine-T or hypochlorite for sulphide and thiosulphate determination.

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In conclusion, the proposed method is sensitive, rapid and accurate, and it offers a simple and convenient alternative to the existing oxidimetric methods for the determination of hydrazine and its derivatives, and of sulphide and thiosulphate. Furthermore, it demonstrates the applicability of the chloramine-T selective electrode to the potentiometric determination of reductants and expands the analytical applications of chloramine-T.

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REFERENCES

1. N. Laksshminarayanaiah, *Membrane Electrodes*, Academic Press, New York, 1976.
2. F. Oehme and L. Dolezalova, *Z. Anal. Chem.*, 1970, **251**, 1.
3. R. Christova, M. Ivanova and M. Novkirishka, *Anal. Chim. Acta*, 1976, **85**, 301.
4. M. A. Koupparis and T. P. Hadjiioannou, *ibid.*, 1977, **94**, 367.
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Summary—Winkler's procedure for the determination of dissolved oxygen has been modified to cope with substantial amounts of oxidizing or reducing substances in the samples. The manganese(III) is treated with an excess of hydroquinone, the unconsumed part of which is then titrated with standard ceric sulphate solution. A blank determination is also carried out, in which the order of addition of reagents is reversed so that the solution is always acidic, to allow for the interfering substances present. Results obtained by using this modified procedure on clean samples are in good agreement with results obtained by the usual Winkler method.

A number of methods have been reported for the determination of dissolved oxygen in water and waste water, the best known being that of Winkler.[1] Reviews by Young *et al.*,[2] and Potter[3] give a critical account of the subject. Physical methods in which the dissolved gas is extracted from water, though relatively accurate, cannot be applied in routine analysis or for waters containing less than 0.3 ppm of oxygen. Most of the colorimetric methods, including the one recently reported employing tris(4,7-dihydroxy-1,10-phenanthroline) iron(II),[4] are affected by the presence of oxidizable and reducible impurities. A radiochemical method based on the measurement of the activity of released ^{204}Tl is relatively expensive. Electrochemical methods such as polarography, coulometry, galvanic cells and membrane electrodes as well as thermal conductivity methods have been widely employed for the measurement of dissolved oxygen and have been reviewed by Brownman.[5] Though continuous recording instruments have largely replaced the chemical methods for routine work, the instruments must be calibrated by physical or chemical methods. Though there are a number of more modern procedures, Winkler's method in its various modified forms, is still the most common method employed in water pollution laboratories.

In Winkler's method, the presence of oxidizable impurities leads to loss of iodine and hence to apparently low values for the dissolved oxygen. Similarly the presence of reducible impurities gives rise to high results. Azide, permanganate, hypochlorite and ammonium fluoride have therefore been suggested as additives when NO_2^-, Fe^{2+}, SO_3^{2-} and Fe^{3+} respectively are known to be present. The azide modification can be applied to waters containing nitrite in the range 0.05–10 ppm if the azide is added as a combined reagent (even 40 ppm can be tolerated if the azide is added separately) and when there is not more than 1 ppm of ferrous iron.[6,7] If the

water sample contains appreciable amounts of nitrite and ferrous iron, the permanganate modification must be used, but preliminary oxidation with permanganate causes errors since the dissolved oxygen may be activated and has then a tendency to oxidize the organic substances present.[8] Alkaline hypochlorite treatment for the determination of oxygen in the presence of sulphite gives low results, the deviation amounting to nearly 1 ppm, and the permanganate modification is ineffective for dealing with sulphite.[6] In all the modifications suggested, the analyst is required to know, prior to the determination of oxygen, the various impurities present, their concentration and the modifications to be used. In view of the complexities involved, there is a possibility that the wrong modification might be adopted. Ion-exchange methods have also been suggested for eliminating the interferences.[9]

We now report a titrimetric method for the determination of dissolved oxygen, making use of hydroquinone to reduce the manganese(III). This reagent has been employed by Berka *et al.*[10] for determination of dissolved oxygen. Their procedure involved forming the pyrophosphate complex of manganese(III), but their modifications suggested for coping with the presence of iron(II) or free chlorine are somewhat laborious. We have found that the procedure can be simplified by reducing the manganese(III) with an excess of hydroquinone and titrating the excess of the reductant with ceric sulphate. The errors due to oxidizable or reducible impurities are compensated for by an appropriate blank titration.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical grade unless otherwise specified.

Hydroquinone solution, 0.025*N*. About 1.500 g of hydroquinone were accurately weighed, dissolved and made up to 1 litre with 2% v/v sulphuric acid.

Ceric sulphate solution, 0.025*N*. About 8.5 g of ceric sulphate were dissolved and made up to 1 litre with 2*N* sulphuric acid. The solution was standardized against freshly prepared hydroquinone solution.

Manganese(II) sulphate solution and *alkaline potassium iodide reagent* (without azide). Prepared according to a standard procedure.[6]

Apparatus

A glass tub of 10 litres capacity was filled with demineralized water stirred continuously with a motor-driven stirrer. The temperature of the water was maintained at $30 \pm 0.2°$. Sampling of water was started only after 6 hr of stirring. A Corning-glass flat-bottomed flask with a ground-glass stopper (24/29) was used as a sampling bottle. The capacity of the flask with the stopper in was found to be 151 ml.

Procedure

After filling the bottle with sample, close it without entraining any air bubbles. Remove the stopper and add 1.5 ml of manganese(II) sulphate solution followed by 1.5 ml of potassium hydroxide solution by means of a long-stemmed pipette, taking care that the tip of the pipette reaches almost to the bottom of the flask before the liquids are released. When the stopper is replaced, 3 ml of water sample will be displaced. Tightly stopper the bottle and shake it by repeated inversion ($\sim$ 15 times) so that the mixed precipitate of Mn(II) and Mn(III) hydroxides is uniformly distributed. Allow the precipitate to settle, carefully remove the stopper without losing any drops of water and add about 1.5 ml of concentrated sulphuric acid down the sides of the bottle by means of a glass tube. Stir the contents with the tube; a dark brown and turbid solution is obtained. Transfer the contents of the bottle into a conical flask, rinse the bottle thrice and add the rinsings to the flask. Add a measured and excessive volume of 0.025*N* hydroquinone slowly while swirling the contents of the flask; the Mn(III) is reduced to Mn(II) as indicated by the loss of colour from the solution. Determine the unconsumed hydroquinone by titration with standard ceric sulphate solution, using 0.025*M* ferroin as indicator, and a 10-ml semi-micro-burette.

Conduct a blank experiment with the same water and sampling bottle, but adding the reagents in the order concentrated sulphuric acid, potassium hydroxide solution, manganese(II) sulphate solution, and then applying the hydroquinone/ceric sulphate procedure. The calculations are based on the amount of ceric sulphate consumed being equivalent to the amount of manganese(III) produced in the volume of water left in the bottle after addition of the 3 ml of reagents.

$$\text{Amount of oxygen} = \frac{V_c \times N_c \times 8 \times 1000}{V_B - 3} \text{ ppm}$$

where V_c = difference in volumes of ceric sulphate used for the blank and test experiments, N_c = normality of the ceric sulphate solution, V_B = volume of sample bottle (ml).

RESULTS AND DISCUSSION

Sixteen determinations of dissolved oxygen in water by the present procedure gave a value of 7.40 ppm with a standard deviation of 0.03 ppm while Winkler's method gave a value of 7.40 ppm with a standard deviation of 0.02 ppm (results corrected to 760 mmHg pressure). The solubility of oxygen in water at 30° and 760 mmHg pressure, as given by APHA, is 7.60 ppm (based on calculations by Whipple and Whipple[6,11]), though various workers have reported solubilities which vary by as much as 0.22 ppm at 25°.

Since the method involves a blank titration, the errors arising from oxidizable and reducible impurities are cancelled. Allowance was also made for their presence by Schwartz and Gurney,[13] who added a known amount of potassium biiodate solution to both the sample and blank before processing and also reversed the order of addition of reagents to the blank [*viz.* alkaline potassium iodide, sulphuric acid, and manganese(II) chloride]. However, as pointed out by Potter,[3]

Table 1. Determination of dissolved oxygen in the presence of interfering ions

Impurity, *ppm*	Dissolved oxygen, *ppm**	Standard deviation, *ppm* ($n = 5$)
NO_2^- 10 (as N)	7.21	0.01
50 (as N)	7.24	0.04
Fe^{2+} 5	7.21	0.02
100	7.22	0.02
Fe^{3+} 100	7.23	0.03
$Cr_2O_7^{2-}$ 100 (as $Cr_2O_7^{2-}$)	7.22	0.01
Free chlorine, 50	7.22	0.03

*Dissolved oxygen in air-saturated water at 30°C and 742.5 mm pressure (conditions under which these determinations were made) is 7.22 ppm.

this technique cannot be applied in the presence of ferrous iron. Our results show that our method can be applied in the presence of relatively high concentrations of either oxidizable or reducible impurities.

Hydroquinone gives a colour reaction with nitrite and moreover the oxidation of nitrite by ceric sulphate is slow. When nitrite is present, the processed sample solution is transferred to the conical flask, and the ceric sulphate solution is added first (from the burette) so that it is in slight excess (as indicated by the colour change of ferroin); the hydroquinone is then added by pipette and the titration continued as usual. In the presence of iron(III), the amount of potassium hydroxide solution added should be sufficient to precipitate all the iron as well as the manganese. The determination of oxygen in the presence of sulphite is very difficult. For example, when sulphite was added to the water in the tub so that its concentration was 5 ppm, we found that all the sulphite was oxidized by aerial or dissolved oxygen within 20 min, the dissolved oxygen content decreasing by 19%. When the concentration of sulphite was increased to 100 ppm, the level of dissolved oxygen after 15 min was found to be only 1 ppm. Results obtained with various impurities present are given in Table 1.

Precautions

(1) It is important that the volumes of water taken for the blank and the determination should be as nearly as possible the same, especially if the amount of oxidizable or reducible impurity is high, as any difference in the volumes will result in an error that is dependent on the concentration of the impurity concerned. For example, if the water contains 100 ppm of iron(II) and there is 1 ml difference in the volumes of water taken for the determination and the blank, this will lead to an error of ± 0.10 ppm of oxygen for a 148-ml sample. Similarly the presence of 100 ppm of nitrite (as NO_2^-) would cause a still higher error, ± 0.23 ppm. Sufficient care must therefore be taken during the addition of reagents when the concentrations of impurities (oxidizable or reducible) are high.

(2) If the water under test is alkaline (pH ~ 10.0), manganese(II) hydroxide may also precipitate in the blank. In such cases, add more sulphuric acid to both blank and sample.

Experiments were also carried out with ferrous ammonium sulphate in place of hydroquinone: the results by the methods were in good agreement.

Application of the method to the analysis of waste water

Sewage samples were collected in duplicate from the sewer adjoining the university campus and were analysed for their dissolved oxygen content. Five determinations gave a value of 4.31 ± 0.02 ppm, while the value obtained by Winkler's method (azide modification) was 4.29 ± 0.02 ppm.

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REFERENCES

1. L. W. Winkler, *Ber.*, 1888, **21**, 2843.
2. R. S. Young, E. T. Pinkey and R. Dick, *Power Eng.*, 1950, **54**, 62.
3. E. C. Potter, *J. Appl. Chem. London*, 1957, **7**, 285.
4. D. P. Poe and H. Diehl, *Talanta*, 1974, **21**, 1065.
5. A. Brownman, *Birmingham Univ. Chem. Eng.*, 1970, **21**, 21.
6. *Standard Methods for the Examination of Water and Waste Water*, 13th Ed., American Public Health Association, 1971.
7. H. A. C. Montgomery, N. S. Thom and A. Cockburn, *J. Appl. Chem. (London)*, 1964, **14**, 280.
8. G. Alsterberg, *Biochem. Z.*, 1926, **170**, 30.
9. E. C. Potter and J. F. White, *J. Appl. Chem. (London)*, 1957, **7**, 459.
10. A. Berka, H. Glassl and P. Hofmann, *Mikrochim. Acta*, 1968, 997.
11. G. C. Whipple and M. C. Whipple, *J. Am. Chem. Soc.*, 1911, **33**, 362.
12. G. A. Truesdale, A. L. Downing and S. F. Lowden, *J. Appl. Chem. (London)*, 1955, **5**, 53.
13. M. C. Schwartz and W. B. Gurney, *Proc. Am. Soc. Testing Materials*, Preprint No. 90, 1934 (1934, **34**, 796).

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DETERMINATION OF CHROMIUM IN LOW-ALLOY STEELS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—Iron causes severe depression of the signal in determination of chromium by atomic-absorption spectrophotometry in an air–acetylene flame. This effect can be eliminated by addition of hydroxylamine hydrochloride and use of a fuel-rich flame. Addition of iron to the standard solutions is not necessary for up to 300 ppm of iron in the test solution.

Chromium is an important element in making low-alloy steels. Its determination by atomic-absorption spectrophotometry in the presence of iron is difficult because of severe depression caused by iron in the air–acetylene flame. Various workers[1–3] prefer the hotter nitrous oxide–acetylene flame, but some loss of sensitivity occurs; Cobb *et al.*[4] found that a fuel-lean flame is best. The depression by iron in the air–acetylene flame may be overcome by adding 8-quinolinol[5] as a releasing agent and interference suppressor. Kinson *et al.*[6] prefer the addition of an equivalent amount of iron to the standard solutions. Pszonicki and Abdallah[7] eliminate interferences by addition of calcium nitrate and acetic acid and use of a lean air–acetylene flame.

The present investigation was undertaken with a view to studying the effect of hydroxylamine hydrochloride as an interference suppressor in a fuel-rich air–acetylene flame.

this technique cannot be applied in the presence of ferrous iron. Our results show that our method can be applied in the presence of relatively high concentrations of either oxidizable or reducible impurities.

Hydroquinone gives a colour reaction with nitrite and moreover the oxidation of nitrite by ceric sulphate is slow. When nitrite is present, the processed sample solution is transferred to the conical flask, and the ceric sulphate solution is added first (from the burette) so that it is in slight excess (as indicated by the colour change of ferroin); the hydroquinone is then added by pipette and the titration continued as usual. In the presence of iron(III), the amount of potassium hydroxide solution added should be sufficient to precipitate all the iron as well as the manganese. The determination of oxygen in the presence of sulphite is very difficult. For example, when sulphite was added to the water in the tub so that its concentration was 5 ppm, we found that all the sulphite was oxidized by aerial or dissolved oxygen within 20 min, the dissolved oxygen content decreasing by 19%. When the concentration of sulphite was increased to 100 ppm, the level of dissolved oxygen after 15 min was found to be only 1 ppm. Results obtained with various impurities present are given in Table 1.

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REFERENCES

1. L. W. Winkler, *Ber.*, 1888, **21**, 2843.
2. R. S. Young, E. T. Pinkey and R. Dick, *Power Eng.*, 1950, **54**, 62.
3. E. C. Potter, *J. Appl. Chem. London*, 1957, **7**, 285.
4. D. P. Poe and H. Diehl, *Talanta*, 1974, **21**, 1065.
5. A. Brownman, *Birmingham Univ. Chem. Eng.*, 1970, **21**, 21.
6. *Standard Methods for the Examination of Water and Waste Water*, 13th Ed., American Public Health Association, 1971.
7. H. A. C. Montgomery, N. S. Thom and A. Cockburn, *J. Appl. Chem. (London)*, 1964, **14**, 280.
8. G. Alsterberg, *Biochem. Z.*, 1926, **170**, 30.
9. E. C. Potter and J. F. White, *J. Appl. Chem. (London)*, 1957, **7**, 459.
10. A. Berka, H. Glassl and P. Hofmann, *Mikrochim. Acta*, 1968, 997.
11. G. C. Whipple and M. C. Whipple, *J. Am. Chem. Soc.*, 1911, **33**, 362.
12. G. A. Truesdale, A. L. Downing and S. F. Lowden, *J. Appl. Chem. (London)*, 1955, **5**, 53.
13. M. C. Schwartz and W. B. Gurney, *Proc. Am. Soc. Testing Materials*, Preprint No. 90, 1934 (1934, **34**, 796).

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DETERMINATION OF CHROMIUM IN LOW-ALLOY STEELS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

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Summary—Iron causes severe depression of the signal in determination of chromium by atomic-absorption spectrophotometry in an air–acetylene flame. This effect can be eliminated by addition of hydroxylamine hydrochloride and use of a fuel-rich flame. Addition of iron to the standard solutions is not necessary for up to 300 ppm of iron in the test solution.

Chromium is an important element in making low-alloy steels. Its determination by atomic-absorption spectrophotometry in the presence of iron is difficult because of severe depression caused by iron in the air–acetylene flame. Various workers[1–3] prefer the hotter nitrous oxide–acetylene flame, but some loss of sensitivity occurs; Cobb *et al.*[4] found that a fuel-lean flame is best. The depression by iron in the air–acetylene flame may be overcome by adding 8-quinolinol[5] as a releasing agent and interference suppressor. Kinson *et al.*[6] prefer the addition of an equivalent amount of iron to the standard solutions. Pszonicki and Abdallah[7] eliminate interferences by addition of calcium nitrate and acetic acid and use of a lean air–acetylene flame.

The present investigation was undertaken with a view to studying the effect of hydroxylamine hydrochloride as an interference suppressor in a fuel-rich air–acetylene flame.

Hydroxylamine should be less toxic than 8-quinolinol and more agreeable to use.

EXPERIMENTAL

Apparatus

All the experiments were performed on a Pye Unicam S.P. 1900 double-beam atomic-absorption spectrophotometer equipped with a digital read-out system and DR 10 printer. A chromium hollow-cathode lamp was used as the energy source, the wavelength being 357.9 nm and the lamp current 8 mA. The band-pass was 0.2 nm, a 10-cm burner was used and the air-flow was 5 l./min.

Reagents

Analytical grade chemicals were used throughout.

Standard chromium solution. Potassium dichromate was dissolved in dilute hydrochloric acid and boiled with dropwise addition of hydrogen peroxide till all the chromium was reduced. The solution was cooled and diluted to give a chromium concentration of 100 μg/ml and 5% free hydrochloric acid.

Hydroxylamine hydrochloride solution, 10%.

Standard iron solution. Pure electrolytic iron powder was dissolved in dilute hydrochloric acid and oxidized by dropwise addition of nitric acid to the boiling solution, which was then cooled and diluted to give an iron concentration of 10 mg/ml and 5% free hydrochloric acid.

Establishment of conditions

Variation of the fuel flow was found to give maximum absorption at a flow-rate of 1.80 l./min. The optimum height of observation was at 9 mm above the burner.

Variation of the acid concentrations showed that with 4–10% free acid the absorption is practically constant. The acidity was therefore set at 5% free hydrochloric acid for convenience.

Varying the amount of hydroxylamine hydrochloride added showed the absorption was constant with 0.5–2.5% of reagent present. Therefore, the reagent concentration was set at 1%.

To study the effect of iron and compare the results with those obtained in the absence of hydroxylamine hydrochloride and those for ammonium chloride added as interference suppressor, three sets of experiments were conducted, each with 5% free hydrochloric acid, 2 ppm of chromium and varying amounts of iron. The results are given in Table 1.

Table 1.

Amount of iron, *ppm*	Absorbance (arbitrary units)		
	No reagent	1% $NH_2OH \cdot HCl$	2% NH_4Cl
0	186	191	186
50	182	191	186
100	162	191	185
150	158	189	184
200	152	189	183
250	145	188	181
300	136	188	180
500	—	175	—
1000	—	161	—
2000	—	143	—

It is evident that with hydroxylamine hydrochloride added, the absorbance is reasonably constant for up to at least 300 ppm of iron and the sensitivity is a little better than with ammonium chloride added. It also can be inferred that preparation of matching standards by addition of equivalent amounts of iron is quite unnecessary provided the iron content in the test solution does not exceed 300 ppm.

The calibration curve was found to be linear up to at least 4 ppm of chromium. Higher amounts can be determined by the burner-rotation technique.

Recommended procedure

Take 0.1 g of sample and dissolve it in 20 ml of conc. hydrochloric acid. Oxidize with a few drops of conc. nitric acid to decompose carbides *etc.*, if any. If black particles remain undissolved, evaporate to dryness and take up in 20 ml of conc. hydrochloric acid and a few drops of nitric acid. Make up to 100 ml in a standard flask. Take a 25-ml aliquot in a 100-ml standard flask, add 10 ml of the reagent and dilute to volume. Allow to stand for half an hour and aspirate. Set the observation height at 0.9 cm above the burner top and fuel flow at 1.8 l./min. Note the absorbance. Compare with a standard solution prepared under similar conditions.

Analysis of standard samples

Several standard low-alloy steels prepared by the Bureau of Analysed Samples Limited, U.K., and the National Metallurgical Laboratory, India were analysed by the recommended procedure. The results are incorporated in Table 2.

Table 2.

Sample	Type	Chromium certified value, %	Chromium found, %
BCS 218/2	Carbon steel	0.10	0.098
BCS 224	Cr–V steel	1.46	1.42
BCS 230	Cast steel	0.46	0.45
BCS 251/1	Low-alloy steel	0.51	0.49
BCS 252/1	Low-alloy steel	0.42	0.41
BCS 253/1	Low-alloy steel	0.99	0.98
BCS 254/1	Low-alloy steel	0.27	0.26
BCS 255/1	Low-alloy steel	0.19	0.18
BCS 256/1	Low-alloy steel	2.33	2.35
BCS 257/1	Low-alloy steel	2.97	2.80
BSC 258/1	Low-alloy steel	1.29	1.32
NML 21.1	Nickel steel	1.06	1.01

DISCUSSION

The absorbance values are affected by slight changes in the fuel flow. Therefore, care should be taken to keep this constant. It is preferred to use a fuel flow-rate of 1.8 l./min for maximum sensitivity. Variation of acid concentration within the range 4–10% does not affect the absorbance. Variation in the amount of reagent also does not matter much if kept within the specified range. From Table 1, it is apparent that hydroxylamine hydrochloride is superior to ammonium chloride, which is most commonly used.

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REFERENCES

1. D. R. Thomerson and W. J. Price, *Analyst*, 1971, **96**, 321.
2. W. Slavin, *Atomic Absorption Spectroscopy*, Interscience, New York, 1968.
3. R. J. Reynolds, K. Aldous and K. C. Thomson, *Atomic Absorption Spectroscopy*, Griffin, London, 1970.
4. W. D. Cobb, W. W. Foster and T. S. Harrison, *Analyst*, 1976, **101**, 255.
5. J. M. Ottaway and M. K. Pradhan, *Talanta*, 1973, **20**, 927.
6. K. Kinsen, R. J. Hodges and C. B. Belcher, *Anal. Chim. Acta*, 1963, **29**, 134.
7. L. P. Pszonicki and A. M. Abdallah, *Chem. Analit. (Warsaw)*, 1975, **20**, 693.

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SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III) AND RHODIUM(III) AFTER EXTRACTION WITH OXINE INTO MOLTEN NAPHTHALENE

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Summary—Conditions have been developed for the extraction of chromium(III) and rhodium(III) as their 8-hydroxyquinolinates into molten naphthalene. The naphthalene is allowed to solidify, separated by filtration, dried with filter paper and dissolved in chloroform. The solution is diluted to 10 ml and its absorbance measured at 410 nm for chromium and 425 nm for rhodium, against a reagent blank. In both cases the solution is stable for 24–36 hr. Beer's law is obeyed over the range of 2.7–48.6 μg of chromium or 2.7–57.5 μg of rhodium in 10 ml of the chloroform solution. The molar absorptivity is 3×10^3 l. mole^{-1} · cm^{-1} for chromium and 3.6×10^4 for rhodium. Solutions containing 27.0 μg of chromium or 10.95 μg of rhodium give a mean absorbance of 0.140 and 0.395 respectively, with standard deviations of 0.002_2 and 0.004_7. Most metal ions that form oxinates may interfere, but can be removed beforehand by normal liquid–liquid extraction.

Chromium(III) and rhodium(III) react with most organic reagents only at high temperature. For example, chromium(III) forms complexes with acetylacetone,[1] 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline,[3] and rhodium(III) with 1-(2-pyridylazo)-2-naphthol,[4] sodium diethyldithiocarbamate (on heating for 24 hr),[5] benzil-α-monoxime[6] and α-benzoinoxime[7] on heating. The ordinary method of liquid–liquid extraction cannot be applied directly for the extraction of these metal chelates into solvents of low boiling point. Some workers[1–7] first precipitate these metals with the reagents at high temperature and then extract the products into the organic phase at room temperature. Thus the method becomes time-consuming. Fujinaga and co-workers developed a new method, analysis by solid–liquid separation after liquid–liquid extraction, based on extraction with molten naphthalene. This method has been successfully applied for the spectrophotometric determination of copper,[8,9] zinc,[10] nickel[11] and palladium.[12] Polarographic methods have also been reported for the determination of Mo(VI),[13] In(III),[14] Ni[15] and Pd(II)[15] after extraction by this method. The main characteristics of this method are that the equilibrium distribution in the two phases is achieved in a few seconds and metal chelates are dissolved merely by contact with the molten naphthalene. The present communication describes conditions for the extraction of chromium(III) and rhodium(III) with 8-hydroxyquinoline into molten naphthalene and subsequent determination of these metals by spectrophotometric methods after dissolution of the naphthalene extract in chloroform. The interference of various ions has been studied and conditions developed for the determination of chromium in various alloys.

EXPERIMENTAL

Reagents

Solutions of chromium nitrate (in the presence of a few drops of nitric acid) and rhodium chloride ($RhCl_3 \cdot 3H_2O$) were prepared in distilled water and standardized by known methods. 8-Hydroxyquinoline was dissolved in 10 ml of glacial acetic acid and diluted to 100 ml to give a final concentration of 0.1*M*. The naphthalene and chloroform were tested spectrophotometrically before use.

General procedure

A portion of chromium nitrate or rhodium chloride solution was taken and to this were added 3.0 ml of oxine solution. The pH was adjusted to 5.8–9.5 for chromium and 5.2–6.8 for rhodium, with ammonia solution or perchloric acid. The solutions were warmed on the water-bath at 60° and naphthalene (2 g) was added and the temperature raised to 90° to melt the naphthalene completely, and then taken off the water-bath and stirred vigorously till the naphthalene separated out as a solid mass. The contents were heated to remelt the naphthalene, shaken vigorously and allowed to stand. The naphthalene was filtered off, dried in filter paper and dissolved in chloroform in a 10-ml standard flask. This solution was dried by adding 2 g of anhydrous sodium sulphate, and the absorbance measured in a 1-cm cell at 410 nm for chromium and 425 nm for rhodium, against a reagent blank. Calibration curves were prepared under similar conditions.

Absorption spectra

The absorption spectra of 8-hydroxyquinoline, chromium oxinate and rhodium oxinate in naphthalene/chloroform solution were measured against water. It was observed that chromium oxinate absorbed strongly in the range 400–420 nm and rhodium oxinate gave two absorption peaks, one at 350 nm and the other at 420–430 nm and the reagent did not absorb at these wavelengths. All measurements of rhodium were made at 425 nm to avoid interference by other metals.

Experimental conditions

Effect of pH. The extraction behaviour of these metal oxinates was studied over a wide range of pH. Chromium was quantitatively extracted over the pH range 5.8–9.5, and rhodium at pH 5.2–6.8. Extraction was incomplete at higher and lower pH values.

Effect of reagent. The amount of reagent was varied, other conditions being kept constant. It was observed that the absorbance remained constant for use of 2.0–3.5 ml of oxine reagent for chromium and 2.5–4.5 ml for rhodium.

Effect of naphthalene. The amount of naphthalene was varied from 0.5 to 4.5 g. With both metals the absorbance remained constant when the amount of naphthalene used was in the range 1.5–3.5 g. The extraction was not complete with less than 1.5 g, and with more than 3.5 g it was difficult to dissolve all the naphthalene in the limited quantity of chloroform.

Effect of aqueous phase volume. Since the volume of the organic phase is very small as compared with that of the aqueous phase, it was necessary to observe the effect of the

Table 1. Determination of chromium in various alloys

Alloy	Composition of the alloy, %	Chromium present, μg	Chromium found, μg	Average, μg	Error, %
Elgiloy (M 1712)	Co:40, Cr:20, Ni:15, Mo:7, Fe:15, Mn:2, Be:0.05, C:0.015	26.9	27.0 27.0 27.1_5 27.2_5 27.1_5	27.1	0.7
Stainless Steel No. 316	Cr:16.5, Ni:12, Mo:2–3	27.5	27.2_5 27.1 27.3_5 27.1_5 27.4_5	27.3	0.7
Stainless Steel No. 304	Cr:18, Ni:8–12,	27.4	27.8 27.3_5 27.8 27.4_5 27.5_5	27.6	0.7
Chrome Steel	C:6.96, Mn:1.3, S:0.01, Ni:0.3, Si:0.42, P:0.04, Cr:66.3, Al:0.05	26.5	27.0 27.0 26.1_5 26.5_5 26.8	26.7	0.8

volume of aqueous phase on the extraction of these metals. Extraction by the general procedure was more than 99% complete in both cases when the volume of the aqueous phase was between 30 and 35 ml. With larger volumes the extraction was considerably decreased. In all further experiments the volume of the aqueous phase was kept at about 30 ml.

Calibration curves. With the optimum conditions described above, the calibration curves for chromium and rhodium were constructed at wavelengths of 410 and 425 nm respectively. They were linear over the concentration range 2.7–48.6 μg of chromium or 2.7–57.5 μg of rhodium in 10 ml of chloroform solution. The molar absorptivity was found to be 3×10^3 l. $mole^{-1} \cdot cm^{-1}$ for chromium and 3.6×10^4 for rhodium. Sample solutions containing 27.0 μg of chromium or 10.95 μg of rhodium gave mean absorbances of 0.140 and 0.395 with standard deviations of 0.002_2 and 0.004_7 respectively.

Interferences

Various ions (50 mg of suitable salts containing the anions or 0.50 mg of salts of the cations) were added individually to a solution containing 27.0 μg of chromium or 10.95 μg of rhodium and the general procedure applied. The anions examined were orthophosphate, borate, oxalate, citrate, tartrate, azide, fluoride, thiocyanate, chloride, bromide and iodide. For chromium the results were low in the presence of oxalate, tartrate, citrate or phosphate but extraction became complete when the amount of these ions was decreased ($C_2O_4^{2-}$ 7.7 mg, PO_4^{3-} 2.5 mg, citrate and tartrate 10.5 mg). For rhodium the results were low in the presence of oxalate, citrate and tartrate but extraction became complete with lower amounts (oxalate 5.5 mg, citrate and tartrate 8.5 mg). Most metal ions interfered to some extent with the determinations. For chromium the tolerance limits were Th 35–40 μg, Mn(II) 25–30 μg, In 15–20 μg, Al 20–25 μg, and U(VI) 40–50 μg. Cu^{2+}, Pd^{2+}, Ni^{2+} and Fe^{3+} interfere seriously but the effect of Fe^{3+} can be eliminated by reducing Fe^{3+} to Fe^{2+} with 5 ml of 5% hydroxylamine solution, and Pd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} may be masked by the addition of 1.5–2.0 g of potassium cyanide. For rhodium the tolerance limits were 65–85 μg for Al, Be, Bi, Hg(II), In, Mb(II), Ni, Pb, Sn(IV), Th, Ti, V(V), W(VI) and Zn, and 40–50 μg for Fe(III), Mo(VI) and U(VI). The interference of Cu(II), Co(II) and Pd(II) was eliminated by prior liquid–liquid extraction at room temperature.

Determination of chromium in alloys

A 0.5-g sample of alloy was dissolved in 15–20 ml of *aqua regia*, and the solution evaporated to about 5 ml. Then 10 ml of conc. hydrochloric acid were added, the solution was warmed, then transferred to a 250-ml standard flask and made up to the mark with water. An aliquot of this solution was boiled for 5 min, cooled, adjusted to pH 6.0–9.0, treated with about 2 g of potassium cyanide and 3.0 ml of oxine solution, and then extracted according to the general procedure. Five determinations were made for each alloy and the results are given in Table 1.

REFERENCES

1. J. P. McKaveney and H. Freiser, *Anal. Chem.*, 1958, **30**, 1965.
2. J. P. Tandon and R. C. Mehrotra, *Z. Anal. Chem.*, 1960, **176**, 87.
3. K. Motojima and H. Hashitani, *Anal. Chem.*, 1961, **33**, 239.
4. J. R. Stokely and W. D. Jacobs, *ibid.*, 1963, **35**, 149.
5. H. Bode, *Z. Anal. Chem.*, 1955, **144**, 165.
6. P. K. Paria and S. K. Majumdar, *J. Indian Chem. Soc.*, 1976, **53**, 546.
7. *Idem, Indian J. Chem.*, 1977, **15A**, 157.
8. T. Fujinaga, T. Kuwamoto and E. Nakayama, *Talanta*, 1969, **16**, 1225.
9. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *Bunseki Kagaku*, 1969, **18**, 1113.
10. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 217.
11. M. Satake, *Mem. Fac. Engng. Fukui Univ.*, 1970, **18**, 225.
12. T. Fujinaga, M. Satake and T. Yonekubo, *Talanta*, 1972, **19**, 689.
13. T. Fujinaga and B. K. Puri, *Z. Anal. Chem.*, 1974, **269**, 340.
14. *Idem, Talanta*, 1975, **22**, 71.
15. *Idem, Indian J. Chem.*, 1976, **14A**, 72.

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ESTIMATION OF METALLIC IRON IN RUSTED SPONGE-IRON: DISSOLUTION OF IRON OXIDES BY BROMINE/METHANOL

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Summary—The extent to which a number of iron oxides dissolved in cold and hot 5% bromine/methanol reagent was examined during analysis for metallic iron in the presence of oxides found in partially-rusted sponge-iron. At room temperature there was only slight attack on the oxides, but at the reflux temperature of the lixiviant and over a period of 2 hr, both the oxyhydroxides and oxides were attacked, the oxyhydroxides considerably and the other oxides slightly.

A solution of bromine in methanol is commonly used as a selective lixiviant for metallic iron in the determination of the metal in sponge-iron (reduced iron ore).[1-3] Sponge-iron also contains gangue compounds (primarily silica, alumina and aluminosilicates) and residual unreduced oxides (haematite, Fe_2O_3, magnetite, Fe_3O_4, and wüstite, FeO). Depending upon the particle size of the metal and how intimately it is bound up in a matrix, leaching is carried out cold or hot for up to 2 hr, with bromine concentrations up to 10% v/v.

Whereas most previous studies were concerned with the dissolution of these residual oxides in bromine/methanol, our experience during the analysis of partially-leached reduced ilmenite suggested that the selectivity of the reagent was impaired if oxides, formed during rusting, were present. The principal oxides produced by atmospheric rusting of iron are goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH) and magnetite.[4] Accordingly, when our attention turned to the analysis of partially-rusted sponge-iron, we decided to examine the solubilizing properties of the reagent for these oxides.

As part of a study of rust formation Sumi *et al.*[5] reported the extent of dissolution of most of the oxide phases in bromine/methanol, but did not disclose the conditions used in their work. The present paper results from tests on the dissolution of the pertinent oxides in the reagent, under conditions proposed for the analysis of sponge-iron pellets.

EXPERIMENTAL

Materials

The iron oxides came from several sources. Those synthesized in the laboratory were FeO, α-Fe_2O_3, and α-, β-, and γ-FeOOH. FeO was prepared by gascous reduction of magnetite at elevated temperature under limited oxygen supply. The remaining four compounds were prepared by established methods.[6-9] Reagent-grade ferrosoferric oxide was obtained from Fisher, a natural magnetite as a concentrate from Savage River, Tasmania and an impure magnetite from an industrial process. This impure magnetite was formed during the aqueous oxidation, under limited oxygen supply, of small iron particles in reduced ilmenite.[10] A sample of "mixed ferric oxides" obtained from the same process when increased oxygen was used, and rust scraped from a steel girder that had been exposed to the atmosphere for about 2 years were also included in the tests. Each material was analysed and its molecular constitution determined by X-ray diffraction (XRD). The results are given in Table 1 and generally confirm the identity of the laboratory-synthesized oxides, although the low total-iron contents of the oxyhydroxides suggest that they contained residual free water. Despite XRD identification as magnetite, reagent-grade ferrosoferric oxide was obviously deficient in ferrous iron, as also was the wüstite. On the other hand, the analysis of the natural magnetite, after

Table 1. Analysis of iron oxides*

Material	Fe(II), %	Fe_{total}, %	Constitution
Fisher ferrosoferric oxide	16.5	71.4	Identified as Fe_3O_4
Natural Fe_3O_4	22.3†	72.0†	Notd determined
Industrial Fe_3O_4	19.6	71.4	Fe_3O_4 + trace lepidocrocite
FeO	59.9	73.6	Identified as FeO
α-Fe_2O_3	not determined	69.9	α-Fe_2O_3
α-FeOOH	not determined	59.2	α-FeOOH
β-FeOOH	not determined	58.2	Identified as β-FeOOH
γ-FeOOH	not determined	60.5	γ-FeOOH
Mixed ferric oxides	0.50	63.5	Lepidocrocite + hematite + trace magnetite
Rust on steel	1.1	59.3	Lepidocrocite + goethite (no apparent magnetite of wüstite)

*Theoretical composition of oxides: FeO, 77.7% Fe(II); Fe_3O_4, 24.1% Fe(II); 48.2% Fe(III); FeOOH, 62.9% Fe(III); Fe_2O_3, 69.9% Fe(III).
†Normalized to account for 2.42% impurities.

Table 2. Dissolution of iron oxides in bromine/methanol

Material	Iron dissolved, %*				
	Room temp. 20 min	Reflux temp. 20 min	Room temp. 2 hr	Reflux temp. 2 hr	Data from Sumi *et al.*[5]
Fisher ferrosoferric oxide	0.11	0.14	0.00	0.94	trace
Natural Fe_3O_4	—	—	0.13	—	—
Industrial Fe_3O_4	0.04	0.00	0.00	0.48	—
FeO	—	—	0.20	1.66	—
α-Fe_2O_3	0.03	0.85	0.05	4.88	trace
α-FeOOH	0.00	2.98	0.02	47.3	0.77
β-FeOOH	0.00	0.28	0.02	52.9	—
γ-FeOOH	0.21	1.97	0.15	41.6	8.08
Industrial mixed oxide	0.00	2.62	0.00	9.92	—
Rust from steel	0.09	0.64	0.09	27.9	—

*Calculated on weight of dried sample.

allowing for a small percentage of gangue constituents (silica and alumina) and moisture, almost matched the theoretical composition of Fe_3O_4.

Procedure

For each dissolution test, 10 mg of oxide, ground to finer than 152 μm grain-size were extracted with 20 ml of 5% v/v bromine/methanol solution at ambient temperature or under reflux. The bromine/methanol was freshly prepared for the tests from BDH AnalaR-grade bromine and methanol, the latter being distilled before use in an all-glass apparatus fitted with a Vigreux fractionation column.[11] The extraction was conducted in a 100-ml round-bottom flask fitted with a water-cooled condenser, the mixture being stirred with a Teflon-coated magnetic stirrer. After an allotted reaction time the mixture was filtered (25 mm × 0.6 μm Polivic Millipore membrane), the solution, if hot, being first quickly cooled to room temperature. The residue was washed free from lixiviant with methanol, the washings being added to the filtrate.

The filtrate was approximately doubled in volume with distilled water and evaporated to dryness in an open beaker. One ml of concentrated perchloric acid was added and traces of organic matter were removed by fuming and evaporating to dryness. The residue was dissolved in 1 ml of 10*M* hydrochloric acid, the solution diluted with distilled water to 50 ml and an appropriate aliquot taken to determine iron spectrophotometrically by the 1,10-phenanthroline method. The absolute error in the method of detection was ±0.05% iron.

DISCUSSION

Results of the dissolution tests (Table 2) indicate that all the iron oxides were essentially unattacked by bromine/methanol at room temperature, but that dissolution increased at the reflux temperature of the reagent, especially with an extended leaching time. FeO, Fe_3O_4 and α-Fe_2O_3 were the most resistant to attack, but the more labile oxyhydroxides, α-, β- and γ-FeOOH, were appreciably dissolved. The high dissolution results for the mixed ferric oxides and rust samples at the reflux temperature are due to the presence of oxyhydroxides.

Anhydrous conditions are required during the leaching of metallic iron, both to obviate the hydrolysis of iron bromides to solid oxide products which would interfere with the analysis, and to minimize the conversion of bromine into hydrobromic acid, which could dissolve oxides. Sumi *et al.*[5] obtained a higher dissolution of iron for γ-FeOOH (8.08%) than for α-FeOOH (0.77%) (see Table 2), which might be the result of insufficient drying of the former compound. This is suspected from their quoted value of only 48.25% (theoretical 62.9%) total iron in the γ-compound, against 54.17% in the α-compound. In the present work, the maximum quantity of water that could have been introduced into the lixiviant from the oxyhydroxide samples was 0.002% w/v, an insignificant amount.

Iron hydroxides were not included in this work, both because they are not normally found in the corrosion product formed by atmospheric rusting, and because they would have contained considerable amounts of unbound water which would nullify the anhydrous conditions desired.

Even in anhydrous solution bromine and methanol react, eventually forming other organic compounds, hydrogen bromide and water[12–14] and, as neither bromine nor methanol attacks iron oxides, it is the reaction products that are responsible for the dissolution found. At elevated temperatures their concentrations would increase rapidly with time, which probably explains the increasing dissolution rates found at the reflux temperature.

It is apparent from these results that, before bromine/methanol solution is used in methods for estimating metallic iron in sponge-iron, the leaching temperature should be considered. When the reduced ore is not rusted, it is generally satisfactory to leach at reflux temperatures as in the methods of Kraft and Fischer[2] and of Blum and Searl.[3] However, prolonged leaching at elevated temperatures introduces errors, because even the more resistant oxides, particularly α-Fe_2O_3, partially dissolve. To determine metallic iron in rusted sponge-iron, leaching of the metal with bromine-methanol should be performed at room temperature.

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REFERENCES

1. R. S. Young, *Chemical Phase Analysis*, Wiley, New York, 1974.
2. C. Kraft and J. Fischer, *Z. Anal. Chem.*, 1963, **197**, 217
3. S. C. Blum and T. D. Searl, *Anal. Chem.*, 1971, **43**, 150.
4. T. Misawa, T. Kyuno, W. Suëtaka and S. Shimodaira, *Corrosion Sci.*, 1971, **11**, 35.
5. K. Sumi, T. Hata and T. Hagiwara, *Bunseki Kagaku*, 1972, **21**, 94.
6. A. I. Vogel, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., p. 468. Longmans, London, 1968.
7. A. M. Van der Draan and J. Medema, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2039.

8. H. B. Weiser, W. O. Milligan and E. L. Cook, *Inorganic Synthesis*, Vol. II, p. 215, McGraw-Hill, New York, 1946.
9. O. Baudish and W. H. Hartung, *Inorganic Synthesis*, Vol. I, p. 185, McGraw-Hill, New York, 1939.
10. B. F. Bracanin, P. W. Cassidy, J. M. MacKay and H. W. Hockin, *Light Metals 1972*, Proceedings 101st AIME Annual Meeting, 1972, p. 209, W. C. Rotsell (ed.).
11. A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 3rd Ed., p. 169. Longmans, London, 1972.
12. H. F. Beeghly, *Anal. Chem.*, 1952, **24**, 1713.
13. K. Kawamura, S. Watanabe and H. Sasaki, *Javan J. Met.*, 1968, **32**, 676.
14. M. J. Nanjan and R. Ganesan, *J. Indian Chem. Soc.*, 1973, **50**, 563.

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ANALYTICAL DATA

DETERMINATION OF THE SALTING COEFFICIENTS OF BENZOYLTRIFLUOROACETONE*

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Summary—The solubilities of benzoyltrifluoroacetone in water and in aqueous solutions of eight electrolytes at 25° were determined. The salting coefficients of benzoyltrifluoroacetone for these electrolytes were obtained from these data, and were found to accord with McDevit–Long theory. Comparison of the salting coefficients for benzoyltrifluoroacetone with those for benzoylacetone suggested that the former has a less polar structure than the latter in their aqueous solutions.

To elucidate the salt effect in solvent extraction systems involving β-diketones and their metal chelates, in a previous paper[1] we dealt with the effect of electrolytes on the liquid–liquid phase distribution and keto–enol tautomeric equilibrium of benzoylacetone (BA). It has been pointed out by many investigators that the trifluoromethyl-substituted β-diketones differ in behaviour from the parent compounds.[2–9] It was therefore thought useful to study the effect of electrolytes on the behaviour of benzoyltrifluoroacetone (BFA), and to compare it with that of its non-fluorinated parent β-diketone, BA.

Thus, we have examined the effect of various electrolytes on the solubility of BFA and tried to correlate it with physical properties of the electrolytes in an attempt to obtain some useful information for interpretation of the salt effect in the solvent extraction of metal chelates.

EXPERIMENTAL

Materials

Reagent-grade BFA was purified by recrystallizing it thrice from n-hexane and dried in a silica gel desiccator (m.p. 38.7–39.4°).

The stock solutions of perchloric acid, hydrochloric acid, sodium perchlorate and sodium chloride were prepared as previously reported.[1] For other salts, reagent-grade chemicals were used without further purification. They were dried at 120° for 2 hr and stock solutions prepared by dissolving accurately weighed amounts in water and diluting to known volumes. Redistilled water was used.

Determination of solubilities

The apparatus and procedure have already been described.[1] In this procedure, the molar concentration of BFA in aqueous solution, C, was calculated from the absorbance at 249.5 nm, A, by means of the equation.

$$C = (A - 0.0041)/1.217 \times 10^4 \qquad (1)$$

obtained by least-squares treatment of the calibration curve at 249.5 nm for three independent series of standard solutions of BFA. The relative standard deviation was 0.3%. The wavelength and absorbance at the absorption maximum were not affected by any of the electrolytes studied. BFA is a weak acid ($pK_a = 6.3$),[10] so to avoid an error due to its dissociation, the solubility was determined for solutions acidified to pH 3 with hydrochloric acid, except for the experiments with hydrochloric and perchloric acids.

Calculation of the salting coefficients

The salting coefficients, k_s, were obtained from the relation[11]

$$\log f = \log (S^0/S) = k_s C_s \qquad (2)$$

where S^0, S, C_s and f denote the solubility of BFA in water and in aqueous electrolyte solution, the electrolyte concen-

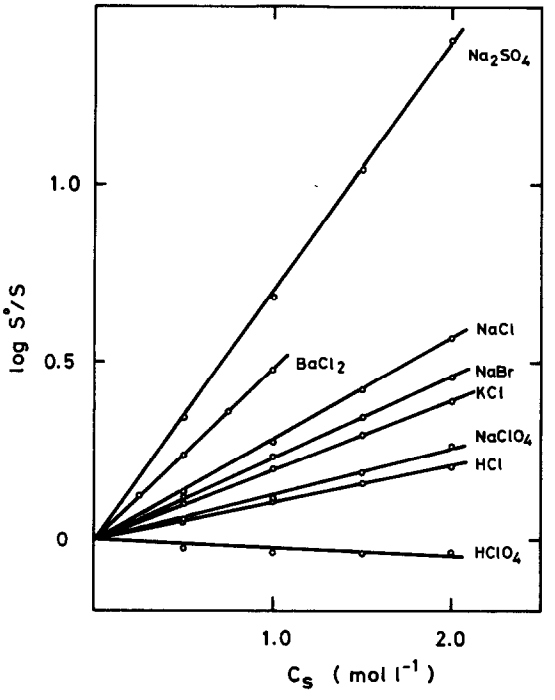


Fig. 1. The plot of log (S^0/S) *vs.* electrolyte concentration (C_s) for benzoyltrifluoroacetone. Straight lines drawn by the method of least squares.

* This paper is part of a doctorate thesis submitted by Y. Yoshimura to the Tohoku University, 1977.

Table 1. Solubility ($10^{-3}M$) of benzoyltrifluoroacetone in aqueous electrolyte solutions at 25°C*

Electrolyte	Electrolyte concentration†, M 0.5	1.0	1.5	2.0
$HClO_4$	$14.5_1 \pm 0.0_2$	$15.0_1 \pm 0.0_4$	$15.0_2 \pm 0.0_3$	$14.8_4 \pm 0.0_4$
HCl	$11.9_9 \pm 0.0_4$	$10.6_5 \pm 0.0_2$	$9.45_5 \pm 0.03_9$	$8.53_0 \pm 0.02_3$
$NaClO_4$	$12.0_5 \pm 0.0_7$	$10.5_1 \pm 0.0_4$	$8.87_2 \pm 0.04_5$	$7.44_5 \pm 0.03_1$
KCl	$10.8_5 \pm 0.0_4$	$8.66_4 \pm 0.02_5$	$6.97_5 \pm 0.01^7$	$5.61_2 \pm 0.02_1$
NaBr	$10.4_3 \pm 0.0_3$	$8.07_6 \pm 0.03_1$	$6.24_0 \pm 0.00_8$	$4.81_9 \pm 0.01_9$
NaCl	$9.98_6 \pm 0.01_4$	$7.30_9 \pm 0.01_8$	$5.20_2 \pm 0.02_1$	$3.72_0 \pm 0.01_2$
Na_2SO_4	$6.25_3 \pm 0.02_9$	$2.85_5 \pm 0.01_3$	$1.25_6 \pm 0.00_8$	$0.539_7 \pm 0.000_7$
$BaCl_2$§	$10.2_9 \pm 0.0_3$(0.25)	$7.93_3 \pm 0.03_3$(0.50)	$5.98_5 \pm 0.02_1$(0.75)	$4.56_7 \pm 0.02_3$(1.0)

* Given as mean value ± standard deviation (6–10 measurements). Salt solutions are $10^{-3}M$ in HCl except for the $HClO_4$ and HCl media. Solubility of benzoyltrifluoroacetone in water ($10^{-3}M$ HCl), S^0, is $13.7_8 \pm 0.0_4 \times 10^{-3}M$.

† Except for $BaCl_2$.

§ The numerals in parentheses are the electrolyte concentrations for $BaCl_2$. Because of its limited solubility, a different concentration was chosen.

tration and the activity coefficient of BFA in the aqueous electrolyte solution, respectively. The plot of log (S^0/S) against C_s gave straight lines for all the electrolytes studied (see Fig. 1). The values for k_s were calculated from the slopes.[1]

RESULTS AND DISCUSSION

The solubilities and salting coefficients of BFA are listed in Tables 1 and 2, respectively. Trifluoromethyl-substituted β-diketones exist principally as the hydrate form in slightly acidified aqueous solutions.[12,13] The ultraviolet spectra of BFA show that it also exists mainly as the hydrate form in acidified aqueous solution, that is, in n-heptane it exhibits the absorption peak at 323 nm due to its enol tautomer, but this peak is completely absent in the spectrum of the acidified aqueous solution. Thus, the solubilities and salting coefficients in Tables 1 and 2 may be regarded as those for the hydrate form of BFA. In most cases, the relative standard deviations of the solubility values (6–10 replicates) were 0.5% or less.

McDevit and Long[14] have estimated the salting coefficient by means of a relation

$$k_s = \frac{\bar{V}_i^0}{2.3\,\beta_0 RT}(V_s - \bar{V}_s^0) \qquad (3)$$

where $\bar{V}_i^0$, V_s, $\bar{V}_s^0$ and β_0 indicate the partial molar volume of non-electrolyte at infinite dilution, the molar volume of pure electrolyte, the partial molar volume of electrolyte at infinite dilution and the compressibility of pure water, respectively. Figure 2 shows that the plot of k_s against $V_s - \bar{V}_s^0$ gives nearly straight lines in accordance with equation (3) for both BFA and benzene. The values for $V_s - \bar{V}_s^0$ were taken from reference 14. Therefore, the effect of electrolytes on BFA can be qualitatively explained by the McDevit–Long theory in the same way as their effect on benzene. This theory is essentially valid only for non-polar non-electrolytes.[14] Therefore, Fig. 2 suggests that the hydrate form of BFA has a polarity low enough for it to be treated as a non-polar non-electrolyte in aqueous solution. The hydrate form of BFA may have a less polar structure because of intramolecular hydrogen-bonds formed between its hydroxyl protons and the fluorine atoms in its trifluromethyl group.[15]

Table 2. Salting coefficients for benzoyltrifluoroacetone at 25°C*

Electrolyte	k_s, *l./mole*
$HClO_4$	-0.022 ± 0.012
HCl	0.107 ± 0.006
$NaClO_4$	0.129 ± 0.008
KCl	0.197 ± 0.004
NaBr	0.229 ± 0.004
NaCl	0.282 ± 0.003
$BaCl_2$	0.481 ± 0.008
Na_2SO_4	0.697 ± 0.009

* Obtained from the slopes of the least-squares straight lines in Fig. 1.

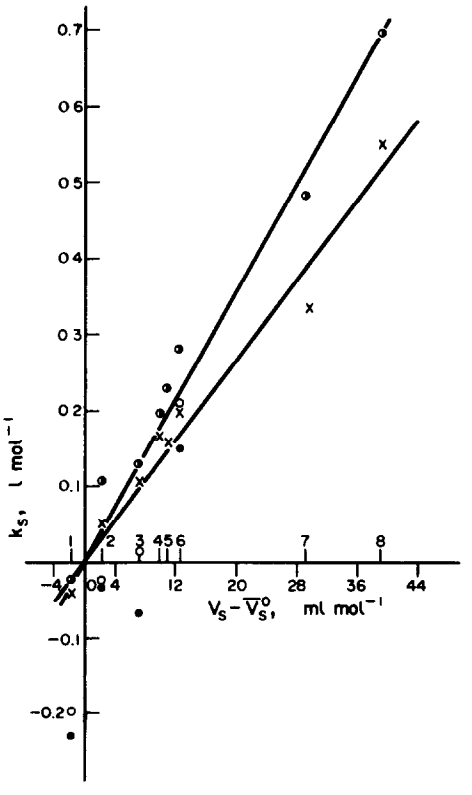


Fig. 2. The plot of salting coefficients (k_s) *vs.* electrolyte property ($V_s - \bar{V}_s^0$) for benzoyltrifluoroacetone, benzene and benzoylacetone. (◑) Benzoyltrifluoroacetone, this work: (○) enol tautomer of benzoylacetone:[1] (●) keto tautomer of benzoylacetone:[1] (×) benzene.[14] (1) $HClO_4$, (2) HCl, (3) $NaClO_4$, (4) KCl, (5) NaBr, (6) NaCl, (7) $BaCl_2$, (8) Na_2SO_4. Straight lines drawn by the method of least squares.

For a given electrolyte, the salting coefficients of both the enol and keto tautomers of BA are smaller than that of the hydrate form of BFA (see Fig. 2). This may be explained by assuming that both the tautomers of BA are more polar than the hydrate form of BFA in aqueous solutions.[1]

The correlation in Fig. 2 gives a useful suggestion for a generalized interpretation of the salt effect in the solvent extraction of metal chelate compounds. This point will be discussed in detail elsewhere.

REFERENCES

1. Y. Yoshimura and N. Suzuki, *Anal. Chim. Acta*, 1977, **91**, 315.
2. B. G. Schultz and E. M. Larsen, *J. Am. Chem. Soc.*, 1949, **71**, 3250.
3. R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, 1956, **2**, 11.
4. K. Sato, Y. Kodama and K. Arakawa, *Nippon Kagaku Zasshi*, 1966, **87**, 821, 1092; 1967, **88**, 968.
5. J. R. Jones and S. P. Patel, *J. Am. Chem. Soc.*, 1974, **96**, 574.
6. K. Kondo, Y. Kondo, T. Takemoto and T. Ikenoue, *Kogyo Kagaku Zasshi*, 1965, **68**, 1404.
7. G. Allen and R. A. Dwek, *J. Chem. Soc. (B)*, **1966**, 161.
8. B. B. Tomazic and T. W. O'Laughlin, *Anal. Chem.* 1973, **45**, 106.
9. M. T. Rogers and J. 'L. Burdett, *Can. J. Chem.*, 1965, **43**, 1516.
10. J. C. Reid and M. Calvin, *J. Am. Chem. Soc.*, 1950, **72**, 2948.
11. F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, **51**, 119.
12. E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, 1951, **73**, 1806.
13. E. H. Cook and R. W. Taft, Jr., *ibid.*, 1952, **74**, 6103.
14. W. F. McDevit and F. A. Long, *ibid.*, 1952, **74**, 1773.
15. J. D. Park, H. A. Brown and J. R. Lacher, *ibid.*, 1953, **75**, 4753.

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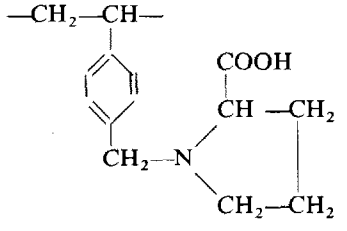
POTENTIOMETRIC DETERMINATION OF THE DISSOCIATION CONSTANTS OF AN ASYMMETRIC SORBENT CONTAINING L-PROLINE, AND THE STABILITY CONSTANTS OF ITS Cu(II) COMPLEXES

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Summary—The dissociation constants of the carboxyl groups ($pK_{a_1} = 2.2$, $n = 1.8$) and amino groups ($pK_{a_2} = 9.5$, $n_2 = 1.6$) of a sorbent prepared by reacting L-proline with a cross-linked chloromethylated styrene polymer have been determined by potentiometric titration. The potentiometrically measured stability constants of the Cu(II) complexes of the resin ($\log\beta_1 = 6.9$ and $\log\beta_2 = 12.4$) were found to be close to the values for the Cu(II) complexes of *N*-benzyl-L-proline. For complexed resins of α-amino-acid type the pH-values of decomplexation do not appear to be directly correlated with the stability constants.

Data reported for the stability constants of metal complexes with chelating resins are highly divergent, the $\log\beta$ values for similar systems given by different authors varying by as much as 4–6 units. The present work was undertaken with the aim of assessing the consistency of the values obtained for these constants by applying different methods to the same system, bearing in mind the importance in ligand-exchange chromatography of being able to characterize quantitatively both stationary complexes of resins with metal ions (*i.e.*, complexes with the metal ions bound to the fixed ligand sites of the resin) and sorption complexes of the resins (*i.e.*, complexes containing the metal ion bound to both resin sites and to mobile ligands). As part of this work, results are presented for potentiometric determination of the carboxyl-group and amino-group dissociation constants of a polystyrene resin containing L-proline:



and of the stability constants of its Cu(II) complexes.

Dissociation constants for amino-acid groups

The acid–base equilibria of polyelectrolytes can be described by a modified Henderson–Hasselbalch equation

$$pH = pK_{char} + n\log\frac{\alpha}{1-\alpha} \qquad (1)$$

where pK_{char} is the dissociation constant characteristic of the functional groups in the polymer, α is the degree of poly-acid dissociation, and n is a proportionality coefficient. Values of pK_{char} calculated according to equation (1) decrease with increasing ionic strength of the solution, whereas the coefficient n decreases with increase in polyelectrolyte concentration as well as in ionic strength.

In calculations of dissociation constants of cross-linked polyelectrolytes account should be taken of contributions from the configurational entropy of the matrix, electrostatic interactions and the specific interactions of the matrix with counter-ions. Some theories partly account for these factors. Thus, Leiden and Underwood[1] have calculated the first and second dissociation constants of the ion-exchanger Dowex A1 with fixed iminodiacetic acid residues, by means of the equation

$$pK_a = pH - \log[Na^+] - \log\left[\frac{\bar{X}}{2}\right] \quad (\alpha = 0.5) \qquad (2)$$

where $[\bar{X}]$ is the concentration of the fixed functional groups in the resin phase: $pK_{a_1} = 2.97 \pm 0.06$; $pK_{a_2} = 8.55 \pm 0.18$ (0.1*M* NaCl medium, 25°). No account was taken, however, of the contributions from specific interactions between the components involved in the ion-exchange and from the electrostatic field effects of the fixed ions.

For evaluating the first carboxyl-group dissociation constant, pK_{a_1}, of this sorbent, Krasner and Marinsky[2] combined the theoretical treatment of polyelectrolytes proposed by Katchalsky[3,4] with the Gibbs–Donnan equation for ionic equilibria in a membrane[5,6] and included the effect of hydrostatic pressure:

$$pH = pK_{a_1} - \log\frac{(1-\alpha)}{\alpha} + \log\frac{\bar{a}_{M^+}}{a_{M^+}} + \frac{0.4343}{kT}\left(\frac{\partial F}{\partial v}\right)_\kappa + \frac{0.4343\pi}{RT}(\bar{V}_{MX} - \bar{V}_{HX}) \qquad (3)$$

Table 1. Dissociation constants of the ionogenic groups of the sorbents and their low-molecular-weight analogues

Electrolyte	pK_a*	n	Swelling, %w/w	Reference
N-Benzyl-L-proline	2.12±0.05			13
	9.77±0.05			13
Resin with L-proline	2.2	1.8	160	
groups*	9.5	1.6	180	
N-Benzyl-D-allohydroxyproline	1.97±0.03			14
	9.13±0.03			14
Resin with	1.65	2.8	60	
D-allohydroxyproline groups	8.8	1.4	110	

*K_{a_1} and K_{a_2}.

where F is the electrostatic free energy of the ionized polyanion carrying ν negatively-charged groups, κ is the inverse Debye radius depending on the concentration of M^+ in the resin phase, $\bar{V}$ is the partial molal volume of the electrolytes MX and HX, π is the contractile pressure of the resin network, and a_{M^+} and $\bar{a}_{M^+}$ are the activities of the counter-ion in the solution and the resin, respectively. The value for the first dissociation constant so obtained, $pK_{a_1} = 2.77 \pm 0.3$ (0.1*M* NaCl, 25°), is somewhat lower than the corresponding dissociation constant of its low-molecular-weight analogue, *N*-benzyliminodiacetic acid, $pK_{a_1} = 2.32$, $pK_{a_2} = 8.88$ (0.1*M* NaCl, 25°).[7]

This led Marinsky *et al.*[2,7-9] to the conclusion that the properties of the polyelectrolyte gels can in general be correlated with those of monomer model compounds provided the poly-ion/co-ion interaction and the Donnan interfacial potential are taken into account. Regrettably, equation (3) was derived from assumptions valid only for weakly cross-linked gels and appears inapplicable for the commonly used ion-exchangers with a high degree of cross-linking.

Finally, the dissociation constant of an ion exchanger can be determined from equation (4), proposed by Soldatov:[10]

$$pH = pK_a + \log \frac{\alpha}{(1-\alpha)} - \log a_{M^+} + \log \frac{\bar{\phi}_{M^+}}{\bar{\phi}_{H^+}} \quad (4)$$

where $\bar{\phi}_{M^+}/\bar{\phi}_{H^+}$ is the ratio of the metal-ion and proton activity coefficients in the resin and a_{M^+} is the metal-ion activity in the external salt solution. A linear dependence has been found[11] between $\log \bar{\phi}_{M^+}/\bar{\phi}_{H^+}$ and $\log \alpha/(1-\alpha)$, leading to the expression

$$pH = pK_a + n \log \frac{\alpha}{(1-\alpha)} - \log a_{M^+}. \quad (5)$$

Equation (5) has been used in the present study for evaluating the dissociation constants pK_{a_1} and pK_{a_2} of the asymmetric polystyrene resin containing L-proline.

The degree of dissociation α was calculated as the ratio of the amount of potassium hydroxide consumed at a given pH value and the overall amount of the amino-acid residues. The activity of K^+ in 1*M* potassium chloride is 0.605 so $\log a_{M^+} = -0.22$. The dissociation constants were determined graphically (Fig. 1). The values obtained proved to be close to those for the dissociation constants of *N*-benzylproline, the low-molecular-weight analogue of the resin (Table 1).

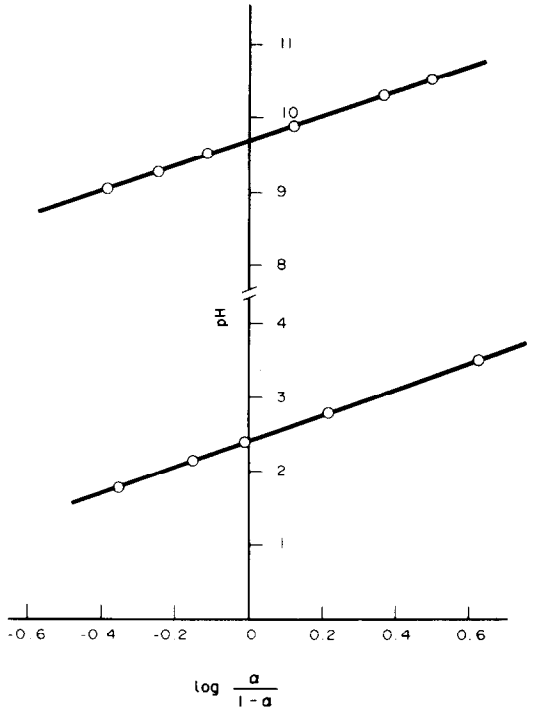


Fig. 1. Graphical evaluation of the results of potentiometric titration of the L-proline-containing resin.

The term n in equation (5) accounts for the effect of the electrostatic field of a polyelectrolyte on its dissociation constant. It was found[12] that the value of n is higher, the greater the resin exchange capacity. We have found that n is also a function of the swelling capacity of the resin. Thus, at pH 2.4 the L-prolinated polystyrene resin swells to the extent of 160% and $n = 1.8$, whereas at pH 9.7 the degree of swelling increases to 180%, resulting in decrease of the n value to 1.6. It should be noted, however, that for this particular resin the swelling capacity varies little on passing from alkaline to acid solution and, concom-

itantly, the variations in n are also small. When the degree of cross-linking permitted a larger range of swelling capacities, as, for instance, with the 5% cross-linked D-allohydroxyproline polystyrene resin (60% swelling at pH 1.85 and 110% at pH 9.0) the difference in the n-values was also markedly greater (Table 1).

Complexation constants for Cu(II) ions

The Cu(II) complexation constant for the chelating resin Dowex A1 containing fixed iminodiacetate groupings was found by the potentiometric method[7] to have a value of $\log\beta = 10.54$, and by the method of partitioning of the copper ions between the resin and a solution of a complexing agent,[15] a value of $\log\beta = 16.9$. Thus, the two methods yield highly divergent results. The value obtained potentiometrically proved to be quite close to that ($\log\beta = 10.61$)[7] for complexation of the copper ion with the low-molecular weight analogue of Dowex A1, *N*-benzyliminodiacetic acid.

In the potentiometric determination of the complex-formation constants of the metal, M^{2+} with the fixed L-proline groupings, AH, the following reaction was considered:

$$iAH + M^{2+} = iH^{+} + A_iM^{+(2-i)}$$

the complex formation equilibrium constant, B_i being

$$B_i = \frac{[A_iM^{(2-i)+}][H^+]^i}{[AH]^i[M^{2+}]}.$$

For similar proton–metal ion exchange reactions[16,17] the equilibrium constants B_i were found to be fairly independent of the degree of polyelectrolyte dissociation.

The constants were determined by a modification of Bjerrum's method:[16]

$$\bar{n} = \frac{\sum_{i=1}^{N} iB_i\left(\frac{[AH]}{[H^+]}\right)^i}{1 + \sum_{i=1}^{N} B_i\left(\frac{[AH]}{[H^+]}\right)^i} \qquad (6)$$

$$B_i = \prod_{i=1}^{i} k_i K_{a_2}^i \quad \text{and} \quad \beta_i = \prod_{i=1}^{i} k_i \qquad (7)$$

where $k_i = [MA_i]/[MA_{i-1}][A]$ is the stepwise constant for the ith step, β_i is the overall stability constant for the ith complex, K_{a_2} is the amino-group dissociation constant.

The main shortcoming of the potentiometric method is the difficulty in determining the number of dissociated and undissociated ionogenic groups in the presence of the metal ions. Gärtner and Wanjek[17] calculated the number of groups co-ordinated to the metal from the difference of the titration curves for an *N*-phenylglycine-containing resin in the presence and absence of metal ions.

In conformity with the procedure adopted for determining the complexing properties of a carboxyl-type cation-exchanger[16] we carried out our calculations assuming that the presence of complexing metal ions does not change the dissociation constant K_a of the ionogenic groups, which thus retains its dependence on the charge of the polyelectrolyte chain in accordance with equation (5). For amino-acid groups this dependence can be written in the following transformed version:

$$K_{a_1} = \frac{[H^+]}{a_{M^+}}\left(\frac{[AH]}{[AH_2^+]}\right)^{n_1}$$

$$= \frac{[H^+][AH]}{[AH_2^+]a_{M^+}}\left(\frac{[AH]}{[AH_2^+]}\right)^{n_1-1}$$

$$= \frac{[H^+][AH]}{[AH_2^+]a_{M^+}}\left(\frac{[A_t]-[AH_2^+]}{[AH_2^+]}\right)^{n_1-1}$$

or

$$K_{a_1} = \frac{[H^+](AH)}{(AH_2^+)a_{M^+}}\left[\frac{(A_t)-(AH_2^+)}{(AH_2^+)}\right]^{n_1-1} \qquad (8)$$

where (A_t) is the total number of amino-acid groups in the resin phase, (AH) is the number of groups in the zwitter-ion form and (AH_2^+) is the number of groups in the acid form.

When the amino-acid resin, in the zwitter-ion form AH, is added to a neutral Cu(II) salt solution, the protons displaced from AH by copper ions are partially bound by the fixed ligands (to form AH_2^+) the rest going into the external solution. The proton concentration in the solution (pH *ca.* 3) is increased by several orders of magnitude, so the proton concentration in the starting solution (pH 7) can be neglected in the following calculations. The number of AH sites occupied by copper ions will be equal to the number of protons displaced, which will be given by (AH_2^+) and the number of protons in the external solutions. If the overall volume of the solution is V, we thus obtain

$$(A_t) = (AH) + 2(AH_2^+) + [H^+]V. \qquad (9)$$

The expression for (AH) from (9) is then substituted into (8). Taking the logarithms gives

$$pH - pK_{a_1} = -n_1\log(AH_2^+) + (n_1-1)\log[(A_t)-(AH_2^+)] + \log\{(A_t)-[H^+]V+2(AH_2^+)\} - \log a_{M^+}. \qquad (10)$$

Equation (10) is solved for (AH_2^+) by the iteration method for each point. To find the values for (AH) the (AH_2^+) values thus obtained are substituted into (9). To arrive at the concentration [AH] the water content of the resin phase must be known. The number of chelate groups interacting with the metal, (A_{Cu}), can then be determined from $(A_{Cu}) = (A_t)-(AH)-(AH_2^+)$ and the degree of complexation can be determined from the expression $\bar{n} = (A_{Cu})/(Cu_t)$, where (Cu_t) is the total copper content of the resin. The dependence of the degree of complexation $\bar{n}$ on the ratio $[AH]/[H^+]$ is shown in Fig. 2.

Equation (6) was solved graphically (Fig. 3) in the form $YP_1 + XP_2 = 1$:[18]

$$\frac{\bar{n}}{(1-\bar{n})\frac{[AH]}{[H^+]}}\cdot\frac{1}{B_1} + \frac{(\bar{n}-2)}{(1-\bar{n})}\frac{[AH]}{[H^+]}\frac{B_2}{B_1} = 1. \qquad (11)$$

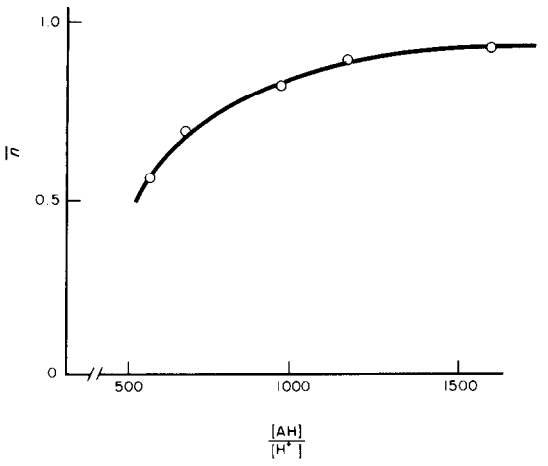


Fig. 2. Extent of Cu(II) complexation with the fixed L-proline groupings.

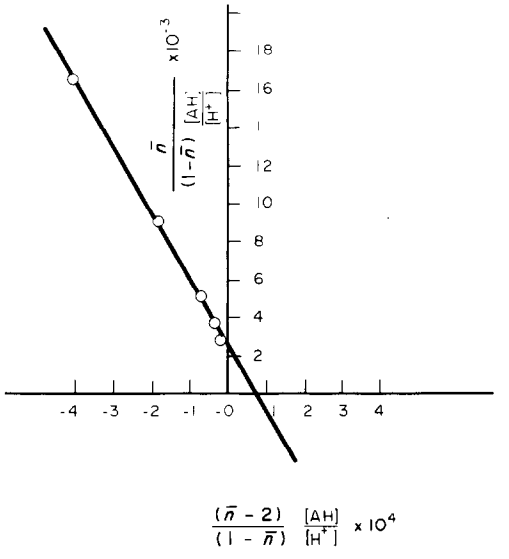


Fig. 3. Graphical determination of complexation constants for the asymmetric sorbent and Cu(II).

The results are given in Table 2. The equilibrium formation constants β_1 and β_2 and the corresponding complex stability constants B_1 and B_2 calculated according to equation (7) are presented in Table 3.

As can be seen from Table 3 the calculated values for the complex stability constants in the resin phase turned out to be close to the corresponding ones for *N*-benzyl-L-proline. Thus, when the potentiometric titration method is used there is a fair consistency between the complexing properties of ion-exchangers and those of their model low-molecular weight analogues. Such a consistency has been shown[7] to exist for the complexing properties of Dowex A1, with a different method being used for calculating the stability constants.

Table 2. Potentiometric determination of the complex formation constants of Cu(II) ions with the fixed L-proline groups

Experimental data					Calculated data					
	Starting amount of Cu(II), *mmole*	Equilibrium solution		Resin phase						
		pH	[Cu], *mmole/ml*	(Cu_r), *mmole*	Water, *g*	(AH_2^+),	(AH),	(ACu),	$\bar{n}$	$\frac{[AH]^*}{[H^+]}$	$\frac{\bar{n}}{(1-\bar{n})\frac{[AH]}{[H^+]}}$	$\frac{(\bar{n}-2)}{(1-\bar{n})}\cdot\frac{[AH]}{[H^+]}$
1	0.273	3.25	0.0148	0.125	0.313	0.113	0.282	0.120	0.960	1600	18.4×10^{-3}	-41.7×10^3
2	0.429	3.15	0.0292	0.137	0.310	0.119	0.269	0.127	0.930	1170	9.20×10^{-3}	-18.0×10^3
3	0.547	3.07	0.0385	0.162	0.306	0.128	0.269	0.135	0.833	978	5.11×10^{-3}	-6.84×10^3
4	1.094	2.96	0.0887	0.207	0.307	0.137	0.226	0.148	0.715	677	3.71×10^{-3}	-3.06×10^3
5	2.186	2.92	0.192	0.266	0.311	0.141	0.220	0.151	0.568	586	2.23×10^{-3}	-1.94×10^3

*[AH] = (AH)/water content of resin phase.

Table 3. Formation and stability constants of Cu(II) complexes

Substance	$\log B_1$	$\log B_2$	$\log \beta_1$	$\log \beta_2$
Resin with L-proline groups*	2.6	6.6	6.9	12.4
N-Benzyl-L-proline[13]	2.93	7.15	6.84±0.03	12.4±0.10

*Degree of cross-linking of the polystyrene matrix 11%, exchange capacity 2.71 mmole/g; external solution 1*M* potassium chloride at 25°.

Complex stability from the pH values of decomplexation, DpH

Hering[19] proposed the use of the quantity DpH for evaluating the stabilities of chelating resin metal complexes. For iminodiacetate groups the following equation was derived:

$$\log \beta = pK_{a_1} + pK_{a_2} - 2\,\mathrm{DpH}. \qquad (12)$$

The equation is based on the fact that in resins of Dowex A1 type, where one bivalent metal ion coordinates to one iminodiacetate group, only half of the fixed groups interact with the metal ions at a solution pH equal to the DpH, whereas the other half will be in the non-complexed H-form. For Cu ions on Dowex A1 the value obtained for DpH was 1.25.[19] The complex stability constant calculated from this value by means of equation (12), $\log \beta = 9.01$, is substantially lower than the stability constant for the Cu complex with *N*-benzyliminodiacetic acid, $\log \beta = 11.09$.[19]

The L-proline-containing asymmetric sorbent used in this work displayed a DpH value of 3.10 when Cu ions were desorbed with 0.1*M* nitric acid under Hering's conditions (Fig. 4); the copper concentration in the eluted solution was [Cu] = 0.026*M*. The data in Table 2 show that under such conditions the extent of complexing in the resin phase is close to unity. With this in mind, the following conclusion can be drawn from analysis of the resin phase composition: in the decomplexing equilibrium only a quarter of the amino-acid groups are interacting with the copper ions, another quarter are protonated and the remaining half are in the form of zwitter-ions.

Thus, acid decomplexing of metals in α-amino-acid type resins differs essentially from that in Dowex A1. Consequently equation (12) does not hold for such type of resins and cannot be used for calculating the stability constants of their metal complexes from the DpH values.

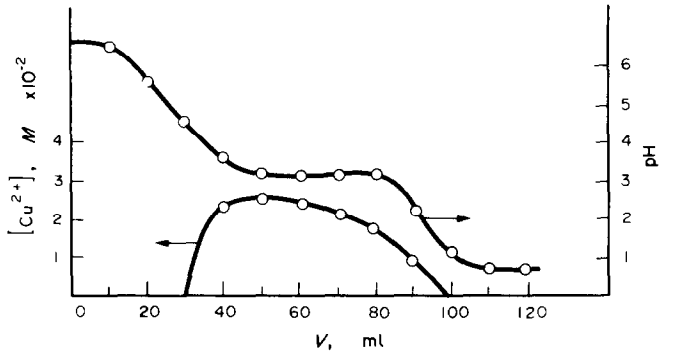


Fig. 4. The pH and copper concentration of the eluate during desorption of copper from the asymmetric resin with 0.1*M* nitric acid.

EXPERIMENTAL

Syntheses

The asymmetric sorbent incorporating L-proline was prepared by aminating a chloromethylated cross-linked polystyrene matrix with methyl L-prolinate.

The isoporous macroreticular matrix, cross-linked to the extent of 11%, was obtained by reacting a 10% solution of polystyrene in dichloroethane with monochlorodimethyl ether in the presence of stannic chloride. Polystyrene (740 g; 7.1 mole) and monochlorodimethyl ether (57.2 g; 0.71 mole) were dissolved in 5.9 litres of freshly distilled dichloroethane. To this solution, cooled to −20°, a solution of 184 g (0.71 mole) of stannic chloride in 100 ml of dichloroethane (also at −20°) was quickly added with stirring. The mixture was then raised to room temperature in the course of 1 hr, without stirring, resulting in a light-yellow cross-linked gel. Following this the temperature was raised to 80° in the course of 3 hr and the mixture was kept at this temperature for 1 hr.

The cross-linked brown gel was then fragmented by shaking; the reaction mixture was cooled to 0°, and 1230 g (15.4 mole) of monochlorodimethyl ether and 400 g (1.54 mole) of stannic chloride were slowly added with stirring. The mixture was kept at 0° for 1 hr, then allowed to stand for 24 hr at 20°. The chloromethylated gel was then filtered off and washed on the filter first with acetone and then with water until free from chloride. The product was dried first in air and then in a desiccator at room temperature. It was then crushed and graded. The 0.064–0.10 mm fraction was used for preparing the ion-exchanger. The chlorine content of the copolymer was 20.4%.

A three-necked 250-ml flask was charged with 21.3 g (0.117

mole) of methyl L-prolinate hydrochloride, 40 ml of absolute methanol and 31.5 g (0.351 mole) of sodium bicarbonate. The mixture was kept at 60° for 1 hr with stirring, then 5.25 g (0.035 mole) of sodium iodide and 20.49 g (0.117 mole) of chloromethylated co-polymer in 150 ml of dioxan were added. The co-polymer was swollen in dioxan beforehand. Amination was carried out at 60° for 20 hr. The product was filtered off, washed with acetone, 1*M* hydrochloric acid and water.

Ester groups in the amination product were hydrolysed with a 1:1 mixture of dioxan with aqueous 2*M* sodium hydroxide for 48 hr at room temperature and the resin was washed successively with 1*M* hydrochloric acid, 1*M* sodium acetate and water, then dried in air and stored in a stoppered flask. The water content of the resin was 37%. The nitrogen content was 3.8%, which corresponds to 2.7 mmole of amino-acid groups per g of dry resin.

Determination of dissociation constants

The dissociation constants were determined by equilibrating the resin with various amounts of acid or base in specially devised 15-ml vials equipped with a porous filter and capable of being stoppered at both ends. The weighed vials were charged with 0.300 g (0.512 mmole) of air-dried resin, different amounts of 0.1*M* sodium carbonate-free potassium hydroxide or hydrochloric acid in 1*M* potassium chloride solution were added and the solutions were made up to 10 ml with 1*M* potassium chloride. The vials were then stoppered and shaken for 48 hr, after which the aqueous layers were filtered and the vials were centrifuged (1600 g, 15 min) to remove the remaining liquid, which was added to the filtrates. Each combined filtrate was then potentiometrically titrated to determine the amount of absorbed acid or alkali. At the same time the degree of swelling of the resin was determined gravimetrically (reproducible to 0.5%). The pH-measurements were made with a precision of 0.01 pH unit.

Determination of the complexation constants

The complexation constants were determined by using the same vials charged with 0.300 g (0.512 mmole) of air-dried resin. To each vial were added different amounts of 0.2*M* cupric chloride solution in 1*M* potassium chloride, and 1*M* potassium chloride was added to make the total volume of solution 10 ml. After equilibration for 72 hr the liquid was separated from the resin in the manner described above, and the extent of swelling of the resin was determined by weighing the vials.

The copper ions were then desorbed by elution with 5*M* hydrochloric acid and the amount of copper in both the filtrate and the eluate was determined by complexometric titration with EDTA in the presence of murexide. The sum of the copper contents tallied well with the overall amount of copper. Simultaneously pH measurements were made on the filtrate.

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REFERENCES

1. E. Leyden and A. L. Underwood, *J. Phys. Chem.*, 1964, **68,** 2093.
2. J. Krasner and J. A. Marinsky, *ibid.*, 1964, **67,** 2559.
3. A. Katchalsky and S. Lifson, *J. Polymer Sci.*, 1953, **11,** 409.
4. S. Lifson and A. Katchalsky, *ibid.*, 1955, **13,** 443.
5. F. D. Donnan and E. A. Guggenkeim, *Z. Phys. Chem. Leipzig*, 1933, **162A,** 356.
6. F. D. Donnan, *ibid.*, 1934, **168A,** 369.
7. C. A. Egor, W. M. Anspach and J. A. Marinsky, *J. Inorg. Nucl. Chem.*, 1968, **30,** 1899.
8. A. Chatterjee and J. A. Marinsky, *J. Phys. Chem.*, 1963, **67,** 41.
9. J. A. Marinsky and A. Chatterjee, *ibid.*, 1963, **67,** 47.
10. V. S. Soldatov, *Simple Ion-Exchange Equilibria*, p. 163. Science and Techniques, Minsk, 1972.
11. F. Helfferich, *Ionenaustauscher*, Verlag Chemie, Weinheim, 1959.
12. L. K. Shataeva, I. A. Chernova, I. Vazik and J. V. Samsonov, *Izv. Aakd. Nauk SSSR, Ser. Khim.*, 1977, 353.
13. V. A. Davankov, S. V. Rogozhin and A. A. Kurganov, *Zh. Neorgan. Khim.*, 1972, **17,** 2163.
14. A. A. Kurganov, *Ph.D. Thesis*, Moscow, 1976.
15. H. Loewenschuss and G. Schmuckler, *Talanta*, 1964, **11,** 1399.
16. H. P. Gregor, L. B. Luttinger and E. M. Loeble, *J. Phys. Chem.*, 1955. **59,** 34. 366.
17. K. Gärtner and H. Wanjek, *Z. Phys. Chem. Leipzig*, 1962, **221,** 391.
18. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants and other Equilibrium Constants in Solution*, p. 115. McGraw-Hill, New York, 1961.
19. R. Hering, *Chelatbildende Ionenaustauscher*, Akademie Verlag, Berlin, 1967.

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DETERMINATION OF STABILITY CONSTANTS OF FIXED-SITE COMPLEXES OF COPPER(II) IONS AND OF SORBED COPPER–L-PROLINE COMPLEXES WITH AN ASYMMETRIC RESIN CONTAINING L-PROLINE GROUPS

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Summary—By study of the distribution of copper(II) and L-proline (Pro) ions between an aqueous phase and a resin phase with L-proline groupings on a polystyrene matrix ($\bar{R}$), the conditional stability constants of fixed-site $\bar{R}_2Cu$ and sorbed $\bar{R}CuPro$ complexes have been determined and a method for calculation of the constants for alkaline and neutral media is proposed. The values obtained reflect the actual behaviour of the system, and strongly depend on the pH and the ionic strength of the solution in equilibrium with the resin phase. It was established that this dependence and the high values of the conditional constants of complex formation in comparison with the stability constants of low molecular-weight model compounds are due to the Donnan distribution of the low molecular-weight participants and to the effect of the electrostatic field of the polyanion. The distribution of the fixed-site ligands on the resin causes considerable differences in the stability of individual fixed-site $\bar{R}_2Cu$ complexes and their capacity to enter into reactions with ligands in the aqueous phase.

The complex formation constants of copper(II) with the iminodiacetate groups on Dowex-A1 resin have been determined by potentiometric titration (log K = 10.54)[1] and by measuring the copper-ion distribution between the resin phase and an aqueous solution of a low molecular-weight chelating agent (log K = 16.90).[2] These values differ considerably but the constant determined potentiometrically is quite close to that for copper-complex formation with the low molecular-weight analogue of the resin—benzyliminodiacetic acid, log K = 10.61.[1]

In a previous study[3] we determined potentiometrically the formation constant of the Cu(II) complex of an asymmetric resin containing fixed L-proline groups, log K = 12.82. This value was in good agreement with the chelation constant of the low molecular-weight analogue of this resin, *N*-benzyl-L-proline, log $K = 12.39 \pm 0.10$.[4]

In the present work the formation constants of the copper complexes with the fixed groups of this L-proline resin, and also the constants for sorption of copper–proline complexes on the resin have been calculated from the results of distribution measurements of Cu(II) and L-proline ions between the resin and aqueous phases, with the aim of studying the effect of conditions of complex formation on the values of these constants.

Factors affecting the interphase distribution of Cu(II) and L-proline ions

In the calculations of concentrational chelation constants it is sometimes assumed that the concentration of the low molecular-weight reaction components in the resin phase is equal to their concentration in the aqueous phase. In our opinion, this assumption is frequently incorrect. This is indicated, for instance, by the strong dependence of the chelating properties of the sorbent on the ionic strength of the external solution. Thus, reduction in chelating ability with increase in ionic strength was reported for resins containing iminodiacetic acid groups[5] and carboxylic groups.[6] In the latter work it was shown that the formation constant of the Cu(II) complex is reduced by two orders of magnitude when the supporting electrolyte concentration is increased from 0 to 2*N*.

In the present work we have studied the chelating properties of an asymmetric sorbent containing L-proline groups, prepared from an isoporous macroreticular matrix with 10% cross-linking.[3] A sharp reduction of chelating power in sorption of copper from ammonia solution is also observed for this sorbent if a neutral electrolyte, potassium chloride, is added in 1*M* concentration (Fig. 1). This apparently reflects the dependence of the copper ion distribution on the ionic strength of the solution, in accordance with the Donnan equilibrium. A similar dependence was also observed for the distribution of L-proline (Fig. 2). At pH values around 7 the distribution coefficient of the L-proline zwitter-ion is $K_d = 0.83$, close to that of the glycine zwitter-ion in a carboxylic acid resin, $K_d = 0.93$.[7] In this range the distribution coefficient of the L-proline zwitter-ion between the solution and the electroneutral resin phase is practically independent of the ionic strength. In the alkaline region, at pH = 11.5, the distribution coefficient describes the behaviour of the L-proline anion in the negatively-charged resin phase. In the absence of a supporting electrolyte, $K_d = 0.1$, whereas in the presence of 1*M* potassium chloride, $K_d = 0.58$. Such a big difference in the distribution coefficients is undoub-

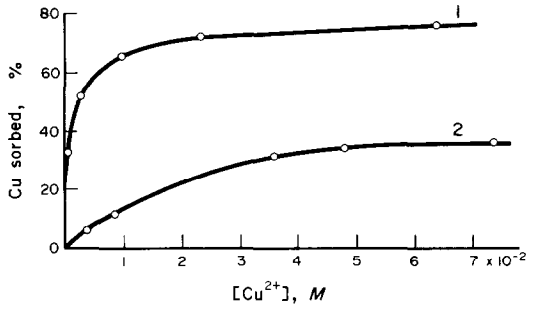


Fig. 1. Sorption isotherm of copper(II) from 2*M* ammonia by an asymmetric resin containing L-proline groupings, in the absence of supporting electrolyte (1) and in the presence of 1*M* potassium chloride (2).

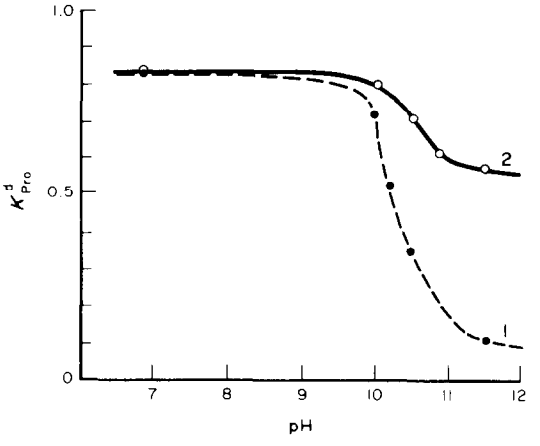


Fig. 2. Coefficient of Donnan distribution of L-proline between the aqueous and asymmetric resin phases as a function of the pH of the aqueous phase, in the absence of supporting electrolyte (1) and in 1*M* potassium chloride (2).

tedly connected with ion-exclusion of the L-proline anion, which in this case acts as a co-ion. It is known that exclusion is greater the larger the volume of the ion and the lower the ionic strength of the solution.[8] The greatest reduction of K_d occurs at the transition of the L-proline zwitter-ion into the anion in the region corresponding to deprotonation of amino groups, $pK_{a_2} = 10.6$. Therefore, at pH $\geqslant$ 11.5 in a Donnan equilibrium the amount of L-proline in the resin phase is only a tenth (in the absence of a supporting electrolyte) of that in the aqueous solution at equilibrium with it. Addition of a supporting electrolyte in 1*M* concentration increases the amount of proline anion in the resin phase by a factor of 5.8.

Evidently, the changes observed in the interphase distribution coefficients of low molecular-weight components with variation in the ionic strength and pH should considerably affect the values of complex formation constants determined by this method.

Calculation of chelation constants in alkaline solutions

To determine the dependence of the chelating and sorption properties of asymmetric sorbents on ionic strength, we studied the distribution of Cu(II) and L-proline between the two phases in the presence and absence of 1*M* potassium chloride.

The conditional concentration of free L-proline, [Pro′], was calculated from the total amount of L-proline and Cu(II) in solution according to the formula

$$[\mathrm{Pro}'] = \frac{m_{\mathrm{Pro}} - 2m_{\mathrm{Cu}}}{V} \qquad (1)$$

where m_{Pro} and m_{Cu} are the numbers of moles of proline and copper in solution respectively, and V is the volume of solution (taking into account the swelling of the resin).

The conditional concentration of free copper in solution was calculated as

$$[\mathrm{Cu}'] = \frac{[\mathrm{Cu(Pro)_2}]}{[\mathrm{Pro}']^2 \beta_2} \qquad (2)$$

where $[\mathrm{Cu(Pro)_2}]$ is the concentration of the bis-proline copper complex (assumed equal to the total concentration of copper in solution, as $[\mathrm{Cu(Pro)_2}] \gg [\mathrm{Cu}]$) and β_2 is the overall formation constant of $\mathrm{Cu(Pro)_2}$, $\log \beta_2 = 16.66$.[9]

The amount of water and the total quantities of copper and L-proline in the resin phase were determined. Naturally, the values obtained include certain amounts of non-absorbed L-proline and copper bis-prolinate. Taking the distribution coefficients as 1 for the copper bis-prolinate, 0.58 for the L-proline anion in the presence of a supporting electrolyte and 0.1 in its absence, and accounting for the volume of water in the resin phase, we calculated the actual quantities of copper, M_{Cu}, and proline, M_{Pro}, participating in the formation of complexes with the stationary phase. The quantity of copper-proline complexes sorbed on the resin phase, $M_{\bar{\mathrm{R}}\mathrm{CuPro}}$, is then equal to the corrected quantity of sorbed L-proline in the resin phase:

$$M_{\bar{\mathrm{R}}\mathrm{CuPro}} = M_{\mathrm{Pro}} \qquad (3)$$

and the quantity of copper complexed with the fixed sites in the resin phase, $M_{\bar{\mathrm{R}}_2\mathrm{Cu}}$ is equal to the difference between the amounts of copper and proline sorbed:

$$M_{\bar{\mathrm{R}}_2\mathrm{Cu}} = M_{\mathrm{Cu}} - M_{\mathrm{Pro}} \qquad (4)$$

The equilibrium number of moles of fixed resin ligands ($M_{\bar{\mathrm{R}}}$) that did not enter into the chelation reaction with copper was determined as

$$M_{\bar{\mathrm{R}}} = M_{\bar{\mathrm{R}}\mathrm{t}} - M_{\bar{\mathrm{R}}\mathrm{CuPro}} - 2M_{\bar{\mathrm{R}}_2\mathrm{Cu}} \qquad (5)$$

where $M_{\bar{\mathrm{R}}\mathrm{t}}$ is the total amount of fixed groups in the resin phase.

The concentration of components in the resin phase was calculated with respect to the volume of water (V_w) in the phase:

$$[\mathrm{X}] = \frac{M_x}{V_w} \qquad (6)$$

The formation constants of the fixed-site complexes with copper and for sorption of the copper–proline

Table 1. Composition of the aqueous solution and resin phase and effective constants of complex formation

	Solution								Resin									
No.*	pH	M_{Cu}, μmole	M_{Pro}, μmole	V, ml	[$CuPro_2$], mM	[Pro], mM	[ProH], mM	pCu	M_{Cu}, μmole	M_{Pro}, μmole	Swelling, mg H_2O	[$\bar{R}CuPro$], mM	[$\bar{R}_2Cu$], mM	[$\bar{R}$], mM	[$\bar{R}H$], mM	log $K_{\bar{R}_2Cu}$	log $K_{\bar{R}CuPro}$	Degree of saturation of resin with copper %†
1	11.62	202.0	1954	13.75	15.0	115.0	—	16.60	11.2	6.0	366	22.3	19.5	1400	—	14.59	15.74	4.4
2	11.60	306.0	1949	13.76	22.0	100.0	—	16.32	14.8	8.2	364	30.4	24.3	1390	—	14.41	15.65	5.8
3	11.55	403.0	1940	13.76	29.5	83.0	—	16.03	24.9	13.3	360	48.2	41.4	1370	—	14.37	15.65	9.7
4	11.50	499.0	1936	13.76	36.6	67.0	—	15.75	35.3	15.9	358	68.1	57.2	1340	—	14.25	15.65	13.8
5	11.45	596.0	1924	13.77	43.6	52.0	—	15.45	44.3	24.5	354	86.5	70.4	1330	—	14.05	15.55	17.3
6	11.40	772.0	1901	13.78	56.5	26.0	—	14.74	84.2	47.3	343	160.0	129.0	1210	—	13.69	15.45	32.9
7	11.20	904.0	1860	13.80	66.0	4.2	—	13.09	169.0	85.0	319	272.0	268.0	890	—	12.62	14.95	65.9
8	10.65	1018.0	2045	14.82	72.0	6.0	—	11.36	247.0	135.0	302	405.0	336.0	617	—	11.30	14.40	96.6
9	11.95	9.8	490	9.99	0.98	47.0	—	17.01	41.4	33.2	362	22.6	91.7	1400	—	15.68	16.55	14.3
10	11.85	70.7	461	9.98	7.07	32.0	—	15.82	92.1	58.4	346	97.4	16.9	1240	—	14.86	16.21	31.8
11	11.80	120.0	437	9.96	12.0	19.7	—	15.17	134.0	79.6	333	165.0	239.0	1100	—	14.46	16.05	46.2
12	11.60	166.0	408	9.95	16.6	7.6	—	14.20	189.0	107.0	321	255.0	333.0	885	—	13.83	15.78	65.2
13	11.20	174.0	370	9.94	17.4	2.2	—	12.11	261.0	141.0	304	395.0	464.0	618	—	12.19	14.57	90.0
14	10.60	175.0	356	9.93	17.6	4.0	—	10.62	303.0	169.0	296	453.0	571.0	355	—	11.27	14.12	104.0
15	8.34	68.1	1928	12.20	5.6	0.878	146.0	12.81	32.3	20.7	324	64.1	33.4	185	1260	12.79	15.40	12.5
16	7.92	170.0	1918	12.30	14.0	0.714	130.0	12.16	39.7	24.3	322	75.5	47.8	102	1320	12.78	15.18	16.0
17	8.24	357.0	1900	12.71	27.7	0.535	91.3	11.66	63.5	42.8	313	133.0	62.0	156	1220	12.06	14.86	25.0
18	8.14	535.0	1869	12.21	40.9	0.349	60.7	11.13	95.9	65.7	308	206.0	98.0	130	1110	11.85	14.83	37.0
19	9.02	679.0	1850	13.76	48.8	0.252	35.8	10.76	166.0	109.0	306	356.0	186.0	301	644	11.07	14.29	65.0
20	8.86	842.0	1806	14.22	59.7	0.058	85.8	9.41	216.0	156.0	298	523.0	201.0	221	570	9.92	14.02	84.3

* 1–8, 1*M* KCl; 9–14, without supporting electrolyte; 15–20, 1*M* KCl.
† Based on formation of $\bar{R}_2Cu$.

complexes may now be determined as

$$K_{\bar{R}_2Cu} = \frac{M_{\bar{R}_2Cu}}{[Cu] \cdot M_{\bar{R}}^2} \quad (7)$$

and

$$K_{\bar{R}CuPro} = \frac{M_{\bar{R}CuPro}}{[Cu] \cdot [Pro] \cdot M_{\bar{R}}} \quad (8)$$

In this calculation of the effective concentrational constants of complex formation, presented in Table 1 and Fig. 3, the concentrations of unchelated copper [Cu] and proline [Pro] ions in the aqueous phase were used.

Since all tests of both series (with and without a supporting electrolyte) were carried out in alkaline solutions (pH $\geqslant$ 11.2, except for samples with maximal copper concentration) it was assumed that all the proline and resin-site ligands were in the anionic form and capable of complex formation (the dissociation constants, pK_{a_2}, of their amino groups are 10.6,[9] and 9.70,[3] respectively).

Calculation of chelation constants in neutral and weakly alkaline solutions

Use of neutral solutions in the study of interphase equilibria makes it possible to minimize the effect of the electrostatic field of the sorbent. However, the acid–base equilibria of both the resin fixed-site ligands and the mobile ligands should be taken into account, since both species are capable of co-ordination with Cu(II) ions when they are in the anionic form, but not when they are in the zwitter-ion form.

In the consideration of the acid–base equilibria in the resin phase we proceeded as follows. The dissociation constant of the amino-acid group in the weak-acid carboxylic acid cation-exchanges is practically the same as the constant for the amino-acid in solution,[7] and for a resin on which no electrostatic charge is present, the distribution coefficient of charged and neutral molecules tends to unity.[8] For the fixed-site groups on resins it is assumed that the acid–base equilibrium is not shifted by the presence of proline zwitter-ions in the resin phase, and that the apparent dissociation constant depends only on the total charge of the polyelectrolyte chain.[6,10]

The amount of sorbed ($M_{\bar{R}CuPro}$) and fixed-site ($M_{\bar{R}_2Cu}$) complexes was determined, as previously, according to equations (3) and (4).

The quantity of sorption groups in zwitter-ion form, $M_{\bar{R}H}$, was obtained from

$$M_{\bar{R}t} = M_{\bar{R}CuPro} + 2M_{\bar{R}_2Cu} + M_{\bar{R}} + M_{\bar{R}H} \quad (9)$$

and substituted into the equation for polyelectrolyte dissociation under conditions of complex formation:[8]

$$K_{a_2} = \frac{[H] \cdot [\bar{R}]}{[\bar{R}H]} \cdot \left(\frac{[\bar{R}]}{[\bar{R}_t] - [\bar{R}]}\right)^{n_2 - 1} = \frac{[H] \cdot M_{\bar{R}}}{M_{\bar{R}H}} \cdot \left(\frac{M_{\bar{R}}}{M_{\bar{R}t} - M_{\bar{R}}}\right)^{n_2 - 1} \quad (10)$$

where M is the number of moles of a species in the sample; $n_2 = 1.6$ and $pK_{a_2} = 9.70$ for an asymmetric resin, in the absence of complex formation.[3]

Equation (10) was solved for $M_{\bar{R}}$ by the method of iteration at each point. The values of $M_{\bar{R}}$ were then substituted into equation (9) to obtain the values of $M_{\bar{R}H}$.

The concentrations of the sorbed and fixed-site complexes as well as of the resin groups in zwitter-ion and anionic forms were determined with due regard to the amount of water in the resin phase, according to equation (6).

The number of moles of copper bis-proline complex in solution, m_{CuPro_2}, was taken as equal to the number of moles of copper determined by analysis of the solution; the amount of unchelated proline, $m_{Pro} + m_{ProH}$, in this case is equal to the difference between the total amount of proline in solution and the amount of its complex with Cu(II).

From the equation for the dissociation constant of proline:

$$K_{a_2} = \frac{[Pro] \cdot [H]}{[ProH]}; \quad pK_{a_2} = 10.6,[14]$$

we found separately the amounts of proline in the zwitter-ion and anionic forms.

The concentration of unchelated copper was determined from equation (2). Finally, the formation constants of the fixed-site stationary and sorbed complexes were calculated from equations (7) and (8).

Results of the calculations are given in Table 1 and Fig. 3.

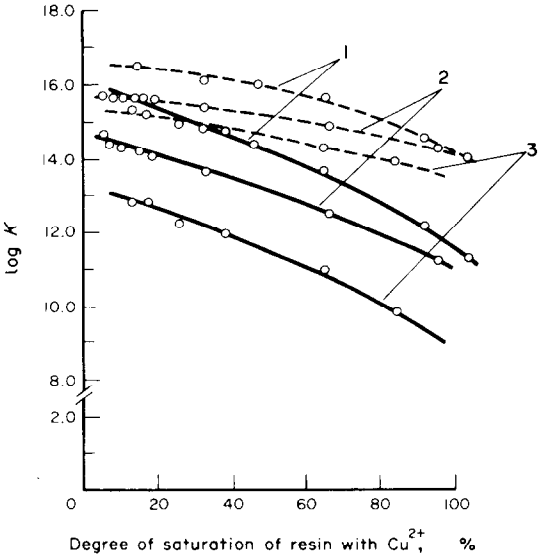


Fig. 3. Stability constants of fixed-site complexes with Cu(II) (———) and of sorbed Cu–Pro complexes (– – –) on an asymmetric resin, as a function of the degree of saturation of the resin with copper(II) (to form $\bar{R}_2Cu$).
(1)—without supporting electrolyte, pH > 11.0;
(2)—1*M* potassium chloride, pH > 11.0;
(3)—1*M* potassium chloride, pH ~ 8.

The dependence of conditional chelation constants on the degree of sorbent saturation with copper ions, pH and the ionic strength of the solution

Three pairs of conditional stability constants of fixed-site ($\bar{R}_2Cu$) and sorbed ($\bar{R}CuPro$) complexes, determined under different conditions, are shown in Fig. 3. As can be seen, they decrease with increase of sorbent saturation with copper ions. The decrease of $K_{\bar{R}_2Cu}$ is especially rapid.

Earlier,[11] we explained the gradual reduction in stability of fixed-site complexes formed by two ligands bonded to the polymer matrix as due to deterioration of the steric conditions for chelation, as the copper ions must react with less and less favourably arranged pairs of fixed-site ligands. Evidently, the stability of individual fixed-site $\bar{R}_2Cu$ complexes varies over a very wide range. This is confirmed by the fact that the average stability constant of these complexes drops by at least 3 orders of magnitude with increase in the degree of saturation with copper ions from 0 to 100%.

The stability of sorbed complexes ($\bar{R}CuPro$) depends to a considerably smaller extent on the copper content of the system. This is to be expected, since the mobile ligand (Pro) in these complexes is not bonded to the polymer chains of the matrix and may arrange itself favourably in space. The fact that the stability of the sorbed complexes nevertheless shows a tendency to reduction with increase of copper content in the resin phase, may be explained by the increase of steric hindrance to formation of bulky complexes in the resin phase and also by variation in the activity coefficients of mobile ions. (The exchange constants have been reported to be dependent on the ionic composition of carboxylic[12] and diallyl phosphate[13] resins.)

Figure 3 demonstrates graphically the dependence of the conditional stability constants of the fixed-site and sorbed complexes on the pH and ionic strength of the equilibrium solution, which, as shown above, considerably affect the distribution coefficients of copper and proline ions. The conditional stability constants of complexes in the resin phase should, undoubtedly, depend on such characteristics of the polymer matrix as the degree of cross-linking and concentration of fixed ligands. The fact that the constants for a similar sorbent with 6% cross-linking and 1.68 meq/g stationary L-proline groupings[11] are slightly higher than those obtained in the present work, and depend to a smaller degree on the amount of copper ions in the sorbent, we also associate with these factors.

The calculated conditional stability constants (Fig. 3) are in good agreement with the actual behaviour of the system under static and dynamic conditions and reflect the following important features of the system.

(*i*) Sharp reduction of the sorption capacity of the resin for copper ions on addition of a neutral electrolyte to the equilibrium solution (see Fig. 1) and on transition from alkaline to neutral solutions.

(*ii*) Considerable increase of resin affinity for mobile ligands with increase of the degree of resin saturation with copper ions. Indeed, the sorption constant of L-proline is determined by the difference between the stability constants of the sorbed complex and of the initial fixed-site complex, $K_{\bar{R}CuPro} - K_{\bar{R}_2Cu}$; this difference rapidly increases with the amount of copper in the system (see Fig. 3).

(*iii*) Noticeable increase of resin affinity for the mobile amino-acid ligand (Pro) with increase in the ionic strength of the equilibrium solution and, in particular, on transition from alkaline to neutral solutions.

Donnan distribution

While the dependence of the conditional constants for chelation with the resin phase on the degree of its saturation is, apparently, primarily associated with steric features of the process, the dependence of the calculated constants on pH and the ionic strength, undoubtedly reflects changes in the distribution coefficients of low molecular-weight components between the two phases. Evidently the latter factor should always be taken into account when comparing stability constants for complexation in resin phases with the stability constants of low molecular-weight model compounds.

Experimental determination of the distribution coefficients of unchelated copper and proline ions in a real system that contains all the components participating in the process is impossible. However, as mentioned above, we determined the distribution coefficients of L-proline (K^d_{Pro}) in the absence of copper ions. The distribution coefficients of unchelated copper ions (K^d_{Cu}) may be estimated from these values, if we assume, according to Helfferich,[14] that formation constants of low molecular-weight complexes in the resin phase do not differ from the same constants in solution and that the distribution coefficient of the electroneutral $CuPro_2$ complex is equal to unity. In this case, at equilibrium

$$Cu + 2Pro \overset{K_{CuPro_2}}{\rightleftharpoons} CuPro_2$$

and $K^d_{Cu} = (K^d_{Pro})^2$. The calculated values of the distribution coefficients of unchelated copper (K^d_{Cu}) are 1.49 for the neutral pH range, and 2.97 and 100 at pH = 11.5 in the presence and absence of 1*M* potassium chloride, respectively. On the basis of the K^d_{Pro} and K^d_{Cu} values the stability constants, $K_{\bar{R}CuPro}$ and $K_{\bar{R}_2Cu}$, corresponding to 50% and 20% sorbent saturation with copper ions may be corrected. The corrected values obtained are given in Table 2 together with $K_{\bar{R}_2Cu}$ determined potentiometrically[3] and the stability constants of the corresponding model complexes bis-(*N*-benzyl-L-prolinato)copper(II)[4] and (L-prolinato)-(*N*-benzyl-L-prolinato)copper(II).[15]

As can be seen from the data presented in Table 2, the corrected values of the stability constants for the sorbed and fixed-site complexes obtained in alkaline solutions in the presence and absence of a supporting electrolyte are in good agreement with each other. Therefore, the differences in the corresponding effec-

Table 2. Stability constants of fixed-site and sorbed complexes in the resin phase and of their low molecular-weight analogues

Test conditions	$\log K_{\bar{R}_2Cu}$ Conditional	Corrected	$\log K_{\bar{R}CuPro}$ Conditional	Corrected
pH > 11; 50% Cu	14.2	12.2	16.0	15.0
pH > 11; 1*M* KCl; 50% Cu	13.0	12.5	15.2	15.0
pH ~ 8; 1*M* KCl; 50% Cu	11.5	11.35	14.6	14.5
pH ~ 8; 1*M* KCl; 20% Cu	12.7	12.55	15.2	15.1
Potentiometry[3]	12.8		—	
Model complexes[4,15]	12.4 ± 0.1		14.9 ± 0.2	

tive chelation constants arise from the high values obtained in the absence of a supporting electrolyte and caused by the Donnan distribution of low molecular-weight participants in the process.

Both the corrected and conditional chelation constants obtained for feebly alkaline 1*M* potassium chloride medium have lower values than those for alkaline solutions. This is evidently connected with the decrease in the charge on the polymer chain on transition to the neutral pH-region, *i.e.* with decrease in the electrical potential of the polymer chain. This conclusion conforms with the results obtained by Gregor[6] who showed for carboxylate linear and cross-linked polymers that the chelating properties of a polyanion significantly exceed the chelating properties of low molecular-weight model compounds. Evidently the polyanion field affects the stability of fixed-site complexes to a considerably greater extent than that of sorbed complexes.

The corrected values of the constants obtained for sorbed and fixed-site complexes in alkaline solutions at 50% saturation of the sorbent with metal-ion are close to the stability constants of low molecular-weight model compounds. Apparently, this is due to compensation by two opposite effects, namely, the effect of the polyanion field and steric hindrance to complex formation.

Both effects should be insignificant in pH-regions close to neutrality and at low degrees of sorbent saturation with copper ions (10–20%). Under these conditions, the values obtained are indeed close to the stability constants of the corresponding low molecular-weight analogues and to the stability constant of the fixed-site complex determined potentiometrically.

EXPERIMENTAL

The asymmetric resin containing L-proline groupings was synthesized on a macro-reticular isoporous polystyrene matrix with 10% crosslinking.[3] The sorbent capacity was 2.71 meq/g.

Distribution of the components in the system was determined under static conditions in 15-ml columns.[3] The air-dried resin was brought to equilibrium with a solution of copper and L-proline by agitation in sealed tubes for 72 hr. The resin phase was isolated by centrifuging at 2000 *g* (3500 rpm) for 15 min. For analysis of the resin phase, copper and L-proline were desorbed by washing the resin in the column with 5*M* hydrochloric acid.

The amounts of copper and L-proline were determined in the aqueous and resin phases. The results obtained agree within experimental error with the amounts of copper and L-proline introduced into the system. Copper was determined spectrophotometrically with diethylcarbamate at 440 nm. L-Proline was determined in 5*M* hydrochloric acid by polarimetry at 436 nm. The pH of the solutions was measured to 0.01 pH unit.

A 0.300-g portion of air-dried resin containing 0.512 meq of functional groups was placed in a column. For studies in alkaline and weakly alkaline media, 2.00 meq of L-proline and 0.2–2.4 meq of Cu(II) were added if a 1*M* potassium chloride medium was used, and 0.53 meq of L-proline and 0.1–1.0 meq of Cu(II) if the supporting electrolyte was omitted.

For studies in alkaline solutions, potassium hydroxide was also added, in quantities equivalent to the total quantity of functional groups in the resin and added proline.

In the case of weakly alkaline solutions potassium hydroxide was added in amounts that would not exceed by more than 5–10% the quantity of protons formed during complex formation.

The volume of equilibrium solution was corrected for the water introduced with the air-dried resin and extracted by the swollen resin.

The amounts of occluded copper bis-prolinate and L-proline were taken into account in the determination of sorbed copper and L-proline. The distribution coefficient of copper bis-prolinate was taken as equal to unity. For proline in alkaline solution in the presence of 1*M* potassium chloride, $K^d_{Pro} = 0.58$, and 0.1 in its absence. In the weakly-alkaline range it was assumed that $K^d_{Pro} = 0.83$ (see Fig. 2).

REFERENCES

1. C. Eger, W. M. Anspach and J. A. Marinsky, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1899.
2. H. Loewenschus and G. Schmuckler, *Talanta*, 1964, **11**, 1399.
3. Y. A. Zolotarev, A. A. Kurganov and V. A. Davankov, *ibid.*, 1978, **25**, M/S 124.
4. A. A. Kurganov, V. A. Davankov and S. V. Rogozhin, *Zh. Neorgan. Khim.*, 1972, **17**, 2163.
5. E. Leyden and A. L. Underwood, *J. Phys. Chem.*, 1964, **68**, 2093.
6. H. P. Gregor, L. B. Luttinger and E. M. Loeble, *ibid.*, 1955, **59**, 34, 336.
7. P. S. Nys and E. M. Savitskaya, *Zh. Fiz. Khim.*, 1969, **43**, 1536.
8. F. Helfferich, *Ion-Exchangers* (in Russian), IL, Moscow, 1962.
9. A. A. Kurganov, V. A. Davankov, S. V. Rogozhin and Yu. D. Koreshkov, *Koord. Khim.*, 1977, **3**, 667.
10. K. Gartner and H. Wanjek, *Z. Phys. Chem.*, 1962, **221**, 391.
11. A. V. Semechkin, S. V. Rogozhin and V. A. Davankov, *J. Chromatog.*, 1977, **131**, 65.
12. H. P. Gregor, H. J. Hamilton and R. J. Oza, *J. Phys. Chem.*, 1956, **60**, 263.
13. J. Kennedy, R. V. Davies and H. Small, *J. Appl. Chem.*, 1959, **9**, 32.
14. F. Helfferich, *J. Am. Chem. Soc.*, 1962, **84**, 3237.
15. V. A. Davankov and P. R. Mittchel, *J. Chem. Soc., Dalton*, 1972, 1012.

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BESTIMMUNG VON STICKSTOFF IN REFRAKTÄRMETALLEN*—II TITAN†

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Zusammenfassung—Es wird über Ringuntersuchungen zur Stickstoffbestimmung in Titan berichtet, die im Arbeitsausschuß "Sonder-und Refraktärmetalle" des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute durchgeführt wurden. Folgende Bestimmungsverfahren kamen zur Anwendung: klassische und modifizierte Kjeldahl-Verfahren, Trägergas-Schmelzextraktion, Vakuum-Schmelzextraktion. Die Heißextraktionsverfahren sind bei Anwendung der Platin-(oder Palladium)Flux-Technik (Edelmetall-/Probegewicht ~ 20; Extraktionstemperatur ≥ 2000°) zur Bestimmung von Stickstoffgehalten ≥ 20 ppm geeignet. Mit den Kjeldahl-Verfahren lassen sich, unter Einhaltung bestimmter Bedingungen, Gehalte > 10–40 ppm (je nach Laboratorium), bei Verwendung einer Mikro-Kreislaufdestillations- und Bestimmungsapparatur in Verbindung mit einem Druckaufschluß > 1 ppm Stickstoff bestimmen. Wegen einer möglichen Beeinflussung durch reduzierbare stickstoffhaltige Verbindungen der Laboratoriumsluft muß der Blindwert in Gegenwart von Reinstaluminium ermittelt werden. Die Ergebnisse von sieben Laboratorien (Kjeldahl 4, Heißextraktion 3) stimmten bei einer Titanprobe mit 138 ppm Stickstoff (Standardabweichung 5 ppm) überein.

Von den nichtmetallischen interstitiellen Elementen Wasserstoff, Kohlenstoff, Stickstoff und Sauerstoff übt Stickstoff den stärksten Einfluß auf die mechanischen Eigenschaften wie Härte, Zugfestigkeit, Bruchdehnung und Streckgrenze von Titan und seinen gängigen Legierungen aus.[1–3] Stickstoff zeigt bei allen Temperaturen eine gute Löslichkeit in Titan.[1,3] Da die Lösungsenthalpie sehr hoch ist, kann eine Entgasung ohne Verwendung von Zuschlägen durch Schmelzen im Ultrahochvakuum nicht durchgeführt werden. Stickstoff kann auch in Form von Nitriden im Metall vorliegen, die sich außer durch hohe thermische Stabilität[1,4] auch durch große Resistenz gegenüber üblichen Reagenzien auszeichnen—Eigenschaften, die im Hinblick auf die analytische Bestimmung von Wichtigkeit sind.

Da schon Stickstoffgehalte < 100 ppm die technologischen Eigenschaften von Titan und seinen Legierungen deutlich beeinflussen, kommt der genauen analytischen Bestimmung von Stickstoff für die Einhaltung vorgeschriebener Festigkeitswerte entscheidende Bedeutung zu.

Von den für die Stickstoffbestimmung in Metallen in Frage kommenden Analysenmethoden,[1,5] wie z.B. der Heißextraktion, den klassisch-chemischen Verfahren oder der Aktivierungsanalyse, findet das Kjeldahl-Verfahren für die Stickstoffbestimmung in Titan am häufigsten Anwendung. Jedoch werden oft starke Abweichungen der Analysenwerte zwischen verschiedenen Laboratorien beobachtet. Die Angaben in der Literatur über die Eignung der Heißextraktionsverfahren sind z.Tl. widersprüchlich,[1,4,6] was aufgrund des Verhaltens des Systems Titan–Stickstoff verständlich erscheint.

Wegen dieser unbefriedigenden Situation hatte sich der Arbeitsausschuß "Sonder- und Refraktärmetalle" des Chemikerausschusses der Gesellschaft Deutscher Metallhütten- und Bergleute die Aufgabe gestellt, die Anwendbarkeit der Heißextraktionsverfahren zu prüfen und den Ursachen für die Abweichungen beim Kjeldahl-Verfahren im Rahmen von Ringuntersuchungen nachzugehen. Bekanntlich erfordern Heißextraktionsverfahren, abgesehen vom apparativen, einen wesentlich geringeren experimentellen und zeitlichen Aufwand. Bei diesen Untersuchungen wurden außer klassischen und modifizierten Kjeldahl-Verfahren, Vakuum- und Trägergas-Schmelzextraktionsverfahren herangezogen.

Es wurde zunächst eine Ringuntersuchung an

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* Ergebnisse einer Gemeinschaftsuntersuchung des Arbeitsausschusses "Sonder- und Refraktärmetalle" im Chemikerausschuß der Gesellschaft Deutscher Metallhütten- und Bergleute (GDMB).

An den Untersuchungen über Stickstoff in Titan waren beteiligt:

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Gesellschaft für Elektrometallurgie m.b.H., Nürnberg: K. Bencker
H. C. Starck-Berlin, Goslar: O. Hilmer
Kernforschungszentrum Karlsruhe, Institut für Material- und Festkörperforschung: H. Schneider
Krupp Forschungsinstitut, Essen: D. Hirschfeld
Max-Planck-Institut für Metallforschung Stuttgart und Schwäbisch Gmünd: E. Grallath
Metallwerk Plansee, Reutte: H. M. Ortner
Süddeutsche Kalkstickstoffwerke, Trostberg: M. Röhrl.

† Teil I: Molybdän und Wolfram, *Talanta*, 1978, **25**, 195.

Titanprobe I und anschließend wurden zwei weitere Untersuchungen an Titanprobe II durchgeführt. Während bei der Analyse der Titanprobe I und der ersten Untersuchung von Titanprobe II keine Absprachen hinsichtlich Probenvorbereitung und Durchführung der Analysen getroffen wurden, erfolgten diese bei der zweiten Ringanalyse an der Probe II.

EXPERIMENTELLER TEIL

Probematerial

Für die Untersuchungen wurde Blech aus unlegiertem Titan (1 mm Dicke) handelsüblicher Qualität TIKRUTAN* RT®, hergestellt nach dem Kroll-Verfahren und in einer wassergekühlten Cu-Kokille niedergeschmolzen, von der Firma Fried. Krupp GmbH zur Verfügung gestellt. In der Tabelle 1 sind die wichtigsten Verunreinigungen der für die Untersuchungen eingesetzten Titanproben I und II angegeben, die sich, was die chemische Zusammensetzung betrifft, im wesentlichen im Sauerstoffgehalt unterscheiden.

Tabelle 1. Chemische Charakterisierung (Richtwerte) der bei den Ringuntersuchungen eingesetzten Bleche aus unlegiertem Titan (Angabe in Masse-%)

Element	Ringanalyse I (TIKRUTAN RT18®)	Ringanalyse II (TIKRUTAN RT12®)
Wasserstoff	0,002	0,002
Kohlenstoff	0,01	0,01
Stickstoff	0,01	0,01
Sauerstoff	0,17	0,06
Mangan	0,005	0,005
Eisen	0,06	0,04
Nickel	0,02	0,02
Titan	Rest	Rest

Probenvorbereitung

Für die zweite Ringuntersuchung an Probe II wurden aus dem Titanblech mechanisch (Diamanttrennscheibe, Schere o.ä.), wenn erforderlich unter Kühlung, Probestücke herausgearbeitet. Ein Zerspanen der Probe sollte unterbleiben, da es bei dieser Behandlung zu lokaler Erhitzung mit verstärkter Aufnahme von Stickstoff aus der Luft kommen kann. Auch die Vergrößerung der Oberfläche ist einer exakten Stickstoffbestimmung, bei der nur der Masse-Stickstoff erfaßt werden soll, nicht dienlich.

Unmittelbar vor der Analyse wurden die Probestücke nach folgender, in einer Gemeinschaftsarbeit des Büro Eurisotop erarbeiteten Beiz-Vorschrift behandelt:[7]

Beizbad: 4 Vol.-T. HNO_3 (65%ig) und 1 Vol.-T. HF (40% ig)
Beizbedingungen: 60 sec; Raumtemperatur
Spülen: 3 × dest. H_2O, 3 × Methanol
Trocknen: Warmluft von ca. 60°

Nach dieser Behandlung ist der Oberflächenstickstoff < 0,1 µg/cm² und bei dem zu erwartenden Stickstoffgehalt zu vernachlässigen.[7] Ein Einfluß einer Lagerzeit bis zu mehreren Stunden im Exsikkator auf die Oberflächenbedeckung mit Stickstoff wurde bisher nicht festgestellt.

Analysenverfahren

Bei der Ringuntersuchung an Titanprobe I und der ersten Untersuchung an Probe II kamen mit einer Ausnahme (Vakuum-Schmelzextraktion) nur klassische bzw. modifizierte Kjeldahl-Verfahren zur Anwendung. Es wurden jeweils die in den Laboratorien üblichen "Hausverfahren" benutzt.

Wie im folgenden noch begründet wird, erfolgte die Durchführung der Analysen bei der zweiten Untersuchung der Titanprobe II unter Einhaltung gewisser Absprachen. In Tabelle 2 sind die wichtigsten Analysenparameter der in den einzelnen Laboratorien angewandten Verfahren zusammengefaßt.

Tabelle 2. Übersicht der von den teilnehmenden Laboratorien angewandten Analysenverfahren sowie wichtigste Analysenparameter

Lab. Nr.	Analysen-Verfahren	Einwaage g	Aufschluß- bzw. Extraktions-Bedingungen	Lösungsmittel bzw. Bad/Flux	Verwendete Apparatur	Bestimmungs-Verfahren	Blindwert, µg N $\bar{x}$	Blindwert, µg N s
1	Makro-Kjeldahl	1	abgedeckte PTFE-Becher; Erwärmen	30 ml HF	handelsübl. Apparatur	LAS mit Neßlers Reagenz[16]	54	3 (n = 4)
2	Makro-Kjeldahl	0,15	abgedeckte Pt-Schale; 30 min bei gelind. Sied.	5 ml HF	handelsübl. Apparatur	LAS; Indophenolverf.[17]	11–14	
3	Makro-Kjeldahl	1	abgedeckte PE-Becher 1 h; 60–70°C	10 ml HF 20 ml H_2O	Apparatur von Ströhlein	LAS mit Neßlers Reagenz[16]	9	1 (n = 4)
4	Halbmikro-Kjeldahl	0,2	abgedeckte PTFE-Becher 15 min; ca. 100°C	5 ml HF	Apparatur nach Parnas	LAS; Indophenolverf.[18]	11,0	0,3 (n = 6)
5	Mikro-Kjeldahl	0,2 bzw. 0,08	Druckaufschluß im PTFE-Gefäß 2–6 h; 120°C	2 ml HF/ $HClO_4$ (10 : 1)	Kreislauf-destill. Apparatur	Coulometr. Titration[8]	1,2	0,1 (n = 12)
	Vakuum-Schmelz-extraktion	0,05	Extraktion 0,5 min/2500°C	Pt-Flux 20 : 1	Leybold-Heraeus VH-9 mit Elektrodenofen	GC mit WLD	für jede Probe aus zugehörigen O_2-Peak mit Fehler < 0,5 µg zu berechnen	
6	Vakuum-Schmelz-extraktion	0,1	Extraktion 1 min/2700°C	Pt-Flux 10 : 1	Balzers EAN 220	Wärmeleitfähigkeits-messung	3–4	
7	Trägergas-Schmelz-extraktion	0,25	Extraktion 2 min/2080°C	Pt-Flux 50 : 1	Ströhlein-Apparatur	Wärmeleitfähigkeits-messung	4,0	1,0 (n = 5)

*TIKRUTAN ist ein eingetragenes Warenzeichen der Fried. Krupp GmbH, Essen.

ERGEBNISSE UND DISKUSSION

Ringuntersuchung an Titanprobe I

Bei der Ringuntersuchung an Titanprobe I (siehe Tab. 3) wandten vier Laboratorien eine Makro- bzw. Halbmikro-Kjeldahlmethode mit Endbestimmung durch Photometrie (Lab. 1, 2, 3), bzw. mit ionensensitiver Elektrode (Lab. 6) an. Ein weiteres Labor (Lab. 5) benutzte eine neu entwickelte Mikro-Kreislaufdestillations- und Bestimmungsapparatur mit coulometrischer Bestimmung des Ammoniaks.[8] Labor 2 zog als weiteres Verfahren die Vakuum-Schmelzextraktion unter Anwendung der Pt-Bad-Technik hinzu.

Von Ausnahmen abgesehen, die in Tab. 3 besonders vermerkt sind, wurden aus dem Analysenmaterial kompakte Probestücke hergestellt.

Die Ergebnisse sind in Tab. 3 zusammengestellt. Obwohl die Werte der meisten Laboratorien eine verhältnismäßig geringe Streuung aufweisen (Variationskoeffizienten $\leqslant 5\%$), unterscheiden sie sich von den Ergebnissen anderer Teilnehmer deutlich. Die Ergebnisse können in zwei Gruppen eingeordnet werden: in eine erste mit den Labormittelwerten 79 und 77 bzw. 84 ppm N (Lab. 1 und 2) und in eine zweite mit 54, 65 und 57 ppm N (Lab. 3, 5 und 6). Das Ergebnis der Vakuum-Schmelzextraktion (Lab. 2) fällt mit $\leqslant 20$ ppm N heraus, was offensichtlich auf eine nicht geeignete Extraktionstechnik, wie zu kleines Pt-Probe-Verhältnis und zu niedrige Extraktionstemperatur zurückzuführen ist.

Tabelle 3. Ergebnisse der Ringuntersuchung an Titanprobe I

Labor-Nr.	Verfahren	$\bar{x}$, ppm	s, ppm	n
1	Makro-Kjeldahl	79*	4	5
2	Makro-Kjeldahl	77*	21	5
	Makro-Kjeldahl	84	13	2
	Vak.-Schmelz-extraktion	$\leqslant 20$		
3	Makro-Kjeldahl	54	2	6
5	Mikro-Kjeldahl	65	3	7
6	Halbmikro-Kjeldahl	57	2	4

*Spanförmiges Probematerial.

Auf grund der ungenügenden Übereinstimmung, deren Ursache bei einer Diskussion der Ergebnisse nicht zu ermitteln war, wurde eine zweite Ringuntersuchung (unter Beteiligung weiterer Laboratorien) an neuem Material durchgeführt.

Erste Ringuntersuchung an Titanprobe II

An dieser Untersuchung nahmen dieselben Labors mit denselben Verfahren wie beim ersten Mal teil, mit Ausnahme der Heißextraktion des Labors 2. Hinzu kamen das Vakuum-Schmelzextraktionsverfahren des Labors 6 und mit Labor 8 ein weiteres Labor mit Kjeldahl-Verfahren.

Wie aus Tab. 4 hervorgeht, zeigen auch die Ergebnisse dieser neuen Untersuchung keine gute Übereinstimmung. Zwei hohen Werten mit 186 und 183 ppm N(Lab. 1 und 8) stehen zwei ebenfalls übereinstimmende Werte von 133 und 138 ppm N (Lab. 3 und 5) gegenüber. Die Werte von Labor 2 mit 162 ppm für spanförmige Proben und 148 ppm für eine kompakte Probe liegen dazwischen; Labor 6 liegt mit dem Ergebnis des Kjeldahl-Verfahrens von 96 ppm N wesentlich niedriger. Der Wert der Vakuum-Schmelzextraktion von Labor 6 fällt aufgrund einer ungeeigneten Extraktionstechnik (Ni-Fe-Bad)[6] ganz heraus. Diese Ergebnisse zeigen, daß sicher nicht, wie nach dem ersten Ringversuch noch vermutet werden konnte, Inhomogenitäten der Probe die Ursache für die Abweichungen waren, sondern daß vielmehr Fehler systematischer Art bei den verschiedenen Verfahren aufgetreten sind.

Hauptsächlich die folgenden Analysenschritte können Fehler beinhalten:

Probenvorbereitung

Aufschluß und damit Ermittlung des Blindwerts bei Kjeldahl-Verfahren

Extraktionsbedingungen bei Heißextraktionsverfahren

Es wurden deshalb Absprachen bezüglich der Vereinheitlichung der Probenvorbereitung (vgl. Abschnitt

Tabelle 4. Ergebnisse der Ringuntersuchung an Titanprobe II

		1. Ringuntersuchung			2. Ringuntersuchung		
Labor-Nr.	Verfahren	$\bar{x}$, ppm	s, ppm	n	$\bar{x}$, ppm	s, ppm	n
1	Makro-Kjeldahl	186*	6	5	164*	4	5
2	Makro-Kjeldahl	162*	10	6			
		148		1	141	2	5
3	Makro-Kjeldahl	133	6	6	135	6	6
4	Halbmikro-Kjeldahl				147	4	6
5	Mikro-Kjeldahl	138	3	9	135	4	4
	Vak.-Schmelzextraktion				140	9	4
6	Halbmikro-Kjeldahl	96	5	4			
	Vak.-Schmelzextraktion	$\leqslant 5$			132	1	3
7	Trägergas-Schmelz-extraktion				139	4	6
8	Makro-Kjeldahl	183	27	6			

*Spanförmiges Probematerial.

Experimentelles), der Analysendurchführung und der Blindwertkontrolle getroffen. Labor 8 schied wegen zu hoher und stark streuender Blindwerte für die weiteren Untersuchungen aus.

Zweite Ringuntersuchung an Titanprobe II

Vereinheitlichungen bei der Durchführung der Kjeldahl-Methode. Der Aufschluß wurde mit Flußsäure durchgeführt, da diese genügend niedrige Stickstoff-Gehalte aufweist. Außerdem ist damit das problemlose Auflösen von Titan und Titannitrid gewährleistet.[4,9,10] Beim Makro- und Halbmikro-Verfahren wurden die Proben (0,15–1 g) unter Verwendung von PTFE-, PE- oder Pt-Geräten in 5–30 ml Flußsäure unter Erwärmen in Lösung gebracht (vgl. Tab. 2). Zur Verminderung von Kontaminationen aus der Laborluft wurden die Aufschlußgefäße abgedeckt; außerdem hat man in den meisten Laboratorien in speziellen, von den übrigen Laborräumen abgetrennten Räumen gearbeitet. Labor 5 führte den Aufschluß in stahlummantelten PTFE-Druckgefäßen mit jeweils 2 ml Flußsäure/Perchlorsäure (10 : 1) bei 120° durch. Eine Kontamination während des Aufschlusses ist dabei ausgeschlossen, was durch niedrige Blindwerte belegt wird.

Von den in den Reagenzien vorliegenden stickstoffhaltigen Verunreinigungen wird bei der üblichen Blindwertbestimmung nur Ammonium-Stickstoff erfaßt. Beim Probenaufschluß können jedoch Verunreinigungen wie Nitrat, Nitrit u.a. durch die reduzierende Wirkung des Metalls zu Ammonium umgesetzt werden und so einen höheren Stickstoffgehalt der Probe vortäuschen.

Diese Überlegung, die in der Literatur[11] bereits diskutiert wurde, wird durch Versuchsergebnisse bestätigt, die in Tabelle 5 zusammengestellt sind: jeweils 1 ml Flußsäure–Perchlorsäure-Mischung (10 : 1) wurde im Druckgefäß 8 h auf 120° gehalten und anschließend der Stickstoffgehalt der Lösung bestimmt. In Zeile 1 sind die Werte für die reine Säure eingetragen. Die Werte der Zeile 2 wurden bei Zusatz von ca. 100 mg Reinstaluminium erhalten, das auf Grund seiner geringen Stickstofflöslichkeit einen vernachlässigbar kleinen Stickstoffgehalt haben sollte. Die Werte sind, ebenso wie die Werte der 3. Zeile, wo 14 µg Stickstoff in Form von Salpetersäure zugesetzt wurden, nur unwesentlich höher als die Werte der 1. Zeile. Bei gleichzeitiger Gegenwart von Salpetersäure und reduzierendem Metall wird jedoch ein unkontrollierbarer Teil des Nitratstickstoffs beim Aufschluß reduziert, wie die Ergebnisse der 4. Zeile zeigen.

Daß die Reduktion nicht quantitativ verläuft, ist sicher darauf zurückzuführen, daß ein Teil der zugesetzten Salpetersäure zu Beginn des Aufschlusses verdampft und als Kondensat an den Gefäßwandungen der Reaktion mit dem Aluminium während des Lösevorganges entzogen ist.

Da ein "stickstofffreies" Titan zur Blindwertkontrolle nicht zur Verfügung stand, wurden auch von den Teilnehmern an dieser Ringuntersuchung einheitlich die Blindwerte in Gegenwart von Reinstaluminium bestimmt. Die auf diese Weise erhaltenen Blindwerte sind in Tabelle 2 aufgeführt.

Vereinheitlichung bei der Durchführung der Heißextraktionsverfahren. Da Titan, wie bereits ausgeführt, große Stickstofflöslichkeit besitzt und die Nitride eine hohe Stabilität aufweisen, ist eine Diffusions- oder Schmelzentgasung weder im Hochvakuum noch im Inertgasstrom ohne Verwendung von Zuschlägen möglich.[1]

Als Hilfsbäder sind die Eisenmetalle vollkommen ungeeignet und nur Platin oder Palladium zu verwenden.[1,5,6] Die Extraktionstemperaturen sollten nicht unter 2000° liegen; die Flux-Technik (Sandwich-Technik), bei der Probe und Zuschlag zusammen eingeworfen werden, ist der Bad-Technik vorzuziehen.

Die an der zweiten Ringuntersuchung an Probe II beteiligten Laboratorien wandten deshalb alle die Pt-Flux- oder eine kombinierte Bad-Flux-Technik an, wobei das Pt-Probe-Verhältnis $\geqslant 10:1$ betrug und der Graphittiegel jeweils nur einmal verwendet wurde (vgl. Tab. 2).

Diskussion der Ergebnisse

Die unter Einhaltung der vorgenannten Absprachen bezüglich Probenvorbereitung und Analysendurchführung an Titanprobe II erhaltenen Ergebnisse sind in Tabelle 4 zusammengestellt. Mit Ausnahme des Wertes von Labor 1 weisen die Labormittelwerte untereinander eine gute Übereinstimmung auf. Als

Tabelle 5. Untersuchungen zur Blindwertbestimmung beim Kjeldahl-Verfahren (Aufschlußbedingungen: 1 ml $HF/HClO_4$ 10 : 1; 8 h/120°; Druckgefäß)

Zusammensetzung des Aufschlusses	Ermittelte Stickstoffmenge, µg		
	Einzelwerte	$\bar{x}$	s
1 ml Säure	0,76; 0,61; 0,77; 0,67; 0,74	0,71	0,07
1 ml Säure + Al*	0,98; 0,92; 0,64; 0,77	0,83	0,15
1 ml Säure + 10 µl 0,1N HNO_3	0,93; 0,81; 0,74	0,83	0,10
1 ml Säure + Al* + 10 µl 0,1N HNO_3	3,03; 4,85; 3,82	3,9	0,9

* 80–100 mg, Al-Späne puriss. (Fluka AG, Buchs/Schweiz)

Mittelwert aller acht Labormittelwerte ergibt sich 142 ppm, die Standardabweichung ist 10 ppm. Der Wert von Labor 1 (164 ppm) ist als Ausreißer zu betrachten (Nalimov-Test).[12] Ob dieser höhere Wert auf die nicht absprachegemäße Probenvorbereitung zurückzuführen ist—in diesem Laboratorium wurde gespantes Material eingesetzt—ist aus dem Ergebnis nicht abzuleiten. Bemerkenswert ist auch, daß in diesem Laboratorium die höchsten Blindwerte aller Teilnehmer an den Ringuntersuchungen erhalten wurden (vgl. Tab. 2), vielleicht eine Folge der für den Aufschluß verwendeten hohen Säuremenge und, trotz aller Sorgfalt, einer möglichen unkontrollierbaren Kontamination aus der Laboratoriumsluft.

Ohne Berücksichtigung des Wertes von Labor 1 liegt der Mittelwert der übrigen Labormittelwerte ($n = 7$) bei 138 ppm N und die Standardabweichung bei 5,0 ppm. Die Einzelwerte der Untersuchungen wurden der Übersichtlichkeit wegen nicht in die Tabelle 4 aufgenommen. Aus diesen ergibt sich, ohne Berücksichtigung der Werte von Labor 1, ein Mittelwert $\bar{x}_E = 139$ ppm mit $s_E = 6{,}5$ ppm bei $n = 34$.

Aus den Einzelwerten ergeben sich für die Heißextraktionswerte ein Mittelwert $\bar{x}_{EH} = 137$ ppm mit $s_{EH} = 6{,}1$ ppm bei $n = 13$ und für die Kjeldahl-Untersuchungen (ohne Berücksichtigung der Werte von Labor 1) ein Mittelwert $\bar{x}_{EK} = 140$ ppm mit $s_{EK} = 6{,}7$ ppm bei $n = 21$. Ein Unterschied zwischen den Werten, die nach dem Kjeldahl-Verfahren, und denen, die nach dem Heißextraktions-Verfahren erhalten wurden, besteht demzufolge nicht. Die Übereinstimmung der Ergebnisse der beiden vom Prinzip her völlig unterschiedlichen Verfahren bestätigt mit hoher Wahrscheinlichkeit die Richtigkeit des Analysenergebnisses.

Schlußfolgerungen

Die Heißextraktionsverfahren liefern bei Anwendung einer geeigneten Extraktionstechnik sowohl nach dem Vakuum- als auch nach dem Trägergas-Schmelzextraktions-Verfahren richtige Analyseuergebnisse. Voraussetzung ist die Anwendung der Pt- oder Pd-Flux-Technik mit einem Pt(Pd)-Probe-Verhältnis von ca. 20 : 1 und Extraktionstemperaturen $\geqslant 2000°$.[1,13] Bad-Probe-Verhältnisse von nur 10 : 1 können zu Minderbefunden führen, vor allem dann, wenn die erreichbare Ofentemperatur nur unwesentlich über 2000° liegt. Ein Pt-Probe-Verhältnis von > 20 : 1 ist jedoch auch bei diesen Geräten nicht erforderlich.

Bei diesen hohen Zuschlag-Probe-Verhältnissen ist die Höhe der Einwaage auf grund des begrenzten Fassungsvermögens der üblichen Tiegel sowie der nicht geringen Edelmetallkosten wesentlich eingeschränkt. Die kleinste noch sicher bestimmbare Stickstoffkonzentration in Titan dürfte deshalb, je nach Gerätetyp, bei 20–30 ppm liegen und im günstigsten Fall 10 ppm betragen. Für Titanlegierungen gelten die gleichen Extraktionsbedingungen und Einschränkungen hinsichtlich des Nachweisvermögens.

Bei diesen Untersuchungen ergab sich auch, daß das Kjeldahl-Verfahren sowohl in seiner üblichen Ausführung—Lösen in Flußsäure, konventionelle Destillation, photometrische Bestimmung—unter Einhaltung bestimmter experimenteller Bedingungen, als auch in modifizierter Form als Mikro-Kjeldahl-Verfahren—Druckaufschluß, Kreislaufdestillation, coulometrische Bestimmung—zur Bestimmung von Stickstoff in Titan geeignet ist.

Diese Ergebnisse können auf die Untersuchung von Titanlegierungen[14,15] und Zirkonium[15] übertragen werden.

Die Nachweisgrenzen sind für jedes Laboratorium verschieden und liegen zwischen 10 und 40 ppm Stickstoff; mit Druckaufschluß und Mikro-Kjeldahl-Verfahren lassen sich noch Gehalte von 1 ppm bestimmen. Voraussetzung für richtige Analysenergebnisse ist beim Kjeldahl-Verfahren die Beherrschung des Blindwertes und der weitgehende Ausschluß von Kontaminationen aus der Laboratoriumsluft. Zu empfehlen ist daher die Ermittlung des Blindwertes unter Verwendung von Reinstaluminium sowie die Durchführung der Bestimmung in einem abgetrennten Raum in ammoniak- und salpetersäurefreier Atmosphäre.

LITERATUR

1. P. A.bert, *Die Bestimmung des Stickstoffgehaltes hochschmelzender Metalle, ihre wirtschaftliche und technologische Bedeutung*, Kommission der Europäischen Gemeinschaften, Informationsheft Nr. 90, Brüssel, 1974.
2. U. Zwicker, *Titan und Titanlegierungen*, Springer-Verlag, Berlin, 1974.
3. E. Fromm und E. Gebhardt (Hrsg.), *Gase und Kohlenstoff in Metallen*, Springer-Verlag, Berlin, 1976.
4. J. Rottmann und H. Nickel, *Z. Anal. Chem.*, 1969, **247**, 208.
5. L. M. Melnick, *Determination of Gaseous Elements in Metals*, Wiley-Interscience, New York, 1974.
6. B. Kysil und O. Engel, *4. Balzers-Kolloquium 1968, Balzers, Liechtenstein.* Tagungsbericht: *Quantitative Bestimmung von Gasen in Metallen*, S. 9.
7. L. Quaglia, G. Weber, D. David, J. van Audenhove und J. Pauwels: *Traitements de surface des métaux non ferreux dans l'analyse des gaz*, Kommission der Europäischen Gemeinschaften, ITE-Bericht Nr. 90, Brüssel, 1976.
8. W. Werner und G. Tölg, *Z. Anal. Chem.*, 1975, **276**, 103.
9. C. Healy und A. Parker, *U.K. At. Energy Res. Estab. Rept.* AERE-R 6491, 1970.
10. H. Schneider und W. Hein, *6. Plansee-Seminar 1969*, F. Benesovsky (Hrsg.), S. 1028. Metallwerk Plansee, Reutte.
11. S. Kallmann, E. W. Hobart, H. K. Oberthin und W. C. Brienza, *Anal. Chem.*, 1968, **40**, 332.
12. R. Kaiser und G. Gottschalk, *Elementare Tests zur Beurteilung von Meßdaten*; Bibliographisches Institut Mannheim, 1972.
13. G. Kraft, Persönliche Mitteilung.
14. D. Hirschfeld, Eigene unveröffentlichte Untersuchungen.
15. E. Grallath und G. Tölg, Vortrag anläßlich der Tagung *Gase in Metallen*, Darmstadt, März 1977.
16. *Analyse der Metalle*, Band: *Schiedsanalyse*, 3. Aufl., S. 133. Springer-Verlag, Berlin, 1966.
17. *Handbuch für das Eisenhüttenlaboratorium*, Band 2, Verlag Stahleisen, Düsseldorf, 1966.
18. *VDI-Handbuch Reinhaltung der Luft*, VDI-Richtlinie 2461, Düsseldorf, März 1974.

Summary—This is a report on round-robin tests concerning the determination of nitrogen in titanium, which were carried out by the refractory-metals group of the chemical board of the Gesellschaft Deutscher Metallhütten- und Bergleute. The following methods were used: classical and modified Kjeldahl methods, inert gas fusion and vacuum fusion extraction. With the platinum (or palladium) flux technique (noble metal to sample ratio ~ 20:1, temperature ≥ 2000°) the reductive fusion methods are capable of determining nitrogen contents ≥ 20 ppm. Under special conditions, contents higher than 10–40 ppm can be determined by the Kjeldahl method (the lower limit varies from laboratory to laboratory). With a micro circulating distillation and determination apparatus, and dissolution of the sample within the pressure vessel, the detection limit can be lowered to 1 ppm. Because of possible interferences by reducible nitrogen compounds from the laboratory air, blanks must be determined with high-purity aluminium. The results from 7 laboratories (Kjeldahl 4; reductive fusion 3) for a titanium sample containing 138 ppm nitrogen were in good agreement (standard deviation 5 ppm).

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MISE AU POINT D'UN PROGRAMME DE CALCUL DES DIAGRAMMES DE REPARTITION DES COMPLEXES A FORCE IONIQUE VARIABLE

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Résumé—Un programme informatique DISCOMP FORTRAN permet le tracé de diagrammes de répartition de différents complexes en fonction de la concentration en ligand, en tenant compte de la variation continue de la force ionique. Le programme est volontairement limité aux systèmes où les complexes sont formés d'un ligand et d'un métal, sans espèces protonnées ou hydrolysées. Cependant, sa structure a été conçue de façon à ce que l'adaptation à chaque cas pratique soit possible. Une première partie de cette étude élabore la théorie et les équations générales de la formation des complexes, puis la seconde explicite le programme étape par étape. La discussion porte sur l'importance de la variation de la force ionique, et il apparaît qu'elle n'est pas négligeable. On remarque aussi que le coefficient empirique C de la relation de Debye et Hückel doit être déterminé pour obtenir une plus grande précision.

Les diagrammes de répartition des complexes en fonction de la concentration en ligand libre sont bien connus des chimistes. Ils peuvent être calculés sur ordinateur à partir de programmes très généraux tels que ceux élaborés par Ingri *et al.*[1] ou par Elgquist.[2] Ils peuvent aussi être tracés dans des cadres beaucoup plus spécifiques: l'équipe de Martin[3] a mis au point un programme permettant de calculer l'influence du pH sur certains complexes organo-métalliques. Le programme de Goldstein concerne uniquement les complexes inorgano-métalliques. Il lui à permis de tracer un grand nombre de diagrammes[4] à partir des constantes de la littérature à force ionique constante et connue.

Malheureusement, ces diagrammes ne sont applicables que si la force ionique est constante, fixée par exemple par une solution plus concentrée d'un sel inerte. Si elle varie, les constantes d'équilibre changent de valeur et les diagrammes sont déplacés. Dans l'étude des transferts de matière, par exemple échange ionique à travers une membrane, fixer la force ionique est très préjudiciable au transfert des ions considérés. On observe un effet de masquage des phénomènes de migration du fait de la prépondérance d'ions étrangers qui peuvent entrer en compétition avec les espèces étudiées.

Si, dans un tel milieu, on veut connaître la répartition des complexes en fonction de la concentration en ligand, il faut que le calcul tienne compte du fait que la force ionique varie avec l'ajout du complexant et qu'elle modifie considérablement les constantes de formation des complexes. Nous avons donc voulu mettre au point un programme de calcul simple et spécifique qui tienne compte de cette variation pour résoudre des problèmes pratiques.

Toutefois, le seul paramètre envisagé ici est la force ionique qui est importante et peu étudiée. L'influence du pH, de la température, pourra se greffer facilement sur le programme, mais nous les avons volontairement écartés pour ne pas faire double emploi avec des programmes déjà existants.

MISE EN EQUATION

Equations générales

La formation d'un complexe peut être mise en équation à partir des bilans, des constantes partielles de formation et du coefficient d'activité γ (l'état de référence étant pris pour une dilution infinie).[5]

$$ML_{n-1} + L \rightleftharpoons ML_n$$

avec

$$k = \frac{[ML_n]}{[ML_{n-1}][L]} \cdot \frac{\gamma_{ML_n}}{\gamma_{ML_{n-1}} \cdot \gamma_L} = K \cdot \Gamma \qquad (1)$$

où k = constante thermodynamique; K = constante apparente; Γ = coefficient global d'activité.

La proportion de l'ion complexé par rapport au total du métal est donné[6] par:

$$y_0 = \frac{1}{1 + K_1[L] + \ldots + K_1K_2 \ldots K_n[L]^n} \qquad (2)$$

$$y_i = y_{i-1} \cdot K_{i-1}[L] \qquad (3)$$

On aura ainsi par exemple pour le complexe cuivre–chlorure:

$$y_2 = \frac{[CuCl^+]}{[Cu]_t}$$

$$= \frac{1}{\frac{1}{K_1}[Cl^-]^{-1} + 1 + K_2[Cl^-] + K_2K_3[Cl^-]^2 + K_2K_3K_4[Cl^-]^3}$$

$$y_3 = \frac{[CuCl_2]}{[Cu]_t}$$

$$= \frac{1}{\frac{1}{K_1K_2}[Cl^-]^{-2} + \frac{1}{K_2}[Cl^-]^{-1} + 1 + K_3[Cl^-] + K_3K_4[Cl^-]^2}$$

La valeur de γ dans l'équation (1) est donnée par la loi de Debye et Hückel[7] où

$$\log\gamma = \frac{-Az^2\sqrt{I}}{1+aB\sqrt{I}} + CI \qquad (4)$$

et A = constante [$= 1{,}825 \cdot 10^6(\varepsilon T)^{-3/2}\rho^{1/2}$, où ε est la constante diélectrique de l'eau et ρ la densité]; z = charge de l'ion; I = force ionique; a = diamètre ionique en cm; B = constante $(0{,}33 \cdot 10^8)$; C = coefficient empirique.

Pour cette étude, nous considèrons que C = coefficient de la littérature, aB = voisin de 1,[6] $A = 0{,}5$ (à 25°). L'équation (4) devient alors:

$$\log\gamma = \frac{-0{,}5z^2\sqrt{I}}{1+\sqrt{I}} + CI$$

Le coefficient d'activité γ dépend donc directement de la force ionique I du milieu quand on choisit C.

$$I = 1/2\sum c_i z_i^2 \qquad (5)$$

avec c_i = concentration de l'espèce i; z_i = charge de l'espèce i.

A force ionique donnée, la seule variable devient la charge de l'ion considéré. On a alors:

$$\log\gamma_i = G(z_i^2) \qquad (6)$$

Calcul de la force ionique réelle du milieu

La force ionique WC est due aux espèces suivantes:
—différents complexes C formés: WC
—ligand libre L: WL
—cation K associé au ligand: WK
—autres ions du milieu: WS
Ces forces ioniques sont calculées en appliquant la formule (5).

Réajustement des constantes à la force ionique du milieu

Dans la pratique, les constantes de la littérature sont établies à force ionique donnée, ou plus rarement extrapolées à force ionique nulle. Nous nous proposons de reporter à chaque instant l'effet de la variation de force ionique sur les constantes d'équilibre.

Pour cela, nous appliquons:

$$k = K_E\Gamma_E$$
$$k = K_L\Gamma_L$$

avec K_E = constante à force ionique calculée; K_L = constante à force ionique donnée par la littérature; Γ_L = coefficient global d'activité calculé à force ionique donnée par la littérature; Γ_E = coefficient global d'activité à force ionique du milieu.

On en déduit

$$K_E = K_L\frac{\Gamma_L}{\Gamma_E} \qquad (7)$$

avec

$$K_L = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad (8)$$

ETABLISSEMENT DU PROGRAMME INFORMATIQUE

A partir des données suivantes:
—constantes de formation de la littérature
—concentration des espèces en solution
—charges des ions en solution
—charges des complexes
—force ionique à laquelles les constantes sont données
—nombre d'ions associés au ligand
nous avons mis au point un programme en FORTRAN IV sur télétype SAGEM relié à un IBM 360 permettant:
— le calcul de la force ionique réelle du milieu
—le calcul de l'exposant de la fonction G pour chaque constante
—le réajustement des constantes de formation à la force ionique du milieu.
—le calcul des pourcentages des différents complexes en fonction du logarithme de la concentration en complexant ajouté
—l'impression des résultats sous forme de tableau.

Calcul de la force ionique réelle du milieu, WR

Calcul de la force ionique due à la formation des différents complexes, WC. Dans le programme, Y(J, I) représente la proportion de complexe formé à une concentration de ligand donnée. On considère que tout le métal participe à la formation des complexes. On a d'après l'équation (5):

$$WC = \tfrac{1}{2}\sum[(Y(J,I)\cdot D(2)\cdot V(J)^2]$$

avec D(2) = concentration du métal (*cf.* lignes 54 à 57).

Calcul de la force ionique due au ligand libre, WL. A chaque ajout de ligand, une partie se complexe avec le métal; l'autre reste en solution, c'est le ligand libre. Avec X(I) = fraction de ligand ajouté; Z(1) = charge

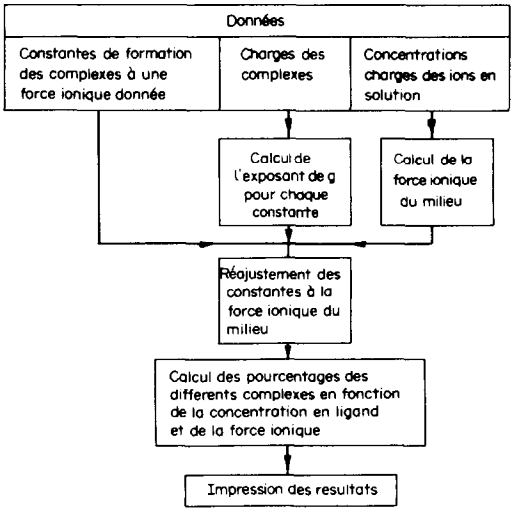


Fig. 1. Structure schématique du programme permettant de calculer la répartition des complexes en fonction de la concentration en ligand.

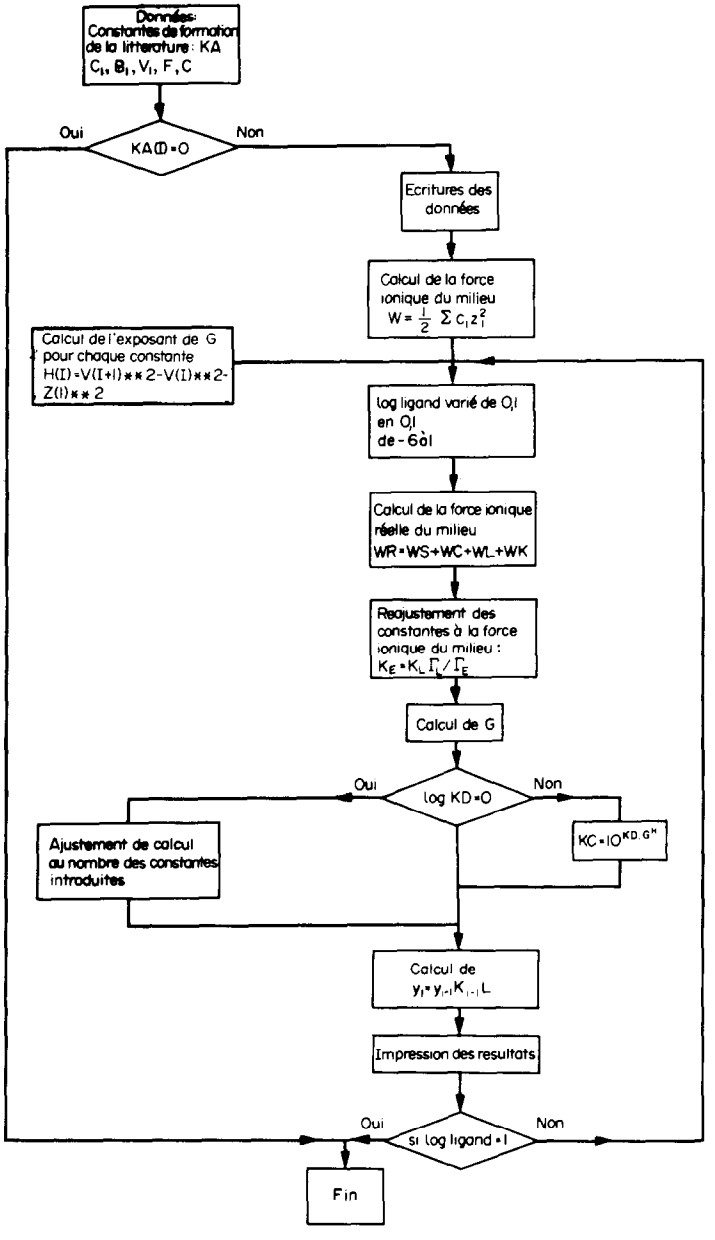


Fig. 2. Organigramme général de calcul de la répartition des complexes en fonction de la concentration en ligand.

du ligand:

$$WL = \tfrac{1}{2}[X(I)\cdot Z(1)^2]$$

[*cf.* ligne 58 du programme (voir Annexe)].

Calcul de la force ionique due à l'ion lié au ligand, WK. Dans le cas de l'ajout d'un ligand possèdant plusieurs charges, il est indispensable de tenir compte de l'action des ions associés dans la force ionique (*cf.* lignes 61 à 64 du programme)

Z(3) = charge de l'ion lié au ligand
NM = nombre d'ions.

Calcul de la force ionique due à tous les autres ions du milieu, WS. Voir lignes 35 à 37 du programme.

La force ionique réelle WR est la somme des forces ioniques partielles: voir lignes 54 à 65 du programme.

Calcul de l'exposant de G pour chaque constante

Nous calculons $\log \Gamma$ [voir formule (1)] pour chaque constante de formation par une récurence simple (*cf.* lignes 43 à 45 du programme).

H(I) est l'exposant de G, donc $\log \Gamma = G^H$.

V(1) charge du métal, V(2) à V(7) charges des complexes par ordre décroissant.

Réajustement des constantes à la force ionique du milieu WR

D'après l'équation (7), nous devons calculer Γ_L et Γ_E pour connaître K_E connaissant K_L.

Soient:

GA: logarithme du coefficient de l'activité calculé à force ionique donnée par la littérature (F).

KA(J): correspond au logarithme des constantes K_{L_J} ($\log K_{L_J}$)

KD(J): correspond au logarithme des constantes K_{E_J} ($\log K_{E_J}$)

GD: logarithme du coefficient de l'activité calculé à force ionique du milieu WR

AG: logarithme du coefficient global d'activité calculé à force ionique donnée par la littérature (F)

DG: logarithme du coefficient global d'activité, calculé à force ionique du milieu WR

(*cf.* lignes 66 à 73 du programme).

Calcul des pourcentages des différents complexes en fonction du logarithme de la concentration en complexant ajouté

L'ordinateur étant digital, nous avons choisi comme pas de variation de la concentration en ligand $10^{0,1}$, de 10^{-6} jusqu'à 10^{1}, soient 70 valeurs (*cf.* lignes 47 à 53 du programme).

WR représente la force ionique réelle du milieu.

G est la fonction de l'équation (5).

La boucle D05... 5 CONTINUE permet d'ajuster le calcul ou nombre de constantes (de 1 à 6) (*cf.* lignes 75 à 76 du programme).

Les boucles D06, D0110, D0111, D0112 permettent le calcul des équations (3) (*cf.* lignes 77 à 78, 79 à 81, 82 à 84, 85 à 87 du programme).

KC(J) correspond aux constantes apparentes K_{E_J}, compte tenu de la variation de force ionique globale.

Les figures 1 et 2 montrent la structure et l'organigramme du programme.

DISCUSSION

L'intérêt d'une telle démarche est démontré par le calcul de la distortion apportée par la variation de la force ionique en fonction de la concentration en ligand ajouté. Nous avons travaillé sur les complexes chlorure cuivrique.

La figure 3A nous montre la distribution des complexes calculés à une force ionique égale à 0,6 sans correction de force ionique (en faisant $G = 1$). La figure 3B par contre fait intervenir la fonction G, donc la correction sur la force ionique, le coefficient C de Debye et Hückel étant nul. En comparant ces deux figures, on peut remarquer qu'avec un tel décalage entre les deux conditions on ne peut pas négliger l'importance de la modification de la force ionique.

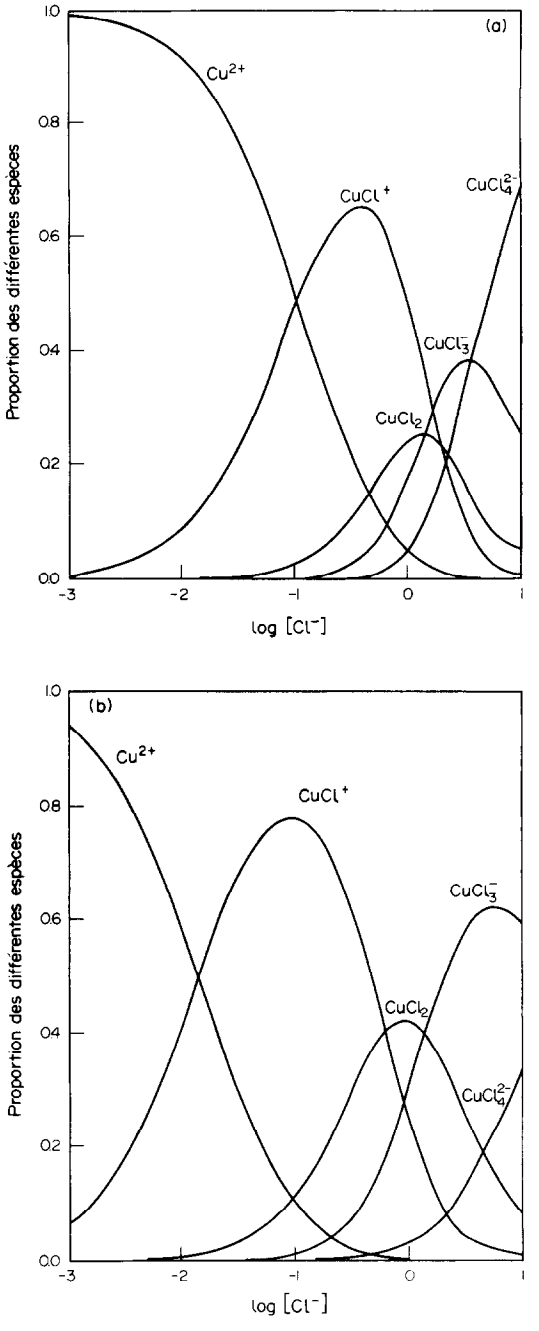


Fig. 3. Diagramme de répartition des complexes chlorure cuivrique en fonction de log [Cl^-].

(*A*) Force ionique constante égale à 0,6

D(1) = 0,0	D(2) = 0,01	D(3) = 0,0	D(4) = 0,6	D(5) = 0,6
$pK_2 = 0,98$	$pK_2 = -0,29$	$pK_3 = -0,14$	$pK_4 = -0,55$	
Z(1) = −1	Z(2) = 2	Z(3) = 1	Z(4) = 1	Z(5) = −1
V(1) = 2	V(2) = 1	V(3) = 0	V(4) = −1	V(5) = −2
	F = 0,6	NM = 1	C(1) = 0	

(*B*) Force ionique variable [même données que (A)].

Nous avons étudié aussi la répartition des complexes ferri-fluorure. La figure 4A montre la répartition des différents complexes à force ionique constante, la figure 4B la répartition en tenant compte

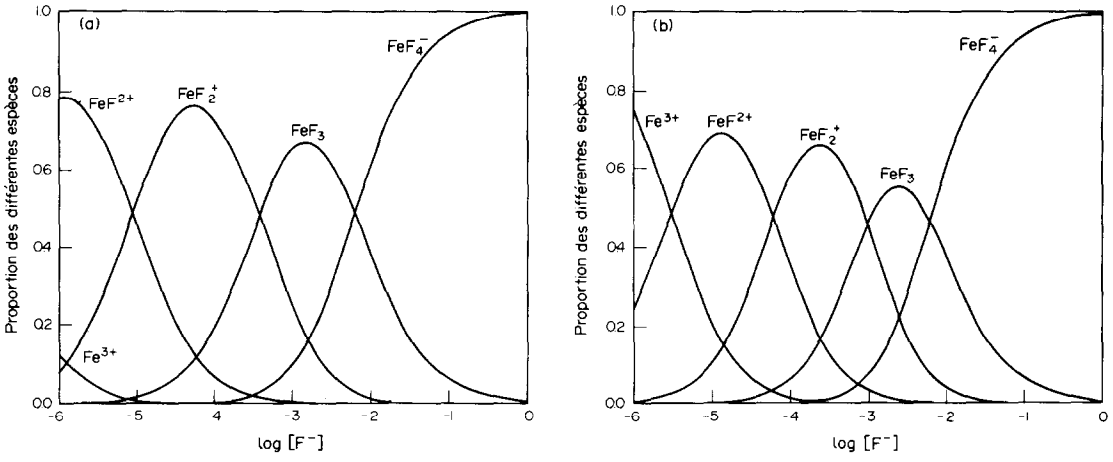


Fig. 4. Diagramme de répartition des complexes ferri–fluorure en fonction de log [F].

(*A*) Force ionique constant égale à 0,53

D(1) = 0,0 D(2) = 0,02 D(3) = 0,0 D(4) = 0,5 D(5) = 0,5

$pK_1 = 5,5$ $pK_2 = 4,2$ $pK_3 = 3,0$ $pK_4 = 2,2$

Z(1) = −1 Z(2) = 3 Z(3) = 1 Z(4) = −1 Z(5) = 1

V(1) = 3 V(2) = 2 V(3) = 1 V(4) = 0 V(5) = −1

F = 0,53 NM = 1 C(1) = 0

(*B*) Force ionique variable [même données que (A)].

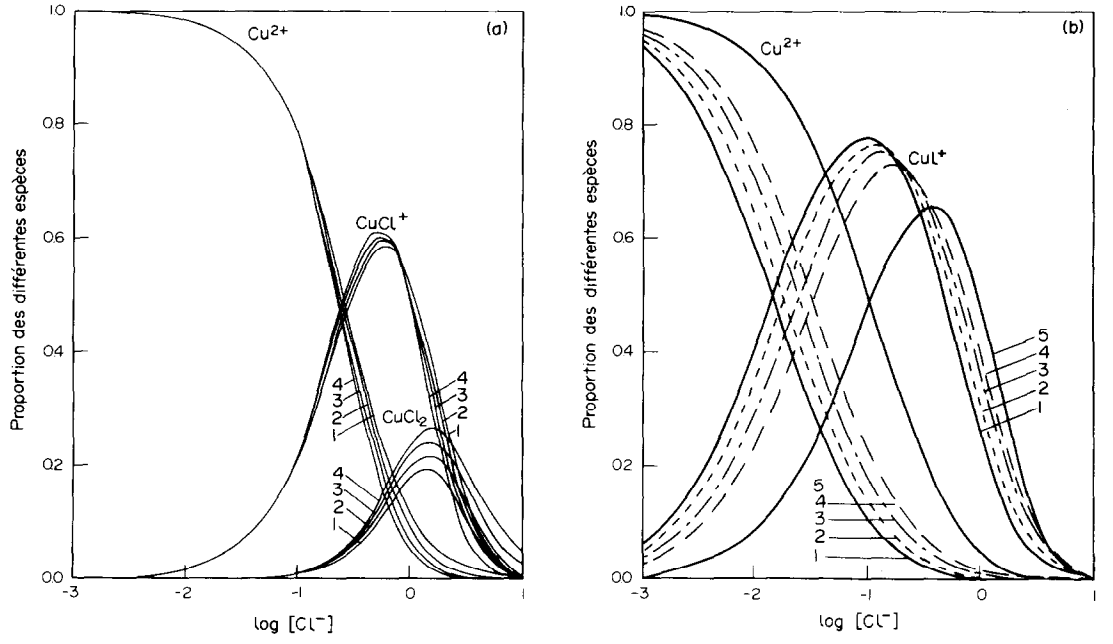


Fig. 5. Influence du coefficient empirique C sur les diagrammes de répartition des complexes chlorure cuivrique en fonction du log [Cl^-], avec correction de force ionique.

(*A*) Le milieu est à force ionique nulle et le facteur C prend les valeurs: 1: $C = 0,05$; 2: $C = 0,10$; 3: $C = 0,15$.

(*B*) Le milieu est à force ionique 0,6 et C prend les valeurs suivantes: 1: $C = 0$; 2: $C = 0,05$; 3: $C = 0,10$; 4: $C = 0,15$ avec la correction continue de la force ionique (fonction G). *Remarque*: Par souci de clarté, seules trois espèces sont représentées: Cu^{2+}, $CuCl^+$, $CuCl_2$.

de la variation de la force ionique. Le décalage observé démontre bien l'importance de cette modification.

L'élaboration du calcul est effectuée par l'intermédiaire de la relation de Debye et Hückel sous sa forme complète (4). Il faut toutefois remarquer que la valeur de C, dans l'état actuel de la recherche fondamentale est empirique et souvent mal connue.

La courbe 5A regroupe les diagrammes montrant l'importance de ce facteur pour des valeurs trouvées dans la littérature:[7] 0,05, 0,10, 0,15 et pour une force ionique initiale nulle, tandis que la courbe 5B montre, pour les mêmes valeurs de C, le décalage quand la force ionique initiale est assez forte: 0,6.

L'examen de cette figure appelle deux remarques:

—on observe un décalage des diagrammes à partir d'une force ionique due à l'adjonction du ligand, dont la valeur est voisine de 0,1. Ce décalage reste néanmoins faible, d'autant plus que les maxima des pics ne sont pas déplacés, mais augmentés ou diminués.

—dans le cas où la force ionique initiale du milieu est

assez forte, par exemple 0,6 (figure 5B), le décalage observé est plus important et commence dès l'ajout du ligand.

La faible répercussion du coefficient C sur les diagrammes de répartition permet d'avoir une approche valable du phénomène, même en négligeant ce facteur, surtout à faible force ionique; aux grandes forces ioniques, une nette amélioration des résultats pourrait être obtenue par une bonne connaissance du coefficient C.

CONCLUSION

Il apparaît donc que le tracé des diagrammes de répartition des complexes doit tenir compte de la variation de la force ionique en fonction de la concentration en ligand ajouté. Ce programme informatique permet de se libèrer de la contrainte du tampon force ionique et de travailler dans les cas où il est souhaitable de ne pas la fixer. D'autre part, aux grandes forces ioniques, une nette amélioration des résultats pourrait être obtenue par une bonne connaissance du coefficient de Debye et Hückel.

LITTERATURE

1. N. Ingri, W. Kakolowicz, L. G. Sillén et B. Warnqvist, *Talanta*, 1967, **14**, 1261.
2. B. Elgquist, *ibid.*, 1969, **16**, 1502.
3. R. P. Martin, Programme ACREF 3AM, *Thèse*, Lyon, Juillet, 1975.
4. G. Goldstein, *Equilibrium Distribution of Metal-Ion Complexes*, Oak Ridge National Laboratory, Tennessee, 1964.
5. A. Ringbom, *Les complexes en chimie analytique*, Dunod, Paris, 1967.
6. G. Charlot, *L'analyse qualitative et les réactions en solution*, Masson, Paris, 1963.
7. S. Glasstone, *An Introduction to Electrochemistry*, Edition revolucionari, Cuba, 1969.

Summary—A computer program DISCOMP FORTRAN permits the drawing of distribution diagrams for different complexes as a function of the concentration of ligand, taking into account the continuous variation of ionic strength. The scope of the program has been limited to cases in which one metal and one ligand are involved, without protonated or hydrolysed species, but an attempt has been made to establish the program so that it can be adapted to each practical case. The first part of the study deals with the theory and general equations corresponding to the formation of complexes, and in the second the program is developed step by step. Because the changes in ionic strength are not negligible, stress has been laid upon their importance. It should be noted that the empirical coefficient C of the Debye–Hückel equation has to be determined to obtain better precision.

Tableau 1.

Liste des symboles	Texte	Programme
Constantes thermodynamiques à temp. donnée	k	
Constantes apparentes	K	
Logarithme des constantes apparentes à force ionique expérimentale	$\log K_E$	KD
Logarithme des constantes apparentes à force ionique du milieu	$\log K_L$	KA
Logarithme du coefficient global d'activité calculé à force ionique de la littérature	$\log \Gamma_L$	AG
Logarithme du coefficient global d'activité calculé à force ionique du milieu	$\log \Gamma_E$	DG
Logarithme du coefficient d'activité calculé à force ionique donné par la littérature dont la référence est prise à dilution infinie	$\log \gamma$	GA
Logarithme du coefficient d'activité calculée à force ionique du milieu	$\log \gamma$	GD
Force ionique du milieu	I	W
Force ionique donnée par la littérature	I	F
Concentration des espèces en solution	C_i	D(I)
Charge des espèces en solution	Z_i	Z(I)

PROGRAM DISCOMP

```
C       D(X) SONT LES CONCENTRATIONS DES COMPOSANTS DE LA SOLUTION
C       D(1) CONCENTRATION DU LIGAND, NULLE AU DEPART
C       D(2) CONCENTRATION DU METAL SEUL
C       D(3) CONCENTRATION DE L'ION LIE AU LIGAND, NULLE AU DEPART
C       KA(X) SONT LES LOG DES CONSTANTES DE FORMATION DES COMPLEXES
C       Z(X) SONT LES CHARGES DES IONS DE LA SOL. CORRESP. AUX D(X)
C       F EST LA FORCE IONIQUE DES CONSTANTES KA(X)
C       V(1) CHARGE DU METAL
C       V(2) A V(7) SONT LES CHARGES DES COMPLEXES (ORDRE D'APPARITION)
C       NM EST LE NOMBRE DE MOLECULES ASSOCIEES AU LIGAND
C       C(1) COEFFICIENT EMPIRIQUE DE DEBYE-HUCKEL
001     REAL WW(7),C(1),D(6),KA(6),KB(6),B(6),X(71),Y(7,71),CA(7)
002     REAL F(1),AG(6),BG(6),KD(6),KC(6),DG(6),CG(6),WS(6),WC(7)
003     INTEGER Z(6),V(7),H(6),U,NM,UK,UT
004     WRITE (6,3Ø)
005  3Ø FORMAT (1ØX,'LES VALEURS DE D(X) SONT:')
006     READ (2,1Ø)(D(I),I=1,6)
007     WRITE (6,1Ø)(D(I),I=1,6)
008     WRITE (6,31)
009  31 FORMAT (1ØX,'LES VALEURS DE KA(X) SONT:')
010     READ (2,1Ø)(KA(I),I=1,6)
011     WRITE (6,1Ø)(KA(I),I=1,6)
012     WRITE (6,33)
013  33 FORMAT (1ØX,'LA VALEUR DE F EST:')
014     READ (2,1Ø) F(1)
015     WRITE (6,1Ø) F(1)
016     WRITE (6,34)
017  34 FORMAT (1ØX,'LES VALEURS DE Z(X) SONT:')
018     READ (2,11)(Z(I),I=1,6)
019     WRITE (6,11)(Z(I),I=1,6)
020     WRITE (6,35)
021  35 FORMAT (1ØX,'LES VALEURS DE V(X) SONT:')
022     READ (2,11)(V(I),I=1,7)
023     WRITE (6,11)(V(I),I=1,7)
024     WRITE (6,36)
025  36 FORMAT (1ØX,'LA VALEUR DE NM EST:')
026     READ (2,11) NM
027     WRITE (6,11) NM
028     WRITE (6,37)
029  37 FORMAT (1ØX,'LA VALEUR DU COEFF C EST:')
030     READ (2,1Ø) C(1)
031     WRITE (6,1Ø) C(1)
032  1Ø FORMAT (2X,6F7.4)
033  11 FORMAT (2X,7I5)
034     IF (KA(1).EQ.Ø.) GO TO 23
035     WS (3)=Ø
036     DO 3 I=4,6
037   3 WS(I)=D(I)* (Z(I)** 2)+WS(I-1)
038     DO 17 J=1,7
039     IF (KA(J).EQ.Ø.) GO TO 26
040  17 CONTINUE
041  26 UK=J-1
042     U=UK+1
043     DO 4 I=1,UK
044     H(I)=V(I+1)** 2-V(I)** 2-Z(1)** 2
045   4 CONTINUE
046  16 FORMAT (2X,6F9.4)
```

```
047         WRITE (6,38)
048    38   FORMAT (16X,'TABLEAU DE RESULTATS')
049         WRITE (6,7)
050     7   FORMAT (3X,'LOG LIGAND',2X, 7(3X,'Y',3X))
051         DO 2Ø I=2,72
052         A=-6.1+(I-1) * Ø.1
053         X(I)=1Ø ** A
054         WC(1)=Ø.
055         DO 19 J=2,U
056         Y(J,1)=Ø.
057    19   WC(J)=(Y((J),(I-1)) * D(2) * (V(J) ** 2)) + WC(J-1)
058         WL=X(I) * (Z(1) ** 2)
059         WW(1)=Ø.
060         UT=U+1
061         DO 41  J=2,UT
062         Y((J-1),1)=Ø.
063    41   WW(J)=Y((J-1),(I-1)) * D(2) * (V(1)-V(J-1))+WW(J-1)
064         WK=(WW(U)+X(I)) *Z(3) ** 2 * NM
065         WR=(WS(6)+WC(U)+WL+WK) * Ø.5
066         GA=-(Ø.5 * SQRT(F)/(1+SQRT(F))) + C(1) * F(1)
067         GD=-(Ø.5 * SQRT(WR)/(1+SQRT(WR))) + C(1) * WR
068         DO 2 J=1,UK
069         AG(J)=GA * H(J)
070         DG(J)=GD * H(J)
071     2   CONTINUE
072         DO 13 J=1,UK
073    13   KD(J)=KA(J)-AG(J)+DG(J)
074         G=1Ø ** ((-Ø.5 * SQRT(WR))/(1+SQRT(WR)) + C(1) * WR)
075         DO 5 J=1,UK
076     5   KC(J)=(1Ø ** (KD(J))) * (G ** (H(J)))
077         DO 6 J=2,U
078     6   B(J-1)=KC(J-1) * X(I)
079         CA(1)=1.
080         DO 11Ø J=2,U
081   11Ø   CA(J)=CA(J-1) * B(J-1)
082         Y(1,I)=1.
083         DO 111 J=2,U
084   111   Y(1,I)=Y(1,I)+CA(J)
085         Y(1,I)=1/Y(1,I)
086         DO 112 J=2,U
087   112   Y(J,I)=Y(1,I) * CA(J)
088         WRITE (6,8)A,(Y(J,I),J=1,U)
089     8   FORMAT (6X,F4.1,4X,7(2X,F5.3))
090    2Ø   CONTINUE
091    23   STOP
092         END
```

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SHORT COMMUNICATIONS

DETERMINATION OF DISSOLVED OXYGEN IN WATER

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Summary—Dissolved oxygen in water is determined by its oxidation of manganese(II) to manganese(III) in alkaline medium and formation of the red manganese(III) ethylenediaminetetra-acetic acid complex on acidification to pH 4. The range of determination is 7-3160 μg of oxygen in a final volume of 500 ml.

The classical Winkler method[1] and its various modifications are widely used for the determination of dissolved oxygen but the method is laborious and time-consuming. In attempts to eliminate errors involved in the Winkler method and to increase its sensitivity several physicochemical methods have been applied, the most significant of which is photometric determination.[2,3] Oxygen has been determined either directly by its action on certain organic compounds or indirectly by reaction with oxygen-fixing substances. The direct methods are based on oxidation of organic compounds such as polyphenols and aminophenols,[4–7] and leuco-dyes.[8,9] In one group of indirect methods manganese(II) is oxidized by dissolved oxygen and the product is treated with iodide, the liberated iodine being estimated;[10,11] in another the product is reacted with *o*-tolidine[12] or certain redox indicators.[3,13,14] In a third group the manganese (III) is reacted with EDTA or DCTA and the resultant colour is measured.[15–17] Carvalho *et al.*[15] observed that the relation between absorbance (A) and concentration of dissolved oxygen was not linear, but that between $A/(1-A)$ and the oxygen concentration was linear. Sastry *et al.*[16] found that if DCTA was used, a linear relation with A resulted.

In the present paper EDTA is used as the colorimetric reagent for the manganese(III) formed, at pH 4 (acetic medium). The intensity of the colour is directly proportional to the concentration of dissolved oxygen. The method is intended to be used for routine estimation of dissolved oxygen in industrial and natural waters. The reaction proceeds as follows:

$$\mathrm{Mn(II)} \xrightarrow{2OH^-} \mathrm{Mn(OH)_2} \xrightarrow{O_2} \text{hydrated Mn(II) oxide} \xrightarrow[pH\sim4]{CH_3COOH} \underset{\text{Mn(III)–EDTA}}{\overset{EDTA}{}}$$

Development of the analytical procedure

Preliminary examination of the reaction of EDTA with Mn(III) indicated that the colour intensity of the complex formed was superior when glacial acetic acid was added to adjust the pH to ~4. It was also observed that the ruby-red complex was formed immediately after addition of EDTA solution and dilution to the mark, but fading occurred after a few minutes. The absorption maximum was at 496 nm. A reagent blank prepared with deoxygenated water gave an almost flat spectrum.

The optimum reagent concentrations were determined and incorporated in the recommended procedure.

Acidity. A wide concentration range of several acids, *e.g.*, acetic, sulphuric, hydrochloric and phosphoric, was tested. The absorbance was highest in buffered acetate medium (pH 4), and the stability was also improved. This may have been because the concentrated acid was added in each case, and local effects would be expected to be higher with the mineral acids. Sastry *et al.*[16] acidified their reaction system with 5*M* sulphuric acid and found it satisfactory.

Protective colloids. The Mn(III)–EDTA complex was stable for only about 3 min even in acetic medium and then gradually faded. An attempt was made to prevent or at least decrease the rate of fading by using some protective colloids (surfactants), such as gelatin, starch, gum arabic, cetyltrimethylammonium bromide (CTAB). Of these CTAB was found to exert a sensitizing and stabilizing action on the coloured product, the reaction reaching equilibrium immediately after addition of all the reagents to the test sample and dilution to the mark, and the absorbance remaining stable for at least 10 min, then gradually decreasing. Several explanations have been proposed for the action of protective colloids, but none of them seems to be satisfactory.[18–20]

Fixation of the dissolved oxygen. A conventional method was used to stabilize the dissolved oxygen in water by adding manganese(II) chloride and sodium hydroxide solution.[21] The other reagents were then added as in the recommended procedure, to produce the ruby-red colour of the Mn(III)–EDTA complex. Addition of the water needed to dilute the solution to the required volume produced no interference, because there was no further oxidation of the manganese(III) in acid medium.

Precision. This was tested by determining the relative standard deviation for 11 replicate analyses of 100-ml samples of distilled water, each containing 790 μg of dissolved oxygen, and was found to be 2.1%.

Interferences. The effects of ten common anions and four cations on determination of about 2000 μg of dissolved oxygen (300 ml of 7-ppm solution) were examined and the results are shown in Table 1. Of the anions, only sulphide interfered appreciably. Iron (III) in 500-fold molar ratio to the oxygen present increased the absorbance but iron (II) in 250-fold ratio decreased the absorbance by about 10%. Iodide and persulphate gave a positive error when present in 250-fold ratio to oxygen, and nitrite at the same level gave a negative error. DL-Alanine, glycine, D(+)-galactose, D(−)-fructose and D(+)-glucose showed no effect even when present in up to 3000-fold ratio to oxygen.

Effect of other complexing agents. In place of EDTA some other complexing agents were added, such as citrate, adipic acid, potassium sodium tartrate and DCTA, but only the last gave useful results; DCTA gives a more stable species (stable for 75 min) but lower sensitivity than EDTA ($\varepsilon = 1.4 \times 10^5$

Table 1. Interfering effect of some anions and cations (absorbance = 0.52 in absence of added ions)

Added ion (X)	Absorbance [X] : [O] = 250	[X] : [O] = 500	[X] : [O] = 1000
Chloride	0.52	0.51	0.51
Nitrate	0.52	0.51	0.52
Carbonate	0.52	0.52	0.51
Thiosulphate	0.52	0.52	—
Hydrogen carbonate	0.52	0.51	0.53
Phosphate	0.51	0.49	—
Iodide	0.54	0.60	0.63
Nitrite	0.48	0.47	0.41
Persulphate	0.55	0.57	0.62
Sulphide	0.11	0.20	—
Magnesium	0.52	0.52	0.51
Calcium	0.51	0.52	0.51
Iron(III)	0.53	0.56	0.62
Iron(II)	0.47	0.42	—

$1.mole^{-1}.cm^{-1}$), and the complex is less susceptible to oxidation by the manganese(III) in it.

EXPERIMENTAL

Reagents

All reagent solutions were made from analytical-grade chemicals.

Manganese (II) chloride tetrahydrate solution, 40%

CTAB solution, 0.5%. Prepared by dissolving 0.5 g of CTAB in 10 ml of ethanol and diluting to 100 ml.

Sodium hydroxide solution, 10%.

EDTA, 0.2 *M*.

Procedure

Stock water samples were prepared and the dissolved oxygen was determined by the Winkler method.[8] These samples were used for preparation of the calibration curve. The dissolved oxygen in amounts ranging from 7 to 3160 μg (*i.e.*, from 1 ml of 7-ppm solution to 400 ml of 7.9-ppm solution) was stabilized by addition of 1 ml of 0.5% CTAB solution, followed by 0.6 ml of manganese chloride solution, 2 ml of sodium hydroxide solution, 2 ml of glacial acetic acid and 3 ml of 0.2 *M* EDTA. The solution was stirred vigorously and the volume made up to 500 ml with distilled water. The absorbances were measured within 10 min of the dilution to the mark, in 2-cm cuvettes at 496 nm, against a reagent blank.

A linear calibration curve passing through the origin was obtained. Beer's law was obeyed over the concentration range 14–6320 μg/l. in the final solution. The apparent molar absorptivity was found to be about 2.02×10^3 $1.mole^{-1}.cm^{-1}$.

The same procedure is used for the analysis of water samples, a sample size of at least 50 ml (and preferably 100 – 300 ml) being recommended.

Application to some natural waters

The dissolved oxygen content of two natural waters was determined by the Winkler method and the present method. The results given in Table 2 show that recovery was satisfactory in the presence of high concentrations of various ions.

Acknowledgements—Thanks and appreciation are due to Professor A. Y. Salim (Alexandria University, Alexandria, Egypt) for his valuable suggestions and various useful discussions.

Table 2. Typical analysis of two natural waters from the vicinity of Mosul (*ppm*)

Value determined	Tigris river water		Nawaran water
	Before clarification	After clarification	
pH	7.8	7.7	8
Total dissolved solids	338	160	75
Total hardness (as $CaCO_3$)	180	158	430
Chloride	5.5	7.5	8
Sulphate	trace	trace	275
Potassium	0.6	0.7	1.1
Sodium	4.7	3.5	125
Calcium	52	4.4	125
Magnesium	12	11.8	31
Dissolved oxygen, Winkler method			
10-ml sample	7.8	7.9	7.7
100-ml sample	7.8_2	7.9_5	7.7_4
250-ml sample	7.84	7.94	7.72
Dissolved oxygen, present method			
10-ml sample	7.8	7.9	7.7
100-ml sample	7.8	7.9	7.7
250-ml sample	7.86	7.95	7.78

REFERENCES

1. L. W. Winkler, *Ber.*, 1888, **21**, 2843.
2. H. Fadrus and J. Maly, *Analyst*, 1971, **96**, 591.
3. W. W. Broenkow and J. D. Cline, *Limnol. Oceanog.*, 1969, **14**, 450.
4. W. M. Mackey and R. E. Middleton, *J. Soc. Chem. Ind.*, 1898, **17**, 1127.
5. R. Tuve, *U.S. Patent* 2,440,315, 27 April 1948.
6. F. W. Gilcreas, *J. Am. Water Wks. Assoc.*, 1935, **27**, 1166.
7. L. W. Winkler, *Z. Angew. Chem.*, 1913, **26**, 135.
8. A. H. Meyling and G. H. Frank, *Analyst*, 1962, **87**, 60.
9. V. B. Aleksovskii, *Zavodsk. Lab.*, 1962, **28**, 159.
10. W. J. Hansen and H. H. Pieters, *Anal. Chim. Acta*, 1948, **7**, 712.
11. M. L. Johnson and R. J. Whitney, *J. Expl. Biol.*, 1939, **16**, 56.
12. F. R. McCrumb and W. R. Kenny, *J. Am. Water Wks. Assoc.*, 1929, **21**, 400.
13. J. Banks, *Analyst*, 1959, **84**, 700.
14. W. F. Stones, *Chem. Ind. London*, 1957, **6**, 37.
15. A. H. de Carvalho, J. G. Calado and M. L. Moura, *Rev. Port. Quim.*, 1963, **5**, 15.
16. G. S. Sastry, R. E. Hamm and K. H. Pool, *Anal. Chem.*, 1969, **41**, 857.
17. H. Fadrus and J. Maly, *Hydrochemia*, 1970, **7**, 41.
18. H. Bechhold, *Z. Phys. Chem.*, 1904, **48**, 385.
19. J. H. Hildebrand and R. E. Powell, *Principles of Chemistry*, 6th Ed., Macmillan, New York, 1958.
20. F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, p. 170. Academic Press, New York, 1949.
21. *Standard Methods for the Examination of Water, Sewage and Industrial Waters*, 12th Ed., p. 405. American Public Health Assn., New York, 1965.

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SEMIMICRO SPECTROPHOTOMETRIC DETERMINATION OF NITROGLYCERINE IN PROPELLANTS BY USE OF 2, 4-XYLENOL

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(*Received* 27 *February* 1978. *Accepted* 27 *March* 1978)

Summary—A semimicro spectrophotometric method using 2,4-xylenol is proposed for the determination of nitroglycerine in propellants. The propellant is extracted with methylene chloride, the extract is diluted, and a 10-ml aliquot is evaporated just to dryness. Then 2,4-xylenol reagent and 63% v/v sulphuric acid are added to hydrolyse the nitroglycerine to nitrate and form 6-nitro-2,4-xylenol which is steam-distilled in a Parnas-Wagner Kjeldahl distillation apparatus into a water–ammonia–isopropyl alcohol mixture. The absorbance of the yellow solution of the anion of the 6-nitro-2,4-xylenol is measured. The calibration curve is prepared from potassium nitrate and an empirical factor (5.50) is used to convert from nitrogen content to nitroglycerine (the theoretical factor is 5.40). The 2,4-xylenol should be added before the sulphuric acid in order to prevent interference from diphenylamine and ethyl centralite. The method is designed for the usual nitrocellulose double-base propellants containing 8–50% of nitroglycerine.

In criminalistics and ordnance there is considerable need for a semimicro method for the determination of nitroglycerine (NG) in propellants, because frequently only a small amount of sample is available. The determination on a macro scale is usually performed by extraction with methylene chloride, evaporation of the solvent, addition of acetic acid, treatment of an aliquot (containing about 0.1 g of NG) with hydrochloric acid, reduction with an excess of iron(II), and titration of the resulting iron(III) with titanium(III).[1–3] Alternatively, the iron(III) can be titrated potentiometrically with EDTA[4] or biamperometrically with sodium thiosulphate (after addition of potassium iodide).[5] Nitroglycerine in propellants can also be determined by infrared spectrophotometry, directly[6] or after thin-layer chromatography,[7] by gas chromatography (using short columns to prevent decomposition of NG),[8, 9] and by polarography.[10]

Yagoda[11] determined NG in blood and urine by extracting it with diethyl ether, evaporating off the solvent, and adding 2,4-xylenol and sulphuric acid to hydrolyse the NG to nitrate which in turn formed 6-nitro-2,4-xylenol. Water was then added, the 6-nitro-2,4-xylenol was steam-distilled into sodium hydroxide solution, and the yellow colour due to the anion of 6-nitro-2,4-xylenol was measured. Yagoda and Goldman[12] applied the 2,4-xylenol method to the determination of NG in air after absorption of the NG in diethylene glycol or propylene glycol.

Recently, an improved version of the 2,4-xylenol method for the determination of inorganic nitrate was described.[13] The present paper describes the application of this method to the semimicro determination of NG in propellants.

EXPERIMENTAL

Reagents and apparatus

Potassium nitrate (dried at 150° for 1 hr), isopropyl alcohol, acetone, ammonia solution (s.g. 0.90), concentrated sulphuric acid to 500 ml of water with cooling by tap water. grade.

Sulphuric acid, 63% *v/v*. Add 850 ml of concentrated sulphuric acid to 500 ml of water with cooling by tap water.

Standard potassium nitrate solution (1 ml ≡ 0.05 mg of nitrogen). Dissolve 0.3610 g of potassium nitrate in water and dilute to 1 litre.

2,4-Xylenol solution, 2.5%. Dilute 5 ml of 2,4-xylenol to 200 ml with acetone.

Parnas–Wagner Kjeldahl distillation apparatus.[13]

Preparation of calibration curve

Transfer 0.00 (reagent blank), 1.00, 2.00, 3.00, and 4.00 ml of the standard potassium nitrate solution to 100-ml beakers and evaporate to dryness by heating gently on a hot-plate.

REFERENCES

1. L. W. Winkler, *Ber.*, 1888, **21**, 2843.
2. H. Fadrus and J. Maly, *Analyst*, 1971, **96**, 591.
3. W. W. Broenkow and J. D. Cline, *Limnol. Oceanog.*, 1969, **14**, 450.
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15. A. H. de Carvalho, J. G. Calado and M. L. Moura, *Rev. Port. Quim.*, 1963, **5**, 15.
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18. H. Bechhold, *Z. Phys. Chem.*, 1904, **48**, 385.
19. J. H. Hildebrand and R. E. Powell, *Principles of Chemistry*, 6th Ed., Macmillan, New York, 1958.
20. F. Feigl, *Chemistry of Specific, Selective and Sensitive Reactions*, p. 170. Academic Press, New York, 1949.
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EXPERIMENTAL

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Parnas–Wagner Kjeldahl distillation apparatus.[13]

Preparation of calibration curve

Transfer 0.00 (reagent blank), 1.00, 2.00, 3.00, and 4.00 ml of the standard potassium nitrate solution to 100-ml beakers and evaporate to dryness by heating gently on a hot-plate.

Cool to room temperature. Add 1 ml of 2,4-xylenol solution and cover with a watch-glass. Add 15 ml of the 63% sulphuric acid from a measuring cylinder and swirl well to dissolve the potassium nitrate. Allow to stand for 10–60 min.

Add 20 ml of water, 35 ml of isopropyl alcohol, and 5 ml of ammonia solution to each of five 100-ml standard flasks. Place one of the flasks under the condenser extension tube of the distillation apparatus so that the extension tube reaches to the bottom of the flask. Introduce the sample into the distillation flask and wash it in with 5–10 ml of water. Distil until the volume in the standard flask is about 95 ml. Wash down the outside of the extension tube and remove the standard flask. Dilute the solution to the mark, mix well, and measure the absorbance at 455 nm against the reagent blank distilled in the same way. Repeat for the other standards. Plot absorbance against mg of nitrogen.

Procedure

Weigh out sufficient sample to contain 8–11 mg of NG (for example, for about 10% NG use 0.1 g and for about 30% NG use 0.03 g) using a balance that will give a precision of 0.1%. Place the sample in a paper thimble in a Soxhlet apparatus and extract with about 85 ml of methylene chloride for 4 hr or more.[2, 14] Transfer the methylene chloride extract to a 100-ml standard flask, cool, and dilute to the mark with methylene chloride. Do not proceed past this point unless there is time to finish the determination. Accurately transfer a 10-ml aliquot to a dry 100-ml beaker (taking care that the methylene chloride does not leak from the tip of the pipette). Place the beaker in a gentle current of air, for example that under the nearly closed door of a fume cupboard, until the methylene chloride has just been driven off (a drop or two of residual methylene chloride will do no harm). Cover with a watch-glass and without delay add 1 ml of 2,4-xylenol solution and 15 ml of 63% v/v sulphuric acid and swirl well. Allow to stand for 10–60 min and proceed as for the calibration curve. Determine the amount of nitrogen present by referring to the calibration curve and calculate the NG content of the propellant from

$$\%\,\mathrm{NG} = \frac{5.50 \times \text{mg of nitrogen in aliquot}}{\text{g of sample}}$$

DISCUSSION AND RESULTS

Yagoda[11] and Yagoda and Goldman[12] added the 2,4-xylenol reagent before the sulphuric acid. Ordinarily it is immaterial which is added first, but in the determination of NG in propellants, it is desirable to add the 2,4-xylenol first to prevent interference from diphenylamine and ethyl centralite (*N,N'*-diethyl-*N,N'*-diphenylurea) which are present in propellants as stabilizers. If the sulphuric acid is added first, the nitrate produced by hydrolysis of the NG reacts with the diphenylamine and the ethyl centralite to produce blue and reddish colours, respectively. When the 2,4-xylenol is added these colours fade, but the results for nitrate tend to be low. On the other hand, if the 2,4-xylenol reagent in acetone is added first to the evaporated extract containing diphenylamine or ethyl centralite, these two substances dissolve in the acetone together with the NG, and there is no reaction. On addition of the acid, the nitrate released from the NG has a greater affinity for the 2,4-xylenol than for the diphenylamine or ethyl centralite and there is no interference. In further experiments 3 ml of standard nitrate solution (0.150 mg of nitrogen) were evaporated to dryness in each of two 100-ml beakers, then 10 mg of diphenylamine were added to one beaker and 10 mg of ethyl centralite to the other, and the samples were carried through the calibration procedure. Recoveries of 0.152 and 0.148 mg of nitrogen respectively were obtained. The amount of diphenylamine or ethyl centralite taken is the same as the maximum amount of sample in the test aliquot (see procedure).

Holler and Huch[15] also added the sulphuric acid last in their rather complex method for the determination of n-amyl nitrate and decyl nitrate in the presence of diphenylamine and ethyl centralite (not in propellants) by reaction with 3,4-xylenol.

The hydrolysis of NG to nitrate is extremely rapid. The same result was obtained on distilling solutions whether they had been standing for 10 or 60 min or heated at 50° for 20 min (after the addition of the sulphuric acid).

The question of what to use as a standard has always been a problem for chemists determining NG spectrophotometrically. Yagoda[11] and Yagoda and Goldman[12] used the theoretical factor (5.40) to calculate the amount of NG from the amount of nitrogen found. We have used an empirical factor (5.50) based on actual determinations. A propellant, previously analysed carefully by the titration method, could be used as a standard each time a sample is run, and a factor calculated. Another means for standardization of the method would be to use a 10-ml aliquot of a standard solution of NG in methylene chloride, but that presupposes that the laboratory has access to NG. The calibration curve should not be prepared by measuring portions of a methylene chloride solution of NG with a burette. Our experience is that methylene chloride is so volatile that the losses on filling the burette will be significant.

Nitroglycerine used in the manufacture of propellants is of high purity. It has a minimum nitrogen content of 18.40% (theoretical content 18.50%).[16]

A 10-ml aliquot of the methylene chloride extract is recommended because this volume of solvent is readily evaporated at room temperature. Larger volumes take longer to evaporate, partly because of the cooling effect (when a 25-ml aliquot was evaporated some ice crystals formed on the bottom of the beaker). A warm water-bath could be used, of course. Volumes less than 10 ml may be taken but the errors will be greater.

To minimize volatilization of NG on standing, the 2,4-xylenol and sulphuric acid should be added immediately after the methylene chloride has evaporated. A drop or two of methylene chloride has no effect on the colour development, though no colour could be developed at all in the presence of 5 ml of methylene chloride.

This method has been developed for the analysis of the usual nitrocellulose double-base propellants containing 8–50% of NG. Nitrocellulose, potassium nitrate, barium nitrate, sodium sulphate, potassium sulphate, graphite and tin dioxide found in propellants are not extracted by methylene chloride and do not interfere. Dinitrotoluene, diethyl phthalate, and dibutyl phthalate are extracted by methylene chloride but do not interefere since they are not readily nitrated. This was checked experimentally in the same way as the effect of diphenylamine and ethyl centralite. 2-Nitrodiphenylamine, which is sometimes added to propellants as a substitute for diphenylamine, is extracted by methylene chloride and can interfere because it also gives a yellow solution on distillation, but a correction can be made for this. The absorbances obtained on treating 0.01, 0.20, 0.50, and 1.0 mg of 2-nitrodiphenylamine as in the method and distilling were 0.00, 0.03, 0.13, and 0.31 respectively. Hence, if an aliquot containing 0.01 g of sample which contains 1% of 2-nitrodiphenylamine were taken, a deduction of 0.015 absorbance units should be made for the 0.1 mg of the compound present.

Nitrate esters (containing the ONO_2 group) such as triethyleneglycol dinitrate, pentaerythritol tetranitrate, mannitol hexanitrate, amyl nitrate, and decyl nitrate would be expected to react with 2,4-xylenol as NG does. Sometimes triethyleneglycol dinitrate is used as a substitute for NG in propellants and there is no reason why it could not be determined by the proposed method (with a different factor, of course).

Low and erratic results were obtained in attempts to apply the method to the determination of nitrocellulose (cellulose nitrate) after dissolution of that material directly in sulphuric

acid (no extraction step).

The results obtained for NG by the proposed method for three propellants which had previously been carefully analysed by the volumetric method[2-3] are shown in Table 1. The

Table 1. Results for nitroglycerine in propellants

Sample	NG by volumetric method, %	NG by spectrophotometric method, %	Mean, %
WC 846*	10.20	10.1; 10.3; 10.1; 10.2	10.2
WC 870†	9.75	9.8; 9.9; 9.6; 9.6	9.7
HPC 13‡	30.6	30.3; 30.3; 30.5; 30.7	30.5

* Contains 1.2% diphenylamine, 1.1% dinitrotoluene, 4.5% diethyl phthalate, 0.25% calcium carbonate, 0.15% sodium sulphate, and 0.2% graphite.

† Contains 1.1% diphenylamine, 0.4% dinitrotoluene, 1.3% dibutyl phthalate, 0.2% calcium carbonate, 0.1% sodium sulphate, and 0.2% graphite.

‡ Contains 3.1% ethyl centralite, 0.9% potassium sulphate, and 0.15% graphite.

spectrophometric results compare favourably with the volumetric results and the precision is satisfactory.

The 2,4-xylenol method (with distillation) seems to be the only spectrophotometric method for nitrate with sufficient accuracy, reproducibility, and freedom from interference to be useful for the determination of NG in propellants. In the course of this study the brucine and diphenylamine spectrophotometric methods were also tried (after the extraction with methylene chloride and evaporation), but the results were very poor.

The proposed method could probably be applied to the determination of NG and related nitrate esters in dynamite, pharmaceuticals and other materials, but this was not investigated.

REFERENCES

1. W. W. Becker and W. R. Shaefer, in *Organic Analysis*. Vol. II, p. 101. Interscience, New York, 1954.
2. F. J. Welcher, *Scott's Standard Methods of Chemical Analysis*, 6th Ed., Vol. 2, Part B, p. 1391. Van Nostrand, New York, 1963.
3. *Military Standard MIL-STD-286B, Propellants, Solid: Sampling, Examination and Testing*, Method 208.1.3, 15 July 1969.
4. R. S. Lambert and R. J. DuBois, *Anal. Chem.*, 1965, **37**, 427.
5. R. A. Gonzalez, J. A. Blanco, A. O. Rucci, E. J. Wood and S. C. Revuelto, *Talanta*, 1977, **24**, 683.
6. F. Pristera, M. Halik, A. Castelli and W. Fredericks, *Anal. Chem.*, 1960, **32**, 495.
7. G. F. Macke, *J. Chromatog.*, 1968, **38**, 47.
8. B. J. Alley and H. W. Dykes, *ibid.*, 1972, **71**, 23.
9. A. Sopranetti and H. U. Reich, *Explosivstoffe*, 1972, **20**, 197.
10. M. Frey, *ibid.*, 1964, **12**, 149.
11. H. Yagoda, *Ind. Eng., Chem., Anal. Ed.*, 1943, **15**, 27.
12. H. Yagoda and F. H. Goldman, *J. Ind. Hyg. Toxicol.*, 1943, **25**, 440.
13. G. Norwitz and H. Gordon, *Anal. Chim. Acta*, 1977, **89**, 177.
14. *Military Standard MIL-STD-286B, Propellants, Solids: Sampling, Examination and Testing*, Method 104.1.3, 30 June 1971.
15. A. C. Holler and R. V. Huch, *Anal. Chem.*, 1949, **21**, 1385.
16. *Military Specification MIL-N-246B, Nitroglycerin*, 19 February 1962.

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CO-EXTRACTION AND SEPARATION OF ZIRCONIUM AND HAFNIUM BY LONG-CHAIN AMINES FROM SULPHATE MEDIA

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(*Received* 12 *April* 1977. *Revised* 22 *March* 1978. *Accepted* 18 *April* 1978)

Summary—The extraction of Zr and Hf from sulphuric acid systems by solutions of Primene JMT (a long-chain primary amine) in kerosene, is described. The effect of contact time, free acidity, solvent concentration and temperature, has been thoroughly examined. A rapid improved method for Hf–Zr separation is suggested.

Intensive development of the application of heavy amines in analysis and hydrometallurgy has resulted in a rapid expansion in commercial applications, particularly in nuclear fuel production.[1] It is a general rule that the extractive power of alkylamines increases in the order primary < secondary < tertiary < quaternary ammonium. In previous work, the types of amine were thoroughly examined as extractants for Zr and Hf in chloride systems.[2] Although it is reported that primary amines are poor extractants in chloride or nitrate media, their extractive capacity is considerably enhanced in sulphate systems.[3] Few observations were made on Zr extraction with primary amines, and still fewer on Hf.[4-9] The present investigation was therefore undertaken to obtain further information on co-extraction and separation of Zr and Hf with Primene JMT (as a model long-chain primary amine) from sulphuric acid solutions.

EXPERIMENTAL

Reagents

Primene JMT (PrJM) (trialkylmethylamine). This is a mixture of isomeric primary amines in the C_{18-22} range, of average molecular weight 279, specific gravity 0.840 and refractive index 1.456 at 25°. PrJM is manufactured by the Rohm and Haas Co., Philadelphia, U.S.A. and was used as received, without further purification; all batches used had the same composition. Odourless kerosene, a commercial product of Shell Ltd. (Sunrise), was used as diluent.

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REFERENCES

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4. R. S. Lambert and R. J. DuBois, *Anal. Chem.*, 1965, **37**, 427.
5. R. A. Gonzalez, J. A. Blanco, A. O. Rucci, E. J. Wood and S. C. Revuelto, *Talanta*, 1977, **24**, 683.
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7. G. F. Macke, *J. Chromatog.*, 1968, **38**, 47.
8. B. J. Alley and H. W. Dykes, *ibid.*, 1972, **71**, 23.
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CO-EXTRACTION AND SEPARATION OF ZIRCONIUM AND HAFNIUM BY LONG-CHAIN AMINES FROM SULPHATE MEDIA

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Summary—The extraction of Zr and Hf from sulphuric acid systems by solutions of Primene JMT (a long-chain primary amine) in kerosene, is described. The effect of contact time, free acidity, solvent concentration and temperature, has been thoroughly examined. A rapid improved method for Hf–Zr separation is suggested.

Intensive development of the application of heavy amines in analysis and hydrometallurgy has resulted in a rapid expansion in commercial applications, particularly in nuclear fuel production.[1] It is a general rule that the extractive power of alkylamines increases in the order primary < secondary < tertiary < quaternary ammonium. In previous work, the types of amine were thoroughly examined as extractants for Zr and Hf in chloride systems.[2] Although it is reported that primary amines are poor extractants in chloride or nitrate media, their extractive capacity is considerably enhanced in sulphate systems.[3] Few observations were made on Zr extraction with primary amines, and still fewer on Hf.[4-9] The present investigation was therefore undertaken to obtain further information on co-extraction and separation of Zr and Hf with Primene JMT (as a model long-chain primary amine) from sulphuric acid solutions.

EXPERIMENTAL

Reagents

Primene JMT (PrJM) (trialkylmethylamine). This is a mixture of isomeric primary amines in the C_{18-22} range, of average molecular weight 279, specific gravity 0.840 and refractive index 1.456 at 25°. PrJM is manufactured by the Rohm and Haas Co., Philadelphia, U.S.A. and was used as received, without further purification; all batches used had the same composition. Odourless kerosene, a commercial product of Shell Ltd. (Sunrise), was used as diluent.

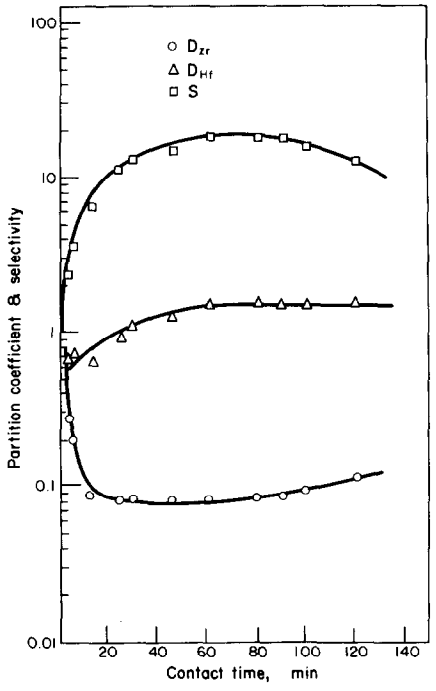


Fig. 1. Effect of shaking time on extraction of Zr(IV) and Hf(IV) by 0.1*M* Primene JMT in kerosene.

Extraction procedure

The organic phase was prepared by adding the calculated amount of extractant to kerosene containing 3% v/v octanol to avoid emulsion. The aqueous phase was prepared from a high-grade hydrated zirconia (with only 1.4% Hf), its exact content of Zr (+Hf) being determined complexometrically by back-titration with iron, with salicylic acid as indicator,[10] and the Hf was measured radiometrically by tracer labelling with $^{175+181}$Hf isotope. The Zr content was computed by difference. The free acidity of the aqueous solution was estimated after addition of excess of standard alkali to the feed, precipitation, and back-titration of the excess of alkali with hydrochloric acid.

Equal volumes (10 ml) of both aqueous and pre-equilibrated organic phases were mixed together in separatory funnels and shaken mechanically for the required contact time. Partition coefficients (D) were calculated as the ratio of the equilibrium concentration of Zr or Hf in the organic phase to that in the aqueous phase. Separation factors (selectivity, S) were computed from

$$S = \frac{D_{Hf}}{D_{Zr}}$$

Table 1. Extraction of Zr(IV) and Hf(IV) from 0.2*M* sulphuric acid in presence of sodium sulphate with 0.1*M* Primene JMT in kerosene

Total sulphate concn., *M*	D_{Zr}		D_{Hf}	
	H_2SO_4	$H_2SO_4 + Na_2SO_4$	H_2SO_4	$H_2SO_4 + Na_2SO_4$
0.2	0.35	0.42	5.4	6.8
0.5	0.25	0.32	9.6	12.2
0.7	0.20	0.24	10.5	14.2
1.0	0.20	0.25	6.3	12.6
2.0	0.20	0.24	4.3	8.4

RESULTS AND DISCUSSION

Effect of contact time

The extraction of Zr and Hf from aqueous solutions that were 0.088*M* in Zr, 6.2×10^{-4}*M* in Hf and 0.3*M* in free sulphuric acid, with organic phases of 0.1*M* PrJM in kerosene at 29°, for various periods (1–120 min), was examined. Results are shown in Fig. 1. It is evident that D_{Zr} decreases steeply with increase in contact time up to about 25 min, then remains more or less constant, whereas D_{Hf} increases gradually over about 1 hr, then remains constant. The same trend was followed by the selectivity curve up to about 80 min. It may be concluded that about 1 hr (or even 45 min) is sufficient to attain equilibrium.

Effect of free acidity and extractant concentration

To find the influence of the acidity, the extraction was investigated under the conditions used for Fig. 1, but with the contact fixed at 1 hr, at 22°, and the acidity varied between 0.2 and 2*M*; the results are shown in Fig. 2. It is inferred that the decrease in D_{Zr} up to 0.7*M* sulphuric acid and in D_{Hf} at higher acidities (>0.7*M*), may be due to competition between Zr(Hf) and sulphuric acid for association with the amine and/or formation of less readily extractable complexes. The higher D_{Hf} values up to 0.7*M* sulphuric acid are presumably due to salting-out effects and formation of an Hf amine complex whereas the nearly constant D_{Zr} values obtained at higher acidities (>0.7*M*) may be attributed to attainment of equilibrium between Zr and sulphuric acid in the competition for association with PrJM. Such an explanation is confirmed by replacing sulphuric acid in the aqueous phase with various concentrations of sodium sulphate (Table 1). The optimum acidity is around 0.7*M* free sulphuric acid, S then being maximal (48).

The effect of extractant concentration was examined by continuing the extraction for 1 hr, using an aqueous solution that was 0.056*M* Zr and 4.2×10^{-4}*M* Hf in 0.7 and 1*M* sulphuric acid, and organic phases of different PrJM concentrations (0.05–0.5*M*) in kerosene. The value of log D increased linearly with increase in log [PrJM] as expected. It was observed that for PrJM concentrations >0.15*M* emulsion starts to be formed, increasing with rise in PrJM

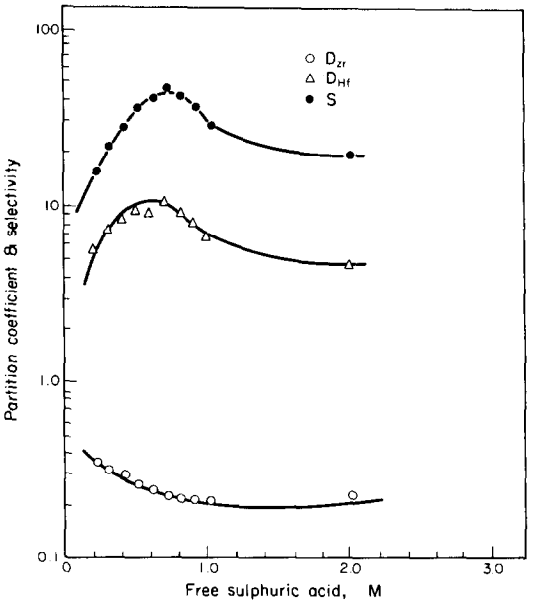


Fig. 2. Effect of sulphuric acid concentration on the extraction of Zr(IV) and Hf(IV) by 0.1*M* Primene JMT in kerosene.

Table 2. Effect of temperature on the extraction of Zr(IV) and Hf(IV) from 0.7*M* sulphuric acid solutions by 0.1*M* Primene JMT in kerosene

Temperature, °C	D_{Zr}	D_{Hf}	S
10	0.31	163.0	525.0
15	0.27	159.0	590.0
20	0.22	49.0	223.0
25	0.20	32.0	159.0
40	0.20	4.0	20.2
50	0.19	3.8	20.0
60	0.20	3.9	19.5

molarity. The optimum extractant concentration is hence recommended as 0.1–0.15*M*.

Effect of temperature

The extraction was continued for 1 hr with aqueous solutions that were 0.056*M* Zr and 4.2×10^{-4}*M* Hf in 0.7*M* free sulphuric acid and organic phases of 0.1*M* PrJM in kerosene at various temperatures (10–60°) (Table 2). It is seen that D_{Zr} decreases slightly with rise of temperature up to 25° then remains nearly constant at higher temperatures whereas D_{Hf} decreases sharply with temperature rise up to 40° then remains more or less constant. The higher D values attained by lowering the temperature may be ascribed to decrease in extractant aggregation and/or increase in activity coefficients in both organic and aqueous phases, a view consistent with that of other investigators.[11] S is also increased pronouncedly by lowering the temperature, a phenomenon also observed by other workers for other commercial amines in chloride systems.[2,5] Since lower temperature favours both D_{Zr} and D_{Hf}, the extraction process is assumed to be exothermic.

Separation of Zr(IV) and Hf(IV)

From this study, a rapid improved method for Hf–Zr separation was developed. It is achieved by shaking mechanically (in separatory funnels or in one-stage mixer-settlers) for 45 min a Zr (+Hf) feed of about 5 g/l. concentration in 0.7*M* free sulphuric acid with an equal volume of pre-equilibrated organic phase of 0.15*M* PrJM in kerosene (containing 3% v/v octanol) at a temperature kept below 15°. It is emphasized here that Hf(IV) is preferentially extracted into the organic phase (with $S > 500$) in contrast to other extraction systems, where Zr is preferentially extracted. A nuclear-pure Zr(IV) product in the aqueous phase, with less than 100 ppm Hf(IV) (as ascertained spectrographically) and more than 90% recovery, was directly obtained in a one-stage operation. The ease of handling, together with the advantage of omitting the traditional re-extraction techniques (scrubbing and stripping) and hence shortening the separation programme, renders the process convenient, economically attractive and satisfactory for analytical as well as industrial purposes.

REFERENCES

1. D. J. Crouse, K. B. Brown and F. G. Seeley, *Solvent Extraction Chemistry of Metals*, p. 327, Macmillan, London, 1966.
2. M. Y. Farah and I. S. El-Yamani, *Proc. 3rd U.N. Intern. Conf. Peaceful Uses Atomic Energy, New York*, 1965, **9**, 131.
3. F. W. Bruenger, B. J. Stever and D. R. Atherton, *Anal. Chem.*, 1963, **35**, 1671.
4. C. F. Coleman, K. B. Brown and J. G. Moore, *Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1958, **28**, 278.
5. E. Cerrai and C. Testa, *Energia Nucleare*, 1959, **6**, 707.
6. E. A. Mason and V. C. Vaughen, *Progress Rept. MIT*, 1959.
7. T. Ishimori and K. Watanabe, *Bull. Chem. Soc. Japan*, 1960, **33**, 1443.
8. E. A. Mason, *Progress Rept.*, TID-15450, 1962.
9. K. S. Venkateswarbu, V. Subramanyan, M. R. Dhaneswar, R. M. Shanker and J. Shankar, *Indian J. Chem.*, 1965, **3**, 448.
10. G. W. C. Milner and P. J. Phennah, *Analyst*, 1954, **79**, 475.
11. G. Scibona, S. Basol, P. R. Danesi and F. Orlandini, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1441.

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BROMAMINE-T AS A NEW OXIDIMETRIC TITRANT

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The status of chloramine-T as an oxidimetric titrant is now well established.[1] In this communication, we report the results of our studies on bromamine-T (BAT), the sodium salt of *N*-bromo-*p*-toluene sulphonamide, which is being used as an oxidimetric titrant for the first time.

EXPERIMENTAL

Preparation of BAT

BAT was prepared from dibromamine-T, which, in turn, was prepared by the bormination of CAT.[2] This procedure might seem a bit circuitous, but although we tried other approaches, this route was found to be the most convenient.

About 33 g of dibromamine-T were dissolved, in small lots at a time and with stirring, in an aqueous solution of about 8 g of sodium hydroxide in 50 ml of water, and the solution was cooled in ice. Pale yellow crystals of BAT separated out. They were filtered off under suction, washed quickly with the minimum quantity of water and dried over phosphorus pentoxide. The yield was *ca.* 28 g. Found: Br 24.4%, N 4.4%, S 9.5%; required for $Na^+(CH_3C_6H_4SO_2NBr)^-.3H_2O$: Br 24.5%, N 4.3%, S 9.8%. On heating to ~800° in air the

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REFERENCES

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compound gave a white residue which proved to be sodium bromide, the loss of weight on heating being the theoretical weight loss of 68.4% for the conversion $Na^+(CH_3C_6H_4SO_2NBr)^-.3H_2O \rightarrow Na^+Br^-$.

Stock solutions of BAT

Approximately 0.1*N* (0.05*M*) stock solutions were prepared by dissolving 16 g of BAT in 1 litre of water, kept in amber-coloured bottles and standardized iodometrically in the same way as CAT.[1] The strengths of a typical stock solution of BAT over a period of one month are given below.

Day no.	0	1	2	4	7	15	30
Normality	0.1068	0.1068	0.1068	0.1065	0.1060	0.1052	0.1047

Daily standardization is recommended.

Reductants studied

Seven typical yet diverse types of reductants were chosen for direct titration, *viz.*, As(III), Sb(III), Fe(II), Tl(I), iodine, hydrazine and ascorbic acid. The substances determined by back-titration were dithiocarbamate, xanthate, trithionate, monothiophosphate, semicarbazide, thiourea and thiosemicarbazide. Standard aqueous solutions of these were prepared by the usual methods.[3] The strengths were checked by CAT procedures.[4-10]

Indicators

The following aqueous indicator solutions were prepared:[11] *p*-ethoxychrysoidine, Bordeaux, Amaranth, Methyl

Table 1. Oxidimetric determinations with bromamine-T

Reductant	Reductant taken, *mmole*	BAT consumed, *meq*	Reductant found,* *mmole*	Error, %	Standard deviation,† *μmole*
(*a*) *Potentiometric titrations*					
As(III)	0.6122	1.225	0.6125	+0.05	2.7
Sb(III)	0.3134	0.6252	0.3126	−0.3	1.9
Fe(II)	0.5936	0.5933	0.5933	−0.05	2.4
Tl(I)	0.2248	0.4488	0.2245	−0.1	2.4
Iodide	0.4878	0.4894	0.4895	+0.35	2.4
Hydrazine	0.2804	0.5623	0.2811	+0.25	1.9
Ascorbic acid	0.1593	0.6354	0.1589	−0.25	3.1
(*b*) *Direct titrations with dyestuff indicators*					
As(III)	0.6678	1.340	0.6701	+0.3	9.4
As(III)	1.307	2.603	1.302	−0.4	
Sb(III)	0.7314	1.463	0.7316	+0.0	5.8
Sb(III)	1.974	3.955	1.977	+0.15	
Fe(II)	0.4749	0.4756	0.4756	+0.15	6.0
Fe(II)	3.700	3.710	3.710	+0.3	
Tl(I)	0.4495	0.8876	0.4488	−0.2	6.7
Tl(I)	1.417	2.824	1.412	−0.4	
Iodide	0.1951	0.1952	0.1952	+0.05	2.5
Iodide	0.7805	0.7850	0.7850	+0.6	
Hydrazine	0.1327	0.5314	0.1328	+0.1	4.9
Hydrazine	0.8917	3.563	0.8906	−0.1	
Ascorbic acid	0.1867	0.3725	0.1862	−0.3	7.2
Ascorbic acid	1.586	3.181	1.591	+0.3	
(*c*) *Direct titrations with starch-KI indicator*					
Results similar to those for (*b*) above. Standard deviations (*μmole*): As(III), 4.2; Sb(III), 2.2; ascorbic acid, 3.8. This procedure was not successful for Fe(II), Tl(I). iodide and hydrazine.					
(*d*) *Andrews titrations*					
Suitable for Fe(II), Tl(I), iodide and hydrazine. Results similar to those for (*b*) above. Standard deviations (*μmole*): Fe(II), 4.8; Tl(I), 2.9; iodide, 2.3; hydrazine, 4.4.					
(*e*) *Back-titrations in acid medium*					
Dithiocarbamate	0.1254	1.750	0.1250	−0.3	5.2
Xanthate	0.1188	1.666	0.1191	+0.25	3.4
Trithionate	0.3433	2.744	0.3430	−0.1	3.4
Monothiophosphate	0.1038	0.8271	0.1034	−0.4	4.6
Semicarbazide	0.3402	1.359	0.3398	−0.1	1.7
Method not successful for thiourea and thiosemicarbazide.					
(*f*) *Modified excess–back-titration procedure*					
All the reductants given under (*c*) could be determined by this procedure as well; the results are similar. Only the modified procedure was possible for thiourea and thiosemicarbazide.					
Thiourea	0.2509	2.005	0.2506	−0.1	4.9
Thiosemicarbazide	0.1356	1.630	0.1358	+0.15	4.1

*Calculated on the assumption that the numbers of equivalents of BAT consumed per mole of the reductant are 1 for Fe(II) and iodide; 2 for As(III), Sb(III), Tl(I) and ascorbic acid; 4 for hydrazine and semicarbazide; 8 for trithionate, monothiophosphate and thiourea; 12 for thiosemicarbazide; and 14 for dithiocarbamate and xanthate.

† Calculated for 6 typical experiments covering a wide range of amount of reductant taken.

Red and Methyl Orange (all 0.1%), Quinoline Yellow (0.5%), starch (1%).

Procedure

The equipment for potentiometric titration was the same as that described earlier.[12]

Direct potentiometric titrations. Reductant solution (5–10 ml) was mixed with 5 ml of conc. hydrochloric acid, diluted to 100 ml with water and titrated with standard BAT solution. The end-points were determined by the graphical method and were checked by the Hostetter-Roberts equation[13] or the Yan equation,[14] whichever was applicable.

In the case of Fe(II) addition of 5 ml of phosphoric acid improves the titration, by the well-known complexation effect. The potential breaks at the equivalence points for the addition of 0.1 ml of 0.1*N* BAT were about 400 mV for As(III), Sb(III), ascorbic acid and hydrazine, 300 mV for Fe(II) and Tl(I), and 100 mV for iodide.

Direct titrations with dyestuffs as indicators. Of the indicators tried, only Quinoline Yellow and *p*-ethoxychrysoidine were found to be suitable. Of the two, the former is preferred except in the case of Fe(II), where *p*-ethoxychrysoidine is recommended. To 5–30 ml of reductant solution, 10 ml of conc. hydrochloric acid were added and the solution was diluted to 100 ml with water. Two or three drops of indicator were added and the solutions were titrated.

Direct titrations with starch as indicator. The procedure was similar to that just described except that 0.1 g of potassium iodide and 1 ml of 1% starch solution were added as the indicator system.

For As(III) and Sb(III) the titrations were successful only in bicarbonate-buffer medium. Therefore, 100 ml of 1*M* $NaHCO_3$ solution were added instead of the acid before the titration.

Andrews-type titrations. The starch method failed for Fe(II), Tl(I), iodide and hydrazine. In these cases, Andrews-type titrations were found to be possible. To 5–20 ml of reductant solutions, 10 ml of conc. hydrochloric acid, 10 ml of carbon tetrachloride and 5 ml of 0.1*N* iodine monochloride solution in 5*N* hydrochloric acid were added (in the case of iodide, no ICI was added). The solution was titrated with BAT, with vigorous shaking, until the violet colour of the organic layer was just discharged.

Back-titrations in acid medium. Aliquots (25 ml) of 0.1*N* BAT were diluted to 100 ml with water and 10 ml of 2*N* sulphuric acid were added, followed by 5–10 ml of the reductant solution (accurately measured). The mixture was left for 10–15 min and the unconsumed BAT determined by adding 10 ml of 10% potassium iodide solution and titrating the liberated iodine with standard thiosulphate.

Modified back-titration procedure. The last procedure was not successful for thiourea and thiosemicarbazide. In these cases, it was found desirable to start the oxidation in alkaline medium. (A similar procedure was found necessary by earlier workers for the CAT oxidation of thiourea.[9]) To 25 ml of 0.1*N* BAT, 10 ml of 2*N* sodium hydroxide were added and the solution was diluted to 100 ml. Then 5–10 ml of reductant solution (accurately measured) were added. After 10–15 min, 20 ml of 2*N* sulphuric acid were added and the unconsumed BAT was determined iodometrically as above.

Blanks were run concurrently for all types of titration except the first. Blank corrections were not needed for starch and Andrews titrations and were very small for the other three types.

RESULTS AND DISCUSSION

Typical results are presented in Table 1. They indicate that BAT is a convenient oxidimetric titrant for a variety of oxidizable substances. The lower oxidation states of sulphur are all oxidized to sulphate and hydrazine to nitrogen.

In the instances studied, oxidation with BAT proceeds very much like that with CAT. The formal redox potential of the bromamine-T/*p*-toluene sulphonamide couple was determined and found to be +1.16 V at 25±0.02°. This is quite comparable to the value of +1.14 V for CAT.[15]

Oxidations with BAT also show some similarities to hypobromite oxidations, *e.g.* in the oxidation of hydrazine to nitrogen. This is interesting from the mechanistic point of view, considering that the seat of oxidant action is the $(NBr)^-$ grouping in BAT and the $(OBr)^-$ grouping in hypobromite. Aqueous solutions of BAT are, however, more stable than hypobromite solutions.

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REFERENCES

1. E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197; 1961, **8**, 22; 1961, **8**, 34; 1961, **8**, 697; 1962, **9**, 581; 1962, **9**, 593; 1962, **9**, 603; 1962, **9**, 679.
2. C. G. R. Nair and P. Indrasenan, *ibid.*, 1976, **23**, 239.
3. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957.
4. C. G. R. Nair, T. Joseph and P. T. Joseph, *Chemist-Analyst*, 1965, **54**, 111.
5. V. R. S. Rao and A. R. V. Murthy, *Talanta*, 1960, **4**, 206.
6. K. Sarada and A. R. V. Murthy, *Z. Anal. Chem.*, 1960, **177**, 401.
7. T. J. Jacob and C. G. R. Nair, *Indian J. Chem.*, 1967, **4**, 501.
8. V. R. Nair and C. G. R. Nair, *Anal. Chim. Acta*, 1971, **57**, 429.
9. V. R. S. Rao and G. Aravamudan, *Talanta*, 1968, **15**, 704.
10. D. S. Mahadevappa and A. S. A. Murthy, *ibid.*, 1970, **17**, 431.
11. A. I. Vogel, *Text-book of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London, 1964.
12. V. N. S. Pillai and C. G. R. Nair, *Talanta*, 1975, **22**, 57.
13. J. C. Hostetter and H. J. Roberts, *J. Am. Chem. Soc.*, 1919, **41**, 1337.
14. J. F. Yan, *Anal. Chem.*, 1965, **37**, 1558.
15. A. R. V. Murthy and B. S. Rao, *Proc. Indian Acad. Sci.*, 1952, **35**, 69.

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STABILITY AND DISTRIBUTION STUDIES ON Sn(IV) AND Cr(III) ARSENOPHOSPHATES: SEPARATIONS OF METAL IONS

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Summary—The stability of tin(IV) and chromium(III) arsenophosphates in mineral acids and sodium hydroxide has been investigated. Structures for the two compounds are proposed, based on the results of thermogravimetric analysis, K_d values for metal ions on these two compounds have been determined and separations of UO_2^{2+}–Th^{4+}, UO_2^{2+}–Zr^{4+} and Na^+–K^+ achieved.

The inorganic ion-exchange materials produced by mixing a solution containing two anionic species with a metal ion solution have shown better ion-exchange properties than the zirconium phosphate type materials.[1] In an earlier publication[2] we reported the preparation of tin(IV) and chromium(III) arsenophosphates. Their composition, ion-exchange capacity, concentration and elution curves, thermal stability and pH titrations have been studied in detail. Infrared and X-ray studies have also been made on these ion-exchange materials. The present paper summarizes the chemical stability of these materials and the distribution behaviour of metal ions on them.

EXPERIMENTAL

Preparation of ion-exchange materials

Tin(IV) arsenophosphate was prepared by mixing equal volumes of 0.1*M* solutions of tin(IV) chloride, sodium arsenate and sodium phosphate. The pH of the mixture was adjusted to 0.0 with nitric acid. The gel thus prepared was kept at room temperature for 24 hr and filtered off. It was washed several times with distilled water and dried at 40°. The dried material was crushed and converted into the hydrogen form with 1*M* nitric acid. The material was finally washed with demineralized water to remove the excess of acid, and dried at 40°. Granules of the required size were obtained by sieving. The chromium(III) arsenophosphate was prepared by mixing 0.1*M* solutions of chromium(III) nitrate, sodium arsenate and sodium phosphate in 2:1:1 volume ratio and treating the precipitate as described above. The ion-exchange capacities of the two arsenophosphates for sodium ions were 1.75 and 0.74 meq/g respectively, as reported earlier.[2]

Chemical stability

Portions of ion-exchange material (500 mg) were placed in 25 ml of various mineral acids and sodium hydroxide solutions (of various concentrations) for 24 hr, with intermittent shaking. The supernatant liquid was then decanted and analysed for Sn(IV), Cr(III), As(V) and PO_4^{3-} by standard spectrophotometric methods.[3–6] The results are summarized in Table 1. The results of a thermogravimetric study of the two arsenophosphates are given in Fig. 1.

Distribution studies

Distribution studies of 16 metal ions on the two arsenophosphates were performed at pH 2 (adjusted with perchloric acid). The results are summarized in Table 2.

Distribution coefficients (K_d) of Na^+, K^+, UO_2^{2+}, Th^{4+} and Zr^{4+}. Sodium nitrate and potassium nitrate solutions were prepared in demineralized water. The amount of the metal solution loaded was so adjusted that it did not exceed 3% of the total ion-exchange capacity of the exchanger. Equilibrium was attained by keeping the solution overnight at room temperature in contact with the ion-exchange material. The

Table 1(*a*). Chemical stability of Sn(IV) arsenophosphate

Solution	Sn(IV) dissolved, *mg*	As dissolved, *mg*	PO_4^{3-} dissolved, *mg*
5M HCl	0.7_5	0.1_5	0.4
7*M* HCl	1.2_5	18.0	36.0
10*M* HCl	dissolved completely		
5*M* HNO_3	—	0.1	0.2
7*M* HNO_3	0.4	0.6	0.8
10*M* HNO_3	1.1	3.7_5	9.0
13*M* HNO_3	1.5	10.4	13.5
16*M* HNO_3	4.0	30.0	54.8
7*M* H_2SO_4	0.4	0.3	0.4
10*M* H_2SO_4	1.5	3.0	4.0
15*M* H_2SO_4	4.2	7.0	8.1
20*M* H_2SO_4	6.0	9.0	18.0
25*M* H_2SO_4	8.0	24.0	54.8
30*M* H_2SO_4	—	dissolved completely	
0.1*M* NaOH	1.5	3.0	6.7
0.5*M* NaOH	3.6	4.4	27.4
1.0*M* NaOH	8.0	30.0	57.3

Table 1(*b*). Chemical stability of Cr(III) arsenophosphate

Solution	Cr(III) dissolved, *mg*	As(V) dissolved, *mg*	PO_4^{3-} dissolved, *mg*
2.5*M* HCl	0.1	0.1_5	0.3
3*M* HCl	0.1	0.2	0.5
5*M* HCl	3.0	3.0	7.7
7*M* HCl	dissolved appreciably		
10*M* HCl	dissolved completely		
3*M* HNO_3	0.1_5	0.2	0.5
5*M* HNO_3	1.1_5	1.5	4.0
7*M* HNO_3	7.0	7.4	18.0
10*M* HNO_3	11.7	10.6	27.0
13*M* HNO_3	dissolved appreciably		
16*M* HNO_3	dissolved completely		
2*M* H_2SO_4	0.0_5	0.1	—
3*M* H_2SO_4	0.2	0.3	0.5
5*M* H_2SO_4	0.4	0.6	1.8
7*M* H_2SO_4	1.4	2.2	4.7
10*M* H_2SO_4	6.0	6.0	13.5
15*M* H_2SO_4	8.2	9.0	16.0
20*M* H_2SO_4	18.4	20.4	54.0
25*M* H_2SO_4	dissolved appreciably		
0.01*M* NaOH	—	1.1	—
0.1*M* NaOH	1.0	3.0	5.3
0.5*M* NaOH	14.0	21.0	12.0
1*M* NaOH	dissolved appreciably		

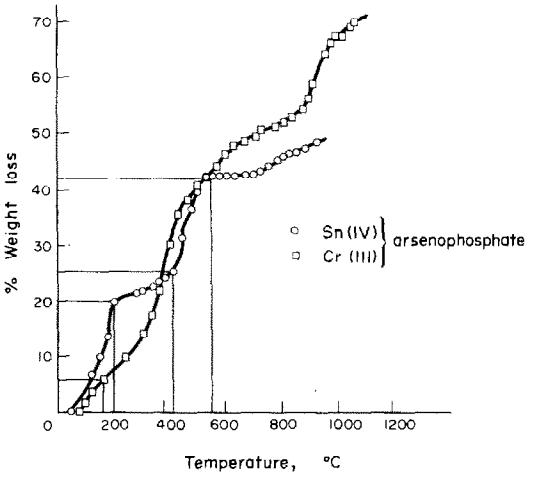


Fig. 1. TGA curves for Sn(IV) and Cr(III) arsenophosphates in the H^+ form.

Table 2. K_d values of metal ions on Sn(IV) and Cr(III) arsenophosphates at pH 2

Metal ion	K_d values, *ml/g**	
	on Sn(IV) arsenophosphate	on Cr(III) arsenophosphate
Na^+	385.0	298.0
K^+	C.A.	C.A.
UO_2^{2+}	7.1	C.A.
Zr^{4+}	C.A.	C.A.
Th^{4+}	C.A.	C.A.
Ag^+	87.4	99.2
Hg^{2+}	2.3	6.2
Zn^{2+}	351.0	19.6
Rb^+	267.0	31.8
Cs^+	119.0	8.6
Sr^{2+}	16.0	0.3
Co^{2+}	47.8	2.4
Mn^{2+}	78.5	32.1
In^{3+}	30.2	94.2
Y^{3+}	288.0	6.4
Tb^{3+}	20.0	0.2

* C.A. = Complete adsorption.

Table 3. K_d values of Na^+ and K^+ in water and mineral acids

Solvent	K_d values, *ml/g**			
	On Sn(IV) arsenophosphate		On Cr(III) arsenophosphate	
	Na^+	K^+	Na^+	K^+
Water	8.65×10^3	C.A.	2.85×10^3	C.A.
0.01*M* HCl	523.0	C.A.	65.0	C.A.
0.1*M* HCl	234.0	8.65×10^3	57.4	C.A.
1.0*M* HCl	85.9	312.0	37.0	C.A.
0·01*M* H_2SO_4	240.0	C.A.	2.12×10^3	C.A.
0.1*M* H_2SO_4	298.0	C.A.	1.04×10^3	C.A.
1.0*M* H_2SO_4	185.0	8.65×10^3	79.8	C.A.
0.01*M* HNO_3	240.0	C.A.	1.68×10^3	C.A.
0.1*M* HNO_3	186.0	8.65×10^3	619.0	C.A.
1.0*M* HNO_3	85.9	C.A.	571.0	C.A.

* C.A. = Complete adsorption.

amounts of Na^+ and K^+ in the solution before and after equilibrium were determined by flame photometry. Determinations were also made in hydrochloric, sulphuric and nitric acids (Table 3).

The K_d values of UO_2^{2+} were determined spectrophotometrically with hydrogen peroxide as the colorimetric reagent.[7] Th^{4+} and Zr^{4+} were determined by EDTA titration.

Distribution coefficients of Ag^+, Hg^{2+}, Zn^{2+}, Rb^+, Ca^+, Sr^{2+}, Co^{2+}, Mn^{2+}, In^{3+}, Y^{3+} and Tb^{3+}. The K_d values of these metal ions were obtained by using radioactive tracers. The solutions were prepared in demineralized water and the pH was adjusted to 2 with perchloric acid. The amount of exchanger taken was 100 mg and 10 ml of $10^{-4}M$ solution were loaded on the material. The equilibrium was attained by keeping the material in the solution overnight at room temperature with occasional shaking. The activity of the solution was measured with a G.M. counter or a scintillation counter.

The formula used for the calculation of K_d values was

$$K_d = \frac{I-F}{F} \times \frac{V}{A} \text{ (ml/g)}$$

where I is the initial concentration of the ion in solution, F is the final concentration of the ion in solution, V is the volume of solution and A the weight of the ion-exchanger.

Separations achieved

The columns were prepared from 0.5 g of the material (200–400 mesh) in a microburette. The metal solutions were then loaded separately and eluted with a suitable solvent. The elution curves were obtained by plotting the weight of metal in the eluate against volume. On the basis of the elution curves, separations of UO_2^{2+}–Zr^{4+}, UO_2^{2+}–Th^{4+} and Na^+–K^+ were attempted. Uranium was completely eluted with demineralized water, and zirconium and thorium were eluted with 1*M* nitric acid. For separating Na^+ from K^+, different concentrations of perchloric acid were used. Na^+ was first eluted with $10^{-3}M$ perchloric acid and K^+ with 0.1*M* perchloric acid. Figures 2 and 3 summarize these separations.

DISCUSSION

It is clear from Table 1 that the materials obtained by mixing arsenates and phosphates with Sn(IV) and Cr(III) are acid-resistant. Hydrochloric, sulphuric and nitric acids at concentrations up to 4*M* have no effect even after 24 hr contact at room temperature. Higher concentrations have an appreciable effect, nitric acid being the least and hydrochloric acid the most effective solvent. Sodium hydroxide also dissolves the samples, forming arsenate and phosphate. In this respect these materials are superior to the analogous single salts such as chromium(III) phosphate,[8] tin(IV) phosphate,[9] chromium(III) arsenate[10,11] and tin(IV) arsenate.[12]

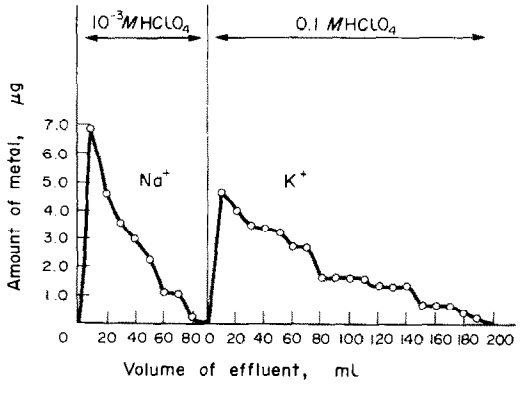


Fig. 2(*a*). Separation of sodium from potassium on Sn(IV) arsenophosphate.

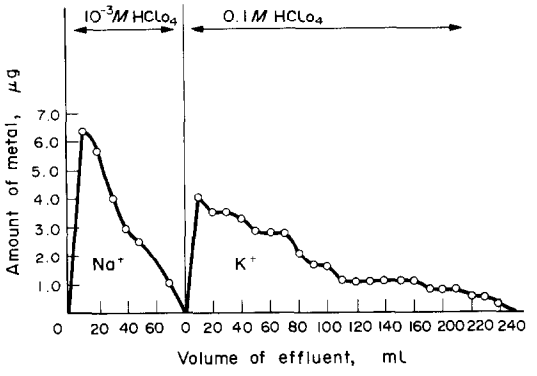
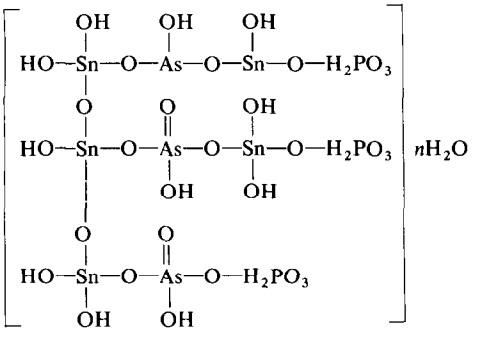


Fig. 2(*b*). Separation of sodium from potassium on Cr(III) arsenophosphate.

Earlier studies[2] gave the ratio of Sn(IV), As and P as 5:3:3 in tin(IV) arsenophosphate. The following formula for this compound can, therefore, be tentatively suggested,

$$[(SnO_2)_5 \cdot (H_3AsO_4)_3 \cdot (H_3PO_4)_3]nH_2O$$

and its structure written as



The number of external water molecules (n) can be estimated from the thermogravimetric study. From Fig. 1 it can be seen that tin(IV) arsenophosphate experiences a weight loss of 20% up to a temperature of 200°. If it is assumed that all the external water molecules are removed on heating to this temperature, then

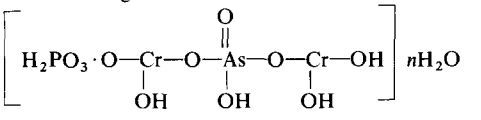
$$18n = \frac{x(M + 18n)}{100}$$

where x is % weight loss at 200°, $M + 18n$ is the molecular weight of the material and n the number of external water molecules. This gives the value of n as ~20.

Similarly the formula for chromium(III) arsenophosphate, based on its composition,[2] can be written as

$$[Cr_2O_3 \cdot H_3AsO_4 \cdot H_3PO_4]nH_2O$$

with the following structure



The number of external water molecules is found to be ~2.

The thermogravimetric curves for these two salts in the H^+ form have some interesting features. The total weight loss is much higher for chromium(III) arsenophosphate than for tin(IV) arsenophosphate. The condensation of the molecule of the tin(IV) salt starts above 400° and is complete at 550°. Chromium(III) arsenophosphate, on the other hand, continues to lose weight up to a temperature of 1100°.

Distribution studies of metal ions on these ion-exchange materials were made at pH 2. It was observed that these

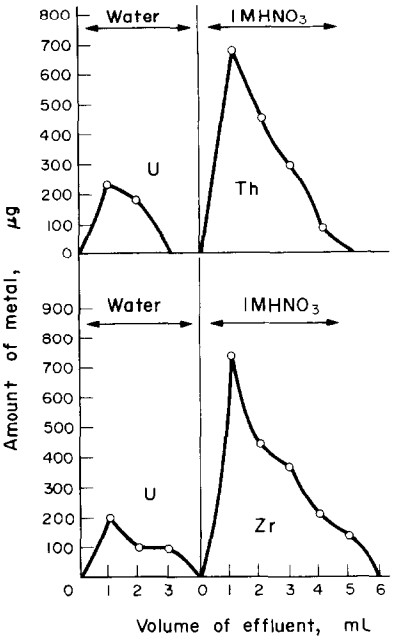


Fig. 3. Separation of uranium from zirconium and thorium from uranium on Sn(IV) arsenophosphate.

arsenophosphates are highly selective for K^+, Zr^{4+} and Th^{4+}. The behaviour of UO_2^{2+} is unusual, however, its adsorption being negligible on tin(IV) arsenophosphate but complete on the chromium(III) salt. UO_2^{2+} has therefore been separated from Zr^{4+} or Th^{4+} on tin(IV) arsenophosphate (Fig. 3). Na^+ has been separated from K^+ on both materials since they have a very wide difference in their selectivities for these two ions. As shown in Table 3 the K_d values of Na^+ and K^+ were also determined in water and in different concentrations of hydrochloric, sulphuric and nitric acids on both ion-exchangers. It is interesting to note that K^+ is completely adsorbed on chromium(III) arsenophosphate in all solvent systems. On the tin(IV) salt also, this metal ion tends to be strongly adsorbed except in 1.0M hydrochloric acid, in which it has a low K_d value.

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REFERENCES

1. V. Pekárek and V. Veselý, *Talanta*, 1972, **19**, 1245.
2. K. G. Varshney and A. A. Khan, *J. Inorg. Nucl. Chem.*, in the press.
3. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., p. 864. Interscience, New York, 1959.
4. *Idem, ibid.*, p. 396.
5. *Idem, ibid.*, p. 282.
6. S. R. Olsen, C. V. Cole, F. S. Watanake and L. A. Dean, *U.S. Dept. Agric. Circ.*, No. 939, 1954, 99.
7. E. B. Sandell, *Colorimetric Determinations of Traces of Metals*, 3rd Ed., p. 916. Interscience, New York, 1959.
8. D. Betteridge and G. W. Stradling, *J. Inorg. Nucl. Chem.*, 1967, **24**, 2652.
9. Y. Inoue, *ibid.*, 1969, **26**, 2241.
10. G. M. Lukaszewski and J. P. Redfern, *J. Chem. Soc.*, 1962, 4802.
11. G. M. Lukaszewski, J. P. Redfern and J. E. Salmon, *ibid.*, 1961, 39.
12. M. Qureshi, H. S. Rathore and R. Kumar, *ibid.*, 1970, 1986.

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USE OF CHROMIUM FERROCYANIDE MEMBRANE ELECTRODE IN THE POTENTIOMETRIC TITRATION OF FERROCYANIDE WITH METAL IONS

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Summary—Membranes based on the inorganic ion-exchanger chromium ferrocyanide have been prepared, which exhibit linear response to ferrocyanide over the concentration range 10^{-1}–$10^{-4}M$. Although the electrode is not very specific for ferrocyanide, it can be used for potentiometric titration of metal ions with ferrocyanide ion or *vice versa*. Hg^{2+}, Th^{4+}, UO_2^{2+}, Pb^{2+}, Cu^{2+} and Zn^{2+} have been determined in this way.

The hexacyanoferrate(II) ion yields stable compounds with many cations. Interest in these arises from their use in quantitative analysis.[1] The chemical composition of the compounds depends on the nature of the metal ion. Bellomo *et al.*[2–4] have used potentiometric methods to study the formation and composition of the ferrocyanide compounds of Cu(II), Zn(II), Ni(II), Co(II) *etc.* In this communication we demonstrate the use of the chromium ferrocyanide membrane electrode in studying the reactions between ferrocyanide and a number of metal ions.

EXPERIMENTAL

Reagents

All the reagents used were of analytical reagent grade. Solutions were prepared in doubly distilled water. Solutions of different concentrations were made by diluting 0.1*M* stock solutions. Solution of potassium ferrocyanide was prepared fresh every day.

Preparation of chromium ferrocyanide

The ion-exchanger material, chromium ferrocyanide, $K_6Cr_2[Fe(CN)_6]_3 \cdot 16H_2O$, was prepared as already reported,[5] by gradually adding chromium chloride solution to potassium ferrocyanide solution in presence of hydrochloric acid at 80°. The final concentrations in the mixture were 0.071*M*, 0.218*M* and 0.01*M* for $CrCl_3$, $K_4Fe(CN)_6$ and HCl respectively. The gel formed after about 5 hr was separated, washed with distilled water and dried at 90°.

Preparation of membranes

The membranes were prepared by mixing 0.3 g of "Araldite" with 0.7 g of chromium ferrocyanide powder, and the mixture was spread thinly on a piece of filter paper and left to dry in air. The hardened membrane was cut into a circular disc of 2.5 cm diameter. The thickness of the membrane was 0.89 mm. The membranes so prepared were then equilibrated with potassium ferrocyanide solution (0.1*M*) for 15 days. If equilibrated for a shorter time the membrane did not attain a steady potential and a drift in potential occurred with time.

Potential measurements

The equilibrated membrane was washed with water several times and dried with filter paper. The membrane was cemented to one end of a "Pyrex" glass tube with "Araldite". The tube was placed in a 50-ml beaker containing potassium ferrocyanide solution of various concentrations. The tube contained 0.1*M* potassium ferrocyanide as internal solution. Saturated calomel electrodes with a potassium chloride salt bridge were employed as reference electrodes. The emf of the resulting cell

Internal reference electrode	Internal 0.1*M* $K_4Fe(CN)_6$ solution	Membrane	External $K_4Fe(CN)_6$ solutions	External reference electrode

was measured on a Cambridge portable potentiometer in conjunction with a sensitive suspended-coil galvanometer.

Titrations were done by taking 20 ml of potassium ferrocyanide solution in a beaker and adding standard metal ion solution from a burette, or *vice versa*. After each addition the emf was measured when a steady state was reached. All the measurements were made at a constant temperature of 35 ±0.5°.

RESULTS AND DISCUSSION

Preliminary investigations showed that the membranes equilibrated with chromic nitrate solution gave a linear relation of potential-response to chromium(III) concentration with a slope of 50 mV/decade. However, when the membranes were equilibrated with potassium or sodium ferrocyanide, they exhibited a linear response to ferrocyanide concentration with a slope of 50 mV/decade (Fig. 1), the direction of potential change being opposite to that for Cr^{3+}, showing that this time the membrane was responding to the anion.[6] A steady emf was obtained in less than a minute and remained constant for about 1 hr; thereafter a drift of about 0.1 mV/min was observed. It is difficult to account for the high slope exhibited by the membrane. Other workers[7,8] have also observed high slopes for membrane electrodes. The mem-

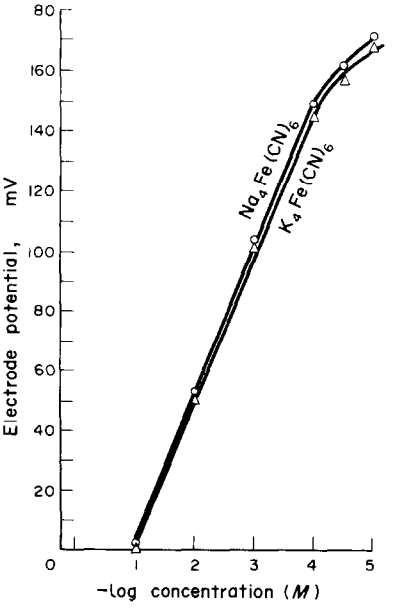


Fig. 1. Electrode potential *vs.* $\log[Fe(CN)_6^{4-}]$.

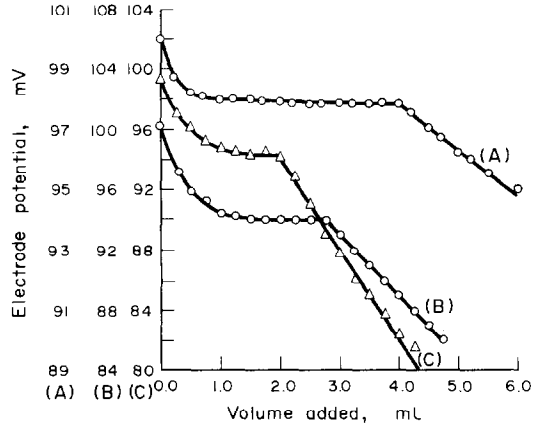


Fig. 2. Titration of 20 ml of $10^{-3}M$ potassium ferrocyanide with $10^{-2}M$ Hg^{2+}(A), UO_2^{2+}(B) and Th^{4+}(C).

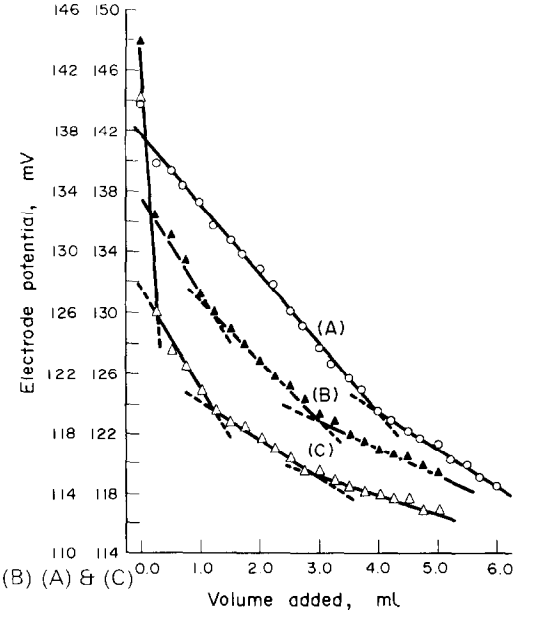


Fig. 3. Titration of 20 ml of $10^{-4}M$ potassium ferrocyanide with $10^{-3}M$ Pb^{2+}(A), Zn^{2+}(B) and Cu^{2+}(C).

brane potential has a standard deviation of 0.2 mV and the membrane gives reproducible electrochemical performance over a period of at least 6 months. Investigations of interference by cations and anions revealed that many of them cause considerable interference. The electrode is therefore not specific for ferrocyanide. However, in spite of this, the electrode can be used for determination of ferrocyanide in the range 10^{-1}–$10^{-5}M$ provided no interfering ions are present.

More important, perhaps, is the use of the electrode for the titration of ferrocyanide with a number of metal cations and *vice versa*. Typical titration curves are given in Figs. 2 and 3. These curves are not of classical shape, because the membrane electrode responds not only to the ferrocyanide but also to other ions added during the titration. However, the resulting interference is not so great that the equivalence point is completely masked. If the last break in the titration curves is taken as the stoichiometric end-point, the compositions of the various compounds formed are found to be $Hg_2Fe(CN)_6$, $ThFe(CN)_6$, $K_4(UO_2)_4[Fe(CN)_6]_3$, $K_2Zn_3[Fe(CN)_6]_2$, $K_2Cu_3[Fe(CN)_6]_2$ and $Pb_2Fe(CN)_6$, in agreement with those already reported by other workers.[3,4]

The electrode can also be used for the reverse titrations

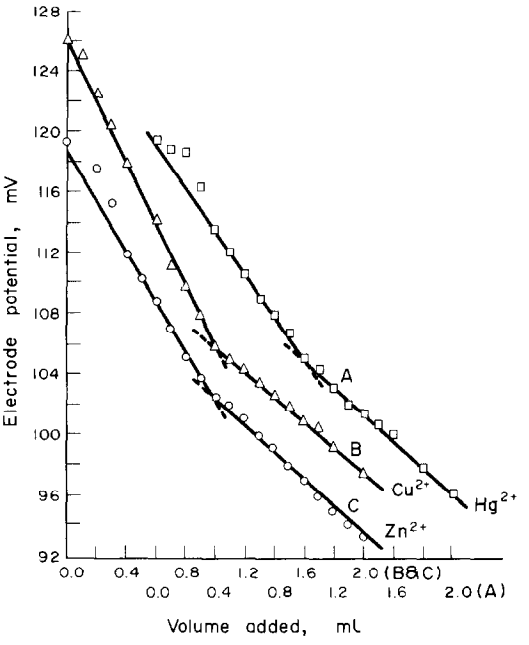


Fig. 4. Titration of 20 ml of $10^{-3}M$ Hg^{2+}(A), Cu^{2+}(B) and Zn^{2+}(C) with $10^{-2}M$ potassium ferrocyanide.

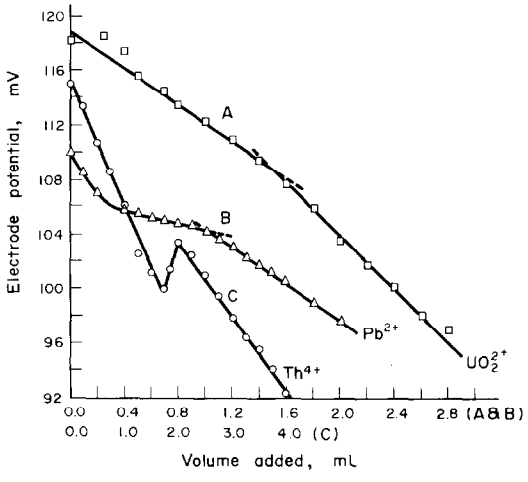


Fig. 5. Titration of 20 ml of $10^{-3}M$ UO_2^{2+}(A), Pb^{2+}(B) and Th^{4+}(C) with $10^{-2}M$ potassium ferrocyanide.

(Figs. 4 and 5). The plots show definite breaks corresponding to the formation of $Hg_2Fe(CN)_6$, $Zn_2Fe(CN)_6$, $Cu_2Fe(CN)_6$, $Pb_2Fe(CN)_6$ and $K_4(UO_2)_4[Fe(CN)_6]_3$, in agreement with the compositions reported by Bellomo *et al.*[3,4] It is thus seen that Zn^{2+} and Cu^{2+} form 2:1 ferrocyanides in the reverse titration whereas in the direct titration they form the 3:2 compound. It is well known that the stoichiometry of the metal–ferrocyanide reaction depends on how the reaction is carried out. In the case of thorium it was observed that the potential shoots up near the equivalence point. It is very difficult to explain this behaviour. However, if we take the second break-point as the equivalence point, the composition of the product comes out as $ThFe(CN)_6$, which is in agreement with Bellomo's results.[4]

Acknowledgement—Financial aid received from the University Grants Commission (New Delhi) is gratefully acknowledged.

REFERENCES

1. G. Jander and H. Wendt, *Lehrbuch der analytischen and präparativen anorganischen Chemie*, Hirzel Verlag, Stuttgart, 1959.
2. A. Bellomo, D. De Marco and A. Casale, *Talanta*, 1972, **19**, 1236.
3. A. Bellomo, *ibid.*, 1970, **17**, 1109.
4. A. Bellomo, D. De Marco, A. Casale, *ibid.*, 1975, **22**, 197.
5. W. U. Malik, S. K. Srivastava, V. M. Bhandari and S. Kumar, *J. Inorg. Nucl. Chem.*, 1976, **38**, 342.
6. G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes*, Merrow, Watford, England, 1971.
7. R. Jasinski, I. Trachtenberg and D. Andrychuk, *Anal. Chem.*, 1974, **46**, 364.
8. E. J. Hakoila, U. O. Lukkari, H. K. Lukkari and A. Takala, *Suom. Kemistilehti*, 1973, **46**, 359.

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DISULPHIDES OF DITHIOPHOSPHINIC ACIDS AS ANALYTICAL REAGENTS—I

EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH SOME BIS(DIALKYLTHIOPHOSPHORYL)- AND BIS(DIARYLTHIOPHOSPHORYL)DISULPHIDES

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(*Received* 24 *January* 1977. *Revised* 24 *January* 1978. *Accepted* 14 *March* 1978)

Summary—The disulphides of dithiophosphinic acids (DS) with the general formula $R_2P(S)SSP(S)R_2$, where $R = C_2H_5$, C_3H_7, C_5H_{11}, C_6H_5 (I–IV) form coloured complexes of 1:3 stoichiometry with Pd(II). The absorption maxima and molar absorptivities are: $\lambda_I = 302$ nm, $\varepsilon_I = 2.04 \times 10^4$ l.mole^{-1}.cm^{-1}; $\lambda_{II} = 305$ nm, $\varepsilon_{II} = 2.58 \times 10^4$; $\lambda_{III} = 303$ nm, $\varepsilon_{III} = 2.60 \times 10^4$; $\lambda_{IV} = 315$ nm, $\varepsilon_{IV} = 3.25 \times 10^4$. The reaction takes about 3 min at room temperature, and the colour is stable for 24 hr. The influence of time, pH, reagent concentration, organic solvents and interferences have been studied. An extractive photometric method of determination of Pd(II) is described and applied to the determination of Pd(II) in a mixture of platinum metals.

Methods based on the complexes of palladium with various organic sulphur-containing ligands, such as thioglycollic acid or alkyldithiophosphoric acids, are widely used in analysis.[1–3] Some disulphides, owing to their selectivity, are of considerable interest and dithiocarbamates,[4] alkyl dithiophosphinates[5] and dithiophosphates[6] have been investigated as reagents for palladium. The complexes of Pd(II) with some disulphides of dithiophosphinic acids are also of analytical importance. In this paper we report on reagents with the general formula $R_2P(S)SSP(S)R_2$, where $R = C_2H_5$, C_3H_7, C_5H_{11}, C_6H_5 (I–IV). The reagents have reasonable stability and can be easily obtained.

EXPERIMENTAL

Reagents

Standard Pd(II) solution. $PdCl_2$ was dissolved in 0.2*M* hydrochloric acid to give a palladium concentration of 0.1g/l. The solution was standardized gravimetrically,[7] and diluted appropriately to give a $5 \times 10^{-4}M$ solution.

Disulphides of the dithiophosphinic acids. The reagents **I–IV** were synthesized by standard methods and recrystallized from isopropyl alcohol.[8,9] Their purity was checked by thin-layer chromatography. The reagents were used as $5 \times 10^{-4}M$ solutions in 95% ethanol.

Buffers. A universal buffer was used, obtained by mixing 0.04*M* acetic, boric and phosphoric acids and 0.2*M* sodium hydroxide.

Dichloroethane. Purified by washing successively with sulphuric acid and potassium hydroxide solution, then dried with calcium chloride and distilled at 83.5°.

Other reagents were of analytical grade and not purified further.

Procedure

Add 4–5 ml of $5 \times 10^{-4}M$ solution of reagent (**I–IV**) to up to 5 ml of 1*M* sulphuric acid containing not more than 40 μg of Pd(II) and dilute to about 10 ml. After 5 min extract with three successive portions of dichloroethane (10, 6, 5 ml) for 2 min each time. Filter the organic phase through a filter paper impregnated with dichloroethane into a 25-ml standard flask and dilute to the mark with the solvent. Measure the absorbance against a reagent blank carried through the procedure.

RESULTS AND DISCUSSION

Absorption spectra

The absorption curves of the disulphides (**I–IV**) and their complexes with Pd(II) are presented in Fig. 1. The maxima for **I–IV** are at 302, 305, 303 and 315 nm respectively and the corresponding molar absorptivities of the palladium complexes are 2.04×10^4, 2.58×10^4, 2.60×10^4 and 3.25×10^4 l.mole^{-1}.cm^{-1}.

For further work the disulphide **IV** was chosen.

Effect of basic parameters

Chloroform, dichloroethane, tetrachloromethane, n-pentane, n-hexane, cyclohexane, benzole, when used as solvents, had no practical influence on the absorption maximum. The molar absorptivity was not affected by chloroform, dichloroethane and tetrachloromethane. Dichloroethane was used for further work.

The dependence of the absorbance of the extract on the acidity of the aqueous phase was studied for various acids (Figs. 2 and 3). The Pd(II) complexes were extracted completely from sulphuric, phosphoric, perchloric or acetic acid

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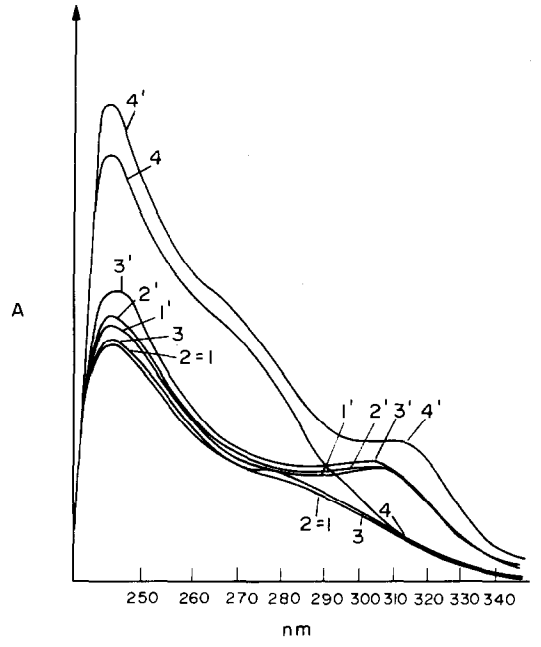


Fig. 1. Spectra of reagents **I–IV** (1, 2, 3, 4) and their complexes with Pd(II) (1′, 2′, 3′, 4′).

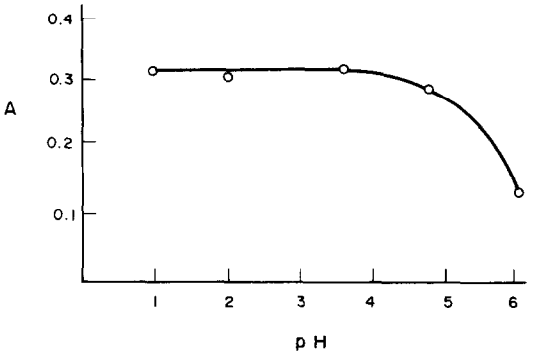


Fig. 2. Influence of acids on the absorbance of the Pd(II) complex [5 ml of $5 \times 10^{-4}M$ reagent **IV**; 0.8 ml of $5 \times 10^{-4}M$ Pd(II)].

Table 1. Effect of various elements on determination of 10 μg of palladium

Added		
Salt	Element, *mg*	Pd found, *μg*
H_2PtCl_6	1.0	9.8
$RuCl_3$	5.0	9.9
Na_2IrCl_6	15.0	10.2
$RhCl_3$	8.0	10.0
$Ni(NO_3)_2$	15.0	9.9
$CoSO_4$	5.0	9.8
$MnSO_4$	20.0	9.8
$Al(NO_3)_3$	8.0	10.0
$CuSO_4$	0.09	9.8
$CdSO_4$	10.0	9.9
Na_2MoO_4	20.0	10.1
$Bi(NO_3)_3$	0.4	10.3
$FeCl_3$	3.0	10.2
SeO_2	5.0	9.9
$MgSO_4$	30.0	10.0
$Pb(NO_3)_2$	5.0	9.8

over the acidity range 0.03–10*N* (Fig. 2) and the absorbance was constant over the pH range 0–4 (Fig. 3).

In order to obtain the maximum absorbance at least a 6-fold molar ratio of reagent to palladium is required. It is necessary to wait for about 5 min before the extraction for the complete interaction of Pd(II) with DS. The absorbance of the extract is stable for 24 hr.

It was found experimentally that the extraction was essentially complete in the first extraction with 10 ml of dichloroethane.

The amount of palladium left in the aqueous phase after the triple extraction is below the limit of detection by means of dimethylglyoxime.

Composition and stability of the complex

The composition of the complex was established by the method of isomolar series, Barbanel's method and the method of equilibrium displacement[10] and found to be Pd:DS = 1:3 (DS = disulphide). When the Pd:DS ratio is 1:1 a product is formed that floats at the interface. The values for the stability constant, determined by two independent methods,[10] were $\beta_3 = 1.4 \times 10^8$ and 3.0×10^8.

The absorbance of the dichloroethane extracts of the Pd(II) compound with **IV** obeyed Beer's law over the palladium range 4–30 μg. The error of the determination generally does not exceed 1%.

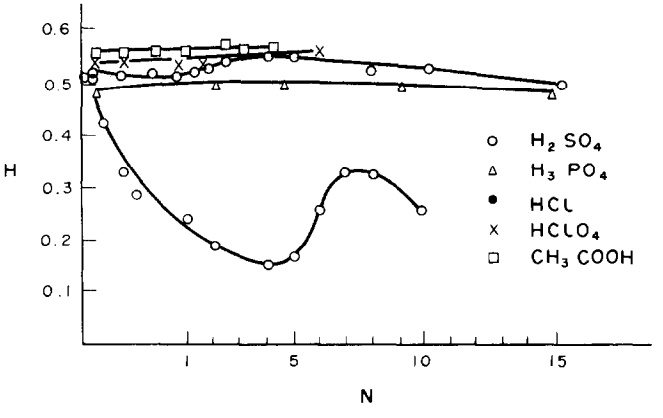


Fig. 3. Influence of pH on the absorbance of the Pd(II) complex of reagent **IV** (reagent concentrations as for Fig. 2).

Table 2. Determination of palladium in presence of Pd:Pt:Ir:Rh:Ru = 1:100:1500:800:500

Pd, μg	$\bar{x}$, μg	Std. devn., μg
10.0	10.0_2	0.08
20.0	20.5_3	0.10
30.0	29.7_6	0.14

The effect of interfering ions

The influence of some potentially interfering ions was investigated (Table 1). Considerable quantities of most platinum metals, Cr(III), Mo(VI), Zn(II), Cd(II), Ni(II), Al(III), NO_3^-, SO_4^{2-}, ClO_4^-, CH_3COOO^- and PO_4^{3-} can be tolerated, but Ag(I), Sb(III), Au(III) and osmium interfere severely and must be absent.

The method has been applied to the determination of Pd(II) in synthetic platinum metal alloys (Table 2).

REFERENCES

1. A. D. Perrin, *Organischeskie analiticheskie reagenty*, "Mir", Moscow, 1967.
2. A. I. Busev and M. I. Ivanyutin, *Organicheskie reagenty v analiticheskoi khimii*, Vol. 11, 1960.
3. *Idem, Zh. Analit. Khim.*, 1958, **13**, 1.
4. A. I. Busev, V. M. Byrko and A. I. Dikusar, *ibid.*, 1971, **26**, 1380.
5. L. A. Ilina and S. V. Larionov, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1968, 1895.
6. A. I. Busev, A. N. Shishkov and N. K. Nikolov, *Zh. Analit. Khim.*, 1975, **30**, 136.
7. G. Charlot, *Metody analiticheskoi khimii*, "Khimia", Moscow, 1960.
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BESTIMMUNG KLEINER NITRIT- UND NITRATKONZENTRATIONEN IN WÄSSRIGEN AMMONIAKLÖSUNGEN

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(*Eingegangen am* 16. *Dezember* 1977. *Angenommen am* 9. *März* 1978)

Zusammenfassung—Für die spektralphotometrische Bestimmung von Nitrit mit Procain im Konzentrationsbereich 10^{-6}–$10^{-2}M$, und von Nitrat mit Chromotropsäure im Konzentrationsbereich 10^{-5}–$10^{-2}M$ in 0.1–16M wäßrigen Ammoniaklösungen werden die optimalen Bedingungen ermittelt und beschrieben. Beide Bestimmungsmethoden wurden mittels Varianzanalyse statistisch überprüft. Die günstigsten Arbeitsvorschriften werden gegeben.

Im Zusammenhang mit Untersuchungen zur strahlenchemischen Oxydation von Ammoniak in wäßrigen Lösungen ergab sich die Notwendigkeit, Nitritgehalte im Konzentrationsbereich 10^{-6}–$10^{-2}M$ zu bestimmen. Daneben waren in den gleichen Lösungen Nitratgehalte im Konzentrationsbereich 10^{-5}–$10^{-2}M$ zu ermitteln, wobei die Nitratgehalte im Durchschnitt zehnmal kleiner als die Nitritgehalte waren.

Es mußten also Bestimmungsverfahren angewendet werden, bei denen keine Beeinflussungen durch die nebeneinander anwesenden Nitrit-bzw. Nitrationen und außerdem durch die gleichzeitig vorhandenen, zum Teil recht hohen Ammoniumionen-bzw. die entstehenden Ammoniumacetatkonzentrationen auftraten. Für diesen Zweck wurden die photometrische Methode der Nitritbestimmung von Jendrassik und Falcsik-Szabó[1] und die photometrische Methode der Nitratbestimmung von West *et al.*[2–4] überarbeitet, korrigiert und vertieft.

*Die Ergebnisse sind ein Teil der Dissertation von Klaus Röhl, Bergakademie Freiberg, DDR, 1977.

EXPERIMENTELLER TEIL

Geräte

Spektralphotometer VSU 1 mit Sekundärelektronenvervielfacher und Skalengalvanometer (VEB Carl Zeiss Jena) bzw. registrierendes Spektralphotometer Specord (VEB Carl Zeiss Jena).

Chemikalien

Procain (*p*-Aminobenzoesäure-β-diäthylaminoäthylesterhydrochlorid) DAB 7. Chromotropsäure (1,8-Dihydroxynaphthalin-3,6-disulfosäure) sowie alle anderen Chemikalien, p.a., Wasser doppelt destilliert.

Nitritbestimmung mit Procain und α-Naphthylamin

Diese Methode basiert auf der Diazotierungsreaktion zwischen Nitrit und Procain und anschließender Kupplung mit α-Naphthylamin in essigsaurer Lösung zu einem roten Azofarbstoff, dessen Absorptionsspektrum ein Maximum bei 531 ± 2 nm aufweist. Beide Reaktionen, Diazotierung und Kupplung, unterliegen einem deutlichen pH-Wert-Einfluß,

Table 2. Determination of palladium in presence of Pd:Pt:Ir:Rh:Ru = 1:100:1500:800:500

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*Die Ergebnisse sind ein Teil der Dissertation von Klaus Röhl, Bergakademie Freiberg, DDR, 1977.

EXPERIMENTELLER TEIL

Geräte

Spektralphotometer VSU 1 mit Sekundärelektronenvervielfacher und Skalengalvanometer (VEB Carl Zeiss Jena) bzw. registrierendes Spektralphotometer Specord (VEB Carl Zeiss Jena).

Chemikalien

Procain (*p*-Aminobenzoesäure-β-diäthylaminoäthylesterhydrochlorid) DAB 7. Chromotropsäure (1,8-Dihydroxynaphthalin-3,6-disulfosäure) sowie alle anderen Chemikalien, p.a., Wasser doppelt destilliert.

Nitritbestimmung mit Procain und α-Naphthylamin

Diese Methode basiert auf der Diazotierungsreaktion zwischen Nitrit und Procain und anschließender Kupplung mit α-Naphthylamin in essigsaurer Lösung zu einem roten Azofarbstoff, dessen Absorptionsspektrum ein Maximum bei 531 ± 2 nm aufweist. Beide Reaktionen, Diazotierung und Kupplung, unterliegen einem deutlichen pH-Wert-Einfluß,

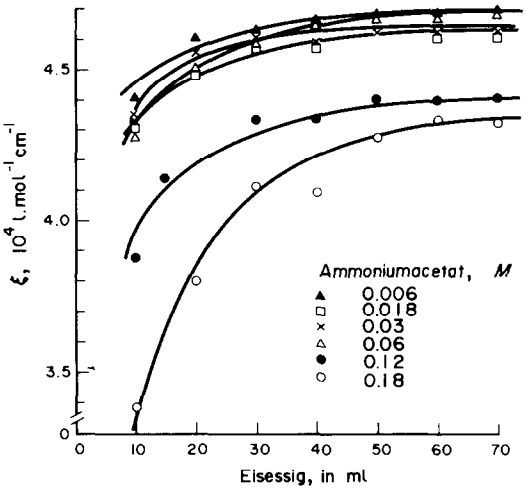


Abb. 1. Extinktionskoeffizienten ε der Nitritbestimmung in Abhängigkeit von der Eisessigmenge und der Ammoniumacetatkonzentration.

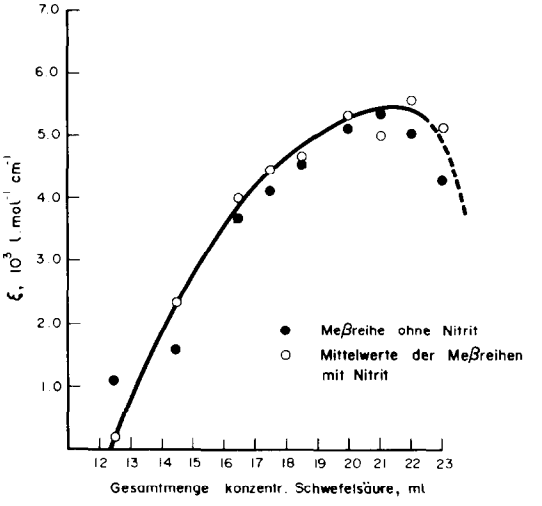


Abb. 3. Extinktionskoeffizienten ε der Nitratbestimmung in Abhängigkeit von der Gesamtschwefelsäuremenge der Farbansätze.

der durch das Entstehen von Ammoniumacetat beim Ansetzen der Bestimmungslösungen noch kompliziert wird.

Optimaler Eisessig- und Ammoniumacetatgehalt. Die Extinktionskoeffizienten steigen mit zunehmender Eisessigmenge an und streben oberhalb von 50 ml Eisessig im Ansatz bei allen angewandten Ammoniumacetatkonzentrationen einem Grenzwert zu (Abb. 1). Diese Grenzwerte erreichen unterhalb von 0,06*M* Ammoniumacetat einen gemeinsamen Streubereich. Folgerungen: die Bestimmungslösungen müssen mindestens 50 ml Eisessig auf 100 ml enthalten. Sie sollen einen Ammoniumacetatgehalt von 0,06*M* nicht übersteigen.

Standzeit. Aus der ermittelten Beziehung zwischen dem Extinktionskoeffizienten und der Standzeit der Meßansätze geht hervor, daß die Messungen zwischen einer Stunde und 24 Stunden durchgeführt werden müssen (Abb. 2).

Nitrat als Fremdstoff. Um die Beeinflussung der Extinktionskoeffizienten durch Nitrationen zu erfassen, wurden Eichmeßreihen mit Nitratzusatz und Meßreihen ohne solchen durchgeführt und in beiden Fällen Geraden mit gleichem Anstieg gefunden. Aus den Regressionskoeffizienten ließen sich mittels *F*-Test keine signifikanten Unterschiede feststellen. Nitrationen stören also nicht.

Extinktionskoeffizient. Zum Ermitteln des durchschnittlichen Extinktionskoeffizienten bei Meßproben mit unterschiedlichen Ammoniumacetatgehalt erfolgten Messungen an Lösungen mit 0,006, 0,018 und 0,06*M* Ammoniumacetat. Diese Gehalte lagen damit im schon erwähnten Streubereich der Extinktionskoeffizienten bezüglich der Ammoniumacetatkonzentration. Alle erhaltenen Extinktionen hingen linear von der Nitritkonzentration ab.

Aus allen Extinktionen dieser Meßreihe errechneten wir die Extinktionskoeffizienten. Die so erhaltenen Extinktionskoeffizienten wurden mittels Bartlett-Test und Varianzanalyse auf signifikante Unterschiede geprüft, wobei zwischen allen Messungen keine signifikanten Unterschiede gefunden wurden.

Auf Grund dieses Resultates faßten wir alle Messungen mit und ohne Ammoniumacetatgehalt, mit und ohne Nitratzusatz zusammen, prüften mittels Varianzanalyse und errechneten mit Hilfe der Regressionsrechnung den Extinktionskoeffizienten ε mit seiner Standardabweichung.

$$\varepsilon = (4{,}60 \pm 0{,}02) \cdot 10^4 \,\mathrm{l.mole^{-1}.cm^{-1}}$$

Arbeitsvorschrift. In einem 100-ml Maßkolben werden 5 ml Procainlösung (1,1*M*, ~ 300 g/l.) vorgelegt. Danach können

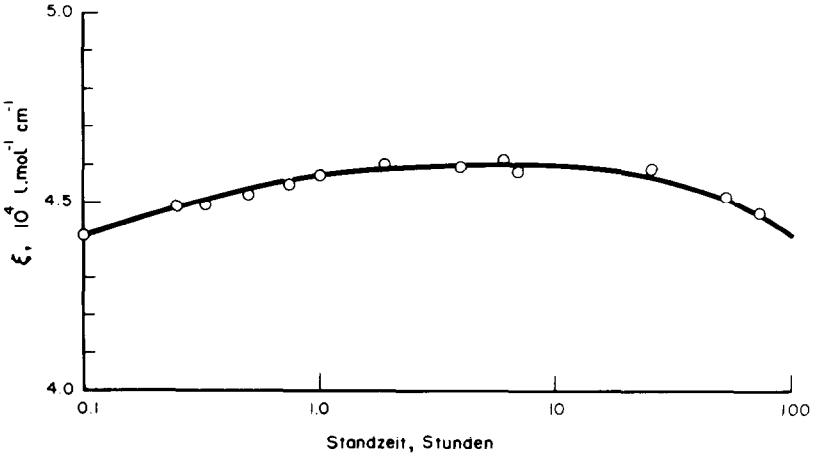


Abb. 2. Extinktionskoeffizient ε der Nitritbestimmung in Abhängigkeit von der Standzeit der Ansätze:— Ansätze ohne Ammoniumacetat.

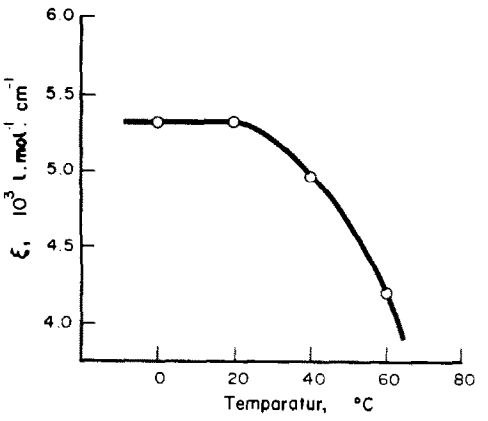


Abb. 4. Mittelwerte des Extinktionskoeffizienten ε der Nitratbestimmung in Abhängigkeit von der Temperatur der Farbansätze.

bis zu maximal 40 ml Probelösung hinzupipettiert werden. Das Volumen der Probelösung muß so bemessen werden, daß die Ammoniumacetatkonzentration 0,06*M* nicht überschreitet: die Lösung ist gegebenenfalls zu verdünnen. Zu diesem Gemisch gibt man in einem Guß 50 ml Eisessig (16,7*M*) und sofort darauf 5 ml α-Naphthylaminlösung (0,05*M*, ~7 g/l.). Die entstehende rote Lösung wird mit doppelt destilliertem Wasser zu 100 ml aufgefüllt. Die Vergleichslösung wird in analoger Weise, jedoch ohne Nitritgehalt, angesetzt. Nach etwa zweistündigem Stehen erfolgen die Extinktionsmessungen der Farbansätze bei 531 nm gegen die Vergleichslösungen. Sie müssen 24 Stunden nach dem Ansetzen abgeschlossen sein.

Um Meßfehler zu vermeiden, ist beim Ansetzen der Meßlösungen streng auf die angegebene Arbeitsweise, insbesondere auf die Reihenfolge der Zugaben zu achten. Bei Einhalten aller genannten Bedingungen treten keinerlei Farbstoffausflockungen auf, und man erhält gut reproduzierbare Ergebnisse.

Nitratbestimmung mit Chromotropsäure

Die Methode basiert auf der Nitrierungsreaktion von Chromotropsäure durch Nitrationen in konzentrierter Schwefelsäure in eine gelbe Nitroverbindung mit Absorptionsmaxima bei ~273 und ~415 nm. Ein Extinktionsmaximum bei 357 nm, wie von West und Lyles angegeben,[3] konnten wir nicht ermitteln. Als Meßwellenlänge wurden 415 nm gewählt, da bei 273 nm noch Störungen durch Absorption nicht umgesetzter Chromotropsäure auftreten.

Optimaler Schwefelsäuregehalt. Aus der Beziehung von Extinktionskoeffizient und Gesamtmenge an konzentrierter Schwefelsäure im Meßansatz von 25 ml werden 20 bis 22 ml als optimal gefunden (Abb. 3), was 8,0 bis 8,8 ml pro 10 ml Ansatz entspricht. Die von West und Mitarbeitern angegebenen Schwefelsäuremengen ($\approx$ 17 bis 18 ml pro 25 ml) liegen noch im ansteigenden Bereich des Extinktionskoeffizienten.

Temperatur. Zur Ermittlung der Temperaturabhängigkeit des Verfahrens verblieben die Ansatzkolben 45 Minuten im Temperaturbad und wurden nach Abkühlung auf Zimmertemperatur mit konzentrierter Schwefelsäure versetzt. Aus der Beziehung Extinktionskoeffizient/Temperatur geht hervor (Abb. 4), daß im Eisbad gearbeitet werden sollte.

Standzeit. Die Ergebnisse der Beziehung zwischen Extinktionskoeffizient und Standzeit (Abb. 5) sagen aus, daß die Messung nicht über 3 Stunden dauern darf.

Ammoniumionen als Fremdstoff. Im untersuchten Konzentrationsbereich 0,1–16*M* an Ammoniumionen treten keine systematischen Veränderungen des Extinktionskoeffizienten auf.

Nitrit als Fremdstoff. In den von uns zu untersuchenden Lösungen waren die Nitritgehalte im Durchschnitt um das Zehnfache größer als die Nitratgehalte. Das Chromotropsäurereagenz liefert jedoch mit Nitriten ebenfalls ein gelbes Reaktionsprodukt, dessen Absorptionsmaximum dicht am Absorptionsmaximum der Nitratbestimmung liegt. Hinzu kommt, daß in saurer Lösung Nitrit durch Disproportionierung Nitrat liefert. Es müssen deshalb die Nitritionen vor der Nitratbestimmung entfernt werden. Harnstoff, Sulfanilsäure und Natriumazid sind für große Nitritüberschüsse ungeeignet, da keine vollständige Nitritzerstörung eintritt. Der Gebrauch von Amidosulfonsäure führt zum Erfolg.

Wir versetzten Nitratlösungen, die zusätzlich die zehnfach molare Menge Nitrit enthielten, stufenweise mit steigenden Mengen von Amidosulfonsäure. Nach Zusatz von 2*M* Schwefelsäure wurde in diesen Lösungen in normaler Arbeitsweise der Nitratgehalt bestimmt und der gefundene mit dem vorgegebenen Nitratgehalt verglichen. Der Vergleich erfolgte mit Hilfe der Mittelwerte der Extinktionskoeffizienten (Abb. 6). Entgegen dem aus der Reaktionsgleichung

$$HNO_2 + H_2NSO_3H \rightarrow N_2 + H_2O + H_2SO_4$$

folgenden Molverhältnis von 1 wird erst bei einem Molverhältnis von über 2 sichere Nitritzerstörung erreicht.

Extinktionskoeffizient. Ausgeführte Eichmeßreihen lieferten eine gute Linearität bei der Abhängigkeit der Extinktionen von der Konzentration im Bereich 0,0004–0,002*M* Nitrat.

Zum Ermitteln des durchschnittlichen Extinktionskoeffizienten der Nitratbestimmung faßten wir die erhaltenen Extinktionskoeffizienten aus den Eichmeßreihen, den Meßreihen zur Zeitabhängigkeit, aus denen zum Ammoniumioneinfluß und aus den Meßwerten zur Nitritzerstörung

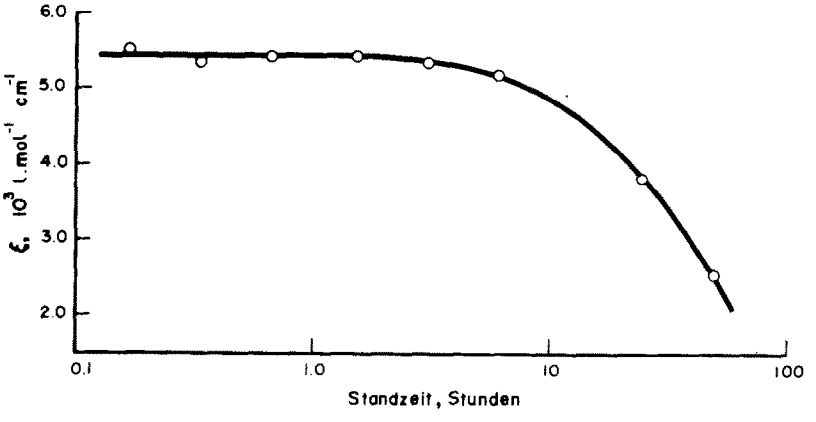


Abb. 5. Mittelwerte der Extinktionskoeffizienten ε der Nitratbestimmung in Abhängigkeit von der Standzeit der Farbansätze.

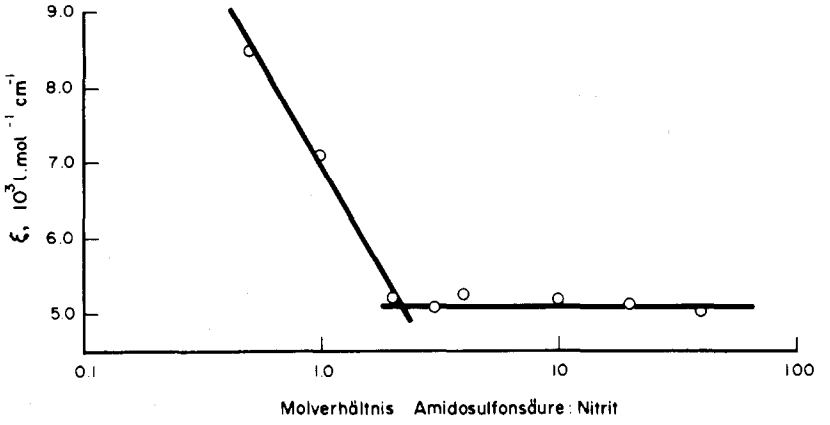


Abb. 6. Mittelwerte des Extinktionskoeffizienten ε der Nitratbestimmung in Abhängigkeit vom Molverhältnis Amidosulfonsäure zu Nitrit.

zusammen, prüften sie mittels Bartlett-Test und Varianzanalyse auf signifikante Unterschiede und errechneten den mittleren Extinktionskoeffizienten ε zusammen mit seiner Standardabweichung. Signifikante Unterschiede ließen sich nicht nachweisen.

$$\varepsilon = (5{,}3 \pm 0{,}4) \cdot 10^3 \,\mathrm{l.mole^{-1}.cm^{-1}}$$

Arbeitsvorschrift. In einem 25-ml Meßkolben werden 5,0 ml Probelösung mit 2,5 ml Chromotropsäurelösung ($3{,}12 \cdot 10^{-3}M$, ~0,1 g pro 100 ml konz. Schwefelsäure) versetzt und danach 17,5 ml konzentrierte Schwefelsäure zugegeben. Das Ansetzen erfolgt im Eisbad. Nach 45 Minuten werden die Ansatzkolben aus dem Eisbad entnommen und nach dem Erreichen von Zimmertemperatur mit konzentrierter Schwefelsäure aufgefüllt. Die Extinktionsmessungen müssen in einer Zeit von 3 Stunden nach dem Ansetzen erfolgen. Gemessen wird bei 415 nm gegen Vergleichslösung. Vorhandene störende Nitritgehalte werden in einem vorangestellten Ansatz durch Zugabe des fünf- bis zehnfachen Äquivalentes von Amidosulfonsäure gegenüber Nitrit zerstört. Hierzu soll die Lösung 1,5–2,0*M* an Schwefelsäure sein.

Durch die Wahl dieser Reaktionsbedingungen liegt der von uns angebene Extinktionskoeffizient etwa um das Fünffache höher als der aus den Messungen von West und Ramachandran[4] berechenbare Wert.

LITERATUR

1. L. Jendrassik und E. Falcsik-Szabó, *Biochem. Z.*, 1933, **261**, 110.
2. P. W. West und P. L. Sarma, *Mikrochim. Acta*, 1957, 506.
3. P. W. West und G. L. Lyles, *Anal. Chim. Acta*, 1960, **23**, 227.
4. P. W. West und T. P. Ramachandran, *ibid.*, 1966, **35**, 317.

Summary—The optimum conditions have been established for the spectrophotometric determination of nitrite with procaine and α-naphthylamine, for the range 10^{-6}–$10^{-2}M$, and of nitrate with chromotropic acid in the range 10^{-5}–$10^{-2}M$, both in aqueous solutions of ammonia at concentrations up to 16*M*. Both methods have been investigated and the results checked by statistical analysis. The procedures for the determinations are described.

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APPLICATION OF AN Al–Ti ALLOY TARGET IN SURFACE ANALYSIS BY X-RAY PHOTOELECTRON SPECTROSCOPY

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(*Received* 4 *April* 1978. *Accepted* 13 *April* 1978)

Summary—An X-ray target of an Al–Ti alloy was used in the determination of the composition of the surface layer (0–200 Å thick) of a Cu–Zn alloy.

The average composition of a surface layer thinner than 30 Å can be determined both by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). For example, the escape depth of Ga $3p_{3/2}$ and Se $3p_{3/2}$ photoelectrons through the lamellar structure of a GaSe semiconductor was estimated to be about 16 Å (9 atomic layers) from the average atomic ratio of Ga to Se of 0.74–0.80.

The escape depth of Ga $3d_{5/2}$ and Se $3d_{5/2}$ photoelectrons was about 20 Å (11 atomic layers) and this value corresponded to that calculated from the intensity ratio of the Ga 3*d* and Ga 2*d* lines.[1]

The surface composition of binary alloys and oxides[2–4] has been determined by means of XPS. On the other hand, the average composition at depths of over 200 Å can be determined by electron probe microanalysis, X-ray fluorescence analysis and chemical analysis. The surface composition of a layer 0–200 Å in thickness, more particularly that between the depths of 30 and 200 Å, has not previously been determined non-destructively. Such layers can be analysed by XPS using a suitable X-ray target if high resolution is not required.

In this communication the results of the application of an Al–Ti alloy target in the surface analysis of Cu–Zn alloys by XPS are reported.

EXPERIMENTAL

The methods for XPS measurements have been described earlier.[1–4]

The Al–Ti alloy target was prepared by the evaporation of Al–Ti alloy (80–20 w/w) on the target-substrate of an AEI ES-200 spectrometer. The excitation conditions were 12 kV and 25 mA. The kinetic energy of the ejected photoelectrons was below 4.5 keV (Ti $K\alpha$). The sample used was a Cu–Zn alloy (60–40 w/w).

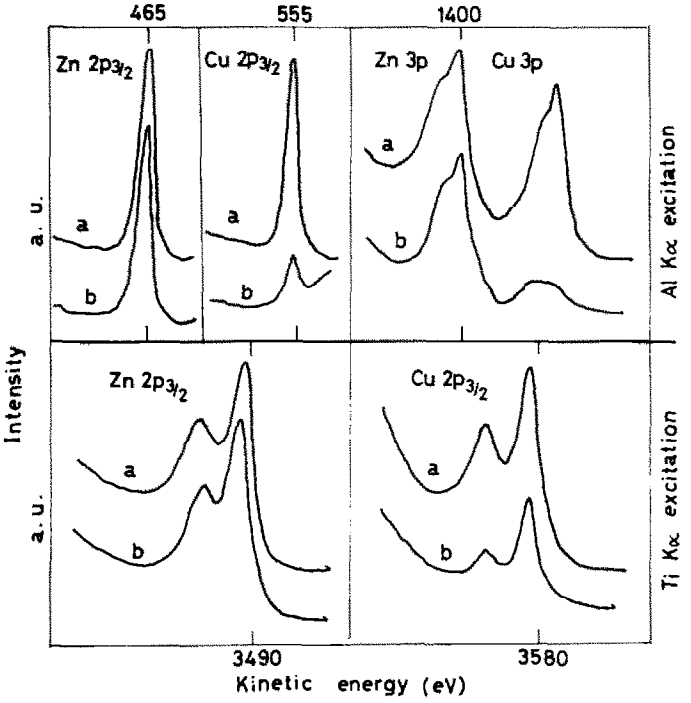


Fig. 1. Examples of X-ray photoelectron spectra from a Cu–Zn alloy (Al–Ti target): *a*, filed; *b*, heated in air at 400° for 1 sec.

Table 1. Intensity ratios of Cu to Zn after various treatments

Treatment	Spectral line pair intensity ratio $\frac{Cu\ 2p_{3/2}}{Zn\ 2p_{3/2}}$ Al K_α*	$\frac{Cu\ 2p_{3/2}}{Zn\ 2p_{3/2}}$ Ti K_α†	$\frac{Cu\ 3p}{Zn\ 3p}$ Al K_α‡
Filed	1.03	1.07	0.96
Dipped in 3*M* HNO_3 at 80° for 10 min	2.78	2.04	1.67
Dipped in 3*M* HNO_3 at 80° for 30 min	1.28	4.02	3.27
Dipped in 3*M* HNO_3 at 70° for 30 min	3.28	3.77	7.43
Heated in air at 400° for 1 sec	0.02	0.20	*ca.* 0.1
Heated in air at 400° for 5 sec	0.0	0.05	0.0

* Kinetic energy: *ca.* 500 eV, escape depth *ca.* 10Å.
† Kinetic energy: *ca.* 3500 eV, escape depth *ca.* 50Å.
‡ Kinetic energy: *ca.* 1400 eV, escape depth *ca.* 20Å.

RESULTS AND DISCUSSION

Examples of X-ray photoelectron spectra of a Cu–Zn alloy obtained by using an Al–Ti alloy target are shown in Fig. 1, curves *a* being the spectra before heating and curves *b* those after heating for 1 sec at 400° in air. The intensity ratios of Cu $2p_{3/2}$ to Zn $2p_{3/2}$ and Cu $3p$ to Zn $3p$ given by Al K_α, and Cu $2p_{3/2}$ to Zn $2p_{3/2}$ given by Ti K_α radiation from the Cu–Zn alloy (after various treatments) are shown in Table 1. The escape depths of electrons in the Cu $2p$–Zn $2p$ and Cu $3p$ regions given by Al K_α and Ti K_α radiation are included in the Table. They were estimated from the so-called "universal curve".[5,6]

The atomic ratio Cu/Zn can be semi-quantitatively determined by multiplying Cu $2p$/Zn $2p$ by 0.79 and Cu $3p$/Zn $3p$ by 1.10 in the case of excitation with Al K_α.[1–4] However, the photoionization cross-section for Ti K_α line excitation has not been measured and the factor used to estimate the atomic ratio for Ti K_α excitation could not be calculated.

The results given in Table 1 indicate that zinc is enriched in the alloy surface (to a depth of 100 Å) by instantaneous heating in air. Copper was enriched (zinc was dissolved away) by treatment with acid solution.

It was recognized that the Al–Ti alloy target can be utilized to estimate the average composition of the 0–200 Å surface layer without the need for ion-milling by use of rare gases.

The high-energy excitation sources Si K_α, Ti K_α and Cr K_α have been reported[7,8] as excitation sources for Auger spectra of nitrogen, phosphorus and sulphur. These high-energy sources are also useful in X-ray photoelectron spectroscopy, for the study of surface layers in the depth range of 50–200 Å. With the combination of low-energy sources the composition at depths of 0–200 Å can be determined.

REFERENCES

1. K Hirokawa and M. Oku, *Z. Anal. Chem.*, 1977, **285**, 192.
2. K. Hirokawa, M. Oku and F. Honda, *ibid.*, 1977, **286**, 41.
3. *Idem, Bunseki Kagaku*, 1977, **26**, T-7.
4. K. Hirokawa and M. Oku, *ibid.*, 1978, **27**, T-5.
5. C. R. Brundle, *J. Vacuum Sci. Technol.*, 1974, **11**, 212.
6. D. R. Penn, *J. Electron Spectrosc.*, 1976, **9**, 29.
7. J. E. Castle, L. B. Hazell and R. D. Whitehead, *ibid.*, 1976, **9**, 247.
8. D. Briggs, *Proc. Anal. Div. Chem. Soc.*, 1977, **14**, 9.

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SERUM CALCIUM AND POTASSIUM DETERMINATION BY THE SPLIT MEMBRANE ION-SELECTIVE ELECTRODE TECHNIQUE

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Summary—Results are presented for the determination by differential potentiometry of calcium and potassium in human and sheep sera, by use of a flow-through cell. The split-membrane ion-selective electrode technique has been used in conjunction with polymer membrane electrodes of the coated-wire type and the type containing an aqueous inner reference solution. The electroactive reagent is di(n-octylphenyl)phosphoric acid for calcium and valinomycin for potassium.

We recently reported the development of calcium- and potassium-sensitive coated-wire ion-selective electrodes based on poly(vinyl chloride) membranes containing the reagents di(n-octylphenyl)phosphoric acid and valinomycin respectively.[1–3] In this paper we report the use of these membranes in both the coated-wire form and in a form with an inner aqueous reference system for the analysis of sheep and human blood serum in a split-membrane continuous-flow cell.

The split-membrane technique of Wawro and Rechnitz,[4] which in our case means the use of two identical membrane electrodes, has the advantage of allowing "double beam" measurements to be made by operating one membrane as a reference. This technique thus compensates for small potential changes associated with changes in the characteristics of the electrode, such as the aging of the membrane or the drift of the inner reference potential, which can be serious with some ion-selective electrodes, particularly coated-wire electrodes.

In a number of previous studies with flow-through electrodes for determination of ionized serum calcium the problem of potential drift was serious enough to require constant restandardization.[5,6]

The use of two high-impedance ion-selective electrodes in this way necessitates employing a fast-response differential voltage amplifier for the potential measurements and such an instrument has been described by Brand and Rechnitz[7,8] and has been constructed for the work presented in this paper.

EXPERIMENTAL

Membrane preparation

Di(n-octylphenyl)phosphoric acid was separated from commercial octylphenylphosphoric acid (70/30% mixture of the di- and mono-esters, Mobil Chemical Co.) by the procedure of Cattrall *et al.*[1] The calcium salt of the di-ester was also prepared according to these workers. Calcium-membrane solutions were obtained by dissolving poly(vinyl chloride), di(n-octylphenyl)phosphoric acid and its calcium salt, and di(2-ethylhexyl)-2-ethylhexylphosphonate (Mobil Chemical Co.) in the minimum amount of tetrahydrofuran. The proportions of the reagents used were such that the dry membranes contained about 30% w/w PVC and had a 10:1 w/w ratio of phosphonate to calcium acid salt. The calcium acid salt was obtained by mixing a 1:2 mole ratio of the calcium salt with the free acid.[1]

Potassium-membrane solutions were obtained according to Cattrall *et al.*[3] by dissolving valinomycin (Calbiochem), di-n-decyl phthalate (Pfaltz and Bauer) and poly(vinyl chloride) in the minimum amount of tetrahydrofuran so that the dry membranes contained about 70% w/w phthalate and 5% valinomycin.

These solutions were used to prepare electrodes of the coated-wire type[1] or to cast films for use with an internal aqueous reference system.[9]

The flow-through cell

A flow diagram of the apparatus is shown in Fig. 1. The flow-through cell consists of a Y-junction made by drilling 1-mm diameter holes for the inlet arms and a 1.5-mm hole for the outlet channel in a small "Perspex" block set into a larger "Perspex" box which can be kept at 37°. The two identical membrane electrodes fit into holes, R (reference) and I (indicator), in the Y-junction so that the membrane surfaces occupy the position of a missing wall in the appropriate inlet channel. The cell is operated with the arms of the Y-junction in the vertical plane and the solutions are continuously pumped (0.7–1.0 ml/min) through the cell from Venoject® tubes through a syringe needle by a variable-speed peristaltic pump (Gilson Model Minipuls II). Standardization was done by passing the middle standard solution through one arm of the cell and the three standards in turn through the sample arm. A calibration graph was constructed and used to determine the concentrations in the sample solutions. Restandardization was done after about 10 samples, to check the calibration graph. After each measurement the sample arm was flushed with distilled water containing 0.50% w/v of trypsin.

The dynamic response of the electrodes was rapid and good reproducibility on a day to day basis was obtained. Also the electrodes showed no protein-poisoning effect even after two weeks of operation.

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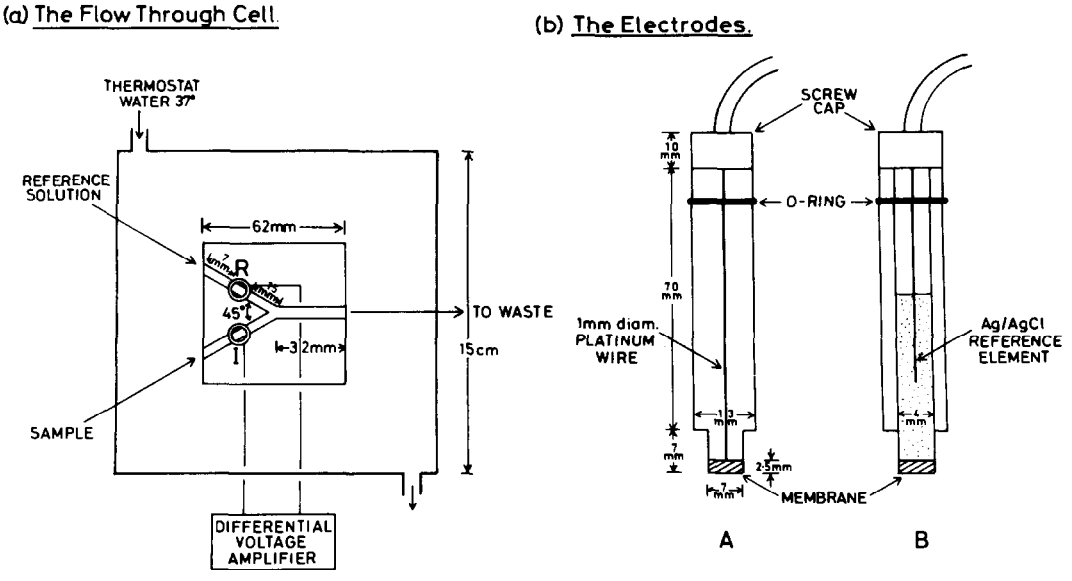


Fig. 1. The cell and electrodes.

It was found necessary to wrap the complete cell in aluminium foil which was grounded to reduce the effects of external fields.

The electrodes

The electrodes (Fig. 1) are constructed from "Perspex" rod drilled with a 1.2-mm hole for the platinum-wire type and a 4-mm hole for the type with an internal aqueous reference system. The electrodes are machined so that they give a very precise fit with the holes in the flow-through cell. With the platinum-wire electrode a cavity, 4 mm in diameter and 2.5 mm deep, is machined at the end of the electrode and the membrane is formed in this. A platinum wire is inserted in the electrode and protrudes into the cavity in order to give adhesion of the wire to the membrane. The membrane is formed by applying the membrane solution to this cavity, allowing the solvent to evaporate, and repeating the process until a film is obtained which is level with the end of the electrode body.

For the electrode with an internal aqueous reference system, the membrane is applied by standing the end of the electrode on a glass plate and inserting the required amount of membrane solution down the 4 mm hole and allowing the solvent to evaporate. In this case the film adheres quite strongly to the sides of the "Perspex" rod and gives a membrane which is flat and level with the end of the electrode body.

The electrodes are fitted with an O-ring to give a watertight seal with the thermostat jacket.

Standard solutions

Calcium. Three calcium standards (A, B and C) were prepared which were 0.141M in sodium chloride, 0.0041M in potassium chloride and 0.605, 1.21 and 2.42 $\times$ $10^{-3}M$ in calcium chloride respectively. These solutions were analysed for calcium, sodium and potassium by standard atomic-absorption spectroscopic and flame spectrophotometric techniques.

Potassium. Three standards that were 3.0, 5.0 and 7.5 $\times$ $10^{-3}M$ in potassium were obtained by addition of potassium chloride to pooled human plasma samples which were previously analysed for potassium by a standard flame-spectrophotometry technique.

Sample preparation

Calcium was analysed in both human and sheep serum. Whole blood was drawn into Venoject® tubes (Thermo Corporation, Tokyo, Japan) and after clotting, was centrifuged for 15 min. The serum was transferred into a second Venoject® tube through its rubber stopper and was frozen

Table 1. Determination of calcium in human and sheep sera

Sample		Ca^{2+}, $10^{-3}M$*	
Human	Sheep	Electrode type A	Electrode type B
1		1.24–1.32	1.19–1.24
2		1.55–1.60	1.52–1.60
3		1.28–1.30	1.30–1.36
4		1.86–1.90	2.08–2.12
5		1.10–1.25	1.12–1.14
6		1.21–1.25	1.09–1.13
7		1.95–2.10	1.94–2.00
8		1.51–1.67	1.46–1.64
9		1.00–1.10	1.00–1.03
10		0.88–1.08	0.97–1.01
11		1.02–1.04	0.87–0.90
12		0.79–1.01	0.79–0.91
13		0.96–1.20	1.13–1.15
14		0.98–1.07	1.00–1.02
15		1.18–1.20	1.27–1.29
16		1.20–1.26	1.28–1.34
	1	1.05–1.20	1.00–1.15
	2	1.36–1.40	1.17–1.20
	3	1.49–1.53	1.43–1.49
	4	1.20–1.26	1.13–1.16
	5	1.22–1.36†	1.23–1.37
	6	1.40–1.44	1.26–1.32
	7	1.21–1.25	1.11–1.17
	8	1.30–1.34	1.21–1.39
	9	1.15–1.19	0.90–1.18

* Range of four determinations.

† Range of three determinations.

Measurements with the two electrode types were made on separate days, and discrepancies due to changes in the sample cannot be eliminated.

Table 2. Potassium in human plasma or serum and Versatol standards

Sample	K^+, $10^{-3}M$* Electrode A	Flame photometry
1	3.40–3.50	4.19–4.21
2	3.90–3.92	3.98–4.02
3	4.26–4.34	4.58–4.62
4	3.68–3.82	3.96–4.04
5	3.10, 3.30†	3.87–3.93
6	4.20, 4.40†	4.39–4.41
7	4.20–4.40§	4.67–4.73
8	3.50–3.60	3.88–3.98
9	4.00–4.20	4.19–4.21
10	4.00–4.20	4.09–4.11
11	3.90–4.10	4.38–4.44
Versatol-Normal	4.60–4.80§ (5.00)‡	4.98–5.02
Versatol-Alternative	6.80–7.10 (7.30)‡	7.18–7.22
Versatol-A-Alternative	3.00, 3.10† (3.10)‡	3.17–3.23

* Range of four determinations.
† Two determinations.
§ Range of three determinations.
‡ Certified value.

when not required immediately. For potassium determination, samples of plasma and serum were used indiscriminately without great care to retain anaerobic conditions. Versatol standards (General Diagnostics Division, Warner-Chilcott Labs., Morris Plains, N.J.) were also analysed for potassium.

RESULTS

The results for ionized calcium in a large number of samples of human and sheep sera are shown in Table 1 for both electrodes. There is generally good agreement and little difference in the precision. In fact, the precision is generally the same as obtained in previous studies[5,6,10] but without the need for continuous restandardization. To test further the response of the electrode system to changes in the ionized calcium level a sheep was infused intravenously with a solution containing 4.4% EDTA (disodium salt) and 0.9% sodium chloride. The infusion rate was approximately 100 ml/hr, and blood samples were taken at 20-min intervals during the infusion and also before it. The results clearly show the expected decrease in the ionized calcium level. The results for potassium in a number of human plasma or serum samples and for the Versatol standards are shown in Table 2 and compared with the results obtained by flame spectrophotometry. The results are in fairly good agreement, but the precision of the flame photometric technique is generally better. In both Tables 1 and 2 the results refer to determinations made on separate days for the comparison of methods, and the possibility of discrepancy caused by changes in the sample cannot be eliminated.

In summary the results show that the split-membrane technique in conjunction with the technique of differential potentiometry yields a promising procedure for the determination of serum potassium and calcium with the electrodes described.

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REFERENCES

1. R. W. Cattrall, D. M. Drew and I. C. Hamilton, *Anal. Chim. Acta*, 1975, **76**, 269.
2. R. W. Cattrall and D. M. Drew, *ibid.*, 1975, **77**, 269.
3. R. W. Cattrall, S. Tribuzio and H. Freiser, *Anal. Chem.*, 1974, **46**, 2223.
4. R. Wawro and G. A. Rechnitz, *ibid.*, 1974, **46**, 806.
5. J. H. Ladenson and G. N. Bowers, Jr., *Clin. Chem.*, 1973, **19**, 565.
6. V. L. Subryan, M. M. Popovtzer, S. D. Parks and E. D. Reeve, *ibid.*, 1972, **18**, 1459.
7. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.* 1970, **42**, 616.
8. *Idem ibid.*, 1970, **42**, 1659.
9. G. J. Moody, R. B. Oke and J. D. R. Thomas, *Analyst*, 1970, **95**, 910.
10. T. K. Li and J. H. Piechocki, *Clin. Chem.*, 1971, **17**, 411.

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FUROIN THIOSEMICARBAZONE AS AN ANALYTICAL REAGENT FOR NICKEL(II), PALLADIUM(II) AND COPPER(II)

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Summary—Furoin thiosemicarbazone (FTS) reacts with Ni(II), Pd(II) and Cu(II) in aqueous medium, giving yellow solutions at pH 9, 6 and 3 respectively. The complexes have absorption maxima at 360 nm for Ni(II) and Pd(II) and 355 nm for Cu(II). At these wavelengths the reagent absorbance is negligible. The molar absorptivities are 1.54×10^4 [$Ni(FTS)_2$], 1.98×10^4 [$Pd(FTS)_2$] and 1.45×10^4 l.mole^{-1}.cm^{-1} (CuFTS). Beer's law is valid up to 4, 5 and 3 ppm for Ni, Pd and Cu respectively. The apparent instability constant of the Ni–FTS system is found to be 6.5×10^{-11}, of the Cu–FTS system 7.1×10^{-7} and of the Pd–FTS system 3×10^{-12} at the recommended pH values. The effect of various ions is reported.

Thiosemicarbazones of ketones and aldehydes form stable five-membered rings with many transition metals,[1] and several have been used as reagents for determination of copper, nickel and palladium,[2–8] but there is strong interference by ions commonly associated with copper and nickel. A common drawback of these reagents is that both they and their complexes absorb in the same region.

The analytical applications of furoin thiosemicarbazone (FTS) in the determination of copper, nickel and palladium are discussed in this paper.

EXPERIMENTAL

Reagents

FTS was synthesized from furoin by the general method of Martine *et al.*[9] and purified by crystallization from ethanol (m.p. 172 ± 2° uncorrected). Elemental analysis confirmed the formula to be $C_{11}H_{10}N_3SO_2$. The reagent was used as a 0.1% (0.004*M*) solution in methanol.

Stock solutions of Ni(II), Pd(II) and Cu(II) were prepared by dissolving the sulphates or chlorides in twice-distilled water and were standardized by well-known methods.[10]

Procedure

Take a portion of metal ion solution containing not more than 75 μg of the metal. Add 2 ml of 0.1% reagent solution, adjust the pH to the appropriate value with dilute hydrochloric acid or ammonia solution and dilute to volume with distilled water in a 25-ml standard flask. Measure the absorbance at the appropriate wavelength against a reagent blank prepared in the same manner. Prepare a calibration curve under identical conditions.

The nickel complex can be extracted into chloroform and measured at 410 nm; this serves for separation of nickel from copper.

Determination of nickel and copper in alloy steel

Dissolve a known weight, ~0.5 g, of steel in 50 ml of 12% sulphuric acid. Heat to dryness with 10 ml of conc. nitric acid, add 5 ml of conc. hydrochloric acid, and heat for 10 min and dilute accurately to 100 ml. Take a suitable aliquot of the solution. Remove the iron by extraction with isobutyl methyl ketone from 6*M* hydrochloric acid medium. Remove excess of the acid from the aqueous phase by evaporation. Determine nickel and copper by the procedure above.

Determination of palladium in palladized carbon

Palladium chloride–carbon catalyst was prepared by the standard method.[11] The palladium chloride was dissolved off with 6*M* hydrochloric acid and determined by the recommended procedure.

RESULTS AND DISCUSSION

Characteristics of the complexes

The absorption spectra are shown in Fig. 1. The absorbance at 360 nm for Ni(II) and Pd(II) and at 355 nm for Cu(II) is not affected by pH over the range 8.75–9.5 for Ni, 2–8 for Pd and 2.5–4.5 for Cu. The recommended pH values are therefore 9, 6 and 3 respectively.

It is found that 0.75 ml of 0.1% reagent solution is adequate for complete colour development with 2 ppm of Ni and 0.5 ml for 2 ppm of Pd or Cu. However, 100% excess is allowed for safety.

Complex formation takes place immediately after mixing of the reactants and the complex is stable for several hours. The order of mixing the reactants has no significant effect on the absorbance of the complex. Table 1 gives the important spectral parameters of the complexes.

The composition of the complexes was determined by Job's method.[13] The curves obtained indicated the formation of a 1:2 complex for nickel and palladium and a 1:1 complex for copper. The results of the mole-ratio method[14] were found to be in agreement with this.

The apparent instability constants were calculated according to Chawla and Singh,[15] and found to be

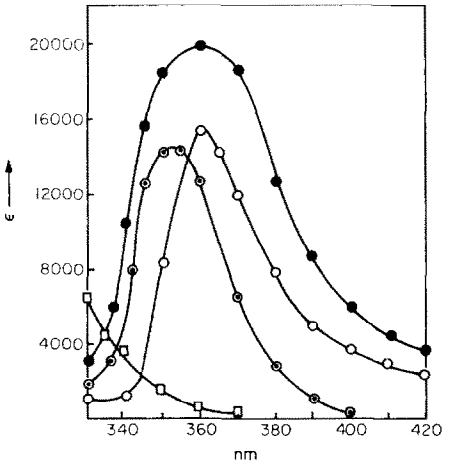


Fig. 1. Absorption spectra: ○ Ni(II), pH 9; ⊙ Cu(II), pH 3; ● Pd(II), pH 6; □ reagent.

Table 1. Photometric determination of Ni(II), Pd(II) and Cu(II) with FTS

Medium	Metal ion	λ_{max}, nm	pH	Range of Beer's law, ppm	Molar absorptivity, $l.mole^{-1}.cm^{-1}$	Optimum conc. range,[12] ppm
H_2O	Ni(II)	360	9	4.0	1.54×10^4	0.8 – 3.4
$CHCl_3$	Ni(II)	410	9	4.0	1.54×10^4	0.8 – 3.4
H_2O	Pd(II)	360	6	5.0	1.98×10^4	2.0 – 4.0
H_2O	Cu(II)	355	3	3.0	1.45×10^4	1.0 – 2.8

Table 2. Effect of diverse ions

Ion	Added as	Tolerance, ppm Ni($CHCl_3$)	Ni(aq)	Pd(aq)	Cu(aq)
V(V)	NH_4VO_3	200	200	*	*
Mo(VI)	$(NH_4)_6Mo_7O_{24}.4H_2O$	200	180	200	100
Ni(II)	$NiSO_4.7H_2O$	—	—	*	100
Ti(IV)	$TiCl_4$	200	120	ppt	ppt
U(VI)	$UO_2(NO_3)_2.6H_2O$	100	100	40	200
Co(II)	$CoSO_4.7H_2O$	200	*	§	‡
Cu(II)	$CuSO_4.5H_2O$	40	40	*	—
Fe(III)	$FeNH_4(SO_4)_2.12H_2O$	‡	‡	*	20
Mn(II)	$MnCl_2$	‡	‡	40	100
F^-	NH_4F	2000	2000	8000	1000
CN^-	KCN	*	*	*	*
EDTA	Na_2H_2Y	*	*	8000	*

* These ions interfere strongly.
† Prepared by standard procedure from potassium titanyl oxalate dihydrate.
‡ Interference due to these ions can be removed by masking with fluoride ion.
§ Interference can be removed by masking with EDTA.

6.5×10^{-11} for the nickel complex, 3.0×10^{-12} for the palladium complex and 7.1×10^{-7} for the copper complex at the recommended pH value.

Interferences

The solutions containing a fixed concentration (2 ppm) of the ion determined and various concentrations of other ions were prepared and the absorbances were measured. Table 2 gives the tolerance limits (*i.e.*, concentration causing 2% error). The amount of iron derived from steel samples is above the tolerance limit, and must be lowered by extraction.

Separation of Ni(II) from Cu(II)

The complex of Ni with FTS is extractable into chloroform; that of Cu is not. The absorptivity of the extracted nickel complex remains unchanged, but the absorption maximum is shifted to 410 nm. The Beer's law range and the composition of the complex are the same for the aqueous and organic systems. Hence nickel is separated from copper by extraction into chloroform at pH 9. Nickel is determined in the organic phase, and the aqueous phase is then heated to remove traces of chloroform, 2 ml of reagent are added to ensure complete complexation of copper, the pH is adjusted to 3 and the absorbance is measured at 355 nm. Typical results are given in Table 3. Analysis of a steel sample gave a mean value of 3.49% Ni (certificate value 3.58%) and 0.130% Cu (certificate value 0.123%). The standard deviations were 0.08% and 0.02% respectively (10 replicates). Analysis of two palladized charcoal samples gave 4.2 and 2.8% Pd (4.3 and 2.8% by the QDT method[16]).

Table 3. Determination of Ni(II) and Cu(II) in a synthetic mixture

Taken, ppm Ni	Cu	Found, ppm Ni	Cu
1.00	3.00	0.98	2.70
2.00	4.00	1.90	3.98
3.00	3.00	3.00	2.97

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REFERENCES

1. B. S. Garg, R. B. Singh and R. P. Singh, *Talanta*, in the press.
2. J. M. Canopavon, D. P. Bendito and F. Pino, *Anales Real. Soc. Espan. Fis. Quim. (Madrid) Ser. B*, 1969, **65**, 667.
3. J. M. Canopavon, A. J. Vazquez, D. P. Bendito and F. Pino, *Inform Quim. Anal. (Madrid)*, 1971, **25**, 149.
4. M. Valcarcel and D. P. Bendito, *ibid.*, 1970, **24**, 49.
5. M. Guzman, D. P. Bendito and F. Pino, *ibid.*, 1973, **27**, 209.
6. F. S. Burgos, M. P. Martinez and F. Pino, *ibid.*, 1969, **23**, 17.
7. J. M. Canopavon and F. Pino, *Anal. Letters*, 1974, **7**, 159.
8. F. E. Beamish, *Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1966.
9. M. P. Martinez, M. Valcarcel and F. Pino, *Anal. Chim. Acta*, 1976, **81**, 157.
10. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed, pp. 479, 511 and 323, Longman, London, 1968.
11. *Organic Syntheses*, Collective Vol. III, p. 686. Wiley, New York, 1962.
12. A. Ringbom, *Z. Anal. Chem.*, 1939, **115**, 332.
13. P. Job, *Ann. Chim. (Paris)*, 1928, **9**, 1113.
14. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
15. R. S. Chawla and R. P. Singh, *Microchim. Acta*, 1970, 332.
16. H. F. Janota and G. H. Ayres, *Anal. Chem.*, 1964, **36**, 138.

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SPECTROPHOTOMETRIC STUDY OF THE REACTION OF Hg(II) WITH CADION A AND CADION 2B

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Summary—The reaction between Hg(II) and Cadion A and Cadion 2B has been studied. Methods are suggested for the determination of Hg(II) in the 0.1–4 ppm range with Cadion A and in the 0.2–8 ppm range with Cadion 2B. Of the 49 ions studied only Hg(I), Sn(II), Br^-, I^-, MnO_4^-, EDTA, SCN^-, CN^- and S^{2-} interfere. The combination ratios and instability constants of the Hg–Cadion complexes were determined. The structural formulae of the complexes were deduced from the infrared spectra and elemental and thermogravimetric analyses.

There are many methods for the determination of Hg(II).[1] The most widely used is based on the reaction of Hg(II) with dithizone but is not entirely satisfactory owing to its sensitivity to any change in experimental conditions. It may be made selective by using EDTA and KSCN as masking agents. Other methods[2–5] in use are based on the extraction into 1,2-dichloroethane of the salt formed by the leuco base of Bindschedler's Green and the bromo-complex of mercury,[2] and on the reactions of mercury with 4,4'-bis(dimethylamino)thiobenzophenone,[3] 1,10-phenanthroline and Rose Bengal B,[4] or with iodide.[5] Although these methods have a remarkable sensitivity their selectivity is low. Among the less sensitive but more selective methods we can cite those using the reagent 6-phenyl-2,3-dihydro-*as*-triazine-3-thione[6] and *p*-dimethylaminobenzylidene-rhodanine.[7] Diazoamino derivatives form very stable complexes with Hg(II), and the reaction of mercury with Cadion A (4-nitrophenyldiazoaminoazobenzene), which takes place in alkaline medium (without extraction) where the reagent is in the aci-form, has been studied,[8] but the method is subject to numerous interferences.

In the present paper we present a study of the reaction of Hg(II) with Cadion A and Cadion 2B (4-nitronaphthyldiazoaminoazobenzene) in neutral or slightly acidic medium. Under these working conditions the complex formed is insoluble in water but easily extracted into benzene.

EXPERIMENTAL

Reagents

Mercuric nitrate solution, 100 ppm mercury. Prepared from metallic mercury and nitric acid.

Cadion A and Cadion 2B solutions, 0.015% in ethanol.

Sodium potassium tartrate solution 20%.

Working procedure

The sample is treated with nitric acid. The solution thus obtained is filtered, adjusted to pH 1–2, then transferred to a standard flask, made up to volume and mixed. An appropriate fraction (depending on the mercury concentration) is transferred to a separating funnel and water is added (if necessary) to make the volume up to about 20 ml. Two ml of sodium acetate buffer are added, followed by 5 ml of reagent solution. The funnel is shaken a few times, and then left for 10 min, to allow formation of the complex. Ten ml of benzene are added and the funnel is shaken for 1 min. After the aqueous and organic phases are fully separated (*ca.* 10 min) the absorbance of the organic phase is measured against a blank. A single extraction is sufficient to extract 98% of the Cadion A complex from the aqueous phase. Toluene, *p*-xylene or chloroform can also be used as solvents. The Cadion B complex is less well extracted, and two extractions with *p*-xylene are necessary.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of a $5.41 \times 10^{-5} M$ solution of Cadion A and of its mercury(II) complex extracted into benzene. The reagent has an absorption maximum at 402 nm whilst that of the complex is at 427 nm. For subsequent work the absorbance was measured at 470 nm, because at this wavelength the absorbance of the reagent is much lower than at 427 nm.

Figure 2 shows the corresponding spectra for Cadion 2B. The absorption maximum of the reagent is at 432 nm, and that of its complex with Hg(II) is at 446 nm. Absorbances were subsequently measured at 500 nm, where the absorbance of the reagent is much lower than at 446 nm.

The curves for both reagents show a single isosbestic point, at 418 nm for Cadion A and 456 nm for Cadion 2B, indicating that only one complex is formed.

Figure 3 shows the variation of absorbance of the extracted Cadion A complex as a function of pH. A $2M$ sodium acetate buffer (2 ml) was used, with nitric acid or sodium hydroxide added in order to obtain the range of pH values studied. We prefer this buffer as it has only a slight tendency to form precipitates with the ions tested in the interference study. The absorbance was found to remain constant for more than 72 hr. The complex was not affected by light.

The Lambert–Beer law is obeyed over the range 0.1–4 ppm with Cadion A and 0.2–8 ppm with Cadion 2B. The molar absorptivity is 4.01×10^4 l. mole^{-1}. cm^{-1} for Cadion A and 3.01×10^4 for Cadion 2B.

The combining ratio of Hg(II) with Cadion A was determined by Job's method for isomolar solutions[9] and by spectrophotometric titration and found to be 1:2. The instability constant of the complex was determined by the Job-plot method (non-isomolar solutions) and found to be about 2.4×10^{-10}.

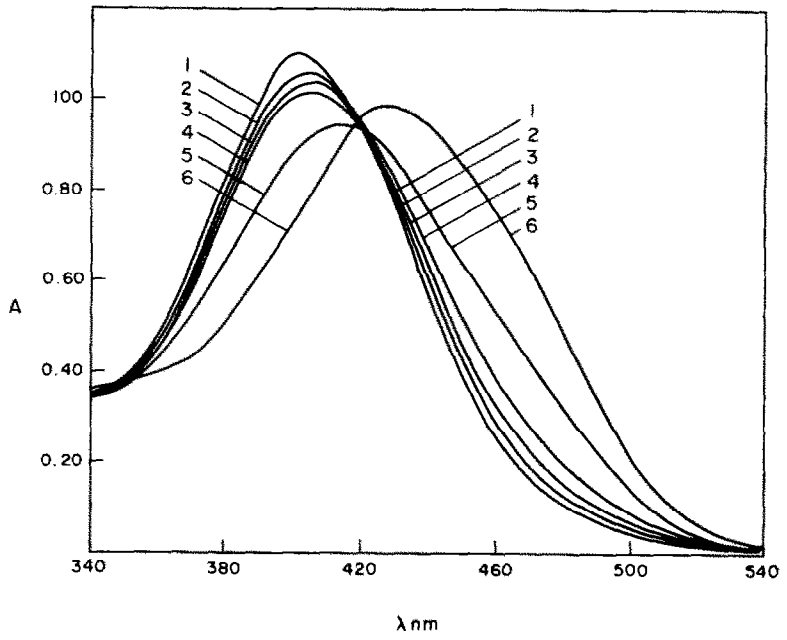
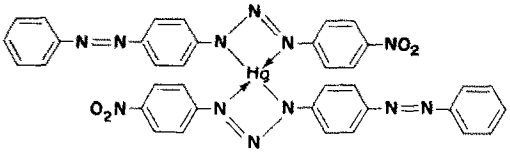


Fig. 1. The absorption spectra of $5.41 \times 10^{-5} M$ Cadion A solutions in benzene, containing Hg(II) in the following concentrations: (1) 0, (2) $1.24 \times 10^{-6} M$, (3) $2.49 \times 10^{-6} M$, (4) $4.98 \times 10^{-6} M$, (5) $9.96 \times 10^{-6} M$, (6) excess of Hg(II). Cells 0.5 cm.

The solid Cadion A complex was obtained by mixing stoichiometric quantities of alcoholic Cadion A solution and aqueous mercuric nitrate solution. The washed and dried precipitate is a red powder (found N 18.8%, Hg 22.1%).

The infrared spectra of the reagent and its mercury complex were compared, and the characteristic vibration of the N–H band[10] at 3200–3300 cm^{-1} was found to be present for the reagent but not the complex. No vibration band attributable to an N–Hg band could be positively identified but we may conclude that the mercury is bound to one nitrogen atom by replacing the hydrogen atom, and co-ordinatively to another nitrogen atom:



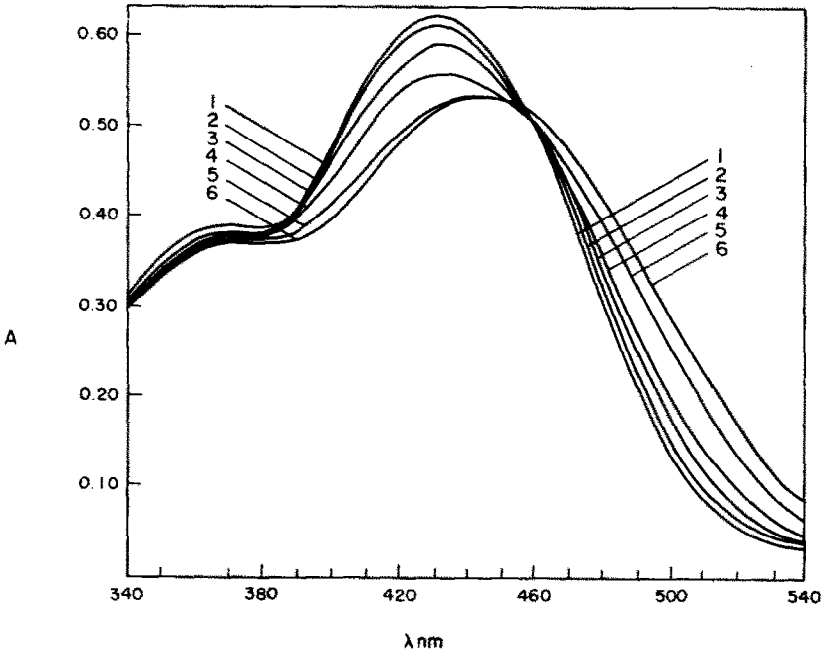


Fig. 2. The absorption spectra of $4.75 \times 10^{-5} M$ Cadion 2B solutions in benzene containing Hg(II) in the following concentrations: (1) 0, (2) $1.24 \times 10^{-6} M$, (3) $2.49 \times 10^{-6} M$, (4) $4.98 \times 10^{-6} M$, (5) $9.96 \times 10^{-6} M$, (6) excess of Hg(II). Cells 0.5 cm.

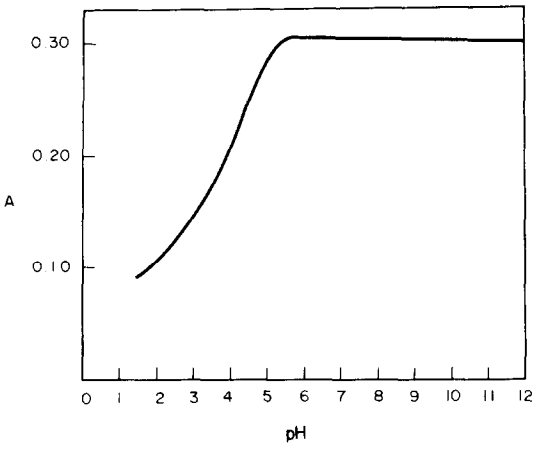


Fig. 3. Variation of absorbance with pH for the mercury complex with Cadion A, extracted into benzene.

According to this formula the complex should contain 18.86% N and 22.52% Hg, close to the values obtained experimentally.

Figure 4 shows the TG, DTA, DTG curves for the reagent and its Hg(II) complex. The complex is stable up to 190° and it should be possible to use Cadion A for gravimetric determination of mercury.

Interferences

The tolerance ratios for various ions ([ion]/[Hg^{2+}]) are 1000:1 for Li^+, Na^+, K^+, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Ga^{3+}, In^{3+}, Tl^+, Te^{3+}, UO_2^{2+}, Pb^{2+}, SO_4^{2-}, PO_4^{3-}, MoO_4^{2-}, WO_4^{2-}, citrate, tartrate; 500:1 for Cu^{2+}, Ag^+, Bi^{3+}, Cr^{3+}, Mn^{2+}, As(V), Sb(V), CrO_4^{2-}, 100:1 for Rh(III), Au(III), Pd(II), Ir(IV), Pt(IV); 50:1 for Cl^-. The following ions interfere at all levels: Hg(I), Sn(II), Br^-, I^-, MnO_4^-, EDTA, SCN^-, CN^-, S^{2-}

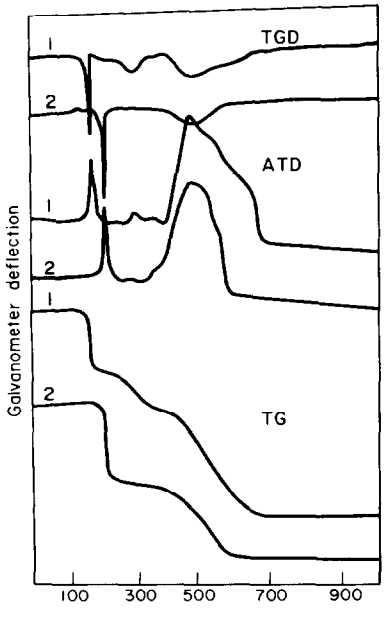


Fig. 4. TG, TGA and TGD curves of Cadion A (1) and of the Hg/Cadion A complex (2).

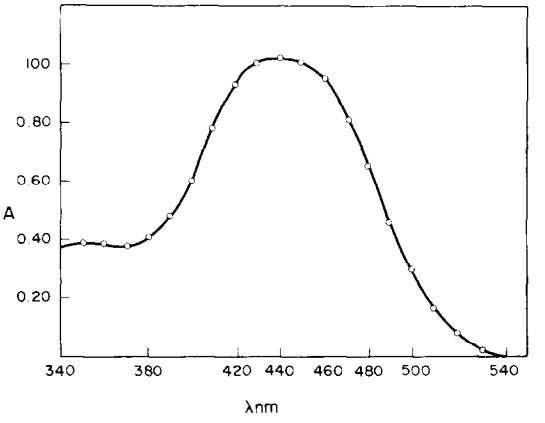


Fig. 5. Absorption spectrum of a benzene solution that is $5.41 \times 10^{-5} M$ in Cadion A and contains Hg_2(II) ions in excess.

Cations were added as their nitrates or sulphates, and anions as their alkali metal salts.

Silver interferes by forming a red complex but it is difficult to extract it into benzene. The interference may be eliminated by precipitating silver as AgCl, but excess of chloride must be avoided. Mercury(I) also forms an extractable complex with Cadion A. The spectrum of this complex is shown in Fig. 5.

From the Job plot for this complex the composition appears to be 1:2 Hg_2^{2+}:Cadion A, but a 1:1 complex and polynuclear species may also be formed. The complexes absorb in the same spectral region as the mercury(II) complex, and thus interfere.

The ions Fe(II), Fe(III) and Mn(II) interfere when present in very large quantities, but can be masked by addition of tartrate (2 ml of 20% sodium potassium tartrate solution). Addition of tartrate also prevents formation of certain precipitates that might adsorb mercury.

Oxidizing and reducing agents interfere by decomposing the reagent or by precipitating the mercury.

Applications

The method has been applied to analysis of waste waters containing mercury and organic substances. The organomercurials were decomposed by treatment with perchloric acid.

REFERENCES

1. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., p. 621. Interscience, New York, N.Y. 1965.
2. M. Tsubouchi, *Anal. Chem.*, 1970, **42**, 1087.
3. B. Gehauf and J. Goldenson, *ibid.*, 1950, **22**, 489.
4. M. M. Tananiko and N. S. Bilenko, *Zavodsk. Lab.*, 1974, **40**, 1049.
5. A. J. Pappas and H. B. Powell, *Anal. Chem.*, 1967, **39**, 579.
6. R. H. Maghssondi and F. A. Shamsa, *ibid.*, 1975, **47**, 550.
7. O. A. Ohlweiler and J. O. Meditsch, *Anal. Chim. Acta*, 1954, **11**, 113.
8. P. Chavanne and Cl. Geronimi, *ibid.*, 1958, **19**, 442.
9. P. Job, *Ann. Chim. Paris*, 1928, **9**, 113.
10. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.

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ANNOTATION

ANALYTICAL EVALUATION OF THE DERIVATIVES USED IN EQUILIBRIUM CALCULATIONS

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Summary—The derivatives of the total concentrations and other measured quantities with respect to the formation constants are calculated in general by a numerical method using finite increments. It is shown in this paper that these values can be calculated analytically, whereby the disadvantages of numerical differentiation may be avoided. The use of this method gives the possibility of writing faster programs for the calculation of the stability constants, based on the SCOGS and LETAGROP principle, without as large a memory requirement as in the LEAST and MINIQUAD programs.

One of the aims of complex equilibrium studies is to determine the compositions and stabilities of associations formed in solution. The calculations used in connection with equilibrium studies are based on the following system of equations which express the mass-balance in terms of the law of mass-action:

$$\begin{aligned} T_1 &= \sum_{j=1}^{n} \alpha_{j1}\beta_j[c_1]^{\alpha_{j1}}\dots[c_i]^{\alpha_{ji}}\dots[c_k]^{\alpha_{jk}} \\ &\vdots \\ T_k &= \sum_{j=1}^{n} \alpha_{jk}\beta_j[c_1]^{\alpha_{j1}}\dots[c_i]^{\alpha_{ji}}\dots[c_k]^{\alpha_{jk}} \end{aligned} \quad (1)$$

where: k = number of components
$T_1 \dots T_k$ = total concentrations of the components
$[c_1] \dots [c_k]$ = equilibrium (free) concentrations of the components
n = number of species (components + association species) in the system
β_j = formation constant of the jth species (the formation constants of the components are unity by definition)
α_{ji} = stoichiometric coefficient, giving the number of the ith component in the jth association species.

The LETAGROP,[1] SCOGS,[2] LEAST[3] and MINIQUAD[4] computer programs are the ones most frequently used to carry out the necessary calculations based on this set of equations. For the refinement of the formation (stability) constants, the derivatives $dT_i/d\beta_j$ [or $dT_i/d(\log\beta_j)$] must be known. The LETAGROP and SCOGS programs require a process of numerical differentiation to evaluate these values. Numerical differentatiation has two disadvantages; it is slow, and it lacks precision owing to the finite increments used in the differentiation. The LEAST and MINIQUAD programs overcome this problem, the necessary derivatives being evaluated analytically. In these cases, however, the stability constants and the free concentrations of the unmeasured components are regarded as unknown parameters on the same level. The partial derivatives $\partial T_i/\partial\beta_j$ and $\partial T_i/\partial[c_j]$ are evaluated simultaneously.

Involving a great number of experimental points, this treatment means the handling of large matrices with a large computer-memory requirement. The function to be minimized in these cases is

$$\sum_{k=1}^{p}\sum_{j=1}^{n}(T_{kj}^{exp}-T_{kj}^{calc})^2,$$

i.e. sum of the squares of the total-concentration deviations (p = number of experimental points).

The aim of the present paper is to show that the derivatives $dT_i/d(\log\beta_j)$ may be calculated analytically, and thus the LETAGROP and SCOGS programs may be made much faster; numerical differentiation can be avoided without the need to treat the β_j values and the concentrations of the free components $c_2 \dots c_k$ as unknown parameters on the same level, *i.e.*, without a large memory requirement.

MATHEMATICAL CONSIDERATIONS

From the first equation of the system of equations (1), the following relation can be derived:

$$\frac{dT_1}{d\beta_j} = \sum_{q=2}^{k}\left(\frac{d[c_q]}{d\beta_j}\right)\sum_{i=1}^{n}\alpha_{i1}\alpha_{iq}\beta_i[c_1]^{\alpha_{i1}}\dots[c_q]^{\alpha_{iq}-1}\dots[c_k]^{\alpha_{ik}}+\alpha_{j1}[c_1]^{\alpha_{j1}}\dots[c_k]^{\alpha_{jk}} \quad (2)$$

(If two of the free component concentrations are measured, then $dT_2/d\beta_j$ may be similarly expressed, and so on.)

It is seen from equation (2) that for the analytical evaluation of $dT_1/d\beta_j$, the $d[c_q]/d\beta_j$ values must be known. These derivatives may be determined from the equations relating to $T_2 \dots T_k$ in the system of equations (1). The assumption is that $T_2 \dots T_k$ are constant, and thus $dT_2/d\beta_j = \dots dT_k/d\beta_j = 0$.

$$\frac{dT_2}{d\beta_j} = \alpha_{j2}[c_1]^{\alpha_{j1}}\dots[c_k]^{\alpha_{jk}} + \sum_{q=2}^{k}\left(\frac{d[c_q]}{d\beta_j}\right)\sum_{i=1}^{n}\alpha_{i2}\alpha_{iq}\beta_i[c_1]^{\alpha_{i1}}\dots[c_q]^{\alpha_{iq}-1}\dots[c_k]^{\alpha_{ik}} = 0 \quad (3)$$

$$\frac{dT_k}{d\beta_j} = \alpha_{jk}[c_1]^{\alpha_{j1}}\dots[c_k]^{\alpha_{jk}} + \sum_{q=2}^{k}\left(\frac{d[c_q]}{d\beta_j}\right)\sum_{i=1}^{n}\alpha_{ik}\alpha_{iq}\beta_i[c_1]^{\alpha_{i1}}\dots[c_q]^{\alpha_{iq}-1}\dots[c_k]^{\alpha_{ik}} = 0$$

The $d[c_q]/d\beta_j$ values can be simply calculated by solving this linear equation system. If the $d[c_q]/d\beta_j$ values are substituted into equation (2), $dT_1/d\beta_j$ can be calculated directly. These values may easily be transformed into $dv/d(\log\beta_j)$, which is used to calculate the normal equations for the least-squares fit of the experimental titration curve in the SCOGS program. This consideration may be used if the concentration of at least one component is directly measured (potentiometric methods).

If spectrophotometric and some similar methods are used, the value of

$$X = \sum_{j=1}^{n} x_j\beta_j[c_1]^{z_{j1}}\dots[c_k]^{z_{jk}} \quad (4)$$

is measured, where x_j is the appropriate intensive property (for example molar absorptivity) of the jth species. In these cases,

$$\frac{dX}{dx_j} = \beta_j[c_1]^{z_{j1}}\dots[c_k]^{z_{jk}} \quad (5)$$

and $dX/d\beta_j$ [or $dX/d(\log\beta_j)$] are used to calculate the normal equations for the least-squares treatment of the experimental X data. For calculation of $dX/d\beta_j$, the LETA GROP program uses numerical differentiation. In a manner very similar to that shown above, $dX/d\beta_j$ may be calculated by

$$\frac{dX}{d\beta_j} = x_j[c_1]^{z_{j1}}\dots[c_k]^{z_{jk}} + \sum_{q=1}^{k}\left(\frac{dc_q}{d\beta_j}\right)\sum_{i=1}^{n} x_i\alpha_{iq}\beta_i[c_1]^{z_{i1}}\dots[c_q]^{z_{iq}-1}\dots[c_k]^{z_{ik}} \quad (6)$$

The only difference is that for calculation of $d[c_q]/d\beta_j$, the equation relating to T_1 is also included in the system of equations (3). It can be easily proved, moreover, that the second derivatives $d^2T_1/d\beta_j^2$ and $d^2X/d\beta_j^2$ may also be calculated analytically, through the appropriate linear system of equations.

A detailed numerical example for the illustration of the methods for calculating $dT_1/d\beta_j$, $dX/d\beta_j$, $d^2T_1/d\beta_j^2$ and $d^2X/d\beta_j^2$ is available from the authors on request. Work is continuing on a flexible general program for the calculation of the formation constants from the experimental data of potentiometric and spectrophotometric methods, using the analytical evaluation of the derivatives.

REFERENCES

1. N. Ingri and L. G. Sillén, *Arkiv Kemi*, 1964, **23**, 47.
2. I. G. Sayce, *Talanta*, 1968, **15**, 1397.
3. A. Sabatini and A. Vacca, *J. Chem. Soc. Dalton*, 1972, 1693.
4. A. Sabatini, A. Vacca and P. Gans, *Talanta*, 1974, **21**, 53.

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GAS CHROMATOGRAPHIC STUDY OF VOLATILE OXIDES AND HYDROXIDES OF Tc, Re, Ru, Os AND Ir—I

INVESTIGATION BY ISOTHERMAL GAS CHROMATOGRAPHY

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Summary—Traces of radioactive elements were produced by the irradiation of uranium foils (93% ^{235}U) with thermal neutrons, and of gold foils with 600-MeV protons. They were volatilized as oxides and hydroxides by heating at 1500° in an O_2 or O_2/H_2O stream and separated by adsorption chromatography on quartz granules. Compounds in the effluent gas were detected with a Ge(Li) detector and the elements identified by γ-spectrometry.

Gas chromatography has become a powerful tool in analytical chemistry in the last two decades. Besides solving separation problems, it is an important method for the study of non-analytical problems such as the determination of adsorption values and kinetic data in the gas phase.[1,2] Its application has been mainly restricted to organic compounds, inorganic compounds being largely neglected.[3–6]

The problems associated with the gas chromatography of inorganic compounds are due to the high temperatures required (>300°) and the difficulties that arise when high temperatures are used. Most stationary phases are volatile at high temperature or decompose. In addition, detectors lose sensitivity at high temperatures or in the presence of corrosive gases. These problems can be solved by the use of solid stationary phases[6–10] (adsorption chromatography) and detectors operating outside the separation tube (emission, radioactivity and fluorescence detectors).[6–9]

Because separations in the gas phase are useful in trace element determination we have carried out a study of volatilization and gas chromatography.[6–9,11] The present paper forms part of this study and deals with oxides and hydroxides. Determinations of the ΔH_{ads} and ΔS_{ads} values for oxides and hydroxides and the species involved in their transport are used to optimize separations of volatile oxides and hydroxides.

EXPERIMENTAL

Apparatus

The experimental arrangement is shown in Fig. 1. The furnace has three heating coils on a ceramic tube 15 mm in diameter and 1 m in length. The first heater is necessary for the revolatilization of condensed compounds and the third for the compensation of the temperature decrease caused by the cooling trap at the end of the column. The oven can be heated to 950°. The quartz separation tube, 8 mm bore, is filled with annealed quartz granules, diameter 315–630 μm.

Materials

The elements studied were produced by nuclear reactions: irradiation of uranium foils (93% ^{235}U) with thermal neutrons and the irradiation of gold foils with 600-MeV protons. The irradiated metal foils were heated in a graphite crucible with a boron nitride casing, by high-frequency induction heating, to 1500°. The nuclear reaction products were volatilized as oxides or hydroxides in an oxygen or oxygen/steam stream. The volatile compounds were either separated directly in the column or they were condensed at the top of the column with a cooling jacket. This condensation assisted in the definition of a starting point for the separation. Compounds in the effluent gas were condensed in front of a Ge(Li) detector and every 30 sec a γ-spectrum was recorded and evaluated by computer. The gas chromatographic peaks were identified by numerical differentiation of the integral curves.[6]

For determination of the dead-volume (hold-up volume, "air-peak"), iodine was used for all experiments with uranium foils and osmium for experiments with gold foils. For experiments with osmium the retention volume of the air-peak was calculated. All the experiments were carried out at a total pressure of one atmosphere. The gas flow-rate was 3 ml/min at room temperature, and the partial pressure of water was 150 mmHg in the experiments with O_2/H_2O.

RESULTS AND DISCUSSION

Determination of adsorption enthalpies and entropies

Table 1 summarizes the measured enthalpies and entropies of adsorption, on a quartz surface, of the oxide and hydroxides investigated. Determinations were carried out by measurement of the retention volumes as a function of the temperature of the column.[12,13]

$$\log V_{R,0} = \frac{-\Delta H^0}{2.3RT} + \frac{\Delta S^0}{2.3R} + \log(RT_0 s)$$

where $V_{R,0}$ is the retention volume referred to $T_0 = 273$ K, ΔH^0 is the standard enthalpy of adsorp-

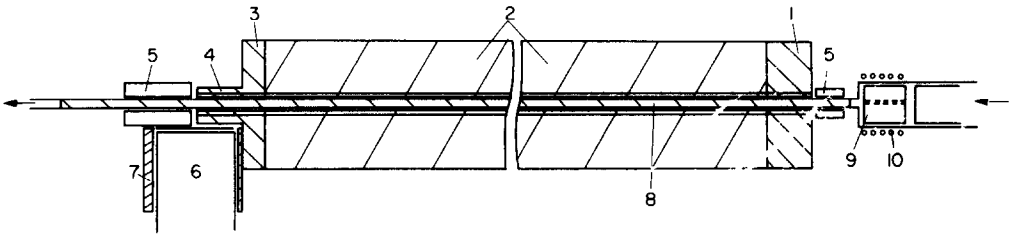


Fig. 1. Experimental arrangement: 1, heating coil 1, 2, heating coil 2, 3 heating coil 3, 4, asbestos insulation, 5, cooling jacket, 6, Ge-(Li) detector, 7, lead screen, 8, column, 9, crucible, 10, induction coil.

tion, ΔS^0 is the standard entropy of adsorption, R is the gas constant, T is the column temperature (K) and s the surface area of the solid phase (*ca.* 4000 cm^2).

As a first approximation it was assumed that ΔH° and ΔS° are independent of temperature. The errors were calculated by regression analysis. In Figs. 2 and 3, log $V_{R,0}$ values for TcO_2, TcO_3, RuO_3 and RuO_4 are plotted against the reciprocal of the column temperature. The enthalpies of adsorption are calculated from the slopes of the straight lines and the entropies of adsorption are calculated from the intercepts.

Table 1. Enthalpies and entropies of adsorption of oxides and hydroxides

Compound	$-\Delta H^\circ$ *kJ/mole*	$-\Delta S^\circ$ *J. mole^{-1}. deg^{-1}*
TcO_2	20.2 ± 1.4	128.2 ± 1.6
TcO_3	64.2 ± 2.9	227.0 ± 4.7
$HTcO_4$	51.9 ± 5.4	188.3 ± 8.2
ReO_3	67.1 ± 5.1	187.0 ± 5.0
$HReO_4$	68.7 ± 2.3	206.4 ± 3.4
RuO_3	40.4 ± 2.0	189.4 ± 3.4
RuO_4	10.2 ± 1.7	139.9 ± 3.1
OsO_4	9.8 ± 2.0	157.5 ± 6.8
IrO_3	42.6 ± 3.8	191.0 ± 6.2

Behaviour of the elements

The volatile compound which is formed in the crucible at 1500° is not necessarily the same as that transported through the column. When the compound which has been formed is condensed before gas chromatographic separation there are three possible patterns of behaviour. (1) The compound condenses and is revolatilized at 950°, the gas chromatogram being the same in either an oxygen or an argon stream. (2) The compound decomposes on condensation and is re-formed on revolatilization, the gas chromatogram being different in an oxygen and in an argon stream. (3) A new compound is formed and the gas chromatogram is different with and without prior condensation.

When argon is used as a carrier gas it is possible to determine whether transport is due to decomposition and re-formation processes or to adsorption and desorption.

Direct determination of the chemical composition of the compound transported is not possible because of the very low amounts of the compounds ($\sim 10^{-15}$ g) used. Some indications of possible structures may be obtained by using other methods such as mass spectrometry or from the measured values of the adsorp-

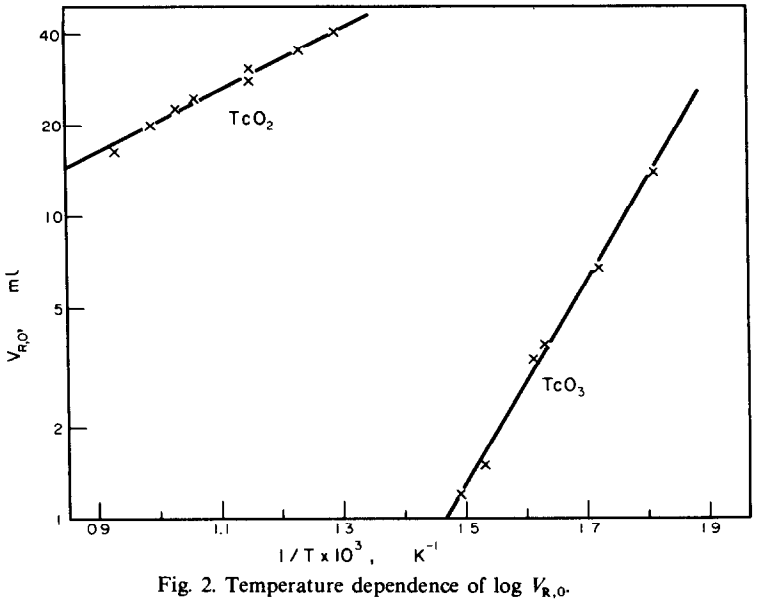


Fig. 2. Temperature dependence of log $V_{R,0}$.

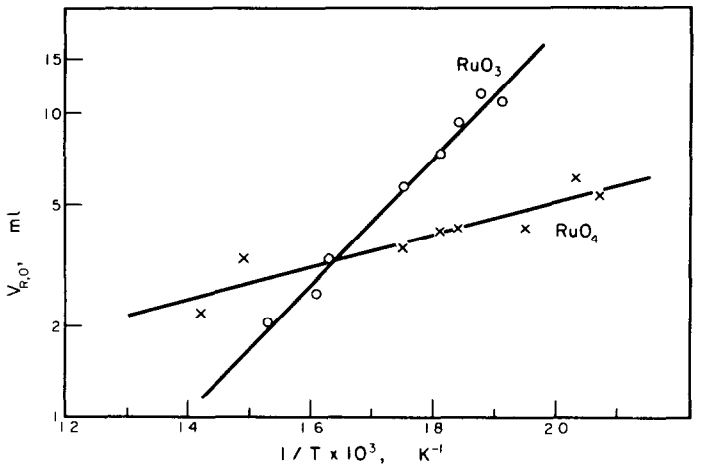


Fig. 3. Temperature dependence of log $V_{R,0}$ for RuO_3 and RuO_4.

tion enthalpies and entropies and from comparisons with compounds of known structure containing other elements.

Rhenium. In the system Re/O_2 only one compound is formed and transported. Previous work has suggested that Re_2O_7 is present in the gas phase[14–16] together with low concentrations of ReO_3. Under our experimental conditions the formation of Re_2O_7 is unlikely, owing to the low concentration of Re. The compound which has been found is ReO_3, which has been observed by Bayar *et al.* under similar conditions.[17] Supporting evidence for the existence of ReO_3 is given by the $\Delta S°$ value of 187.0 ± 5.0 $J.mole^{-1}.deg^{-1}$ which is similar to that for IrO_3 and RuO_3.

When a mixture of O_2 and H_2O is used as carrier gas, $HReO_4$ is formed as described previously.[18,19] $HReO_4$ has been identified in the gas phase by mass spectrometry.[14,15] There is no indication of decomposition of $HReO_4$.

Technetium. Two different technetium oxides have been separated by gas chromatography (Fig. 2). They are probably TcO_2 and TcO_3. TcO_3 is formed in the crucible at 1500° and decomposes continuously in the column to TcO_2, as shown by the pronounced tailing of the TcO_3 peak and the decrease in yield with decrease in column temperature (60% at 500° and 7% at 280°). When TcO_3 was condensed it decomposed and only TcO_2 was transported. With the exception of Tc_2O_7, the oxides of technetium have not previously been studied in the gas phase although it has been reported that TcO_2 sublimes at 1100° without decomposition. The values of the enthalpies of adsorption of ReO_3 and TcO_3 are the same within experimental error but those of IrO_3 and RuO_3 are lower, perhaps because the electronegativities of Ir and Ru (2.2) are higher than those of Re and Tc (1.9). The adsorption entropies of ReO_3, IrO_3 and RuO_3 are similar (Table 1), but that of TcO_3 is higher. This could be an indication of an alternative composition for this oxide but it is more likely to be due to a large systematic error in the determination. The fact that unlike ReO_3, TcO_3 decomposes during transportation, agrees with the rule that for transition elements the stability of the higher oxidation state increases with atomic weight.

The compound identified as TcO_2 has been found in earlier studies, but there is no proof of its chemical composition.[18,20,21] A comparison of the measured enthalpy and entropy of adsorption with those of IrO_2 (determined by thermochromatography) shows a rough agreement,[11] but there are no thermodynamic values available for the adsorption of comparable dioxides. In the O_2/H_2O system the compound $HTcO_4$ is transported and behaves similarly to $HReO_4$.[18,20,21]

Osmium. In the gas chromatographic separations of Os only one oxide was detected. Mass spectrometric investigations of the Os/O_2 system and a study of the thermal decomposition of OsO_2 showed that two oxides, OsO_3 and OsO_4, exist in the gas phase.[22–24] The ratio OsO_4/OsO_3 is increased with decreasing temperature.[24] It is possible that both oxides are formed in the crucible at 1500° but at the temperature of transportation only OsO_4 is present. These assumptions are supported by the similarity in the measured adsorption enthalpies and entropies of the osmium oxide and RuO_4 (Table 1). The adsorption enthalpy is quite low, probably because of the screening effect of the four oxygen atoms.

When an O_2/H_2O mixture is used OsO_4 is transported, but with a reduced yield (about 50%) owing to the reduction of OsO_4 by H_2O.

Ruthenium. Two oxides of ruthenium, RuO_3 and RuO_4, have been separated by gas chromatography (Fig. 3). At 1500° RuO_3 was formed with about 20% of RuO_4. When the oxides were condensed before separation, decomposition occurred and during revolatilization at 950° reoxidation produced a mixture containing about 70% of RuO_4. In Fig. 4, integral curves are presented for the experiments with and without condensation at a separation temperature of 270°. At temperatures higher than 300° it is no longer possible to differentiate between the two peaks, since

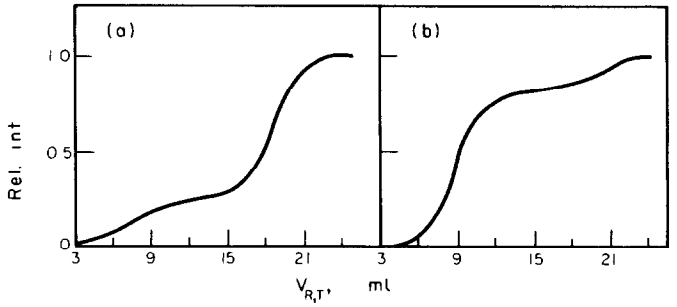


Fig. 4. Integral curves for an Ru experiment at 270°. (*a*) without condensation, (*b*) with condensation before separation.

the retention volumes of RuO_3 and RuO_4 are similar (Fig. 3). With argon as carrier gas no transportation of Ru was possible after the condensation, suggesting that RuO_3 and RuO_4 decompose to another, non-volatile, oxide. Decomposition processes were also observed during the transportation in the chromatographic column. At 350° the yield was 100%, whereas at 210° it was only 10%. The decomposition product is non-volatile and probably RuO_2.[26] Figure 5 summarizes these processes. RuO_3 and RuO_4 are described as gaseous species at temperatures up to 2000°.[23,25–27]

As discussed earlier, a further indication of the presence of RuO_3 and RuO_4 is the agreement of the adsorption enthalpy and adsorption entropy with those for compounds of similar structure.

In the system Ru–O_2/H_2O no other species could be found but the yield decreased to 10%, because of the reduction of RuO_4 and RuO_3 and the formation of RuO_2.[26]

Iridium. In the gas chromatographic separations of iridium oxides, two species could be detected, which were probably IrO_2 and IrO_3. There was no difference in the separation behaviour of the oxides in experiments with or without condensation before separation and with argon instead of oxygen as carrier gas. In the chromatograms a peak with a very long tail was found. This tailing decreased with increasing temperature and was not observed above 700°. Thermochromatographic separations demonstrated that the tailing was caused by the simultaneous transportation of IrO_2 and IrO_3. Because of the unfavourable ratios of the concentrations and the very similar retention volumes, the two peaks could not be resolved. It was therefore not possible to determine the adsorption enthalpies and entropies for IrO_2 in isothermal experiments although with thermochromatographic experiments the determination is possible.[11] IrO_2 and IrO_3 have already been described as stable compounds in the gas phase.[28–30] With O_2/H_2O as carrier gas the yield of oxides of Ir is reduced (~5%) compared with those for Ru and Os.

Separations

The oxides or hydroxides which have been investigated are volatile over different temperature ranges, so a separation by isothermal gas chromatography is not possible and temperature-programme methods must be used. Figure 6 shows a chromatogram of a temperature-programmed separation with O_2 as reactive gas and a heating rate of 20°/min. The elements osmium and rhenium are separated, whereas the peaks of ruthenium and iridium (IrO_3) and the peaks of technetium and iridium (IrO_2) overlap and a further separation is necessary.

Figure 7 shows a chromatogram of a temperature-programmed separation with O_2/H_2O as reactive gas and a heating rate of 20°/min. The peaks of technetium and rhenium are not completely resolved. The elements ruthenium and iridium could not be deter-

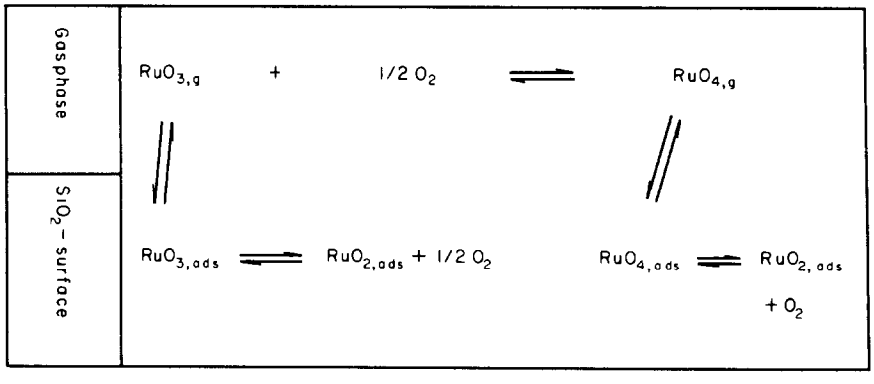


Fig. 5. Reaction scheme for the Ru/O_2 system.

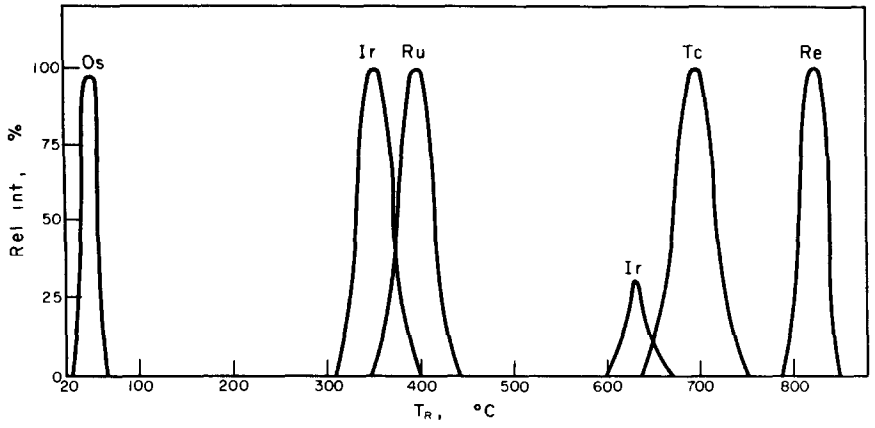


Fig. 6. Chromatogram from a temperature-programmed experiment with O_2 as reactive gas heating rate: 20°/min).

mined in this experiment and osmium was identified in the water condensed.

Separation of Tc from Ir and Ru. With a mixture of O_2/H_2O it is easy to separate technetium from Ir and Ru, since iridium and ruthenium are not volatilized (Fig. 7), but the technetium yield with O_2/H_2O is lower than with dry O_2. The temperature range for technetium transport is different from that for ruthenium and iridium in isothermal experiments with O_2 and with condensation and revolatilization before the separation (Fig. 8*b*). A separation of ruthenium and technetium can be obtained without condensation before the separation whereas the technetium and iridium peaks are only partly resolved (Fig. 8*a*).

When part of the column is filled with potassium chromate, this acts as a chemical filter, technetium being completely retained and ruthenium partly. The ruthenium which is deposited on the potassium chromate is volatilized over a long period, especially at higher temperatures. This method results in a separation of technetium and iridium and over a longer period an additional separation of technetium and ruthenium.

Separation of ruthenium and iridium. The complete separation of ruthenium and iridium as oxides is not possible on a quartz surface. These two elements behave similarly and a separation is not possible by changing the grain size of the silica or the column temperature since two ruthenium oxides are transported simultaneously. The ruthenium peak always shows tailing which overlaps the iridium peak. The best separation was obtained in isothermal experiments with condensation before separation (Fig. 8*b*). In cases where a simultaneous determination of iridium and ruthenium is not possible a separation can be achieved. The volatilized oxides are first deposited and then the IrO_3 and IrO_2 are revolatilized with argon as carrier gas. A revolatilization of ruthenium under these conditions is not possible because the volatile ruthenium oxides RuO_3 and RuO_2 decompose during the condensation.

Separation of rhenium and technetium. With a mix-

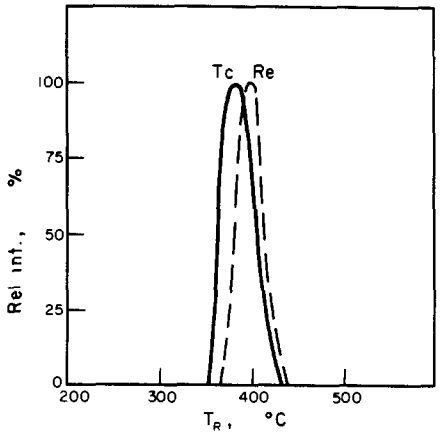


Fig. 7. Chromatogram from a temperature-programmed experiment with O_2/H_2O as reactive gas (heating rate: 20°/min).

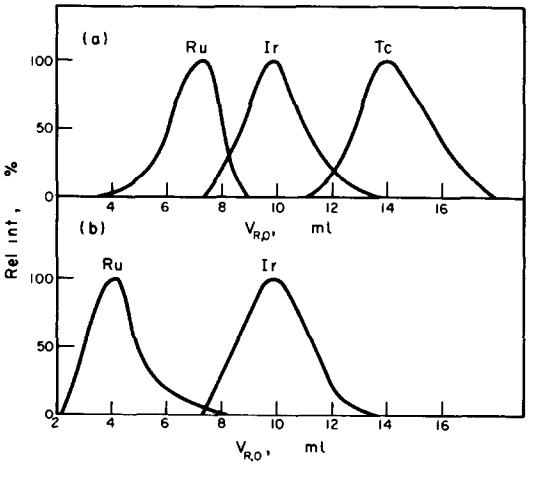


Fig. 8. Separation of Ru, Ir and Tc. Reactive gas: O_2, column temperature: 280°. (*a*) without condensation, (*b*) with condensation before separation.

ture of O_2/H_2O as reactive gas, a separation of rhenium and technetium is not possible since both the transported species, $HReO_4$ and $HTcO_4$, are similar in their behaviour. However, rhenium and technetium show different behaviour with dry O_2 as reactive gas and can be separated satisfactorily (Fig. 6). When a potassium chromate "filter" is used, this separation is not possible, since the rhenium and technetium oxides react, probably by formation of pertechnetate and perrhenate.

CONCLUSION

The results of this work show that isothermal gas chromatography is a good method for determining values of the enthalpies and entropies of adsorption of volatile oxides and hydroxides on silica surfaces and investigating the behaviour of the compounds in the gas phase. For analytical purposes temperature-programmed gas chromatography is advantageous, because the compounds are volatile over different temperature ranges and separation by isothermal gas chromatography is not possible.

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REFERENCES

1. V. Hopfe and G. Marx, *Z. Chem.*, 1972, **10**, 370.
2. J. Rudolph and K. Bächmann, *Vortrag 8. Radiochem. Conf.*, Bad Marienbad, April, 1975.
3. H. Rüssel and G. Tölg, *Anorganische Gaschromatographie*, Springer Verlag, Berlin, 1972.
4. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965).
5. G. Guichon and C. Pommier, *Gas Chromatography in Inorganics and Organometallics*, Ann Arbor Science, Ann Arbor, 1973.
6. K. Bächmann and J. Rudolph, *J. Radionanal. Chem.*, 1976, **32**, 243.
7. K. Bächmann, V. Matschoß, J. Rudolph, A. Steffen and S. Tsalas, *Nucl. Instr. Methods*, 1976, **139**, 343.
8. S. Tsalas and K. Bächmann, *Anal. Chim. Acta*, in the press.
9. J. Rudolph and K. Bächmann, *Chromatographia*, in the press.
10. A. V. Kiselev and Y. I. Yashin, *Gas-Solid Chromatography*, Masson, Paris, 1969.
11. A. Steffen and K. Bächmann, to be published.
12. E. Leibnitz and H. G. Struppe, *Handbuch der Gaschromatographie*, Verlag Chemie, Weinheim, 1970.
13. A. Steffen, *Dissertation Technische Hochschule*, Darmstadt, 1977.
14. J. E. Battles, G. E. Gundersen and R. K. Edwards, *J. Phys. Chem.* 1968, **72**, 3963.
15. H. B. Skinner and A. W. Searcy, *ibid.*, 1973, **77**, 1578.
16. G. A. Semenov and K. V. Ovchinnikov, *J. Gen. Chem. USSR*, 1965, **35**, 1521.
17. B. Bayar, N. B. Zaitseva and A. F. Novgorodov, *Radiochem. Radional. Lett.* 1973, **15**, 231.
18. B. Eichler, *Dissertation B*, Dresden, 1976.
19. B. Bayar, I. Votsilka, N. G. Zeitseva and A. F. Novgorodov, *Sov. Radiochem.* 1974, **16**, 871.
20. W. Bögl, *Dissertation Technische Hochschule*, Darmstadt, 1973.
21. V. Matschoß, *Dissertation Technische Hochschule*, Darmstadt, 1976.
22. R. T. Grimley, R. P. Burns and M G. Inghram, *J. Chem. Phys.* 1960, **33**, 308.
23. A. B. Nikolskii and A. N. Ryabov, *Russ. J. Inorg. Chem.*, 1965, **10**, 1.
24. A. B. Nikolskii, G. A. Semenov and E. N. Veshnyakova, *ibid.*, 1967, **12**, 571.
25. H. Schäfer, W. Gerhardt and A. Tebben, *Angew. Chem.*, 1961, **73**, 27.
26. W. E. Bell and M. Tagmi, *J. Phys. Chem.*, 1963, **67**, 2432.
27. H. Schäfer, A. Tebben and W. Gerhardt, *Z Anorg. Allgem. Chem.*, 1963, **321**, 41

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REDOX TITRATIONS—II

LOCATION OF INFLECTION POINTS OF TITRATION CURVES FOR HOMOGENEOUS REDOX REACTIONS

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Summary—The relative positions of the inflection points and equivalence point of a homogeneous redox reaction have been studied by using the redox buffer capacity to derive an equation for the titration curve. The position of the inflection point corresponding to the maximum slope of the titration curve relative to the equivalence point depends on the electron transfers of the analyte and the titrant (the stoichiometric coefficients of the reaction equation) and on the difference between the formal potentials of the redox couples in a more complicated way than has been described previously.

Several investigators have studied theoretically the relative positions of the equivalence point and the inflection points on the titration curve of a homogeneous redox reaction.[1–8] The equations proposed are cumbersome to handle, so most of the work has been confined to one special case, the symmetrical redox reaction.

Murgulescu and Dragulescu[2] observed when studying asymmetric homogeneous redox reactions that the inflection point corresponding to the maximum slope is located after the equivalence point if the electron transfer of the analyte is greater than that of the titrant, *i.e.*, if the stoichiometric coefficient of the titrant is greater than that of the analyte in the redox equation; and before the equivalence point if the coefficient of the titrant is smaller than that of the analyte. They stated that the inflection point and the equivalence point can never coincide in redox titrations. However, Goldman[7] has demonstrated that the inflection point corresponding to the maximum slope can coincide with the equivalence point if the coefficient of the titrant is greater than that of the analyte. For any given pair of coefficients this occurs at a particular value of the difference between the formal potentials. If the difference is smaller than this value, the inflection point is before the equivalence point, and after it if the difference is greater.

It has also been observed that the inflection point corresponding to the maximum slope of the titration curve in symmetrical redox titrations is always before the equivalence point.[1,6]

The redox poising (buffer) capacity has been used previously to describe redox titrations, but the functions derived were hyberbolic.[3] However, the same premise may lead to simpler equations.[8] When the redox buffer capacity is used the dilution of the solution does not have to be considered separately.

In this paper we shall study homogeneous redox titrations in detail.

BASIC EQUATIONS

For a homogeneous redox reaction

$$m\,\mathrm{Ox}(1) + n\,\mathrm{Red}(2) \rightleftharpoons m\,\mathrm{Red}(1) + n\,\mathrm{Ox}(2) \quad (1)$$

the following expressions are valid during the titration:

$$E = E_1^* + \frac{RT}{nF}\ln\frac{c_{\mathrm{Ox}(1)}}{c_{\mathrm{Red}(1)}} \quad (2)$$

$$E = E_2^* + \frac{RT}{mF}\ln\frac{c_{\mathrm{Ox}(2)}}{c_{\mathrm{Red}(2)}} \quad (3)$$

where E_1^* and E_2^* are the formal potentials ($E_1^* > E_2^*$).

If we write

$$e^x = \frac{c_{\mathrm{Ox}(1)}}{c_{\mathrm{Red}(1)}} = \exp\{(E - E_1^*)nF/RT\} \quad (4)$$

and

$$e^y = \frac{c_{\mathrm{Ox}(2)}}{c_{\mathrm{Red}(2)}} = \exp\{(E - E_2^*)mF/RT\} \quad (5)$$

the following expressions are obtained for the total molar concentrations,

$$C_1 = c_{\mathrm{Ox}(1)} + c_{\mathrm{Red}(1)} = c_{\mathrm{Red}(1)}\left(1 + \frac{c_{\mathrm{Ox}(1)}}{c_{\mathrm{Red}(1)}}\right) = c_{\mathrm{Red}(1)}(1 + e^x) \quad (6)$$

$$C_2 = c_{\mathrm{Ox}(2)} + c_{\mathrm{Red}(2)} = c_{\mathrm{Ox}(2)}\left(1 + \frac{c_{\mathrm{Red}(2)}}{c_{\mathrm{Ox}(2)}}\right) = c_{\mathrm{Ox}(2)}(1 + e^{-y}). \quad (7)$$

If Ox(1) is the titrant, the redox buffer capacity is given by the expression

$$P = \frac{\mathrm{d}C_1}{\mathrm{d}E} = \frac{\mathrm{d}c_{\mathrm{Red}(1)}}{\mathrm{d}E}(1 + e^x) + \frac{nF}{RT}e^x c_{\mathrm{Red}(1)}. \quad (8)$$

When the concentration of the titrant is very large compared with that of the analyte and the addition

of titrant is very small then the change in the total concentration of the analyte from dilution is negligible. Thus

$$-\frac{dC_2}{dE} = -\frac{dc_{Ox(2)}}{dE}(1 + e^{-y}) + \frac{mF}{RT}e^{-y}c_{Ox(2)} = 0. \quad (9)$$

During the titration

$$c_{Red(1)} = \frac{m}{n}c_{Ox(2)} \quad (10)$$

and

$$\frac{dc_{Red(1)}}{dE} = \frac{m}{n}\frac{dc_{Ox(2)}}{dE}. \quad (11)$$

From equations (4), (5) and (8)–(11) the redox buffer capacity can be expressed as

$$P = \frac{F}{RT}\left[\frac{m^2}{n}\frac{(1 + e^x)}{(1 + e^y)}e^y c_{Red(2)} + nc_{Ox(1)}\right] \quad (12)$$

Correspondingly, when Red(2) is the titrant, the redox buffer capacity is given by the expression

$$P' = \frac{F}{RT}\left[\frac{n^2}{m}\frac{(1 + e^y)}{(1 + e^x)e^y}c_{Ox(1)} + m c_{Red(2)}\right]. \quad (12')$$

From equations (6), (7) and (10), the ratio of the total concentrations is

$$\frac{C_1}{C_2} = \frac{m(e^y + e^{x+y})}{n(e^y + 1)} \quad (13)$$

and this applies throughout the titration. By comparison of equation (13) with the condition for the equivalence point

$$\frac{C_1}{C_2} = \frac{m}{n} \quad (14)$$

it can be seen that when Ox(1) is the titrant, the equivalence point of the titration and the inflection point of the titration curve coincide if $(e^{x+y})_i = 1$. If $(e^{x+y})_i < 1$ the inflection point is *before* the equivalence point and if $(e^{x+y})_i > 1$ the inflection point is *after* the equivalence point.

When Red(2) is the titrant, the inflection point and the equivalence point again coincide when $(e^{x+y})_i = 1$. When $(e^{x+y})_i > 1$, the inflection point is *before* the equivalence point and when $(e^{x+y})_i < 1$, the inflection point is *after* the equivalence point.

The inflection points of the titration curve correspond to the maximum and the minimum in the redox buffer capacity. These are obtained by differentiating equations (12) and (12') and equating the derivatives dP/dE to zero. To allow study of the relationship between the inflection points and the equivalence point, the equation $dP/dE = 0$ must be solved for (e^{x+y}).

Equation (12) leads to the expression

$$(e^{x+y})_i = \frac{m^2e^y - m^2 - (m + n)^2e^x}{n^2e^y + 2mn + 2n^2 - m^2} \quad (15)$$

and equation (12') to

$$(e^{x+y})_i = \frac{(m + n)^2e^{2x} + (2m^2 - n^2 + 2mn)e^x + m^2}{n^2(1 - e^x)}. \quad (15')$$

At the equivalence point of the titration

$$E_e = \frac{nE_1^* + mE_2^*}{m + n} \quad (16)$$

where E_e is the potential at the equivalence point. Equations (4) and (5) lead to the expression

$$(x + y) = \frac{(m + n)E}{RT/F} - \frac{nE_1^* + mE_2^*}{RT/F} \quad (17)$$

(which is valid throughout the titration).

The difference between the potential at the inflection points and that at the equivalence point is

$$\Delta E_i = E_i - E_e = \frac{RT}{F}\frac{(x + y)_i}{(m + n)} \quad (18)$$

The influence of the difference between the formal potentials of the redox couples, ΔE^*, on the relationship between the positions of the inflection points and the equivalence point can be studied by means of equations (15) and (15'):

The equilibrium constant for redox reaction (1) is

$$K = \left(\frac{c_{Red(1)}}{c_{Ox(1)}}\right)^m\left(\frac{c_{Ox(2)}}{c_{Red(2)}}\right)^n. \quad (19)$$

At equilibrium, from equations (2) and (3)

$$E_1^* + \frac{RT}{nF}\ln\frac{c_{Ox(1)}}{c_{Red(1)}} = E_2^* + \frac{RT}{mF}\ln\frac{c_{Ox(2)}}{c_{Red(2)}} \quad (20)$$

and

$$\ln K = \frac{mn\Delta E^*}{RT/F} \quad (21)$$

Equation (19) can be written in the form

$$K = \exp\{ny - mx\} \quad (22)$$

or

$$\ln K = ny - mx \quad (23)$$

Equations (4)–(7), (10), (12) and (12') lead to the following expressions for the calculation of the redox buffer capacity:

$$P = \frac{F}{RT}C_2\left[\frac{m^2}{n}\frac{(1 + e^x)e^y}{(1 + e^y)^2} + m\frac{e^{x+y}}{(1 + e^y)}\right] \quad (24)$$

which applies when Ox(1) is the titrant and

$$P' = \frac{F}{RT}C_1\left[\frac{n^2}{m}\frac{(1 + e^y)e^x}{(1 + e^x)^2e^y} + \frac{n}{(1 + e^x)e^y}\right] \quad (24')$$

when Red(2) is the titrant.

RESULTS AND DISCUSSION

A particular value of the equilibrium constant K corresponds to each value of ΔE^*. Equations (15) and (15') were solved numerically with the aid of a Wang 2200B minicomputer. Pairs of values of $(e^x)_i$ and $(e^y)_i$ were found by substituting a series of numerical values for $(e^y)_i$ and finding the corresponding values of $(e^x)_i$. Values of K [equation (22)], ΔE^* [equation (21)], buffer capacity [equation (24)], and ΔE_i [equation (18)] could then be calculated. Some of these results are presented in Table 1 (25°, $2.303RT/F = 0.05916$ V). Calculations of the same kind can be performed for each pair of coefficients m and n when either Ox(1) or Red(2) is the titrant.

The redox titration can be inspected more closely with the aid of the calculated values given in the tables and the corresponding graphs (Fig. 1).

It should also be noted that when Ox(1) is the

Table 1. A sample calculation [Ox(*1*) as titrant; $m = 2$, $n = 1$]

ΔE^*, *mV*	42.34	46.00	50.00	100.0	200.0	300.0	400.0
$(e^x)_{i(max)}$	0.3333	0.2365	0.1874	2.04×10^{-2}	4.165×10^{-4}	8.47×10^{-6}	1.73×10^{-7}
$(e^y)_{i(max)}$	3.000	2.008	1.722	1.064	1.001	1.00002	1.0000005
$(e^x)_{i(min)}$	0.3333	0.3651	0.3505	0.1145	8.829×10^{-3}	6.60×10^{-4}	4.93×10^{-5}
$(e^y)_{i(min)}$	3.000	4.778	6.022	31.53	450	6052	81080
$\Delta E_{i(max)}$, *mV*	0	−6.378	−9.685	−32.53	−66.64	−100.0	−133.3
$\Delta E_{i(min)}$, *mV*	0	4.782	6.398	11.00	11.82	11.87	11.87
K	27.00	35.90	49.02	2.403×10^{3}	5.77×10^{6}	1.39×10^{10}	3.33×10^{13}
$(RT/FC_2)P_{(max)}$	1.500	1.413	1.341	1.042	1.001	1.00002	1.0000003
$(RT/FC_2)P_{(min)}$	1.500	1.383	1.261	0.3548	2.65×10^{-3}	1.98×10^{-3}	1.48×10^{-4}

Note: i(max) [or i(min)] represents the maximum (or minimum) point of the redox buffer capacity.

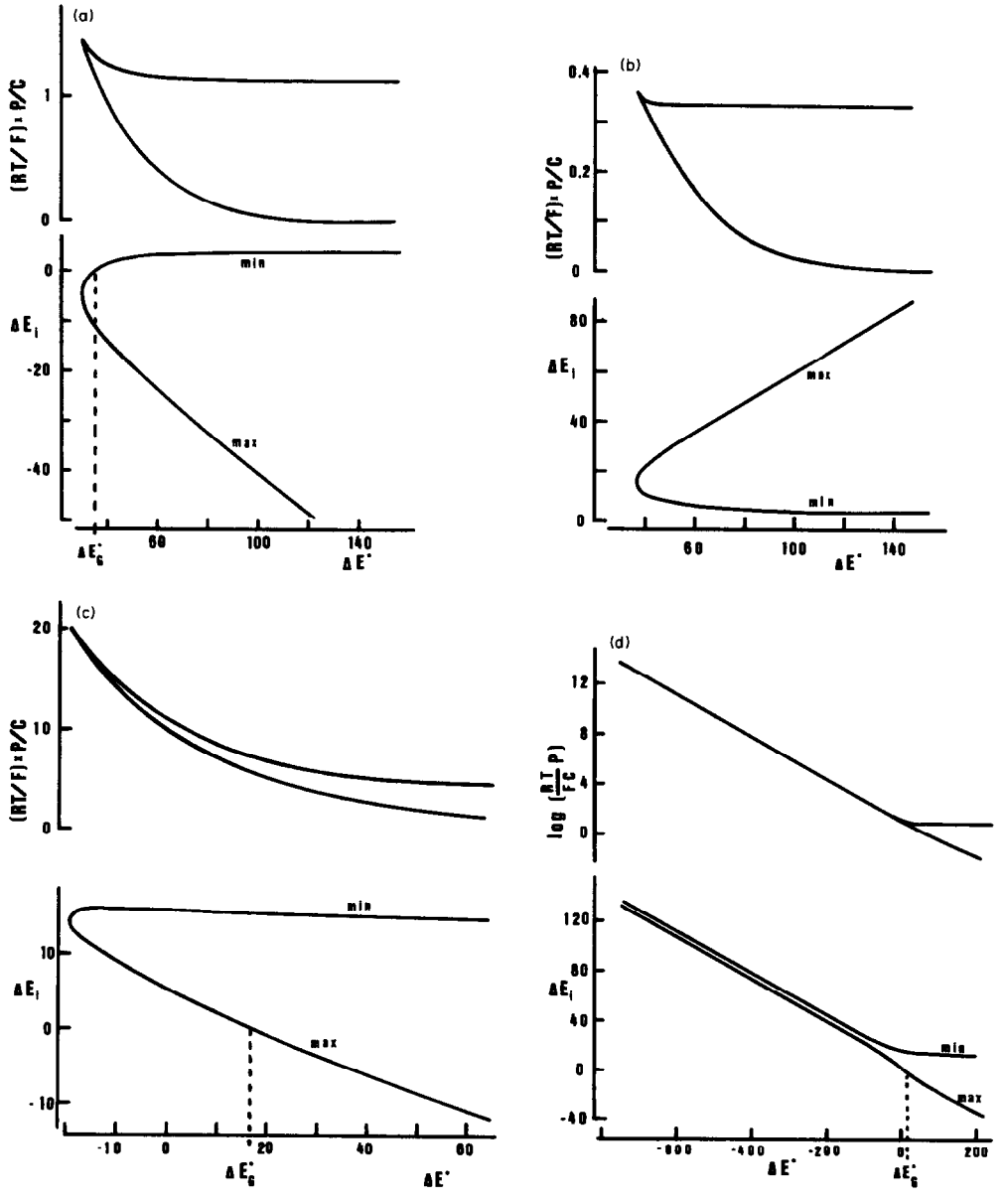


Fig. 1. ΔE_i and redox buffer capacity as a function of the difference between the formal potentials, ΔE^*. (*a*) Ox(1) as titrant, $m = 3$, $n = 2$. (*b*) Red(2) as titrant, $m = 3$, $n = 2$, (*c*) Ox(1) as titrant, $m = 4$, $n = 1$. (*d*) Ox(1) as titrant, $m = 5$, $n = 1$.

titrant, a positive value for ΔE_i indicates that the inflection point comes after the equivalence point and a negative value for ΔE_i indicates that the inflection point is before the equivalence point. When Red(2) is the titrant the situation is reversed.

(a) The condition required for the existence of the inflection points

Goldman[6] has shown that for symmetrical redox titrations, the difference, ΔE^*, between the formal potentials of the redox couples decreases to a value, ΔE^*_{min}, at which there is only one inflection point in the titration curve. He gives a value of $85.6/p$ mV for ΔE^*_{min} when $p = m = n$ (p = number of electrons transferred) and a value of $-25.68/p$ mV for the difference between the potentials of the inflection point (at the point of maximum slope of the titration curve) and the equivalence point, $\Delta E_{i(min)}$. Nightingale[3] stated that the inflection point corresponding to a minimum in the redox poising capacity would not be observed if the difference between the formal potentials was less than 85.6 mV.

For a homogeneous redox titration there is for each coefficient pair m and n such a minimum value, ΔE^*_{min}. The values of the limiting titration parameters are presented in Table 2 (Ox(1) as titrant). There is no inflection point on the titration curve if the values of ΔE^* are below those given. This indicates that the redox buffer capacity has neither a maximum nor a minimum, and that equations (15) and (15′) have no real solution.

When Ox(1) is the titrant,

$$\frac{c_{Ox(2)}}{c_{Red(2)}} = (e^y)_i = \frac{m+n}{n} \qquad (25)$$

corresponds to ΔE^*_{min}.

The same values of ΔE^*_{min} and K are valid when Red(2) is the titrant if the numerical values of m and n in equation (1) are exchanged. The numerical values of ΔE_i are the same but the sign is changed. Thus

$$\frac{c_{Ox(1)}}{c_{Red(1)}} = (e^x)_i = \frac{m}{m+n} \qquad (26)$$

corresponds to ΔE^*_{min}.

(b) The conditions for the inflection points to lie between the formal potentials

In the redox titration corresponding to equation (1), since either Ox(1) or Red(2) may be the titrant, $e^y = 1$ at the point on the titration curve where the potential of the solution $E = E^*_2$, and $e^x = 1$ when $E = E^*_1$. In practice the inflection points of the titration curve have to fall between the potentials E^*_2 and E^*_1, so $(e^y)_i \geq 1$ and $0 < (e^x)_i \leq 1$.

Table 2. The smallest values of ΔE^*, *i.e.*, ΔE^*_{min}, required for an inflection point to be observed on the titration curve

m	n	ΔE^*_{min}, mV	ΔE_i, mV	K
1	1	85.61	−25.00	28.00
1	2	64.81	−32.78	1.552×10^2
1	3	52.23	−31.78	4.456×10^2
1	4	44.13	−29.57	9.643×10^2
1	5	38.44	−27.35	1.776×10^3
2	1	42.34	0	27.00
2	2	42.80	−12.50	7.839×10^2
2	3	37.01	−15.64	5.671×10^3
2	4	32.40	−16.39	2.410×10^4
2	5	28.88	−16.30	7.616×10^4
3	1	12.80	8.67	4.461
3	2	30.29	−4.27	$1\,182 \times 10^3$
3	3	28.54	−8.33	2.195×10^4
3	4	25.89	−10.00	1.785×10^5
3	5	23.55	−10.69	9.390×10^5
4	1	−19.54	14.24	4.768×10^{-2}
4	2	21.17	0	7.290×10^2
4	3	22.62	−4.25	3.887×10^4
4	4	21.40	−6.25	6.146×10^5
4	5	19.90	−7.28	5.345×10^6
5	2	13.52	2.57	1.931×10^2
5	3	18.00	−1.71	3.673×10^4
5	4	17.96	−3.81	1.183×10^6
5	5	17.12	−5.00	1.721×10^7

Equation (15) can be used to find which combinations do not fulfil these conditions when Ox(1) is the titrant. When $(e^x)_i = 1$ is substituted in equation (15)

$$(e^y)_i = \left(\frac{m^2}{n^2} - \frac{m}{n} - 1\right) \pm \sqrt{\left(\frac{m^2}{n^2} - \frac{m}{n} - 1\right)^2 - \frac{m^2}{n^2} - \left(1 + \frac{m}{n}\right)^2}. \qquad (27)$$

Substitution of various values for the coefficients m and n into this equation leads to the following conclusions. (*i*) When $m/n < 3$, equation (27) has no real solution, so the potentials corresponding to the two inflection points lie in the range E^*_2–E^*_1. (*ii*) When $m/n = 3$ and $(e^y)_{i(min)} = 5$, the value of $(e^x)_{i(min)}$ is unity. With a ΔE^* value of 13.78 mV, corresponding to $(e^y)_{i(min)} = 5$, the inflection point $ip_{(min)}$, which corresponds to the minimum of the redox buffer capacity, falls at the point E^*_1, *i.e.*, $E_{i(min)} = E^*_1$, and the inflection point $ip_{(max)}$, which corresponds to the maximum of the redox buffer capacity, falls in the range E^*_2–E^*_1. (*iii*) When $m/n = 4$, $(e^x)_i \geq 1$ if $(e^y)_i$ has a value between $11 - 4\sqrt{5}$ and $11 + 4\sqrt{5}$ More detailed location of the inflection points is given in Table 3. (*iv*) When $m/n = 5$, $(e^x)_i \geq 1$ if $(e^y)_i$ has a value between $19 - 10\sqrt{3}$ and $19 + 10\sqrt{3}$. More detailed information is given in Table 3.

Similarly, equation (15′) can be used for cases where Red(2) is the titrant. By setting $(e^y)_i = 1$ we get

$$(e^x)_i = \frac{-(m^2 - n^2 + mn) \pm \sqrt{(m^2 - n^2 + mn)^2 - m^2[(m+n)^2 + n^2]}}{(m+n)^2 + n^2}. \qquad (27')$$

Table 3. Location of the inflection points when the stoichiometric coefficient ratio m/n is large

m/n	ΔE^*, mV	Location of ip *vs* ep: $ip_{(max)}$	Location of ip *vs* ep: $ip_{(min)}$	Value of E_i compared with E_1^*	
4	$\Delta E^* < 4.65$	after	after	$E_{i(max)} > E_1^*$	$E_{i(min)} > E_1^*$
	$4.65 < \Delta E^* < 16.40$	after	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$\Delta E^* = 16.40$	= ep	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$16.40 < \Delta E^* < 19.23$	before	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$\Delta E^* > 19.23$	before	after	$E_{i(max)} < E_1^*$	$E_{i(min)} < E_1^*$
5	$\Delta E^* < 2.64$	after	after	$E_{i(max)} > E_1^*$	$E_{i(min)} > E_1^*$
	$2.64 < \Delta E^* < 12.50$	after	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$\Delta E^* = 12.50$	= ep	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$12.50 < \Delta E^* < 18.46$	before	after	$E_{i(max)} < E_1^*$	$E_{i(min)} > E_1^*$
	$\Delta E^* > 18.46$	before	after	$E_{i(max)} < E_1^*$	$E_{i(min)} < E_1^*$

Substitution of various values of m and n into this equation leads to the following conclusions. (*i*) When $n/m < 3$, equation (27′) has no real solution so the inflection points lie in the range E_1^*–E_2^*. (*ii*) When $n/m = 3$, $(e^y)_{i(min)} = 1$ if $(e^x)_{i(min)}$ has a value of 0.200, so $E_{i(min)} = E_2^*$. (*iii*) When $n/m = 4$, the $(e^y)_i$ values corresponding to $(e^x)_i$ values between $(11 - 4\sqrt{5})/41$ and $(11 + 4\sqrt{5})/41$. (*iv*) When $n/m = 5$, the $(e^y)_i$ values corresponding to $(e^x)_i$ values between $(19 - 10\sqrt{3})/61$ and $(19 + 10\sqrt{3})/61$ do not fulfil the conditions and thus $ip_{(min)}$ does not lie in the range E_1^*–E_2^*.

(c) The coincidence of equivalence point and inflection point

According to Murgulescu and Dragulescu[2] the inflection point and the equivalence point can never coincide in a redox titration. Goldman[7] has shown, however, that in asymmetrical redox titrations the equivalence point and the inflection point corresponding to the maximum slope of the titration curve can coincide if the electron transfer of the analyte is greater than that of the titrant and if ΔE^* has a particular value.

In Part I[8] this special case was studied with the aid of the redox buffer capacity. The inflection point and the equivalence point coincide if $(e^{x+y})_i = 1$ in equations (15) and (15′). This occurs only if the conditions presented by Goldman are fulfilled.

More information can be found by solving equations (15), (15′) and (18) to find the cases where $(e^{x+y})_i = 1$, and the inflection point and the equivalence point coincide. At the same time the redox buffer capacity may be used to find which of the inflection points coincides with the equivalence point.

The results of the calculations for Ox(1) as titrant are given in Table 4. The same table gives values for ΔE_i for the inflection point which does not coincide with the equivalence point but which appears on the same titration curve. The particular values of ΔE^* corresponding to coincidence of same equivalence point and the inflection point are denoted by ΔE_G^*.

Similar results can be obtained when Red(2) acts as titrant.

The calculations lead to the following conclusions (the difference between the formal potentials, ΔE^*, is equal to ΔE_G^*, and the coefficient of the titrant is denoted by m and that of the analyte by n). (*i*) When $m/n \leq 1$, the inflection point and the equivalence point never coincide. The inflection point corresponding to the *minimum* of the redox buffer capacity is always *before* the equivalence point. (*ii*) When $1 < m/n < 2$, the inflection point corresponding to the *minimum* of the redox buffer capacity coincides with the equivalence point. If $\Delta E^* < \Delta E_G^*$, both inflection points appear *before* the equivalence point and if $\Delta E^* > \Delta E_G^*$, the inflection point corresponding to the *minimum* of the redox buffer capacity appears *after* the equivalence point. (*iii*) When $m/n = 2$, only one inflection point, which coincides with the equivalence point, appears on the titration curve and then $\Delta E_G^* = \Delta E_{min}^*$. If $\Delta E^* > \Delta E_G^*$, the inflection point corresponding to the *minimum* of the redox buffer capacity appears *after* the equivalence point. (*iv*) When $m/n > 2$, the inflection point corresponding to the *maximum* of the redox buffer capacity and the equivalence point coincide. If $\Delta E^* < \Delta E_G^*$, both inflection points appear *after* the equivalence point and if $\Delta E^* > \Delta E_G^*$, the inflection point corresponding to the *minimum* of the redox buffer capacity appears *after* the equivalence point.

On the basis of the results presented above, it can

Table 4. Calculated parameters for the coincidence of the inflection point and the equivalence point; the values of ΔE_i for the other inflection points (which do not coincide with the equivalence points) are also given [Ox(1) as titrant]

m	n	ΔE_G^*, mV	K	$\Delta E_{i(min)}$	$\Delta E_{i(max)}$
2	1	42.34	27.0	0	0
3	1	23.74	16.0	12.80	0
3	2	34.46	3.12×10^3	0	−10.3
4	1	16.40	12.9	15.45	0
4	2	21.17	7.29×10^2	0	0
4	3	29.16	8.23×10^5	0	−11.2
5	1	12.50	11.4	15.66	0
5	2	15.24	3.77×10^2	4.39	0
5	3	19.00	6.55×10^4	0	−3.85
5	4	25.40	3.87×10^8	0	−10.6

When $\Delta E_{i(min)} = 0$, ip_{min} and ep coincide.
When $\Delta E_{i(max)} = 0$, ip_{max} and ep coincide.

Table 5. Limiting values of $\Delta E_{i(min)}$, for large differences between the formal potentials, ΔE^*, when Ox(1) or Red(2) acts as titrant (for the inverse values of m/n, the $\Delta E_{i(min)}$ values are negative).

	m/n	2/1	3/1	4/1	5/1	3/2	4/2	5/2	4/3	5/3	5/4
$\lim\Delta E_{i(min)}$,	mV	11 87	14.11	14.25	13.78	4 167	5.936	6 726	2.112	3.281	1.274

be stated that the conclusion by Murgulescu and Dragulescu[2] that the inflection point corresponding to the maximum slope of the titration curve should appear after the equivalence point when the coefficient of the titrant is greater than that of the analyte is only partly valid. Also the deduction by Goldman[7] that if $\Delta E^* < \Delta E^*_C$, the inflection point corresponding to the maximum slope of the titration curve appears before the equivalence point (and after the equivalence point if $\Delta E^* > \Delta E^*_C$) is valid only when $m/n \leq 2$.

(d) Titrations in practice

In practical titrations the difference between the formal potentials is always large. This allows the relative positions of the inflection points and the equivalence point to be described more simply. From the calculations it can be noted that, for a titration corresponding to equation (1), (Ox(1) or Red(2) as titrant) as ΔE^*, which is generally high in a practical titration, is increased, the difference $\Delta E_{i(min)}$ between the potentials corresponding to the minimum of the redox buffer capacity and the equivalence point either increases or decreases to a limiting value which depends only on the temperature and the coefficients m and n. The limiting values, $\lim\Delta E_{i(min)}$, are presented in Table 5.

Furthermore, it can be noted that (*i*) when $m/n < \frac{1}{3}$, $\Delta E_{i(min)}$ is always negative and its numerical value decreases, regardless of the titrant, when the difference between the formal potentials, ΔE^*, increases; (*ii*) when $1/3 \leq m/n < 1$, $\Delta E_{i(min)}$ is always negative, and it increases with increasing ΔE^* when Ox(1) is the titrant and decreases when Red(2) is the titrant; (*iii*) when $m/n = 1$, $\Delta E_{i(min)}$ is negative when Ox(1) is the titrant and positive when Red(2) is the titrant. In both cases $\Delta E_{i(min)}$ approaches zero when ΔE^* increases; with the same ΔE^* value, the value of $\Delta E_{i(min)}$ becomes smaller as the number of electrons transferred $p = m = n$ is increased; (*iv*) when $1 < m/n \leq 3$, $\Delta E_{i(min)}$ is always positive, and it increases with increasing ΔE^* when Ox(1) is the titrant and decreases when Red(2) is the titrant; (*v*) when $m/n > 3$, $\Delta E_{i(min)}$ is always positive, and it decreases, regardless of the titrant, with increasing ΔE^*.

The results of Murgulescu and Dragulescu[2] are valid for high ΔE^* values.

The solutions of equations (15) and (15') also clarify the relative positions of the inflection point, corresponding to the maximum of the redox buffer capacity, and the equivalence point. The calculations show that with small ΔE^* values the $ip_{(max)}$ occurs after the "half-titrated" position. The larger the ΔE^* value, the closer is the potential $\Delta E_{i(max)}$ to the formal potential E^* of the analyte.

(e) Approximate equations for practical titrations

The considerations presented above require computer calculations, but an approximate value for $(e^{x+y})_{i(min)}$ may be used instead. In practical titrations ΔE^* is large, and at the inflection point $e^y =$

$$\frac{c_{Ox(2)}}{c_{Red(2)}} \gg 1 \quad \text{and} \quad e^x = \frac{c_{Ox(1)}}{c_{Red(1)}} \ll 1.$$

When Ox(1) is the titrant this leads to

$$(e^{x+y})_{i(min)} \approx (m/n)^2 \tag{28}$$

as an approximation to equation (15). From equation (28)

$$(x + y)_{i(min)} = 2\ln(m/n) \tag{29}$$

Then, according to equation (18)

$$\Delta E_{i(min)} = E_{i(min)} - E_e = \frac{RT}{F}\frac{2}{(m+n)}\ln\frac{m}{n}. \tag{30}$$

When Red(2) is the titrant, the approximation of equation (15') is the same as in equation (28), and hence equation (30) is again valid.

Calculations with these simplified equations give the same $\lim\Delta E_{i(min)}$ values (to four digits) for the various pairs of coefficients m and n given in Table 5.

For symmetrical redox titrations ($m = n = p$) equations (28) and (30) give $(e^{x+y})_{i(min)} = 1$. Thus $\Delta E_{i(min)} = 0$ and $ip_{(min)}$ coincides with the equivalence point, For this, equations (15) and (15') must be used instead of the simplified version (28). When Ox(1) is the titrant, from equation (15) $(e^{x+y})_{i(min)} \approx 1 - e^{-y}$, so $\Delta E_{i(min)} < 0$, and in this case $ip_{(min)}$ lies before the equivalence point. When Red(2) is the titrant, then $(e^{x+y})_{i(min)} \approx 1 + 3e^x$ and $\Delta E_{i(min)} > 0$ so $ip_{(min)}$ again lies before the equivalence point.

REFERENCES

1. I. M. Kolthoff and N. H. Furman, *Potentiometric Titrations*, 2nd Ed., Chap. 3. Wiley, New York, 1931.
2. I. G. Murgulescu and C. Dragulescu, *Z. Phys. Chem. A*, 1940, **185**, 375; 1942, **190**, 174.
3. E. R. Nightingale Jr., *Anal. Chem.*, 1958, **30**, 267.
4. E Bishop, *Anal. Chim. Acta*, 1952, **7**, 15; 1962, **26**, 397; 1962, **27**, 253.
5. J. A. Goldman, *J. Electroanal. Chem.*, 1966, **11**, 255; 1966, **11**, 416.
6. *Idem, ibid.*, 1968, **16**, 47.
7. *Idem, ibid.*, 1968, **18**, 41
8. A. Meretoja, O. Lukkari and H. Lukkari, *Finn. Chem. Lett.* 1976, 77.

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EXTRACTION OF MERCURY(II) FROM AQUEOUS THIOCYANATE SOLUTIONS WITH 5-(4-PYRIDYL)NONANE IN BENZENE, AND ITS SUBSEQUENT ATOMIC-ABSORPTION SPECTROMETRIC DETERMINATION

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Summary—Tracer ($\sim 10^{-8}M$) mercury(II) can be quantitatively extracted with 5-(4-pyridyl)nonane in benzene from aqueous thiocyanate solutions that are up to $6M$ in HCl, $1M$ in H_2SO_4 or $0.25M$ in HNO_3, in a single extraction. Optimal conditions for the extraction are given, based on a critical study of the relevant factors such as the effects of the acids, thiocyanate, salting-out and complexing agents and the reagent concentration. The mechanism underlying these extractions is discussed on the basis of the results obtained from partition and slope-analysis data. The extraction of the metal as $Hg(PyN)_2(SCN)_2$ is indicated. The extracted mercury can be stripped from the non-aqueous layer with various aqueous solutions, including nitric acid ($\geq 2M$), sodium citrate ($\geq 1M$) and sodium thiosulphate ($\geq 0.1M$). Common salts do not depress the extraction. Distribution coefficients and separation factors of several elements relative to mercury(II) are reported for media that contain the optimal concentrations of the mineral acids and are in $0.2M$ in potassium thiocyanate. The data have been applied for the determination of mercury in soil and water samples by atomic-absorption spectrometry.

The extraction and determination of traces of mercury have attracted considerable attention owing to the toxicity of mercury and its compounds. Numerous analytical methods for the extractive determination of mercury in various matrices have been described. Reviews have been published recently by Ure[1] and Chilov.[2] A commonly used reagent for the extraction and preconcentration of mercury(II) is ammonium pyrrolidinedithiocarbamate (APDC) dissolved in methyl isobutyl ketone, (MIBK), which also co-extracts many other metal ions quantitatively. This paper is concerned with the use of 5-(4-pyridyl)-nonane dissolved in benzene as an extractant for mercury(II) from various matrices. The method is rapid and fairly selective and the various parameters have wide tolerance; it has been adapted for the determination of the element by atomic-absorption spectrophotometry. The main purpose was to demonstrate the applicability of the procedure for the extraction and possible preconcentration of the metal from spiked soil and water samples, without particular stress on low levels of detection. However, this extraction procedure could well be used in combination with the cold vapour atomic-absorption technique for the determination of low levels of mercury.

EXPERIMENTAL

Reagents and instrumentation

5-(4-Pyridyl)nonane (PyN) was used as extractant. The characteristics of this compound are given elsewhere.[3,4] Stock mercury(II) solution was made by dissolving the appropriate amount of analytical grade mercuric nitrate in 250 ml of distilled water and diluted as required to make standards of low concentrations. All solutions were prepared in doubly-distilled demineralized water. ^{203}Hg tracer solutions were prepared by dissolving a weighed quantity of irradiated HgO in high-purity acids and diluted to volume with distilled water. The equipment used for the radiochemical assay was described previously.[5,6] Atomic-absorption analyses were done on a Carl-Zeiss FMD 3 Atomic Absorption Spectrophotometer equipped with a deuterium lamp for automatic background compensation, a 10-cm titanium universal burner using acetylene/air as gas mixture, and a Westinghouse mercury hollow-cathode lamp.

Extraction procedure

Partition coefficients were determined by a procedure similar to the one used for the corresponding zinc system [4] The period of equilibration was varied from 0.5 to 15 min. The extraction was quantitative with 1 min equilibration or more. A 5-min equilibration time was used. The concentration of mercury(II) in the original aqueous phases was $10^{-8}M$

Procedure for opening out soil samples

Of the various methods used[7] for opening out soils for mercury determination, the one recommended by Iskandar *et al.*[8] was adopted for our purpose. (Procedures requiring hydrochloric acid in the initial acid mixtures were avoided, because although it increases the sensitivity of mercury determination,[9] the varying amounts of the acid left after evaporation caused a large fluctuation in the atomic-absorption signals; hydrochloric acid was added to the final solution before aspiration into the flame, to make use of the increase in sensitivity.) The container with 1 g of soil sample (as received or spiked with Hg) was placed in an ice-water bath and 15 ml of 2:1 sulphuric acid–nitric acid mixture were added slowly. After expulsion of nitrous fumes the mixture was digested for 2–3 hr on a water-bath at 50–60°. The solution was filtered through a porosity-3 sintered-glass disc, neutralized with conc. sodium hydroxide solution and adjusted to give 100 ml of solution $0.1M$

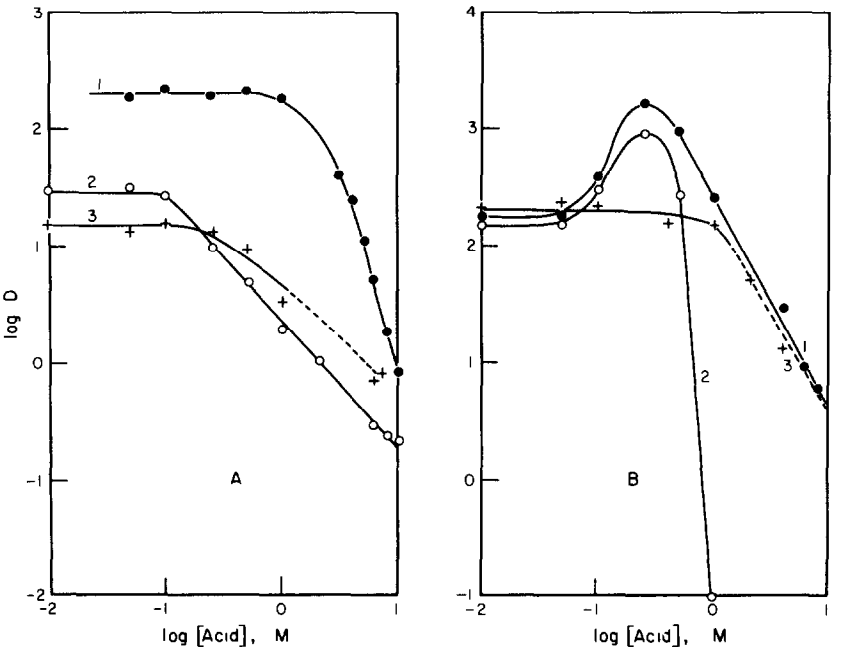


Fig. 1. Distribution of Hg(II) between 0.1*M* PyN/benzene and aqueous mineral acid solutions (A) without and (B) with thiocyanate (0.02*M*).

in nitric acid and 0.2*M* in thiocyanate, before extraction by the described procedure. Blanks and standard mercury(II) solution were treated in the same manner.

RESULTS AND DISCUSSION

In Fig. 1A log *D* is plotted against the concentration of hydrochloric, nitric and sulphuric acid in the aqueous phase for the extraction of trace amounts ($\sim 10^{-8}M$) of mercury(II) by 0.1*M* PyN in benzene. In the hydrochloric acid system, the extraction from dilute acid solutions can be ascribed to the hydrolysed species while the extraction from moderately concentrated acid solutions is evidently due to the extraction of anionic chloride complexes of the metal; these are obviously present since trioctylamine extraction[10] in this region is high. The decrease of the partition coefficient with increase of acidity in the aqueous phase can be attributed to the fact that the acid itself is extracted by the organic reagent and much less of the reagent is available for extraction of the complex. In nitric and sulphuric acid solutions, appreciable extraction is observed from the dilute solutions, probably of hydrolysed metal species of the type Hg(OH)(A) where A is the anion of the supporting acid. The decrease in extraction at high acidities can be explained as due to the competition of the acids for association with the free base. In the sulphuric acid system, an intermediate third phase is formed at acid concentrations above 1*M* as in the corresponding zinc system[4] and can be explained similarly.

Figure 1B shows the effect of thiocyanate (0.02*M*) on the extraction of mercury(II) by 0.1*M* PyN in benzene from various concentrations of the mineral acids. The addition of thiocyanate promotes extraction in all three systems probably because thiocyanate ions give larger and less hydrated complexes. In the hydrochloric and nitric acid systems, the distribution coefficients for mercury(II) first rise with aqueous thiocyanate concentration, pass through maxima at initial thiocyanate concentrations of 0.1–1*M* and then fall again. In the sulphuric acid system, the shape of the extraction isotherm is almost similar to that for the extraction from the acid alone, but the distribution ratios are greater by an order of magnitude.

The extraction of trace amounts of mercury(II) by 0.1*M* PyN in benzene was also investigated as a function of thiocyanate concentration at several concentrations of mineral acid (Fig. 2). All the curves show maxima at around 0.1–0.5*M* potassium thiocyanate in the initial aqueous phase. The extraction is quantitative over the whole region of thiocyanate concentration investigated except when the concentration of nitric and sulphuric acid solutions is too low or that of hydrochloric acid is too high. The variation of the distribution coefficient may be attributed to the formation of metal ion–thiocyanate complex and to the competition between metal ion and thiocyanate for association with the pyridine.

Experiments were performed to ascertain the composition of the extractable species by extracting mercury(II) at fixed acid concentration with varying concentrations of PyN, with benzene as diluent. The experiments were carried out with and without thiocyanate ions present. Figure 3A shows the plots of log *D* *vs.* log[PyN] for 0.1*M* solutions of the mineral acids without thiocyanate. For the hydrochloric acid

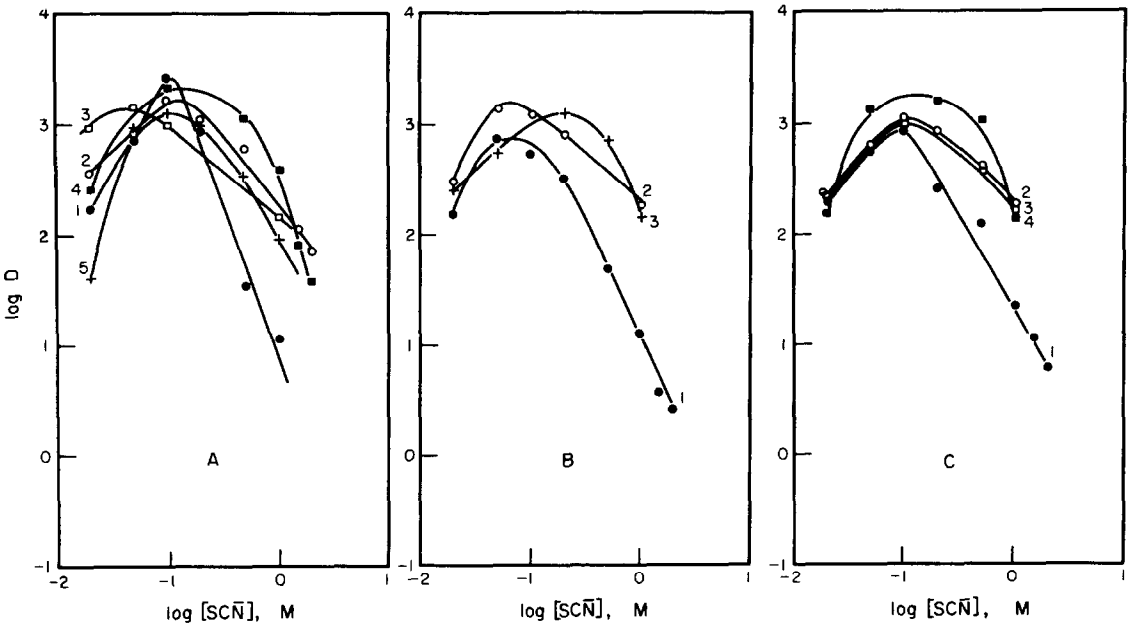


Fig. 2. Variation of the distribution coefficients of Hg(II) as a function of thiocyanate concentration in constant acidity solutions; extractant 0.1*M* PyN/benzene. (A) HCl system: (1) 0.01*M*; (2) 0.1*M*; (3) 0.5*M*; (4) 1.0*M*; (5) 3.0*M*. (B) HNO_3 system: (1) 0.01*M*; (2) 0.1*M*; (3) 0.5*M*. (C) H_2SO_4 system: (1) 0.01*M*; (2) 0.1*M*; (3) 0.5*M*; (4) 1.0*M*.

system the slope was around 2, whereas for the nitric and sulphuric acid systems, the slope of the linear part of the curves was ~1.5, suggesting the extraction of a mixture of compounds containing one and two molecules of the extractant. Figure 3B shows the dependence of log *D* on the reagent concentration, for 0.1*M* mineral acid solutions 0.2*M* in thiocyanate. The linear parts of the curves below 0.01*M* concen-

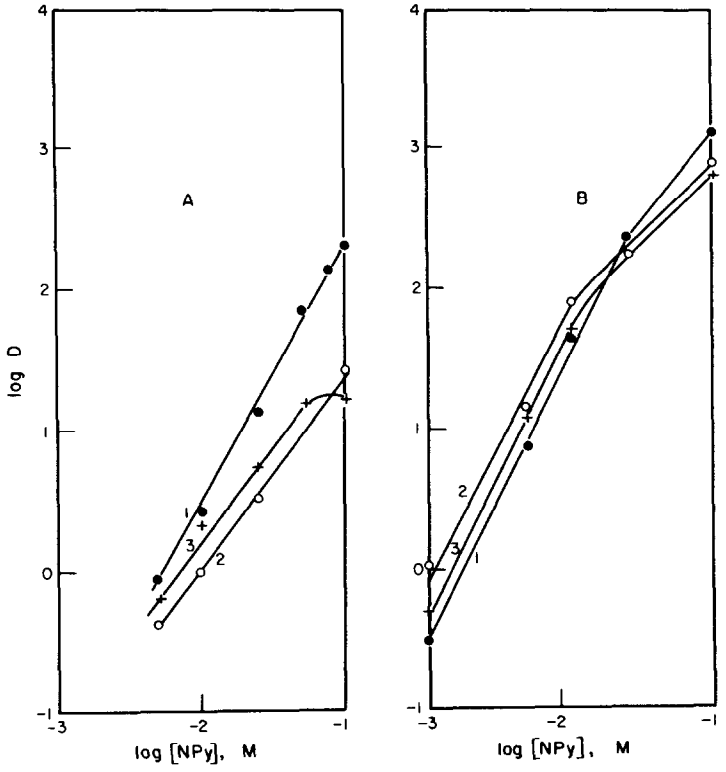


Fig. 3. Influence of PyN concentration on the extraction coefficient of Hg(II) from constant acidity solutions (A) without thiocyanate and (B) 0.2*M* in KSCN. (1) 0.1*M* HCl; (2) 0.1*M* HNO_3; (3) 0.1*M* H_2SO_4.

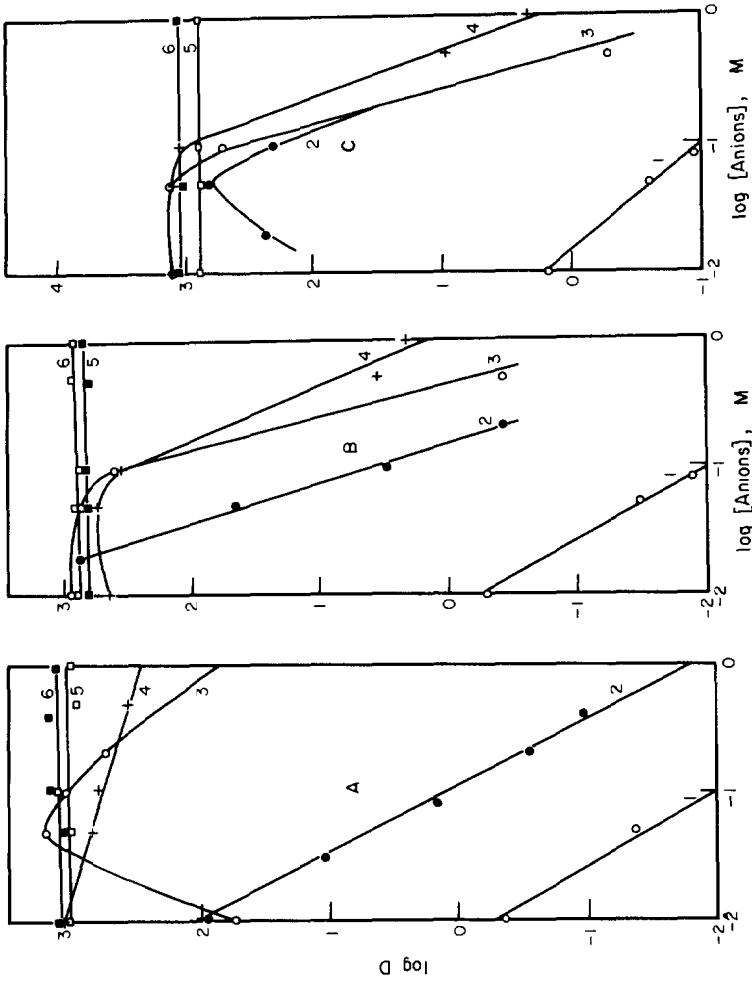


Fig. 5. The effect of various anions on the distribution coefficient of Hg(II) from 0.1*M* acid solutions 0.2*M* in KSCN. A: HCl; B: HNO_3; C: H_2SO_4. (1) thiosulphate; (2) citrate; (3) acetate; (4) oxalate; (5) ascorbate; (6) sulphate.

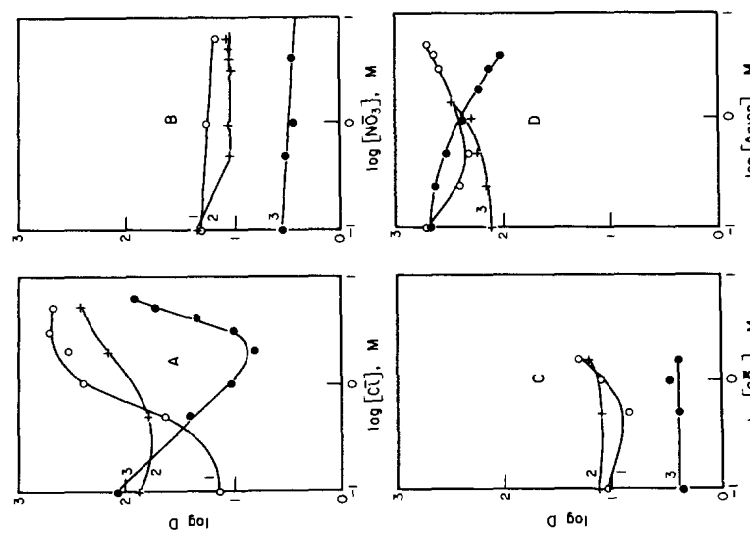


Fig. 4. The effect of the addition of chloride, nitrate and sulphate salts on the extraction behaviour of Hg(II) with 0.1*M* PyN/benzene and the corresponding constant acidity solutions without thiocyanate ions (A, B, C) and 0.2*M* in KSCN (D). (A) HCl system: (1) 0.01*M*; (2) 0.1*M*; (3) 1*M*. (B) HNO_3 system: (1) 0.01*M*; (2) 0.1*M*; (3) 1*M*. (C) H_2SO_4 system: (1) 0.01*M*; (2) 0.1*M*; (3) 1.0*M*. (D): (1) 0.1*M* HCl + 0.2*M* KSCN; (2) 0.1*M* HNO_3 + 0.2*M* KSCN; (3) 0.1*M*. H_2SO_4 + 0.2*M* KSCN.

Table 1. Distribution coefficients and separation factors of different metal ions from 0.1*M* PyN/benzene-mineral acid (0.2*M* with respect to KSCN) extraction systems

Metal ion	Concentration, *M*	Distribution coefficients			Separation factors		
		0.1*M* HCl	0.1*M* HNO_3	0.1*M* H_2SO_4	0.1*M* HCl	0.1*M* HNO_3	0.1*M* H_2SO_4
Hg(II)	10^{-8}	1113	839	900	—	—	—
Tc(VII)	C.F*	6.2	4.7	5.6	1.8×10^2	1.8×10^2	1.6×10^2
U(VI)	10^{-3}	21.8	26.3	15.3	51	32	59
Cr(VI)	C.F	2.3	2.6	0.35	4.8×10^2	3.2×10^2	2.6×10^3
Mo(VI)	10^{-5}	0.23	1.0	4.7	4.8×10^3	8.4×10^2	1.9×10^2
Mo(V)	10^{-5}	18.8	110	15.9	59	76	57
Ru(IV)	10^{-6}	0.1	0.47	0.07	1.1×10^4	1.8×10^3	1.3×10^4
Hf(IV)	10^{-7}	0.3	1.2	1.43	3.7×10^3	6.9×10^2	6.3×10^2
Cr(III)	C.F	0.04	0.11	0.12	2.8×10^4	7.6×10^3	7.5×10^3
Y(III)	10^{-8}	1.1	1.03	1.17	1.0×10^3	8.1×10^2	7.7×10^2
Ce(III)	10^{-8}	0.00	0.00	0.00	$>10^5$	$>10^5$	$>10^5$
Nd(III)	10^{-8}	0.14	0.01	0.02	7.9×10^3	8.4×10^4	4.5×10^4
Fe(III)	10^{-6}	7	2.04	17	1.6×10^2	4.1×10^2	52
La(III)	10^{-6}	0.05	0.05	0.27	2.2×10^4	1.7×10^4	3.3×10^3
Pm(III)	10^{-7}	0.00	0.00	0.00	$>10^5$	$>10^6$	$>10^5$
Ir(III)	10^{-7}	0.06	0.02	0.03	1.8×10^4	4.2×10^4	3.0×10^4
Sr(II)	10^{-8}	0.01	0.00	0.00	$>10^5$	$>10^5$	$>10^5$
Zn(II)	10^{-5}	1197	243	1046	0.9	3.5	0.9
Co(II)	10^{-5}	204	359	119	5.5	2.3	7.6
Cu(II)	10^{-6}	47	39	30	24	22	30
Cs(I)	10^{-8}	0.00	0.00	0.00	$>10^6$	$>10^6$	$>10^6$
Ag(I)	10^{-8}	189	239	144	5.9	3.5	6.3
Br^-	10^{-4}	0.18	0.25	0.24	6.2×10^3	3.4×10^3	3.7×10^3

C.F. = carrier-free

tration of the reagent have a slope of about 2. The linearity breaks down above 0.01*M* concentration of the reagent and the slope decreases, probably because of aggregation of the pyridine salts.

The effect of common salts on the extraction of mercury was investigated at constant acidity with and without thiocyanate. The results are presented in Fig. 4. The addition of sodium chloride (Fig. 4A) to the (0.1 or 0.5*M*) hydrochloric acid system appears to have a depressant effect on extraction up 0.1*M* concentration of added chloride. This is possibly due to a shift in the equilibrium, favouring formation of relatively less extractable neutral chloride complexes of mercury(II). With 1*M* hydrochloric acid, the *D* value decreases with added chloride concentration up to 1*M*. This is probably because the comparatively less extractable neutral chloride complexes are more readily formed at relatively high acid concentrations. A subsequent increase in extraction at salt concentration above 1*M* can be ascribed to the salting-out effect and/or to the formation of anionic chloride species. However, over the whole range of added salt concentration, the extraction is almost quantitative. In the nitric and sulphuric acid systems (Figs. 4B and 4C), the corresponding metal salts do not appear to have much salting out and/or complexing effect on the extraction, which remains more or less constant.

We also recorded the effect of neutral chloride, nitrate and sulphate salts on the extraction of mercury(II) from 0.1*M* solutions of the corresponding mineral acids (0.2*M* in thiocyanate). The results presented in Fig. 4D show that in these systems the extraction is not very much influenced by the presence of neutral salts in the aqueous phase.

The extraction of mercury(II) was also studied as a function of the concentration of different complexing agents added to 0.1*M* aqueous solutions of the mineral acids (0.2*M* in thiocyanate)—Fig. 5. In the thiosulphate and acetate systems, the extraction decreases with increasing concentration of these ions in the original aqueous solutions but the decrease is not very pronounced. Oxalate and citrate almost com-

Table 2.

Hg added, *ppm*	Hg found by extraction and AAS determination, *ppm*		
	Soil	Water	Water + 0.25*M* K_2SO_4
25	24 ± 1	—	—
50	48.5 ± 2	48.5 ± 1.5	51.0 ± 2
100	98.8 ± 1	98.5 ± 1	99.5 ± 1.5

pletely suppress the extraction when present in above 0.1*M* concentration.

To find the selectivity the behaviour of a number of metal ions, including other inorganic pollutants, was examined. The data presented in Table 1 show that it is possible to separate mercury(II) from a number of elements in a single extraction followed by a few scrub stages. Zinc, cobalt and copper, however, are quantitatively co-extracted, indicating that the reagent has potential for the preconcentration of toxic metal ions from solutions.

For quantitative stripping of the metal into the aqueous phase, the organic phase containing mercury(II) was equilibrated with an aqueous phase 2*M* in nitric acid 0.2*M* in thiocyanate and containing 1% of hydrochloric acid. Table 2 shows the recoveries of added Hg after extraction and stripping steps, as determined by atomic-absorption spectrophotometry. Nitric acid (2*M*) without thiocyanate also strips mercury but less efficiently. Moderately concentrated perchloric acid was also found to strip mercury. Oxalate and citrate also act as stripping agents although but there is a loss of mercury activity, the cause of which was not elucidated.

REFERENCES

1. A. M. Ure, *Anal. Chim. Acta*, 1975, **76**, 1.
2. S. Chilov, *Talanta*, 1975, **22**, 205.
3. M. Iqbal and M. Ejaz, *Anal. Chem.*, 1975, **47**, 936.
4. M. Iqbal, A. Qureshi and M. Ejaz, *Talanta*, 1978, **25**, 371.
5. M. Ejaz, *Sep. Sci.* 1975, **10**, 425.
6. M. Iqbal, M. Ejaz, S. A. Chaudhri and R Ahmed, *ibid.*, 1976, **11**, 255.
7. H. Agemian and A. S. Y. Chau, *Analyst*, 1976, **101**, 91.
8. I. K. Iskandar, J. K. Syers, L. W. Jacobs, D. R. Keeney and J. T. Gilmour, *ibid.*, 1972, **97**, 388.
9. J. W. Owens and E. S. Gladney, *Anal. Chem.*, 1976, **48**, 787.
10. M. Y. Mirza and M. Ejaz, *Anal. Chim. Acta* 1967, **37**, 402.

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DETERMINATION OF RHENIUM IN GEOLOGICAL MATERIALS BY RADIOCHEMICAL NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method for the determination of rhenium in geological materials is described. Radiochemical separation, using Re-carrier and liquid–liquid extractions, yields ^{186}Re in a state of radiochemical purity. The gamma-ray activity of the radionuclide is counted with an NaI(Tl) crystal scintillation detector, and the chemical yield is determined spectrophotometrically. Results for the contents of rhenium in the standard rock W-1 and in nickeliferous lateritic profiles are reported. Particular problems arising in neutron-activation analysis for rhenium in lunar surface materials are discussed.

Rhenium is an extremely rare element, with a crustal abundance of 0.1–1 ppM* on the Earth, although it is concentrated in a few minerals, such as dzhezkazganite.[1] It follows that for studies of its geochemistry a method of analysis that provides exceptionally high sensitivity is essential. Neutron-activation analysis satisfies this demand. Naturally occurring rhenium consists of two isotopes, ^{185}Re and ^{187}Re, with the terrestrial abundances 37.07 and 62.93%, respectively†. The heavier isotope is radioactive[2] and decays to ^{187}Os by β^--emission with a half-life of $\sim 4.3 \times 10^{10}$ y.

On irradiation with neutrons of thermal energies, rhenium gives rise to radionuclides by the following nuclear reactions.

$$^{185}\mathrm{Re} \xrightarrow{n} {}^{186}\mathrm{Re}_{(t_{1/2}=90.6\,\mathrm{hr})} \begin{cases} \xrightarrow{\beta^-(95\%)} {}^{186}\mathrm{Os\ (stable)} \\ \xrightarrow{EC(5\%)} {}^{186}\mathrm{W\ (stable)} \end{cases} \quad (1)$$

$$^{187}\mathrm{Re} \xrightarrow{n} {}^{188}\mathrm{Re}^{m}_{(t_{1/2}=18.7\,\mathrm{min})} \xrightarrow{IT} {}^{188}\mathrm{Re}_{(t_{1/2}=17.0\,\mathrm{hr})} \xrightarrow{\beta^-} {}^{188}\mathrm{Os\ (stable)} \quad (2)$$

Isotopic thermal neutron-activation cross-sections, σ, for the nuclear reactions[3] are

$$^{185}\mathrm{Re}(n,\gamma)^{186}\mathrm{Re}\ \sigma = 110\ \mathrm{barns}$$

$$^{187}\mathrm{Re}(n,\gamma)^{188}\mathrm{Re}^{m}\ \sigma = 1.3\ \mathrm{barns}$$

$$^{187}\mathrm{Re}(n,\gamma)^{188}\mathrm{Re}\ \sigma = 70\ \mathrm{barns}$$

Rhenium-186 was used in the present study. Its decay scheme[4] is shown in Fig. 1. The radionuclide was separated in a radiochemically pure condition by using Re-carrier and its gamma-radiation was assayed by NaI(Tl) crystal-scintillation counting. Extraction of the active species as ReO_4^- from alkaline solution by Aliquat 336 in methyl isobutyl ketone (MIBK) achieved a good separation from other activities (*cf.* Lakshmanan and Lawson[5]). Other impurities were removed by solvent extraction with sodium dinonylnaphthalenesulphonate (NaD) in solution in n-heptane.[6] Finally traces of technetium-99m ($t_{1/2}$ = 6 hr), formed predominantly by the process $^{98}\mathrm{Mo}(n,\gamma)^{99}\mathrm{Mo}\ (t_{1/2} = 66.7\ \mathrm{hr}) \xrightarrow{\beta} {}^{99}\mathrm{Tc}^{m}$, were separated by extraction with xanthate into carbon tetrachloride.[7,8] The chemical yield of rhenium (usually ~93%) was determined spectrophotometrically, as in the procedure of Terada *et al.*[8,9]

EXPERIMENTAL

Irradiation

Samples of powdered geological material, about 0.4 g, were accurately weighed into pure silica tubes of 4-mm internal diameter, which were closed with pure aluminium caps. Comparison standards were prepared by weighing out *ca.* 0.1-ml aliquots of freshly prepared standard solution of rhenium (Re 0.1 mg/ml) into 4-mm bore silica tubes which were then sealed. Samples and controls were packed

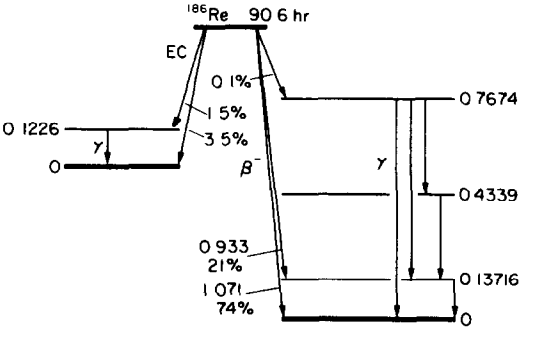


Fig. 1. Decay scheme for ^{186}Re—energies in MeV.

* Parts per milliard (10^9).

† See results and discussion section for alteration of the abundance ratio in lunar surface materials.

together with silica wool in standard aluminium screw-top cans and sent to the Atomic Weapons Research Establishment, Aldermaston, for neutron activation. Irradiations were for periods of 28 hr in the nuclear reactor HERALD in a thermal neutron flux of 1.8×10^{12} n.cm^{-2}.sec^{-1}. Samples and standards were left to "cool" for 5 days after the end of irradiation, before radiochemical processing at Brunel University. At this stage a typical set of irradiated materials gives a dose rate of ~10 mR/hr at a distance of 1 m

Radiochemical separation

Preparation and standardization of rhenium carrier solution [Re(VII) 1 mg/ml]. Potassium perrhenate (Johnson Matthey) (0.1554 g) was dissolved in 100 ml of distilled water. Alternatively, 0.1 g of pure rhenium (Johnson Matthey) was dissolved in 1 ml of conc. nitric acid by heating on a steam-bath, and the solution was neutralized with sodium hydroxide and diluted to 100 ml with distilled water. Aliquots of carrier solutions (10 ml) were standardized gravimetrically by precipitation of tetraphenylarsonium perrhenate.[10]

Reagents. Aliquat 336, commercial grade tricaprylmethylammonium chloride (General Mills Inc.), 0.1% in MIBK; sodium peroxide; sodium hydroxide solutions, 2 and 10*M*; sodium chloride solutions, 3.5, 5 and 10%; sodium perchlorate solution, 0.25*M*; NaD, 0.2*M* in n-heptane; conc. hydrochloric acid; conc. nitric acid; sodium thiocyanate, 10% solution; tin(II) chloride dihydrate, 20% solution in dilute hydrochloric acid; potassium ethyl xanthate; carbon tetrachloride; tetraphenylarsonium chloride solution, 0.05*M*.

Procedure for geological samples. Irradiation tubes were removed from the can and opened. The powdered geological samples were transferred quantitatively to nickel crucibles. To each 2.5 g of sodium peroxide were added and mixed thoroughly. The mixture in each crucible was covered with a layer of sodium peroxide and heated in an electric muffle furnace at 500° for 10 min. The crucibles were removed from the furnace and immediately cooled in a shallow dish of water. After transfer to a 150-ml beaker which was then covered with a watch-glass, the cake in a crucible was carefully dissolved in a small quantity of distilled water. Exactly 2 ml of rhenium carrier were added and the solution was digested on a steam-bath.*

Sufficient conc. hydrochloric acid was added to the solution to make it ~3*M* in the acid and heating was continued in the steam-bath. After centrifuging, the supernatant liquid was transferred to a clean 50-ml glass centrifuge tube. Enough 10*M* sodium hydroxide was added to produce a 2*M* final concentration of alkali. Any precipitate was removed by centrifuging. The clear supernatant liquid was transferred to a 50-ml separatory funnel; the residue was washed with 4 ml of distilled water and, after centrifugation, the washings were added to the separatory funnel. Ten ml of Aliquat 336–MIBK reagent were added and rhenium was extracted into the (upper) organic phase by shaking for 10 min. The lower layer was then rejected, and the extract washed with two consecutive 10-ml portions of 2*M* sodium hydroxide containing 10% of sodium chloride. Rhenium was then stripped into aqueous solution by agitating the organic phase with two consecutive 10-ml portions of 0.25*M* sodium perchlorate. The aqueous back-extracts were combined in a separatory funnel and shaken with 10 ml of NaD–heptane reagent. The aqueous (lower) layer was run off into a brown glass separatory funnel and the organic layer discarded. One ml of conc. hydrochloric acid was added, making the final hydrogen-ion concentration about 0.5–0.6*M*, and 0.1 g of potassium ethyl xanthate was introduced. Technetium was extracted by shaking with 10 ml of carbon tetrachloride for 30 min. The (lower) organic phase was run off and discarded, and finally the aqueous phase was washed with 5 ml of carbon tetrachloride and the organic washings were rejected.

The residual aqueous solution was transferred to a 25-ml standard flask and made up to the mark with distilled water. Then 5 ml were transferred by pipette into another 25-ml standard flask, and 6 ml of conc. hydrochloric acid, 4 ml of 10% sodium thiocyanate solution and 3 ml of 20% tin(II) chloride solution were added, and the solution was diluted to volume with distilled water. After 30 min the absorbance of the solution was measured at 378 nm (in 10-mm glass cells) and the amount of rhenium was calculated from a calibration curve.

Treatment of irradiated standards. At a suitable time the silica tubes containing the Re controls were opened. With a transfer pipette drawn to a fine point, a standard was transferred quantitatively to a 100-ml standard flask. Both parts of the silica ampoule were rinsed very thoroughly with distilled water and the washings transferred to the flask. The solution was then diluted to the mark with distilled water and shaken. A suitable measured aliquot, depending in volume on the amount of Re expected in the corresponding geological samples, was transferred to a 25-ml standard flask and diluted to the mark with distilled water.

Measurement of radioactivity

The final solutions from samples and standards were counted with a well-type gamma-ray scintillation counter [1¾ in. diameter × 2 in NaI(Tl) crystal, with Panax scaler unit]. Five ml of the final solutions (25 ml) were transferred to standard polyethylene tubes which were then inserted in the detector. All activities measured were corrected for background and for chemical yield.

Decay measurements were performed on the final samples. Semi-logarithmic plots of activity against time were always linear and corresponded to a half-life of 90.7 ± 1.3 hr.

From the activity of samples and standards at any arbitrarily chosen time, the rhenium content of the original material could be found from the relationship

$$\text{Weight of Re in sample} = \text{weight of Re in standard} \times \frac{\text{corrected count rate of the sample}}{\text{corrected count rate of the standard}}$$

In most of the geological samples analysed by us in the present study the activity was too low to permit reliable measurement of the 0.137-MeV photopeak of ^{186}Re with a Ge(Li) semiconductor gamma-ray spectrometer.

RESULTS AND DISCUSSION

Table 1 shows the results of the neutron-activation analysis for rhenium in the U.S. Geological Survey standard basalt ("diabase") W-1 from Centerville, Virginia. Magnitudes obtained by the procedure agree well with those obtained previously. The earlier method of Morris and Fifield[10] has the advantage that by employing β^--counting, where a low and fairly constant background count-rate pertains, more accurate measurement of radiation should be achieved. However, the newer method is rather more elegant, particularly in that it dispenses with precipitation processes in the radiochemical separation.

Owing to the extremely low rhenium contents and

* N.B. All the operations must be performed quantitatively until exchange with carrier has been achieved.

Table 1. Rhenium content of the standard basalt ("diabase") W-1 determined by neutron-activation analysis, *ppM*

This work	0.7_1	0.7_0	0.7_0	0.7_2		mean 0.7_1
Morris and Fifield[11]	0.70	0.59	0.83	0.56	0.84	mean 0.7_1
Ishida *et al.*[12]	0.26	0.24				
Morgan and Lovering[13]		0.44	0.41	(reported by Morgan[14], apparently mistakenly, as 10 times as great)		

Tungsten analyses: 0.42, 0.40, 0.41 ppm (this work) 0.42, 0.42, 0.41, 0.47 ppm (Atkins and Smales)[12]

The differences between the first and second pairs of results for Re could be due to variations in the homogeneity of W-1, as this standard was not prepared with such rare elements as rhenium in mind. Lack of uniformity of distribution of gold in samples of such material has been demonstrated experimentally.[15]

the possibility of contamination, *e.g.*, in the grinding of samples. it is felt that all the results for Re should be considered as representing maximum values.

This study was undertaken as part of an investigation of the geochemical occurrence of elements in nickeliferous lateritic profiles.[17–20] Some results of analyses of such deposits as a function of depth are given in Table 2. Reproducibility of the determinations of rhenium is often considerably poorer than would be expected from the counting statistics. This may be due primarily to inhomogeneity of distribution of the element at such low concentrations in the samples. However, the results appear to be sufficiently accurate for reliable geochemical deductions to be made; thus the identification of bands of enrichment of rhenium appears to be unequivocal. Further conclusions will be reported elsewhere.[21]

The figures quoted for tungsten in Table 2 were obtained by neutron-activation analysis, using a slightly modified version of the method of Lustenhouwer *et al.*[22]

It has been demonstrated that errors due to self-shielding differences for neutrons between common rocks[10] or laterite[17] and the dilute aqueous solutions used as controls are not significant. However, there are other geological materials, e.g. lepidolite, colemanite, pyrolusite, smaltite, monazite, which contain as major constituents some elements with high neutron-absorption cross-sections; in such cases preparation of comparators by small standard additions of Re to analysis samples is probably the best answer.[23]

In activation analysis for rhenium by using thermal neutrons attention must be given to the possibility of formation of rhenium radionuclides from tungsten by the sequences

$$^{184}W(n,\gamma)\,^{185}W_{(t_{1/2}=75d)} \xrightarrow{\beta^-} {}^{185}Re(n,\gamma)\,^{186}Re \quad (3)$$

$$^{186}W(n,\gamma)\,^{187}W_{(t_{1/2}=24hr)} \xrightarrow{\beta^-} {}^{187}Re(n,\gamma)\,^{188}Re \quad (4)$$

If only ^{186}Re is counted, as in the method reported here, interference from (3) and (4) is unimportant. It

Table 2. Neutron-activation analysis for rhenium in lateritic profiles (results for tungsten are also listed)

Profile	Sample No.	Depth *m*	Description	Re *ppM*	W *ppm*
Guatemala	L1	1.5–2	Surficial laterite	8.9, 9.2	0.15
Lake Izabel	L2	2.5–3	Plastic laterite	6.8, 6.2	0.13
region	L3	3.5–4	Saprolite	1.9, 2.7	0.32
	L4	5.25–5.75	Boulders in saprolite zone	1.3, 1.2, 0.9	0.10
	L5	8–8.5	Weathered rock	1.9, 1.0, 1.2	0.04
	L6	8–8.5	Fines of weathered rock	1.7, 2.0	0.08
	L7	10.25–10.75	Rock	1.0, 1.1	0.03
New Caledonia	BNC1	0–2	Ferricrete	1.8, 1.7, 1.8, 1.9	0.26
Lat. 22°17'S	BNC2	2–7	Limonite	0.6, 0.8, 0.9	0.08
Long. 166°58'E	BNC3	7–11	Limonite	8.0, 9.0, 6.0	0.12
	BNC4	11–13	Limonite	1.6, 1.9	0.14
	BNC5	13–14	Limonite and asbolite	1.6, 1.8	0.11
	BNC6	14–17	Limonite and asbolite	0.7, 0.9	0.19
	BNC7	17–20	Saprolite	0.8, 0.8	0.13
Indonesia	BIP1	11–13	Limonite and asbolite	4.5, 5.3, 4.4	0.07
Pomalea district	BIP2	13–17	Saprolite	3.1, 3.9	0.06
of Sulawesi	BIP3	18–19	Saprolite and quartz boxwork	1.1, 1.0	0.05
Lat. 4°10'S					
Long. 121°37'E					

has been shown by irradiation of tungsten standards that under the prescribed experimental conditions for a geological sample containing 50 ppm of tungsten the ^{186}Re activity produced by sequence (3) corresponds to that from only 3×10^{-6} ppM of rhenium. On the other hand, if neutron-activation analysis for rhenium is to be based on the counting of ^{188}Re, in addition to ^{186}Re, interference from sequence (4) should be taken into consideration.[10] This is one reason for the "cooling" time of 5 days between the end of irradiation and the commencement of radiochemical processing which is prescribed in the present procedure. Moreover, with shorter cooling times it was found that the final rhenium was contaminated with ^{77}As($t_{1/2}$ = 39 hr) but *not* with ^{76}As($t_{1/2}$ = 26.8 hr). The extraction with Aliquat 336–MIBK separates rhenium from arsenic, and so the ^{76}As found by activation of arsenic in a sample [^{75}As(n, γ)^{76}As] is removed. However, ^{77}As is formed from germanium by the reaction

$$\begin{matrix} & & ^{77}\mathrm{Ge}^{m}_{(t_{1/2}=54\,\sec)} & \xrightarrow{\beta} & ^{77}\mathrm{As}. \\ ^{76}\mathrm{Ge(n,\gamma)} & & & & \\ & & ^{77}\mathrm{Ge}_{(t_{1/2}=11.3\,\mathrm{hr})} & & \end{matrix}$$

Hence in the procedure the ^{77m}Ge + ^{77}Ge activity is permitted to decay away before the extraction with the quaternary ammonium compound is performed.

Rhenium-186 can be produced by the nuclear reaction ^{186}Os(n, p)^{186}Re. However, this is of no significance in the present method for rhenium in geological materials, except in the case of a few rare matrices, *e.g.*, osmiridium.

Additional complexities arise in the determination of rhenium in lunar materials by neutron-activation analysis. Michel *et al.*[24–26] have applied the technique for the isotopic analysis of lunar samples for rhenium in the subnanogram range. They found, by comparing the 0.137–MeV photopeak of ^{186}Re with the 0.155–MeV photopeak of ^{188}Re, measured with a Ge(Li)-detector and a multichannel analyser, that ^{187}Re is enriched in lunar material relative to the terrestrial value by 1.4–1.8% (in 14 regoliths) and by as much as 29% in one of the Apollo 14 breccias. The (tungsten/rhenium) ratios varied between 1.1×10^3 (soils) and 4.1×10^4 (breccia 14321), and this suggested that the isotopic anomaly is mainly caused through neutron capture by ^{186}W giving rise to ^{187}Re. This is considered to be primarily due to epithermal neutrons of energies up to ~100 eV in the lunar flux. It follows that a proper analysis for the rhenium content of materials on the lunar surface by neutron activation should involve the determination of both the individual isotopes ^{185}Re and ^{187}Re, together with simultaneous analysis for tungsten in order to correct for interference from reaction (4). To apply the present procedure to the determination of ^{185}Re it would be necessary to remove germanium in the radiochemical separation before the extraction with Aliquat 336–MIBK; this could be done by adjusting the aqueous phase to ~9*M* in hydrochloric acid and extracting the germanium with carbon tetrachloride.[27,28]

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REFERENCES

1. D. F. C. Morris and E. L. Short, in *Handbook of Geochemistry* (ed. K. H. Wedepohl) Vol. II-1. Springer-Verlag, Berlin, Heidelberg, New York, 1969.
2. B. Hirt, G. R. Tilton, W. Herr and W. Hoffmeister, *Earth Science and Meteoritics*, p. 273. Interscience, New York, 1963.
3. D. T. Goldman, *Chart of the Nuclides* (1964, 1965); General Electric Co. Schenectady, N.Y.; also private communications.
4. C. M. Lederer, J. M. Hollander and I. Perlham, *Table of Isotopes*, 6th Ed., Wiley, New York, 1968.
5. V. I. Lakshmanan and G. J. Lawson, *Proc. Intern. Solvent Extraction Conf ISEC71*, 1971, **1**, 631.
6. D. F. C. Morris, *Chem. Ind. (London)*, 1973, 624.
7. T. Kiba, K. Terada, N. Okawa and S. Osaki, *Talanta*, 1966, **13**, 1385.
8. K. Terada, Y. Yoshimura, S. Osaki and T. Kiba, *ibid.*, 1967, **14**, 53.
9. K. Terada and T. Isohara, *Bunseki Kagaku*, 1965, **14**, 745.
10. D. F. C. Morris and F. W. Fifield, *Talanta*, 1961, **8**, 612.
11. *Idem, Geochim. Cosmochim. Acta*, 1961, **25**, 232.
12. K. Ishida, R. Kuroda and K. Kawabuchi, *Anal. Chim. Acta*, 1966, **36**, 18.
13. J. W. Morgan and J. F. Lovering, *Earth Planet Sci. Lett.*, 1967, **3**, 219.
14. J. W. Morgan, *Anal. Chim. Acta*, 1965, **32**, 8.
15. K. Fritze and R. Robertson, in *Modern Trends in Activation Analysis*, ed. J. R. De Voe, Vol. II, p. 1279. NBS Spec. Pubn. 312, 1969.
16. D. H. F. Atkins and A. A. Smales, *Anal. Chim. Acta*, 1960, **22**, 462.
17. I. Ahmad, S. Ahmad and D. F. C. Morris, *Analyst*, 1977, **102**, 17.
18. S. Ahmad and D. F. C. Morris, *ibid.*, 1977, **102**, 395.
19. *Idem, Radiochem. Radioanal. Letters*, 1977, **28**, 165.
20. *Idem, Min. Mag.* 1978, **42**, 143, M4.
21. A. Gharib and D. F. C. Morris, *ibid.*, in press.
22. J. W. A. Lustenhouwer, H. A. Das and H. A. van der Sloot, *Radiochem. Radioanal. Letters*, 1976, **26**, 57.
23. D. F. C. Morris and R. A. Killick, *Talanta*, 1961, **8**, 129.
24. R. Michel, V. Herpers, H. Kulus and W. Herr, *Proc. Third Lunar Science Conf.* (Supplement 3, *Geochim Cosmochim. Acta*), 1972, **2**, 1917.
25. *Idem, Am. Soc. Testing Mater., Spec. Tech. Publ.* No. 539, 140 (1973).
26. *Idem, J. Radioanal. Chem.*, 1973, **17**, 177.
27. D. F. C. Morris and J. S. P. Batchelor, *Geochim. Cosmochim. Acta*, 1966, **30**, 737.
28. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959.

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RAPID ANALYSIS OF SMALL GLASS FRAGMENTS BY ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—A rapid method is described for the determination of magnesium, iron and manganese in small glass fragments (250–500 μg). The speed of the analytical procedure is made possible by the use of a convenient cold digestion stage allied to a discrete sampling method which permits the three elements of interest to be determined by flame atomic-absorption spectrophotometry.

Previous work[1–3] has shown that glass samples, indistinguishable on the basis of the physical parameters of density and refractive index, can have very different chemical compositions. Thus the forensic scientist can enhance the evidential value of glass by measuring not only its physical properties but also its chemical composition. As glass commonly occurs as evidence in forensic investigations it is of importance to establish a method which provides precise, accurate results.

Hughes *et al.*[1] described a method for the determination of magnesium and manganese in small (1 mg) glass fragments by a combination of flame and electrothermal atomic-absorption spectroscopy (AAS). This method showed considerable promise but was slow, as it involved dilution of the sample solutions and electrothermal atomization was required for the determination of manganese. The determination of iron, though of interest, would also have required electrothermal atomization, which would have made the method unacceptably time-consuming. AAS has also been used for the determination of manganese and iron in very small glass samples (*ca.* 100 μg).[4] In this method electrothermal atomization was used for both elements and consequently high sample through-puts were not possible.

The simultaneous determination of six elements in 1-mg glass samples by emission spectrography has also been described.[2] Again the results were promising, but the method involved an arduous sample preparation stage and the time-consuming extraction of quantitative data from photographic plates.

The proposed method covers the measurement of magnesium, manganese and iron in small glass fragments (250–500 μg) by flame atomic-absorption spectroscopy. The sample preparation stage is simple and all three elements are determined in single solution without dilution. With minor modification, magnesium and iron can be determined in 100-μg glass fragments.

EXPERIMENTAL

Instrumentation

An Instrumentation Laboratories IL 151 single-beam atomic-absorption spectrophotometer was used (air–acetylene flame) for all the analyses. The acid matrix of the sample solution necessitated the use of a Teflon-lined nebulizer with a platinum/iridium capillary (available from the manufacturer). The instrument was fitted with a 4-lamp turret and a deuterium-lamp background correction system. Signals were recorded on a Varian A-25 fast-response chart recorder, with 100-mV full-scale deflection and integration for 0.25 sec; the chart speed was 2 cm/min. The gain used was 620 V. Other instrument conditions are listed below

	Mg	Mn	Fe
Bandpass, *nm*	1.0	0.3	0.3
Wavelength, *nm*	202.5	279.5	248.3
Scale expansion	1×	20×	5×
Analysis mode (A, measurement without background correction. A–B, measurement with background correction)	A–B	A	A
Lamp current (mA)	2	0.5	3

Reagents

"Aristar" grade acids and commercially available 1-mg/ml stock solutions of magnesium, manganese and iron (BDH) were used.

Procedure

The samples were digested in 5-ml polystyrene tubes (Sterilin Ltd.) cleaned with 4 ml of 1:2:9 of a mixture of hydrofluoric and hydrochloric acids and water, by agitation in an ultrasonic bath (Megason 60-1, Schuco Scientific Ltd) for 30 min, rinsed three times with distilled water, then with ethanol and dried at 60–80°.

Glass samples (250–500 μg) were soaked in concentrated nitric acid for a minimum of 30 min and washed and dried in the same way as the tubes. The glass fragments were weighed and placed in the clean tubes. After the addition of 0.5 ml of hydrofluoric–hydrochloric acid mixture (1:2) they were agitated in the ultrasonic bath for 30 min. A number of cleaned tubes containing the mixed acid but no glass samples were run as blanks. Then each solution was treated with 1.5 ml of distilled water. These solutions were then nebulized. Standards covering the following ranges were prepared in the 1:2:9 acid–water mixture: Mg, 2.5–15 μg/ml; Mn, 0.025–0.10 μg/ml; Fe 0.125–0.75 μg/ml.

Analysis of small volumes (200 μl). For the analyte to be at a suitable concentration level for flame AAS, the volume of the final solution must not exceed 2 ml, for the size of glass fragments generally encountered in forensic investigations. As typical uptake rates for AAS nebulizers are 5–15 ml/min it is important to conserve the sample solu-

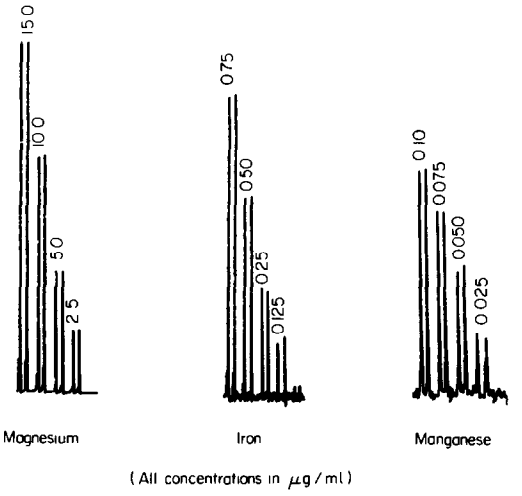


Fig. 1. Chart traces of the standards for the three elements used in the analysis of glass.

tion to allow the determination of three elements for each piece of glass. Previous workers have shown the possibilities of discrete sampling for maximizing the number of determinations on a given sample volume. Slavin[5] indicated that acceptable results could be obtained if the sample was aspirated in the conventional manner with the aspiration time restricted to 1 sec. Thompson and Godden[6] placed 200 μl of solution in a 20-ml polystyrene beaker for aspiration into the flame. Sebastiani *et al.*[7] and Manning[8] used a small cup, the interior of which tapered to a point at the base, attached directly to the metal nebulizer inlet capillary. We deposit 200-μl aliquots in 2-ml sampling cups (Technicon Ltd.) which have a similarly shaped interior, but are not attached to the nebulizer. Distilled water is aspirated continuously between determinations in the normal way, the nebulizer tube is removed from the water and the sample aspirated from the sampling cup; the tube is then returned to the distilled water and the next aliquot prepared.

The blanks and samples are analysed in duplicate, with duplicate determinations of standard solutions at the beginning and end of each run. The analysis for the other two elements is carried out in a similar fashion. The use of the 4-lamp turret means that baseline drift is not a problem and a turn-round time of 10 min between elements is satisfactory. Chart traces typical of those obtained for the standards are shown in Fig. 1.

Reduction in sample size. The method and instrument conditions described here allow the determination of magnesium, manganese and iron in glass fragments as small as *ca.* 250 μg. If required, magnesium and iron can be determined in samples of *ca.* 100 μg by using 0.25 ml of the acid mixture (1:2) to dissolve the glass and then making up to 1 ml with distilled water. The concentrations of the standards used need to be halved and the scale expansions doubled. With the instrumentation available to us manganese cannot be determined at the levels encountered in glass if the samples are smaller than *ca.* 200 μg.

Table 2. Analysis of 20 samples (*ca.* 100 μg) of a typical sheet glass (refractive index = 1.5171) by flame AAS

	Mg, %	Fe, %
Mean	1.91	0.054
Std. devn.	0.11	0.006
Relative std. devn., %	5.6	11.0
Range	1.64–2.02	0.046–0.071

RESULTS AND DISCUSSION

Precision

The results for ten pieces (each *ca.* 500 μg) of the same sheet glass analysed by this method are given in Table 1. These results were obtained on the same day under ideal conditions; coefficients of variation of 5% for magnesium, 5–10% for manganese and not greater than 10% for iron have been found to be more typical for routine analysis. The magnesium and iron results for twenty pieces of the same glass, weighing 100 ± 30 μg, are shown in Table 2. It can be seen that acceptable precision can be obtained on fragments of this size but care is required, in the analysis of small samples, to avoid problems due to iron contamination.

Accuracy

Table 3 shows the results obtained when standard glasses[1,2] were analysed by this method. Also included are the known concentrations of the elements of interest and results obtained by other methods. The results from the proposed method show good agreement for all three elements.

Dissolution of glass fragments

Decomposition of silicate materials has often been done in specially constructed PTFE vessels with various hydrofluoric acid mixtures with subsequent heating under pressure.[9–12] A vapour-phase digestion has also been reported,[13] but this again required a sealed PTFE container for heating under pressure. It was felt that a successful cold digestion method could help in the development of a much quicker and simpler analytical method. Adams[14] had gone some way towards such a system, but the method involved a grinding stage, followed by mechanical stirring. By using ultrasonic agitation and a suitable acid medium, it was thought that small fragments (*ca.* 500 μg) might be dissolved without heating.

Table 1. Analysis of 10 samples (*ca.* 500 μg) of a typical sheet glass (refractive index = 1.5171) by flame AAS

	Mg, %	Mn, *ppm*	Fe, %
Mean	2.03	84	0.057
Std. devn.	0.041	2.6	0.002
Relative std. devn., %	2.0	3.1	3.5
Range	1.96–2.12	79–88	0.052–0.058

Table 3. Comparison of accuracy of methods by using standard glasses of known composition*

Standard glass	Mg, % Previous AA method[1]	Mg, % Emission spectrography[2]	Mg, % Proposed AA method	Mg, % Theoretical	Mn, *ppm* Previous AA method[1]	Mn, *ppm* Emission spectrography[2]	Mn, *ppm* Proposed AA method	Mn, *ppm* Theoretical	Fe, % Previous AA method[1]	Fe, % Emission spectrography[2]	Fe, % Proposed AA method	Fe, % Theoretical
A	0.025	0.05	N.D.†	0.052	338	300	306	303	—	0.187	0.178	0.189
B	0.020	0.095	0.12	0.096	174	170	150	170	—	0.118	0.133	0.122
C	0.51	1.1	1.1	1.1	135	132	121	119	—	0.096	0.098	0.087
D	1.3	1.5	1.8	1.6	238	220	200	206	—	0.051	0.043	0.045
E	2.1	2.2	2.5	2.2	97	98	81	82	—	0.026	0.027	0.029
F	3.4	3.9	4.1	4.1	40	31	42	33	—	0.022	0.009	0.008

* All results are the mean of duplicate determinations
† N.D. not detected.

Table 4 Digestion procedures—Ca and Mg levels detected in a typical sheet glass (refractive index = 1 5171)

Procedure	Mg, %	Ca, %
Mean of emission spectrography results (12 samples)—no digestion involved	2.0 ± 0.2	5.5 ± 0.5
Concentrated hydrofluoric acid—ultrasonic agitation		
initially	1.86 ± 0.1	1.52 ± 0.2
on standing for several days	1.56 ± 0.1	1.34 ± 0.2
after standing but shaking the sample	2.18 ± 0.2	1.34 ± 0.2
HF/HCl (2·1)—ultrasonic agitation		
initially	1.85 ± 0 1	4.83 ± 0.5
on standing for several days	1.87 ± 0.1	4.12 ± 0.5
after standing but shaking the sample	1.87 ± 0.1	4.10 ± 0.5

Examination of Table 3 shows that the results obtained for magnesium by the previous AAS method are considerably lower than the theoretical levels, but those obtained by emission spectrography are satisfactory. It would appear that the dissolution procedure used in the earlier AAS method may influence the measured magnesium concentration. Trials were therefore carried out with various dissolution procedures. The levels of magnesium and calcium present were monitored (flame AAS) since it was suspected that insoluble CaF_2 was co-precipitating the magnesium and reducing the level observed. All studies were carried out on the sheet glass which was used to obtain the results in Tables 1 and 2 and had been analysed many times before by a variety of methods. The results obtained and the procedures studied are given in Table 4. Digestion of the glass in concentrated hydrofluoric acid rather than in the 1:1 mixture with water used earlier (both with ultrasonic agitation) resulted in acceptable magnesium values. The magnesium concentrations determined varied with time, however, and the calcium levels indicated poor dissolution of this element. The use of a 2:1 mixture of hydrofluoric and hydrochloric acids gave magnesium levels similar to those observed with concentrated hydrofluoric acid alone. In this case the magnesium concentration of the solution did not vary with time (over a period of several days) and the calcium content indicated considerably improved dissolution. Digestion of the glass with either acid mixture and heating in a PTFE bomb at 110° for 1–2 hr did not give rise to acceptable results (magnesium and calcium very low). Dissolution with the 2:1 acid mixture and mechanical agitation gave results for both elements slightly lower than those obtained by using ultrasonic agitation, but considerably higher than those from use of the PTFE bomb. Satisfactory digestion of glass samples (100 μg) in a PTFE bomb with hydrofluoric acid alone has been reported.[4] The smaller sample size (100 μg) compared to that used in this work (500 μg) may explain this apparent contradiction in digestion efficiency.

Consideration of the iron levels determined in the standard glass samples resulted in the final choice of an acid matrix consisting of a 1:2 mixture of hydrofluoric and hydrochloric acids. This was shown to give satisfactory results for all three elements (Table 3) over the concentration ranges generally encountered in glass. Table 5 compares the results obtained by using two different acid mixtures for the determination of iron in the standard glasses.

This improved digestion procedure was the first stage in the modification of the earlier AAS method. Also, the standards were altered and suitable resonance lines chosen to allow the determination of magnesium, manganese and iron without further dilution of the solution. The analysis was carried out with flame AAS for magnesium and flameless AAS for iron and manganese and under these conditions a further problem was encountered.

Influence of the magnesium content of glass on the level of manganese detected by using electrothermal AAS

Results obtained for manganese (Table 3) by the earlier AAS method show reasonable agreement with the theoretical. Some dilution of sample solutions was required for the glasses containing higher concentrations of manganese. In the new method there was no such dilution and the results obtained by electrothermal AAS for previously analysed glass samples

Table 5 Dependence of iron concentration determined in standard glasses on acid matrix used

Standard glass	Iron concentration, % HF/HCl 2:1	HF/HCl 1:2	Theoretical
A	0.121	0.171	0.189
B	0.093	0.133	0.122
C	0.074	0.098	0.087
D	0.049	0.043	0 045
E	0.025	0.027	0.029
F	0.007	0.009	0.008

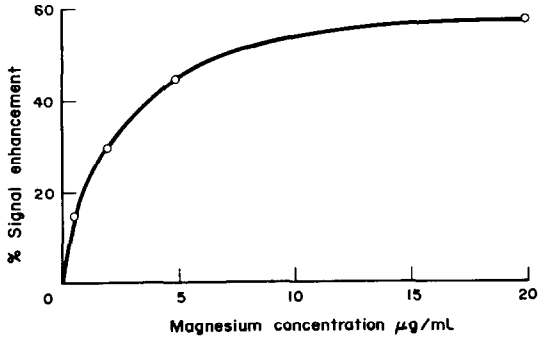


Fig. 2. Signal enhancement for a 0.05-μg/ml manganese solution in the presence of different concentrations of magnesium.

gave spuriously high manganese levels. This enhancement was found to be related to the magnesium content of the solution. The influence of varying amounts of magnesium on the results obtained for 0.05 μg/ml manganese in the 1:2 hydrofluoric–hydrochloric acid mixture is shown in Fig. 2. Improved design in modern AA spectrometers has permitted the determination of both iron and manganese by flame excitation. When the experiment described above was repeated with an air–acetylene flame the enhancement of the manganese signal by magnesium was not observed. These results were consistent with those reported by other workers. A number of authors[15–18] have found that results of acceptable accuracy can be obtained for manganese in the presence of excess of magnesium by using flame excitation. Cresser[18] emphasized the need to be wary of changes in instrumentation or instrumental parameters, but found that suitable interference-free results could be obtained. Smeyers-Verbeke *et al.*[19] used electrothermal atomization and found that the manganese enhancement by $Mg(NO_3)_2$ and $MgSO_4$ was *ca.* 50%, in good agreement with the present work. $MgCl_2$ however, influenced the response so that not only the magnitude, but also the sign of the interference changed with the magnesium concentration.

CONCLUSION

The method described provides a rapid, cheap, precise and accurate method for the analysis of small glass samples (250–500 μg). It shows marked improvements over the previously reported AAS methods in speed and accuracy and offers the possibility of analysing large numbers of small glass samples on a routine basis. Whilst it does not provide the range of elements which can be determined by d.c. arc emission spectrography, it allows the analysis of smaller samples by a much quicker and less ardous analytical procedure.

REFERENCES

1. J. C. Hughes, T. Catterick and G. Southeard, *Forensic Sci.*, 1976, **8**, 217.
2. E. C. Blacklock, A. Rogers, C D. Wall and B. B. Wheals, *ibid.*, 1976, **7**, 121
3. G. C. Goode, G. Wood, N. Brooke and R. F. Coleman, *AWRE Rept. No.* 0 24/71, 1971.
4. C. R. Howden, B. German and K. W. Smalldon, *J. Forensic Sci. Soc.*, 1977, **17**, 153.
5. W. Slavin, *Atomic Absorption Spectroscopy*, p. 16. Interscience, New York, 1968.
6. K. C. Thompson and R. G. Godden, *Analyst*, 1976, **101**, 96.
7. E. Sebastiani, K. Ohls and G. Riemer, *Z. Anal. Chem.*, 1973, **264**, 105.
8. D. C. Manning, *At. Absorption Newsletter*, 1975, **14**, 99.
9. B. Bernas, *Anal. Chem.*, 1968, **40**, 1682.
10. W. J French and S. J Adams, *Anal. Chim. Acta*, 1973, **62**, 324.
11. C. W. Fuller and J. Whitehead, *ibid.*, 1974, **68**, 407.
12. P. Knoop, *Anal. Chem.*, 1974, **46**, 965.
13. J. F. Wooley, *Analyst*, 1975, **100**, 896.
14. P. B. Adams, *Anal. Chem.*, 1961, **33**, 1602.
15. J. E. Allan, *Spectrochim. Acta*, 1959, **15**, 800.
16. M. Beyer, *At. Absorption Newsletter*, 1965, **4**, 212.
17. J. Y. Hwang, *Appl. Spectry.*, 1970, **24**, 371.
18. M. S. Cresser, *Lab. Practice*, 1977, **26**, 171.
19. J. Smeyers-Verbeke, Y. Michotte, P. van den Winkel and D. L. Massart, *Anal. Chem.*, 1976, **48**, 125.

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ION-EXCHANGER COLORIMETRY—III
MICRODETERMINATION OF ZINC IN WATER

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Summary—An ion-exchanger colorimetric method for the determination of zinc(II) with Zincon has been developed. Zinc in a water sample can be determined by sorption onto an anion-exchange resin from 2*M* chloride solution followed by transformation into a coloured complex with Zincon. With use of a 1-litre sample the sensitivity is 10 times greater than that for conventional colorimetry. Most metals, except cadmium(II), lead(II) and bismuth(III), do not interfere when present in up to 100 times the concentration of zinc. The zinc:Zincon ratio of the complex in the resin phase was found to be 1:1 by the molar ratio method.

Zinc occurs widely in the earth's crust and in minute amounts in rocks, soils and natural waters. At present, the most widely used colorimetric method for zinc is the one employing solvent extraction with dithizone.[1] On the other hand, a zinc complex with Zincon (2-hydroxy-5-sulphonylazobenzylidenehydrazinobenzoic acid) is soluble in aqueous solution and zinc in aqueous sample solution can be determined with Zincon after ion-exchange separation.[2]

A new colorimetric method based on the direct measurement of the absorbance of the resin phase after the sorption of sample species has been developed for the determination of some transition metals.[3–6] This "ion-exchanger colorimetry" is much more sensitive than the conventional method. There are three ways for colour development in the resin phase, depending on the properties of the colour reagents.

(*i*) A constant amount of an ion-exchange resin is added to a sample solution together with a colour reagent. This procedure can be applied when the coloured complex species of the metal in the sample solution and the colour reagent are sorbed in the resin and the colour reagent has high selectivity. An example is the system chromium–1,5-diphenylcarbohydrazide.[3–6]

(*ii*) A constant amount of an ion-exchange resin in which a colour reagent is presorbed is added to a sample solution. The procedure is applied when the coloured complex species is not sorbed but the colour reagent and the complex species can be retained irreversibly in the resin. A high selectivity is also required in this case. An example is the system copper–Zincon.[3–5]

(*iii*) The metal in a sample solution is selectively sorbed in a fixed amount of an ion-exchange resin and then a colour reagent is sorbed in the resin. This procedure is applied when the colour reagent has poor selectivity.[4,5] In this study, zinc could be selectively sorbed in an anion-exchange resin, as the anionic complexes with chloride.

Kraus and Nelson have demonstrated the possibility of separating zinc by using an anion-exchange resin dowex 1 from 2*M* chloride solution.[7] Cadmium(II), mercury(II) and bismuth(III) are also sorbed but beryllium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and molybdenum(VI), which are interfering ions for the Zincon method, are not. A partial separation of iron(III) and lead(II) from zinc may also be achieved.

EXPERIMENTAL

Reagents

Ion-exchanger. Dowex 1-X2 (100–200 mesh) and 1-X8 (200–400 mesh) anion-exchange resins in the chloride form were used. They were conditioned, air-dried and stored in polyethylene containers.

Standard zinc(II) stock solution. An appropriate amount of zinc chloride was dissolved in 1*M* hydrochloric acid and standardized by EDTA titration with Eriochrome Black T as indicator.

Zincon solution, 0.05% in 0.1M sodium hydroxide.

Borate buffer solution, 0.2M, pH 9.0.

All chemicals used were of analytical grade.

Apparatus

Spectrophotometer. Hitachi recording spectrophotometer, Model EPS-3T A perforated metal plate of absorbance 1.0 or 2.0 was used in the reference beam to balance the light intensities.

Procedures

Absorbance measurements on the resin phase. Absorbance measurements on the resin phase in a 1-mm quartz cell were carried out by the same procedure as that described in the previous papers.[3–6] The absorbances at two different wavelengths, one corresponding to the absorption maximum of the zinc–Zincon complex species (650 nm) and the other in a range where only the resin absorbs (800 nm), were used. The net absorbance of the complex species sorbed on the resin at 650 nm, $A_{RC(650\ nm)}$, is expressed

by the equation

$$A_{RC(650\ nm)} = A_{(650\ nm)} - A_{R(650\ nm)} - A_{RI.(650\ nm)} \quad (1)$$

where $A_{(650\ nm)}$, $A_{R(650\ nm)}$ and $A_{RI.(650\ nm)}$ are the observed overall absorbance, the absorbance of the resin background and the absorbance of the colour reagent, respectively, at 650 nm. In this case $A_{RI.(650\ nm)}$ cannot be neglected. The molar absorption coefficient of the free Zincon in the resin phase is, however, fairly small (Fig. 1) and $A_{RI\,(650\ nm)}$ may be constant. The value of $A_{R(650\ nm)} + A_{RI.(650\ nm)}$ in equation (1) was calculated from the difference between the absorbances at the two wavelengths for the measured absorption spectrum of a resin layer containing no zinc and the measured value of $A_{R(800\ nm)}$ for a resin layer containing zinc.

Molar ratio method for the resin phase. Zinc was sorbed beforehand onto Dowex 1-X2 (100–200 mesh) in the chloride form from 2*M* hydrochloric acid solution. The zinc sorbed was determined by EDTA titration after stripping with 0.1*M* hydrochloric acid. Then, 0.40 g of the resin, 0.325 μmole of zinc, 0.05–0.70 ml of $1.66 \times 10^{-3}M$ Zincon solution and 5 ml of the borate buffer were mixed and stirred for 2 hr. The resin was collected and the resin slurry transferred to the cell. The absorption spectra were measured.

Procedure for the determination of zinc with Zincon. To a 200-ml water sample containing 0.1–2 μmole of zinc, 7 g of sodium chloride and 25 ml of concentrated hydrochloric acid were added to make the chloride concentration about 2*M*. To sea-water samples, only hydrochloric acid was added. Then, 0.50 g of Dowex 1-X2 (100–200 mesh) in the chloride form was added. The mixture was stirred for 10 min and then the resin was collected. The resin, 0.50 ml of 0.5*M* sodium hydroxide and 5 ml of the borate buffer were then added to 2 ml of 0.05% Zincon solution. The mixture was stirred for 10 min, the resin collected, and the resin slurry transferred to the cell. The absorbances at 650 and 800 nm were measured. The concentration of zinc was determined by use of a calibration curve or by the standard addition method.

To a 1-litre water sample containing 0.1–3 μmole of zinc, 35 g of sodium chloride, 125 ml of concentrated hydrochloric acid and 0.50 g of Dowex 1-X8 (200–400 mesh) in the chloride form were added. The resin which had sorbed the zinc was treated in the same manner as that described above.

In sampling of tap-water and sea-water, 10 ml of concentrated hydrochloric acid per litre of sample solution was added immediately after filtration. The sample solution was stored in a polyethylene container.

Distribution measurements. To a 200-ml water sample containing 2.0 μmole of zinc, sodium chloride, concentrated hydrochloric acid and 0.50 g of Dowex 1-X8 (200–400 mesh) in the chloride form were added in the manner described above. The zinc concentration, C (mole/l.) was determined by ion-exchanger colorimetry. The distribution ratio, D (ml/g of dry resin), was calculated from

$$D = \frac{(2.0 \times 10^{-3} - 200\,C)/0.50}{200\,C/225} = (4.5 \times 10^{-3}/C) - 450.$$

RESULTS AND DISCUSSION

Absorption spectra of the resin and solution

Almost all the free Zincon reagent is sorbed irreversibly by an anion-exchange resin from alkaline solution within 1 min. The absorption spectrum of the sorbed Zincon varies with time, giving the broad absorption peak near 550 nm after 2 hr, whereas the maximum for Zincon in solution is at about 470 nm (Fig. 1). It seems that the species sorbed onto the resin is not the same as that in solution. However, there was a linear relationship between the amount of the sorbed species and the resin phase absorbance. The Zincon sorbed in the resin phase may, therefore, be a single species and the difference of the absorption spectra in both phases may occur because the Zincon in the resin phase is deformed owing to spatial restriction and subjected to non-electrostatic interaction with the resin skeleton.

As shown in Fig. 1, the Zincon complex of zinc has an absorption maximum at 650 nm in the resin phase, and 620 nm in solution. In the pH range 8.5–9.5, this complex is stable.

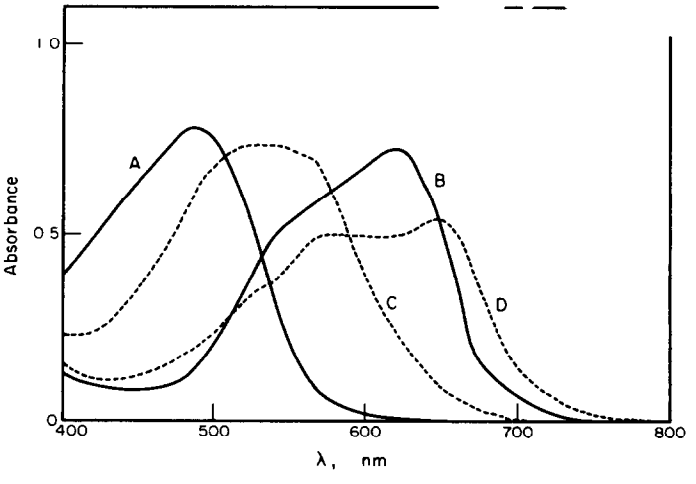


Fig. 1. Absorption spectra of Zincon and its zinc complex. Solid line: solution spectra (cell; 10 mm). A; $2.5 \times 10^{-5}M$ Zincon. B; $2.5 \times 10^{-5}M$ zinc–Zincon complex. Dotted line: resin spectra (cell; 1 mm). C; 1.0 μmole of Zincon/g of resin. D; 1.0 μmole of zinc–Zincon complex/g of resin. Resin; Dowex 1-X2 (100–200 mesh, Cl^- form). pH of the solution: 9.0.

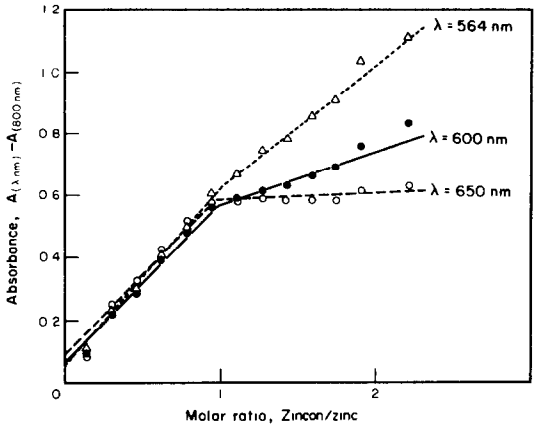


Fig. 2. Molar ratio method applied to the zinc–Zincon complex in the anion-exchange resin phase. Resin: Dowex 1-X2 (100–200 mesh, Cl^- form), 0.42 μmole of Zn/0.40 g of resin. pH: 9.0 (borate buffer). Time for colour development: 2 hr.

Composition of the complex in the resin phase

The reagent-to-metal molar ratio of the complex in solution at pH 9.0 has been found to be 1:1 by the slope ratio method, the molar ratio method and the continuous variation method.[2] The composition of any complex formed by zinc and Zincon in the resin phase was studied by the molar ratio method. Various amounts of Zincon were sorbed onto the resin from a solution containing the standardized reagent solution and 5 ml of the buffer solution. As shown in Fig. 2, the plots at 564, 600 and 650 nm indicate a 1:1 ratio, as found in solution.

Sorption of zinc chloro-complexes by the resin

Horne *et al.*[8] and Yoshimura *et al.*[9] have shown that the principal zinc chloro-complex sorbed in the resin from 2*M* chloride solution is $ZnCl_4^{2-}$, accompanied by a small quantity of $ZnCl_3^-$. Ion-exchange equilibrium was reached within 10 min both in the system of 200 ml of sample solution and 0.50 g of Dowex 1-X2 (100–200 mesh) resin and in the system of 1 litre of sample solution and 0.50 g of Dowex 1-X8 (200–400 mesh) resin.

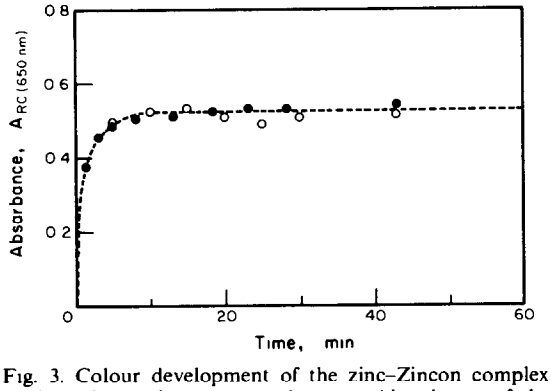


Fig. 3. Colour development of the zinc–Zincon complex in the anion-exchange resin phase. ●: Absorbance of the resin separated from Zincon solution after 30-sec stirring. ○: Absorbance of the resin stirred with Zincon solution. Resin: Dowex 1-X2 (100–200 mesh, Cl^- form), zinc presorbed. Solution: 0.05% Zincon (2 ml) + 0.5*M* NaOH (0.50 ml) + borate buffer (pH 9.0) (5 ml).

Time dependence of colour development

When the resin which had sorbed zinc was added to a Zincon solution at pH 9.0, the colour reagent was completely sorbed in the resin within 1 min and then the colour developed as the colour reagent displaced the chloride ions co-ordinated to the zinc. Figure 3 shows that the time-dependence curve of the absorbance of the resin separated from the solution after 30-sec stirring agreed very closely with that for the resin stirred with the solution till measurements were carried out. The colour development in both cases was almost complete within 10 min. The colour may be developed by the diffusion of the colour reagent within the resin phase. The zinc sorbed in the resin may not be desorbed during this procedure.

Calibration and precision

The calibration curves are reasonably linear in the concentration ranges of 5×10^{-7}–$1 \times 10^{-5}M$ for the system of 200 ml of sample solution, and 1×10^{-7}–$1.4 \times 10^{-6}M$ for the system of 1 litre of sample solution, respectively. Precision was measured with 1-litre sample solutions 2.2×10^{-7} and $1.1 \times 10^{-6}M$ in zinc, respectively. For 10 determinations, the relative standard deviations were 13.1 and 4.0%, respectively, as shown in Table 1. For the 200-ml sample system the precision may be higher than that for the 1-litre sample system, because the separation and packing of the resin are easier. Different lots of Dowex 1-X8 (200–400 mesh) resin gave somewhat different sensitivities. It is recommended that a calibration curve be prepared for each lot of resin.

Sensitivity

The sensitivity for each system has been compared with that obtained with a conventional colorimetric method (Table 2). The sensitivity is about 4 times higher when a 200-ml sample is used and 10 times higher for a 1-litre sample. The sensitivity for the system with a 200-ml sample and 0.50 g of Dowex 1-X8

Table 1. Reproducibility of measurements

Zn(II), *M*	$A_{RC(650\ nm)}$†	Relative standard deviation, %
0	$0.224 \pm 0.009_2$ (A^*)‡	4.1
2.2×10^{-7}	0.107 ± 0.014	13.1
1.1×10^{-6}	0.530 ± 0.021	4.0

Resin: Dowex 1-X8 (200–400 mesh, Cl^- form), 0.50 g.
Solution: 1 litre + NaCl (35 g) + conc. HCl (125 ml).
Time for stirring: 10 min.
Time for colour development: 10 min.
† $A_{RC(650\ nm)} = A_{(650\ nm)} - A_{(800\ nm)} - A^*$.
‡ $A^* = A_{(650\ nm)} - A_{(800\ nm)}$ (for blank).

Table 2. Comparison of the sensitivity of ion-exchanger colorimetry with that of conventional colorimetry (metal concentration giving a final absorbance of 0.50)

Ion-exchanger colorimetry	$4.9 \times 10^{-6}M$	(Sample volume: 200 ml. Resin: Dowex 1-X2, 100–200 mesh)
	$3.1 \times 10^{-6}M$	(Sample volume: 200 ml. Resin Dowex 1-X8, 200–400 mesh)
	$1.6 \times 10^{-6}M$	(Sample volume: 1 litre. Resin: Dowex 1-X8, 200–400 mesh)
Conventional colorimetry	$1.7 \times 10^{-5}M$	

(200–400 mesh) is higher than that for the system of Dowex 1-X2 (100–200 mesh) because of the longer effective light-path of the resin layer in the cell. The distribution ratio is 560 for the system of a 200-ml sample solution and Dowex 1-X8 (200–400 mesh) and the ratio of the sensitivities for both the systems, S_{1000}/S_{200}, as calculated by equation (2) in the previous paper,[6] is 1.9. This value is in good agreement with the experimental value (3.1/1.6) from Table 2. For the system with a 1-litre sample solution, the relative detection limit (the concentration that produces an absorbance equal to twice the magnitude of the fluctuation in the background absorbance) was $7.6 \times 10^{-8}M$, *i.e.*, 4.9 μg/l. (Table 1). This value is somewhat larger than that for atomic-absorption spectrophometry.[10] For samples of sea-water, however, the contribution of the molecular absorption band of sodium chloride to the signal should be taken into consideration for atomic-absorption determination of zinc at low levels. The proposed method is free from such trouble.

Effect of foreign ions

Rush and Yoe[2] have reported that the following ions interfere in the conventional colorimetric method when present in a molar ratio to zinc of 1:1 or more: aluminium(III), chromium(III), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), molybdenum(VI), cadmium(II), mercury(II), lead(II) and bismuth(III). For the ion-exchanger colorimetry, most of the metals, except for cadmium, lead and bismuth, the anionic chloro-complexes of which are sorbed, do not interfere when present at up to 100 times the concentration of zinc (Table 3). Cadmium and lead interfere at 100:1 ratio to zinc, and bismuth at 10:1 ratio. The mercury chloro-complex is more stable than the mercury–Zincon complex so mercury does not interfere.

Determination of zinc in tap-water and sea-water

The present method has been applied to the determination of zinc in Fukuoka tap-water and sea-water from Hakata Bay. The results of the analyses by use of the standard addition method are given in Fig. 4. For the tap-water, the concentration of zinc was $2.5 \times 10^{-6}M$, *i.e.*, 0.16 ppm. This value was in fair agreement with that, $2.4 \times 10^{-6}M$, obtained by atomic absorption. For the sea-water, the concen-

Table 3. Effects of foreign ions on the determination of zinc(II)

	Added, molar ratio to Zn	Zn taken, $\times 10^{-6}M$	$A_{RC(650\ nm)}$	Zn found $\times 10^{-6}M$	Relative error, %
		2.12	0.194	1.93	−9.0
		5.29	0.528	5.22	−1.3
Al(III)	100	5.29	0.570	5.63	+6.4
Cr(III)	100	5.29	0.563	5.57	+5.3
Mn(II)	100	5.29	0.510	5.04	−4.7
Fe(III)	10	5.29	0.568	5.61	+6.0
	100	5.29	0.551	5.44	+2.8
Co(II)	10	5.29	0.479	4.74	−10.4
	100	5.29	0.549	5.43	+2.6
Ni(II)	100	5.29	0.553	5.47	+3.4
Cu(II)	10	5.29	0.498	4.93	−6.8
	100	5.29	0.585	5.78	+9.3
Mo(VI)	100	5.29	0.571	5.63	+6.4
Cd(II)	10	5.29	0.514	5.08	−4.0
	100	5.29	0.264	2.62	−50.5
Hg(II)	10	5.29	0.550	5.43	+2.6
	100	5.29	0.485	4.80	−9.3
Pb(II)	10	5.29	0.559	5.53	+4.5
	100	5.29	0.422	4.17	−21.2
Bi(III)	1	5.29	0.483	4.78	−9.6
	10	5.29	0.411	4.06	−23.3
	100	indeterminable			

$A_{RL(650\ nm)} + A_{R(650\ nm)} = A_{(800\ nm)} + 0.158$

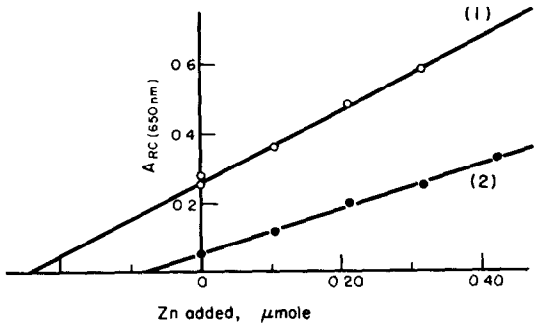


Fig. 4. Standard addition method for zinc in tap-water and sea-water. Place of sampling: (1) tap-water, Fukuoka. (2) Hakata Bay (Fukuoka). Date of sampling: (1) 20 February 1976. (2) 24 February 1976. Sample: (1) 200 ml + NaCl (7 g) + conc. HCl (25 ml). (2) 1 litre + conc. HCl (125 ml). Resin: (1) Dowex 1–X2 (100–200 mesh, Cl^- form), 0.50 g. (2) Dowex 1–X8 (200–400 mesh, Cl^- form), 0.50 g.

tration of zinc was $1.7 \times 10^{-7}M$, *i.e.*, 11 μg/l. The natural abundance of zinc in sea-water has been reported to be in the range 2×10^{-8}–$3 \times 10^{-7}M$.[11] The present method may be useful for determining zinc in sea-water.

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REFERENCES

1. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience, New York, 1959.
2. R. M. Rush and J. H. Yoe, *Anal. Chem.*, 1954, **26**, 1345.
3. K. Yoshimura, H. Waki and S. Ohashi, *Talanta*, 1976, **23**, 449.
4. K. Yoshimura, *Doctoral Thesis*, 1977.
5. K. Yoshimura, H. Waki and S. Ohashi, *Kagaku no Ryoiki*, 1977, **31**, 885.
6. K. Yoshimura and S. Ohashi, *Talanta*, 1978, **25**, 103.
7. K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, 1st, Geneva*, 1956, **7**, 113.
8. R. A. Horne, R. H. Holm and M. D. Meyers, *J. Phys. Chem.*, 1957, **61**, 1655.
9. K. Yoshimura, H. Waki and S. Ohashi, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1697.
10. W. Slavin, *Atomic Absorption Spectrophotometry*, Interscience, New York, 1968.
11. L. G. Sillén, *Kagaku no Ryoiki*, 1968, **Zokan 84**, 71.

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A NON-IONIC SURFACTANT AS A NEW SOLVENT FOR LIQUID–LIQUID EXTRACTION OF ZINC(II) WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Summary—A new method for extracting zinc(II) with 1-(2-pyridylazo)-2-naphthol (PAN) has been developed, based on the fact that a micellar solution of a non-ionic surfactant separates into two phases above a certain temperature, defined as the cloud point. Polyoxyethylene nonyl phenyl ether, (PONPE-7.5; average number of ethylene oxide units 7.5) was used as the surfactant. The cloud point of a 0.40% PONPE-7.5 solution is 1°, and hence the solution is turbid at room temperature. The two phases can be separated by centrifuging for 8 min at room temperature. The zinc chelate of PAN is quantitatively extracted from 50 g of the solution into a small volume (about 1 ml) of the lower (surfactant-rich) phase over the pH range 8.0–11.5. After most of the supernatant solution has been removed, the amount of final solution is adjusted to 2.00 g with 0.5 g of 10% of PONPE-20 solution and water. This mixture is transparent at room temperature. The absorbance is measured as 535 nm. Concentration factors of up to 25 can be obtained by choosing appropriate amounts of final ($\geq$ 2.0 g) and initial solution ($\leq$ 50 g). This new technique has been applied to the determination of zinc(II) in tap water.

The ability of surfactants to dissolve organic compounds which are insoluble or only slightly soluble in water, is a distinctive feature referred to as solubilization. The usual explanation offered for this phenomenon suggests that the solubilized compounds are incorporated into a hydrocarbon environment in the interior of micelles.[1] This leads to these species being regarded as distributed between a micellar phase and a bulk aqueous phase,[2] with the micellar phase playing the same role as the organic solvent in ordinary liquid–liquid extraction. Water-insoluble metal chelates, such as those of 1-pyrrolidinecarbodithioic acid,[3–6] 1-(2-pyridylazo)-2-naphthol (PAN),[7] dithizone[8] and 1-(2-thiazolylazo)-2-naphthol (TAN),[9] can be solubilized with micellar solutions of non-ionic surfactants. Hence, if the two phases can be separated physically, it should be possible to concentrate the metal chelates into a small volume of the micellar phase in a similar manner to liquid–liquid extraction.

It is well known that a micellar solution of a non-ionic surfactant separates into two phases when heated above a certain temperature, and suddenly becomes turbid at a temperature called the cloud point.[10] At a temperature somewhat higher than the cloud point, and after a suitable equilibration time, the micellar solution will separate into two distinct phases. The concentration of the surfactant is higher in one of these phases than the other.

One of us has already developed a method for extracting nickel(II) with TAN, by use of a micellar solution of Triton X-100 at above its cloud point (about 70°).[11] The micellar solution was heated, and allowed to stand at 95°, a phase rich in Triton X-100 then separating to form a lower layer in which the nickel chelate of TAN was concentrated. Complete separation of the two phases took at least 20 min. Centrifuging was tried to speed up the separation, but the recovery of the nickel chelate was then low because the temperature of the micellar solution gradually fell to below the cloud point during the centrifugation, and an appreciable fraction of the Triton X-100 was redissolved in the supernatant solution.

This drawback could be overcome if a non-ionic surfactant, having a lower cloud point than Triton X-100, was used. In the present study it has been found that polyoxyethylene nonyl phenyl ether, with on average 7.5 ethylene oxide units (PONPE-7.5), is a satisfactory substitute and that the zinc chelate of PAN can be effectively extracted into a small volume of the phase rich in PONPE-7.5. As the cloud point of a dilute micellar solution of PONPE-7.5 is below 20°, the two phases can be separated rapidly by centrifuging at room temperature. This new technique has been applied to the spectrophotometric determination of trace zinc(II) in tap water with PAN.

EXPERIMENTAL

Reagents

A standard solution of zinc(II) was prepared from the high-purity metal. Other metal-ion solutions were prepared from high-purity reagents dissolved in 2*M* hydrochloric acid and then diluted to the desired concentration. The final acid concentration of the solutions was about 0.01*M*. Other reagents used were of analytical grade.

A 0.020% PAN solution containing various amounts of PONPE-7.5 was prepared by dissolving 0.020 g of PAN in 2 ml of 5*M* sodium hydroxide, and mixing this with various amounts of PONPE-7.5 (Tokyo Kasei Industries) and 60 ml of distilled water. Finally, the mixture was neutralized with 5*M* hydrochloric acid and diluted to 100 g with distilled water. The concentrations of PONPE-7.5 were in the range 0.40–30%.

A 10% PONPE-20 solution was also prepared by dissolving 10 g of PONPE-20 (Tokyo Kasei Industries, average

number of ethylene oxide units = 20) in 80 g of distilled water. This solution was used to increase the cloud point of the final solutions before the absorbance of the zinc chelate was measured.

Buffer solution of pH 10.0 was made by mixing 0.5*M* sodium bicarbonate and 0.5*M* sodium carbonate.

One of the masking agents used, *N*-dithiocarboxylglycine, (DTCG), was synthesized by the method described by Budevsky *et al.*[12] DTCG was used as the solid because its aqueous solution is rather unstable

Procedure for cloud-point determination

A 50.00-g portion of a PAN solution was cooled in an ice-bath until the solution became clear. Then the temperature was raised slowly until the solution became turbid. This temperature was recorded as the cloud point of the solution.[10]

The influence of PONPE-20 concentration on the cloud point of a PAN solution (in 20% PONPE-7.5 solution) was also examined by mixing 1.00-g portions of the PAN solution and various amounts (0–2.00 g) of 10% PONPE-20 solution, making up to 5.00 g with distilled water and determining the cloud points.

Standard procedure for determining zinc(II)

An aliquot of standard zinc solution (and of other metal ions if necessary) was transferred to a glass centrifuge tube, which had been dried and weighed (the volume of the tube was about 60 ml). Next, a 1.00-g portion of 0.20% PAN solution containing 20% of PONPE-7.5, and 2 ml of pH 10.0 buffer (with additions of suitable amounts of sodium hydroxide or hydrochloric acid if required) were added. Masking reagents, if required, were added prior to the addition of the PAN solution. The whole solution in the tube was made up to 50.00 g with distilled water on a top-loading balance. The resulting turbid solution will be referred to as the initial solution. The initial solution was then spun in a centrifuge at 4000 rpm for a certain period to help separate the two phases. On cooling to about 0° in an ice-bath the PONPE-7.5 phase which had separated became a viscous gel, and then most of supernatant solution could be poured off. The total amount remaining in the tube was adjusted to 5.00 g by addition of a 0.5-g portion of 10% PONPE-20 solution and an appropriate amount of distilled water. This clear solution will be referred to as the final solution. The absorbance of the final solution was measured at the wavelength of maximum absorption (555 nm) of the zinc chelate, against a blank, in 1-cm cells.

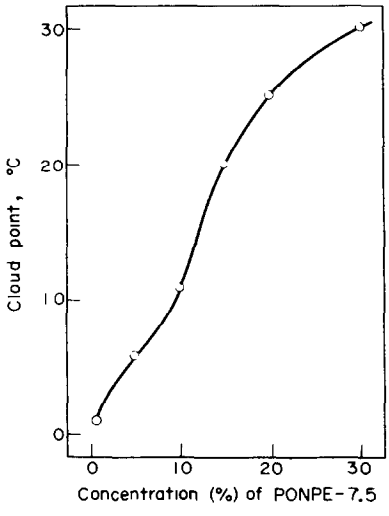


Fig. 1. Variation of cloud point with concentration of PONPE-7.5.

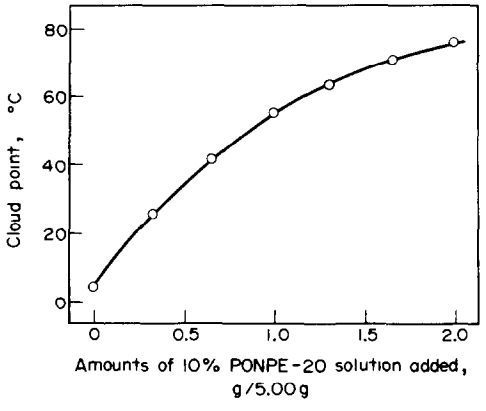


Fig. 2. Influence of PONPE-20 on the cloud point of PONPE-7.5 aqueous solution (PONPE-7.5: 0.20 g/5.00 g).

RESULTS AND DISCUSSION

Cloud point of micellar solutions of PONPE

As seen in Fig. 1 the cloud point of an aqueous solution of PONPE-7.5 depends largely on its concentration. At concentrations below 15% the solution becomes turbid and separates into two phases after equilibration at room temperature (about 20°) since the cloud point is below this. The PAN solutions used in these studies contained 20% of PONPE-7.5 and were consequently quite clear at room temperature. In contrast, the cloud point of a 10% PONPE-20 solution is above 100°—it was not possible to determine its exact value experimentally. Non-ionic surfactants with shorter polyoxyethylene chains generally show lower cloud points[1].

The concentration of PONPE-7.5 in the initial solutions prepared according to the standard procedure is 0.40% and the cloud point is 1°. This corresponds to the lowest point in Fig. 1. When this turbid solution is allowed to stand for a while at room temperature, a lower phase rich in PONPE-7.5 separates out of the solution during equilibration. The two phases can then readily be separated by centrifuging at room temperature.

It is generally accepted that the concentration of the non-ionic surfactant in the supernatant solution separated from a micellar solution is very low and is approximately equal to the critical micelle concentration (CMC).[1] The CMC of PONPE-7.5 in aqueous solutions has not been determined but is probably about $8 \times 10^{-5}M$ (about 0.004%) since the CMCs of PONPE-10, PONPE-15 and PONPE-20 have been reported as $8.5 \times 10^{-5}M$, $12 \times 10^{-5}M$ and $15.5 \times 10^{-5}M$ respectively.[13] Therefore, the added PONPE-7.5 will be recovered quantitatively in the lower phase and hence in the final solution. The concentration of PONPE-7.5 in this final solution

should be close to 4.0% since the concentration factor in the standard procedure is 10. As can be seen in Fig. 1, the cloud point of a 4.0% PONPE-7.5 solution is 5°. It is thus necessary to raise the cloud point of the final solution so that this will be transparent for the absorbance measurement at room temperature. Addition of PONPE-20 to the mixture achieves just this (see Fig. 2). It is generally accepted that the cloud point of a mixed solution of two non-ionic surfactants lies somewhere between the cloud points of the two components.[1] In this investigation 0.5 g of a 10% PONPE-20 solution was added in preparing each final solution, the cloud point of which was about 30°, as shown in Fig. 2.

Phase separation by centrifuging at 4000 rpm

In this experiment 3.00-μg portions of zinc(II) were taken and the pH of the initial solution was adjusted to 10.0; the centrifugation time was varied. When centrifuging is carried out for longer than 8 min the absorbance of the final solution at 555 nm remains constant, and that of the supernatant solution is almost equal to that of a reagent blank (0.010). This suggests that the zinc chelate is quantitatively extracted into the lower PONPE-7.5 phase. The volume of the lower phase was estimated to be 1.1 ml. In all further work centrifuging was carried out for 10 min.

Degree of concentration

In the standard procedure the concentration factor is 10. If this factor is to be increased, the volume of the final solution should be reduced or that of the initial solution should be increased. The latter cannot exceed 50 g because of the limited volume of the tube used.

The highest concentration factor will be obtained if the absorbance of the PONPE-7.5 phase can be measured directly without the addition of PONPE-20, but this is not practical, for reasons already stated. The PONPE-7.5 phase retains considerable amounts of water (85.0 ± 0.5% at room temperature). The cloud point of the PONPE-7.5 phase would be expected to be about 20° from Fig. 1, but there will be more than 85% of water in the liquid remaining in the tube as the supernatant liquid cannot be separated quantitatively simply by pouring off, and the final solution will not be transparent at room temperature. When 0.2 g of a 10% PONPE-20 solution was added to the tube containing the PONPE-7.5 phase, along with small portions

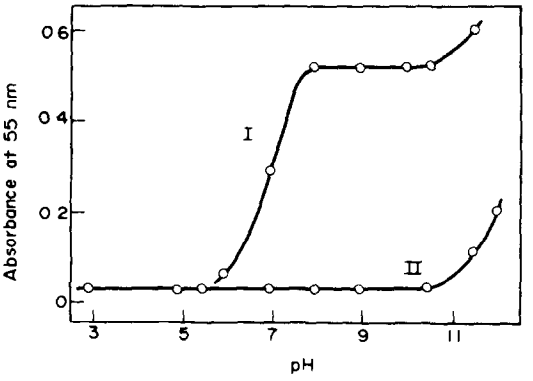


Fig. 3. Influence of pH on the absorbance of the zinc chelate and a reagent blank at 555 nm.
I: zinc chelate (ref., water), zinc taken 3.0 μg
II: reagent blank (ref., water)

(about 0.2 g) of supernatant solution, and the whole made up to 1.50 g with distilled water, the cloud point of this final solution was raised to about 30°.

It is therefore recommended that the final solution should be made up to not less than 1.5 g with 10% PONPE-20 solution. For absorbance measurements with ordinary 1-cm cells at least 1.5 g of solution will be required, again making this the minimum amount of the final solution. In the present study the amount was chosen as 2.00 g, and hence the highest concentration factor obtained was 25. The cloud point of the final solution prepared by addition of 0.5 g of 10% PONPE-20 solution was 50°.

Determination of zinc(II) in tap water

Figure 3 shows the influence of pH on the absorbance of the zinc chelate and a reagent blank at 555 nm. The reaction between zinc(II) and PAN is rapid and quantitative in the pH range 8.0–11.5. As the reagent blank increases if the pH is >10.5 the pH chosen was 10.0. The chelate formed is stable for at least 24 hr.

PAN is not a specific reagent for zinc(II), and appropriate masking agents must be used for the determination of zinc(II) in tap water. Table 1 summarizes the effectiveness of some masking agents at pH 10.0. The sign, (+), indicates complete, (±) incomplete and (−) no colour formation. It is apparent from Table 1 that the combination of DTCG, metaphosphate and triethanolamine is effective for masking other ions except for nickel(II) and iron(II). Any iron

Table 1. Effectiveness of masking agents at pH 10.0

Masking agent	Concentration*	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}	Mn^{2+}	Cd^{2+}	Fe^{2+}	Fe^{3+}
None	—	+	+	+	±	+	+	±	±
Sodium tartrate	$10^{-2.7}M$	+	+	+	±	±	+	±	±
Sodium metaphosphate	0.2% w/w	+	+	+	±	−	+	±	−
DTCG	$10^{-2.5}M$	+	+	−	−	+	−	±	±
Triethanolamine	$10^{-2.4}M$	+	+	+	±	±	+	±	−

* This is the concentration in the initial solution (50.00 g).
colour formation complete (+); partial (±); completely absent (−).

Table 2. Influence of foreign ions on the determination of zinc

Foreign ions	Added, μg	Absorbance at 555 nm
None	—	0.696
Co^{2+}	3	0.728
Cu^{2+}	6	0.740
Cd^{2+}	10	0.723
Fe^{3+}	40	0.714
Mn^{2+}	100	0.707
Mg^{2+}	5×10^3	0.721
Ca^{2+}	1×10^4	0.745
Na^{+}	5×10^4	0.735
K^{+}	2×10^4	0.729
Ni^{2+}	2	1.243
	2	0.700*
	3	0.691*

Zn taken: 1.5 μg
*The correction method

in samples must be oxidized to iron(III). Copper(II), cobalt(II) and cadmium(II) are masked by DTCG, and iron(III) and manganese(II) by metaphosphate and triethanolamine. Tartrate was used to prevent formation of calcium carbonate.

Nickel(II) cannot be masked, but its concentration in tap water seems to be extremely low, and any interference from it would be most unlikely. When nickel(II) in quantities up to 3 μg is present, it is possible to correct for the absorbance due to the nickel PAN chelate by measuring at two suitable wavelengths as reported earlier,[14] e.g., 555 and 568 nm, the latter being the wavelength of the absorption maximum of the nickel chelate. If the absorbance ratio of the two wavelengths is constant for each of the complexes, then

$$(A_{568} - aA_{555}^{Zn})/(A_{555} - A_{555}^{Zn}) = b$$

where A_{555} and A_{568} are the total absorbances at the wavelengths indicated, and a and b are the zinc and nickel absorbance ratios (A_{568}/A_{555}) respectively, from which A_{555}^{Zn} can be determined. The experimental value of a was found to be 0.515 ± 0.003 and that of b was 1.331 ± 0.030. In the presence of the masking agents at pH 10.0 the formation of the nickel chelate is slow, so that, before centrifuging, the initial solution has to stand for at least 20 min with occasional stirring.

In the procedure recommended for tap water, an aliquot (≤ 50 g) of a test solution containing less than 3 μg of zinc(II) is taken in the tube together with 2 ml of pH 10.0 buffer that is 0.1 *M* in triethanolamine, 0.1 *M* in potassium tartrate and contains 10% of sodium metaphosphate, and then 10 mg of DTCG and 1.00 g of the PAN solution (20% PONPE-7.5) are added successively. After centrifuging at 4000 rpm for 10 min, most of the supernatant solution is removed. The final solution is made up to 2.00 g by addition of 0.5 g of 10% PONPE-20 solution and appropriate amounts of distilled water. The mixture is thoroughly mixed till clear and the absorbance of the zinc chelate is measured at 555 nm. In this procedure the concentration factor is 25. When nickel(II) is present the absorbance is measured at both 555 nm and 568 nm. A calibration curve is prepared by the same procedure.

The calibration curve is linear over the range 0.1–3.0 μg of zinc(II). Table 2 shows the influence of other ions on the determination of 1.5 μg of zinc(II). Iron(III), manganese(II) and copper(II) are tolerated in quantities of 40, 100 and 6 μg respectively. Nickel up to 3 μg does not interfere if the correction procedure is followed.

As a test of the present method zinc(II) was determined in a sample of tap water (municipal water, Muroran). To check the recovery of zinc(II) a 40.00-g sample was analysed both alone and when spiked with 1.00 μg of zinc(II). The average of five determinations and the coefficient of variation are shown in Table 3. The results indicate that the method is apparently satisfactory.

When metal ions are extracted with PAN solutions in organic solvents such as chloroform it may take several hours before equilibrium is reached.[15] Because of this, methanolie PAN solution is often added to the aqueous solutions.[16, 17] Further, when metal ions are to be extracted from large volumes of aqueous solutions it may be necessary to heat the aqueous solution for a relatively long time, but in the present method the zinc chelate is formed rapidly although the initial solution containing zinc(II), PAN and PONPE-7.5 is not homogeneous at room temperature. The reason is not clear but may be due to the PAN being concentrated locally on the surface of the micelles.

The method is fairly simple and is sensitive enough for the determination of zinc(II) in the range from several ppM to several tens ppM. A feature of the method is the use of small amounts of non-ionic surfactant as a solvent. Accordingly the method requires smaller amounts of sample solutions for obtaining degrees of concentration similar to those obtained in ordinary liquid–liquid extraction which often involves handling large volumes of aqueous solutions. In this study the amount of the initial solution was also increased to 90 g when a larger centrifuge equipped

Table 3. Determination of zinc in tap water

	Sample taken, g	Zn added, μg	Absorbance* at 555 nm	Zn found, μg	Zn found, μg/kg	C.V., %
A	40.0	—	0.518	1.12	28.0	1 8
B	40.0	1.00	0.961	2.10	27.5	0.8

* Average of five determinations

with polycarbonate tubes (capacity about 120 ml) was employed. When 90 g of the initial solution were kept in the centrifuge at 8000 rpm for 5 min, a concentration factor of 45 was obtained under the same analytical conditions as were used previously. The two surfactants PONPE-7.5 and PONPE-20 would seem to be attractive as solvents because they are not volatile and have no smell, and waste solutions containing them are easily treated.

Treatment of waste water containing PONPE

In the treatment of waste solutions of PONPE-7.5 use can be made of the fact that micellar solutions of PONPE-7.5 separate into two phases above a certain temperature. The concentration of non-ionic surfactant in the supernatant solution separated from a micellar solution is accepted as almost equal to the CMC.[1] This means that the surfactant is dissolved in molecular dispersion and can therefore be treated effectively with active charcoal, in either a batch or a column method.

The PONPE-7.5 phase gels at about 0°, so the supernatant solutions can simply be poured off. The concentration of water in the PONPE-7.5 phase depends on the temperature at which the micellar solution separates into two phases. The concentration of water was found to be about 50% if this temperature was 90°, and the PONPE-7.5 phase was quite viscous. Thus all the supernatant solution can be removed by inverting the container after cooling the PONPE-7.5 phase to about 0°. As the PONPE-7.5 phase contains water, it does not burn well, but when mixed with suitable amounts of waste acetone or ethanol it burns gently and completely without producing any fume or smoke.

The cloud point of a 10% PONPE-20 solution is above 100° and that of the final solution prepared in the recommended procedure is 50°. It would thus seem not to be possible to treat these waste solutions effectively. However, the addition of suitable amounts of PONPE-7.5 results in pronounced lowering of their cloud points, making it possible to apply the same treatment to these waste solutions as to the others.

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REFERENCES

1. K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, *Colloidal Surfactants*, pp. 97–178. Academic Press, New York, 1963.
2. S. J. Dougherty and J. C. Berg, *J. Colloid Interfac. Sci.*, 1974, **48**, 110.
3. K. Hayashi, Y. Sasaki, M. Nakanishi and S. Ito, *Bunseki Kagaku*, 1968, **19**, 1673.
4. K. Hayashi and K. Ito, *ibid.*, 1971, **20**, 1550.
5. K. Hayashi, Y. Sasaki and K. Ito, *ibid.*, 1972, **21**, 1338.
6. K. Hayashi, K. Sato and M. Ochi, *ibid.*, 1975, **24**, 156.
7. H. Watanabe and Y. Sakai, *ibid.*, 1974, **23**, 396.
8. H. Watanabe and J. Miura, *ibid.*, 1977, **25**, 196.
9. H. Watanabe and H. Matsunaga, *ibid.*, 1976, **25**, 35.
10. T. Nakagawa, in *Nonionic Surfactants (Surfactant Science Series*, Vol. I) ed. M. J. Schick, pp. 481, 571, 843. Dekker, New York, 1967.
11. H. Ishii, J. Miura and H. Watanabe, *Bunseki Kagaku*, 1977, **26**, 252.
12. O. Budevsky, E. Russeva and B. Mesrob, *Talanta*, 1961, **13**, 277.
13. L. Hsiao, H. N. Dunning and P. B. Lorenz, *J. Phys. Chem.*, 1956, **60**, 657.
14. H. Watanabe, *Talanta*, 1974, **21**, 295.
15. G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, 1963, **84**, 639.
16. S. Shibata, in *Chelates in Analytical Chemistry*, Vol. 4, ed. H. A. Flaschka and A. J. Barnard, Jr., p. 1. Dekker, New York, 1972.
17. R. Puschel, E. Lassner and K. Katzengruber, *Z. Anal. Chem.*, 1966, **223**, 414.

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SHORT COMMUNICATIONS

DETERMINATION OF THIOUREAS BY REACTION WITH PHENACYL BROMIDE

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Summary—Thioureas react quantitatively with phenacyl bromide in ethanolic solution to give hydrobromides of aminothiazoles/iminodihydrothiazoles which can be titrated with sodium carbonate, Thymol Blue being used as indicator.

There is hardly any titrimetric method of general application for the determination of thioureas though for *sym*-diphenylthiourea and phenyl thiourea an acid–base titration is possible in dimethylformamide with Azo Violet and *o*-nitroaniline respectively, as indicators.[1] The gravimetric method[2] of determination as silver sulphide formed by treating a thiourea with ammoniacal silver nitrate solution is quite time-consuming. Thioureas have been observed to react quantitatively with phenacyl bromide and this reaction can be utilized for their titration. A thiourea is treated with an excess of phenacyl bromide in ethanolic solution; the hydrobromide of aminothiazole/iminothiazole thus formed is titrated with sodium carbonate, with Thymol Blue as indicator. The procedure has been applied to the determination of a selection of thioureas (Table 1). The procedure appears to be of general applicability and merits recommendation. Although phenacyl bromide reacts with nucleophiles, under the conditions used the only likely interference would seem to be amines present as impurity in thioureas, the extent of interference depending on the nucleophilicity. Sodium hydroxide is unsuitable as titrant, giving erratic results.

EXPERIMENTAL

A weighed quantity of a thiourea (*ca.* 50–150 mg) is dissolved in 10 ml of ethanol and phenacyl bromide (in 10–50% excess) is added. After about 15 min, the solution is titrated with 0.1*N* sodium carbonate with 2 drops of Thymol Blue (0.3% solution in ethanol) added as indicator. The colour change at the end-point is stable for about a minute.

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REFERENCES

1. J. Kucharsky and L. Safarik, *Titrations in Non-Aqueous Solvents*, p. 231. Elsevier, Amsterdam, 1965.
2. C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. Ib, p. 736, Elsevier Publishing Company, London, 1960.

Table 1. Determination of thioureas

Sample*	Weight range, *mg*	Average recovery %	Standard deviation, %
Thiourea (4)	40–100	98.9	0.4
N-Allylthiourea (4)	50–125	99.6	0.2
sym-Diphenylthiourea (4)	56–127	99.8	0.4
N-Phenyl-*N'*-(4-chlorophenyl) thiourea (4)	57–170	99.8	0.2
N-Phenyl-*N'*-(2-methoxyphenyl)thiourea (3)	50–125	99.9	0.1
N-Phenyl-*N'*-(4-ethoxyphenyl)thiourea (3)	59–140	100.3	0.1
N-Phenyl-*N'*-(2-methylphenyl)thiourea (3)	58–153	100.0	0.1
N-Phenyl-*N'*-(β-oxyethyl)thiourea (3)	55–150	99.8	0.1
N-Phenyl-*N'*-(β-oxydiethyl)thiourea (3)	50–120	99.9	0.3
N-Phenyl-*N'*-pentamethylene thiourea (3)	51–125	100.0	0.1

* Figures in parentheses represent number of determinations.
The first three thioureas were commercial samples, the others were synthesized by reacting phenyl isothiocyanate with suitable amines and recrystallizing the product from ethanol.

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DIRECT PHOTOMETRIC DETERMINATION OF COBALT(II) WITH *N*-METHYLAMINOTHIOFORMYL-*N'*-PHENYLHYDROXYLAMINE

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(*Received* 8 *December* 1977. *Accepted* 1 *May* 1978)

Summary—*N*-Methylaminothioformyl-*N'*-phenylhydroxylamine forms a 1:2 (metal:ligand) greenish yellow complex with cobalt(II). This complex has maximum absorption at 470 nm with a molar absorptivity of 1.65×10^4 $l.mole^{-1}.cm^{-1}$. Beer's law is obeyed over the concentration range 6×10^{-6}–$6 \times 10^{-5} M$. The effect of diverse ions is described.

N-Methylaminothioformyl-*N'*-phenylhydroxylamine (MTPH) acts as a non-selective ligand towards transition metal ions.[1-3] The complexation between this reagent and cobalt is attributed to the presence of the thioketo and oxime groups. The use of this reagent for spectrophotometric determination of cobalt offers advantages over the most frequently employed reagent, nitrosonaphthol.[4]

EXPERIMENTAL

Reagents

N-Methylaminothioformyl-*N'*-phenylhydroxylamine was prepared[5] by refluxing equimolar quantities of methyl isothiocyanate (14.5 g) and phenylhydroxylamine (30 g) in 225 ml of ether for 20 min, then cooling in the refrigerator for 20 min, filtering off, and recrystallizing twice from ethanol. A 1% solution in 50% aqueous ethanol was used.

A solution of cobalt was prepared by dissolving about 18 g of hydrated cobalt perchlorate in a litre of distilled water, and standardized by electro-deposition.

All chemicals used were of reagent grade.

Procedure

A portion of cobalt solution (pH about 8) is taken in a 25-ml standard flask; 7 ml of reagent solution are added and the mixture is shaken. After 15 min, 5 ml of 7*M* hydrochloric acid are added and the solution is diluted to volume with water. The absorbance is measured against an ethanol blank at 470 nm. The amount of cobalt present is read from a calibration curve.

RESULTS AND DISCUSSION

In 50% aqueous ethanol, MTPH reacts with cobalt (II) to form a highly coloured complex having maximum absorption at 470 nm. The slope-ratio method[6] and Job's method[7] indicate that the complex has a metal to ligand ratio of 1:2. The rate of complex formation increases with increasing ligand concentration and pH. The apparent pH of the system is about 8.0 before the acidification.

The cobalt complex is kinetically inert towards hydrogen ions. No dissociation of the complex (once formed) is observed over a hydrogen-ion concentration range of 1.5×10^{-8}–$2.5 M$. The complex has maximum absorbance at 470 nm and a molar absorptivity of 1.65×10^4 $l.mole^{-1}.cm^{-1}$. Beer's law is obeyed over a cobalt concentration range of 6×10^{-6}–$6 \times 10^{-5} M$.

Table 1.

Sample	Co present, %	Co found, %
Cu–Ni–Zn alloy (58–12–29%)	0.024	0.021
Ni steel	0.044	0.042
Co–Mo–W steel (8.9% Mo, 1.8% W)	8.44	8.66

The effect of diverse ions on the cobalt–MTPH complex has been examined. Interference due to overlapping of absorption bands may be eliminated by the addition of acid, which will cause labile metal complexes to dissociate, but not the cobalt complex. The other transition metals do not seriously interfere in the system, nor do alkali and alkaline earth metals. Most anions do not interfere. Zn^{2+}, Cd^{2+}, Pb^{2+} and Mn^{2+} in 500 ppm concentration do not interfere. Molybdenum, tungsten, vanadium and uranium are precipitated if their concentration is too high, the amounts tolerated being 0.4 mg of molybdate, 0.25 mg of tungstate or vanadate, and 1.5 mg of uranium (in the 25 ml of solution measured).

The direct photometric determination of cobalt with MTPH reagent is found to be suitable and accurate for steel analysis. Typical analyses are shown in Table 1.

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REFERENCES

1. S. P. Mathur and M. R. Bhandari, *Chem. Ind. London*, 1975, 572.
2. *Idem*, *ibid.*, 1975, 745.
3. *Idem*, *Indian J. Tech.* 1976, **14**, 359.
4. E. B. Sandell, *Colorimetric Determination of Trace Metals*, 3rd Ed. pp. 420–422. Interscience, New York, 1969.
5. M. R. Bhandari, *Ph.D. Thesis*, Rajasthan University, Jaipur, India, 1965.
6. A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 1950, **72**, 4488.
7. P. Job, *Ann. Chem. Paris*, 1928, **9**, 113.

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ON THE CONFIDENCE INTERVAL OF THE EQUIVALENCE POINT IN LINEAR TITRATIONS

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Summary—As the point of intersection in linear-branch titration curves results from two optimized linear regressions, calculated by least-squares from n_1 and n_2 pairs of values of the signal y as a function of the added volume of titrant v, the value of the equivalence volume V_e has the character of an estimated average $\bar{V}_e$, hence a confidence interval is associated with it. If the point of intersection $\bar{V}_e$ belongs concomitantly to both regressions then the same value of $\bar{y}_e$ should correspond to the two extreme values V'_e and V''_e of the confidence interval as to $\bar{V}_e$ itself. Consequently, the two segments of the confidence interval are obtained by averaging each of the two unequal segments of the separate confidence intervals. Alternatively, considering that multiple estimates of $\bar{V}_e$ can be obtained, the confidence interval can be calculated from the normally distributed random variables $\Delta a'$ and $\Delta b'$ of the two linear regressions.

In titrations in which the end-point is located graphically as the point of intersection of two straight lines obtained by plotting some quantity linearly related to concentration against the volume of titrant added, the two lines can be evaluated by the least-squares method. We can use the equation.

$$y = a'_1 + b'_1 V \tag{1}$$

before the equivalence point, and

$$y = a'_2 + b'_2 V \tag{2}$$

after it. The estimated value of the equivalence point[1,2] will then be given by the expression:

$$\bar{V}_e = \frac{a'_2 - a'_1}{b'_1 - b'_2} = \frac{\Delta a'}{\Delta b'}. \tag{3}$$

As the point of intersection results from two optimized linear regressions, calculated by the least-squares method from n_1 and n_2 pairs of (y, V) values, the value $\bar{V}_e$ has the character of an estimated average, hence a confidence interval is associated with it.

Given that each value of signal y has a normal distribution with respect to the two linear regressions of the titration curve, with the same variance s_y^2, several procedures for estimating the confidence interval of the true value of the equivalence volume $\bar{V}_e$ have been suggested.[1–7]

From the data for a conductometric linear titration shown in Table 1, the equations (1) and (2) of the two straight lines are:

$$(y)_1 = 1.403 - 0.06367V \tag{4}$$

$$(y)_2 = -0.4908 + 0.05171V, \tag{5}$$

so according to expression (3), $\bar{V}_e = 16.41_3$ ml.

The confidence interval (V'_e, V''_e) would result, as may be seen in Fig. 1, by the projection on the abscissa of the surface between the four hyperbolic arcs.[3] Using the data in Table 1, for $P = 0.90$, we obtain $V'_e = 16.27$ ml, $V''_e = 16.57$, so $16.27 \text{ ml} < \hat{V}_e < 16.57$ ml where $\hat{V}_e$ is the true value.

Janders *et al.*[3] approximate by line segments the hyperbolas limiting the confidence band for the two straight lines, so that the value of the confidence interval, $\Delta V_e = V''_e - V'_e$, consists of two equal segments. Using the data in Table 1, for $P = 0.90$ we obtain in this case: $\Delta V_e = 0.354$ ml, so that $V'_e = \bar{V}_e - \Delta V_e/2 = 16.23$ ml and $V''_e = \bar{V}_e + \Delta V_e/2 = 16.59$ ml, or $16.23 \text{ ml} < \hat{V}_e < 16.59$ ml.

Liteanu and Cörmös[4] approximate by straight lines the hyperbolas limiting the confidence band for the two linear regressions, so the value of the confidence interval is $\Delta V_e = V''_e - V'_e$, again consisting of two equal segments. Using the data of Table 1 and taking the same probability $P = 0.90$, we obtain $\Delta V_e = 0.306$ ml, hence $V'_e = 16.26$ ml and $V''_e = 16.57$ ml, or $16.26 \text{ ml} < \hat{V}_e < 16.57$ ml.

Lark *et al.*,[5] referring to the papers of Fisher[6] and Kastenbaum[7] show that the limits of the confidence interval of the intersection point of two linear regressions, if this consists of two equal segments, are given by the roots of a second-order equation. For the data of Table 1, with $P = 0.90$, we obtain by this method $\Delta V_e = 0.25$ ml so that $V'_e = 16.29$ ml and $V''_e = 16.54$ ml; $16.29 < \hat{V}_e < 16.54$ ml.

If we assume a closely correlated two-dimensional normal distribution (for y and for V), for each branch of the titration curve,[9] the value of the confidence interval, ΔV_e again consists of two equal segments. The data in Table 1, for $P = 0.90$, give $\Delta V_e = 0.30$ ml, so $V'_e = 16.26$ ml and $V''_e = 16.56$ ml; $16.26 \text{ ml} < \hat{V}_e < 16.56$ ml.

If we consider the point of intersection $\bar{V}_e$ as belonging to the linear regression before the equivalence point, then

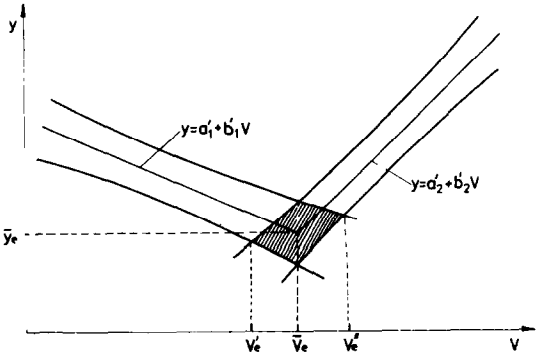


Fig. 1. The confidence interval of the equivalence point $\bar{V}_e$ in a linear titration, from the intersection of the hyperbolic confidence-bands of the two linear regressions[3].

Table 1. Data for conductometric titration of 0.1*M* HCl with 0.1*M* NaOH[8]; degrees of freedom $\nu_1 = 6$ and $\nu_2 = 3$

No.	V, ml 0.1*M* of NaOH (x)	$(1000\text{-}l)/l$* (y)	No	V, ml 0.1*N* of NaOH (x)	$(1000\text{-}l)/l$* (y)
1	2	1.265	8	16	0.372
2	4	1.141	9	17	0.388
3	6	1.028	10	18	0.441
4	8	0.906	11	20	0.544
5	10	0.777	12	22	0.644
6	12	0.641	13	24	0.752
7	14	0.510			

* l = mm length on conductimetric bridges.

from Fig. 2 a certain confidence interval $(\Delta V_e)_1 = (V_e'')_1 - (V_e')_1$ is associated with it. If it is regarded as belonging to the other linear regression, however, another confidence interval $(\Delta V_e)_2 = (V_e'')_2 - (V_e')_2$ is associated with it.

As the equivalence point belongs concomitantly to both linear regressions, the two segments of its confidence interval can be obtained by taking the weighted averages of the branches of the two separate sets of confidence intervals.

Therefore, in principle, the two segments are not equal. They are equal only in the case of the Jander method,[3] but in that case $(y)_{V_e'} \neq (y)_{V_e''} \neq (y)_{\bar{V}_e}$.

However, it is intuitive that the value of y for the two extreme values of the confidence interval, V_e' and V_e'', should be the same as the value for $\bar{V}_e$, *i.e.*, $(y)_{V_e'} = (y)_{V_e''} = (y)_{\bar{V}_e}$. This condition is not fulfilled by the methods listed.

If the weighted averages are taken, we obtain

$$\frac{\nu_1(V_e')_1 + \nu_2(V_e')_2}{\nu_1 + \nu_2} < \hat{V}_e < \frac{\nu_1(V_e'')_1 + \nu_2(V_e'')_2}{\nu_1 + \nu_2} \tag{6}$$

where $\nu_1 = n_1 - 2$ and $\nu_2 = n_2 - 2$. From Fig. 2 the two values of the limits of the confidence interval for each of those two bands will be the two solutions of the equations:

$$\bar{y}_e = a_1' + b_1'(V_e)_1 \pm t_{(P;\nu_1)}(s_y)_1\sqrt{\frac{1}{n_1} + \frac{[(V_e)_1 - \bar{V}_1]^2}{(S_{VV})_1}} \tag{7}$$

$$\bar{y}_e = a_2' + b_2'(V_e)_2 \pm t_{(P;\nu_2)}(s_y)_2\sqrt{\frac{1}{n_2} + \frac{[(V_e)_2 - \bar{V}_2]^2}{(S_{VV})_2}} \tag{8}$$

where

$$S_{VV} = \sum_{i=1}^{n} V_i^2 - \left(\sum_{i=1}^{n} V_i\right)^2 \Big/ n$$

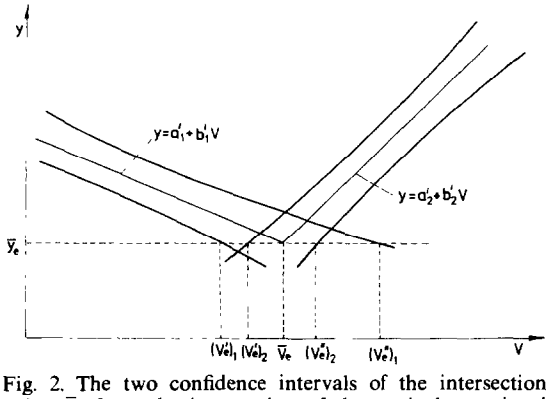


Fig. 2. The two confidence intervals of the intersection point $\bar{V}_e$ from the intersection of the equivalence signal $\bar{y}_e$ with the hyperbolic confidence-bands of the two linear regressions.

and

$$s_y = \sqrt{\frac{S_{yy} - b'S_{Vy}}{n-2}},$$

where

$$S_{Vy} = \sum_{i=1}^{n} V_i y_i - \left(\sum_{i=1}^{n} V_i \sum_{i=1}^{n} y_i\right) \Big/ n$$

and

$$S_{yy} = \sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} y_i\right)^2 \Big/ n.$$

From equations (4) and (5) $\bar{y}_e = 0.358$ results for $\bar{V}_e = 16.413$ ml, and using the data from Table 1 we obtain: $\nu_1 = 6$, $\bar{V}_1 = 9.00$, $(S_{VV})_1 = 168$, $(s_y)_1 = 1.034 \times 10^{-2}$, $\nu_2 = 3$, $\bar{V}_2 = 20.20$, $(S_{VV})_2 = 38$, $(s_y)_2 = 2.049 \times 10^{-3}$. Since $t_{(0\,90,6)} = 1.943$, and $t_{(0\,90,3)} = 2.353$, the equations (7) and (8) have the form:

$$0.358 = 1.403 - 0.06367(V_e)_1 \pm 0.02009\sqrt{0.125 + \frac{[(V_e)_1 - 9.00]^2}{168}} \tag{7'}$$

$$0.358 = -0.4908 + 0.05171(V_e)_2 \pm 0.004622\sqrt{0.2 + \frac{[(V_e)_2 - 20.20]^2}{32.8}}. \tag{8'}$$

The solutions of equation (7') are $(V_e')_1 = 16.02$ ml and $(V_e'')_1 = 16.81$ ml, and those of equation (8') are $(V_e')_2 = 16.34$ ml and $(V_e'')_2 = 16.49$ ml, so according to expression (6) $V_e' = 16.13$ ml and $V_e'' = 16.71$ ml. Summarizing: 16.13 ml $< \hat{V}_e <$ 16.71 ml.

If one of the linear regressions has $b' = 0$, the two values of the limits of the confidence interval are calculated by using either equation (7) if $b_2' = 0$, so that $(V_e')_1 < \hat{V}_e < (V_e'')_1$, or equation (8), if $b_1' = 0$, so that $(V_e')_2 < \hat{V}_e < (V_e'')_2$.

The flow-chart of the program for computer-calculation of the confidence interval according to this method is shown in Fig. 3.

Assuming[10] that the value $\bar{V}_e$ is a function of the normally distributed independent variables a_1', a_2', b_1' and b_2', for the data in Table 1 we obtain: $\Delta V_e = 1.30$ ml and hence 15.76 ml $< \hat{V}_e <$ 17.06 ml.

From expression (3) it appears that the estimated value $\bar{V}_e$ normally distributed is a function of the two independent variables $\Delta a'$ and $\Delta b'$. Hence, from the repetitive estimation of the average value $\bar{V}_e$ originating from the $n_1 + n_2$ pairs of values (y_i, V_i), the following variable may also be considered:

$$t = \frac{\bar{V}_e - \hat{V}_e}{s_{\bar{V}_e}} \tag{9}$$

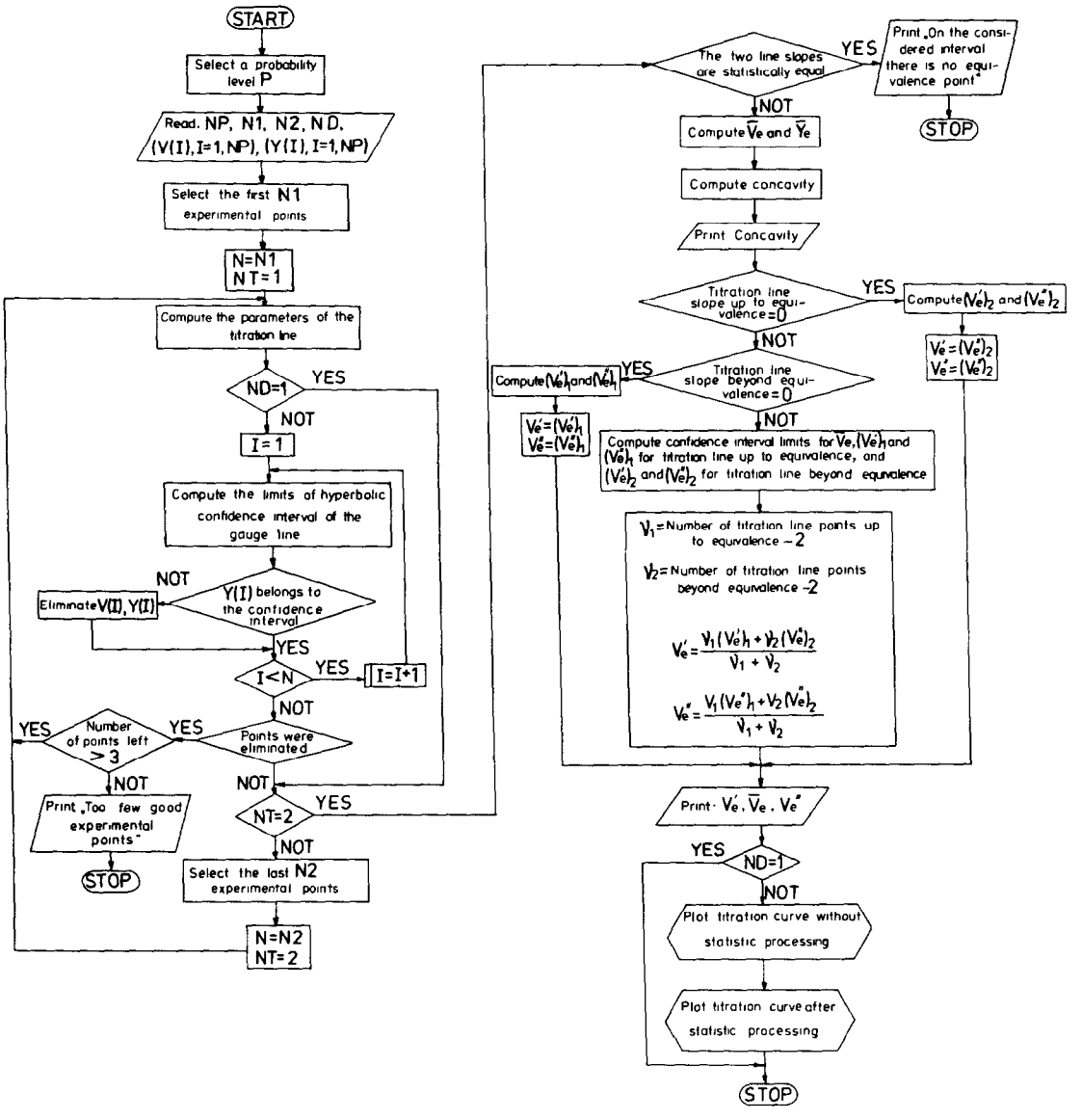


Fig. 3. Flow-chart of the program for computer calculation of the confidence interval of the equivalence volume $\bar{V}_e$, according to the method shown in Fig. 2.

and the expression of the confidence interval with two equal segments for the true value of the equivalence point $\hat{V}_e$ is

$$\bar{V}_e - t_{(P;\nu_1+\nu_2)} s_{\bar{V}_e} < \hat{V}_e < \bar{V}_e + t_{(P,\nu_1+\nu_2)} s_{\bar{V}_e} \qquad (10)$$

From the variance of the ratio of two independent variables we have

$$s^2_{\bar{V}_e} = \frac{1}{(\Delta b')^2} s^2_{\Delta a'} + \frac{(\Delta a')^2}{(\Delta b')^4} s^2_{\Delta b'} \qquad (11)$$

in which $s^2_{\Delta a'} = s^2_{a_1'} + s^2_{a_2'}$, where

$$s^2_{a'} = s^2_y \sum_{i=1}^{n} V_i^2 \Big/ n \sum_{i=1}^{n} (V_i - \bar{V})^2,$$

and

$$s^2_{\Delta b'} = s^2_{b_1'} + s^2_{b_2'},$$

where

$$s^2_{b'} = s^2_y \Big/ \sum_{i=1}^{n} (V_i - \bar{V})^2.$$

Using the data of Table 1, we obtain: $s^2_{\Delta a'} = 0.000963$, $s^2_{\Delta b'} = 0.0000026$ and $s^2_{\bar{V}_e} = 0.126$, or $s_{\bar{V}_e} = 0.35$. For $P = 0.90$ and $\nu = \nu_1 + \nu_2 = 9$, $t = 1.833$, so that $ts_{\bar{V}_e} = 0.65$, giving the same result: $\Delta V_e = 1.30$ ml: 15.77 ml $< \hat{V}_e <$ 17.06 ml.

REFERENCES

1. J. Mika, *Z. Anal. Chem.*, 1936, **106**, 248.
2. C. Liteanu and D. Cörmös, *Talanta*, 1960, **7**, 18.
3. P. Janders, S. Kolda and S. Kotrlý, *ibid.*, 1970, **17**, 443.

4. C. Liteanu and D. Cörmös, *Rev. Roumaine Chim.*, 1965, **10**, 361.
5. P. D. Lark, E. R. Craven and R. C. L. Bosworth, *The Handling of Chemical Data*, p. 177. Pergamon, London, 1968.
6. R. A. Fisher, *Statistical Methods for Research Workers*, 13th Ed., Oliver & Boyd, Edinburgh, 1963.
7. M. A. Kastenbaum, *Biometrics*, 1959, **15**, 323.
8. C. Liteanu and E. Hopîrtean, *Studia Univ. Babeş-Bolyai, Ser. Chem. (1)*, 1966, **11**, 135.
9. D. Ceauşescu and V. Eliu-Ceauşescu, *Rev. Roumaine Chim.*, 1977, **23**, 563.
10. *Idem, Z. Anal. Chem.*, 1976, **282**, 45.

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SODIUM TETRACHLOROFERRATE AS A DEHYDRATING AGENT

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Summary—Fused $NaFeCl_4$ shows a great affinity for moisture, which reacts chemically with it. By passage through a heated column filled with $NaFeCl_4$ coated on bioglass, gases such as nitrogen are found to have retained some moisture when dried over a molecular sieve. The compound also acts as a self-indicator, as the colour changes from yellow to brown after the reaction. It is more efficient than molecular sieves and is regenerated by passing HCl gas through the column.

A number of chemical methods are known for removal of water from liquids and gases. Those of most practical interest in research work are absorption or chemical desiccation and adsorption[1–9] Besides the drying agents mentioned elsewhere[1–9] there are many other compounds such as glycerol, glycol, some polyhydric alcohols, H_2SO_4, CaO, $CuSO_4$, LiBr, $ZnBr_2$, $ZnCl_2$, $CaBr_2$, CaC_2 *etc.* These substances do not remove moisture completely and are only employed when small amounts of moisture are permissable.[7]

In the present work a study has been made of the properties of sodium tetrachloroferrate as a dehydrating agent, especially for gases, and it is compared with the above-mentioned drying agents.

EXPERIMENTAL

$NaFeCl_4$ was prepared from NaCl and $FeCl_3$, which are known to form a 1:1 addition compound.[9] A known amount of anhydrous and resublimed $FeCl_3$ was taken in a glass tube and treated according to the method described earlier.[10,11] $NaFeCl_4$ melts at a fairly low temperature, 158°, and boils at 1060°. It reacts with moisture in gases at room temperature, but is more efficient and reacts completely only in the fused state. Therefore it can only be applied as a drying agent at higher temperatures.

At a temperature of 200° it reacts with moisture completely and its vapour pressure is extremely low, 0.0936 mmHg, calculated from the equation[12]

$$\log P = -(3900/T) + 5.80$$

where T is the absolute temperature. The vapour pressure at 300° is 0.099 mmHg and the compound starts to bleed.

The procedure adopted by Zado and Juvet[13] was used for preparation of the column. Bioglass-2500 (80–100 mesh) dried at 400° and flushed with anhydrous Cl_2 or HCl gas and finally with dry nitrogen to eliminate impurities, if present, was used as solid support for the $NaFeCl_4$ melt. The relatively high density of the melt permits a maximum loading of 45% w/w. The following reaction explains the "absorption" of moisture by the fused melt:

$$2NaFeCl_4 + 3H_2O = Fe_2O_3 + 2NaCl + 6HCl$$

Moist air was passed through a column containing 1.276 g of $NaFeCl_4$ and heated to 200°. As the moisture was "absorbed" the column turned from yellow to brown. The brown zone moved in the direction of the flow of gas. The colour indicated when the whole of the $NaFeCl_4$ was spent. The "absorption" of moisture resulted in loss of weight of the column, in agreement with the equation above. The results show that 100 g of $NaFeCl_4$ are capable of removing 11.72 g of water.

The first 70% of the melt reacts very rapidly but later the reaction runs slowly because the Fe_2O_3 formed outside the bioglass particles protects the $NaFeCl_4$ inside the pores from moisture.

Helium and nitrogen, already dried over a molecular sieve, could be still further dried in an $NaFeCl_4$ column at 200°, showing that $NaFeCl_4$ is more efficient than a molecular sieve for removal of water. Similarly chlorine previously dehydrated by $Mg(ClO_4)_2$ was also further dried on $NaFeCl_4$. Oxygen and carbon dioxide passed through the column at 200°. The column changed colour, indicating some reaction. Carbon dioxide and oxygen were detected at the outlet. The column retained moisture from natural gas but the gas could not be detected at the outlet. Apparently the methane reacts with $NaFeCl_4$.

The reaction with water is reversible and $NaFeCl_4$ can be regenerated by passing dry HCl gas through the column at 200°. HCl gas also reacts at room temperature, but more efficiently at higher temperatures. If the gas is passed carefully at constant flow-rate, it takes 5–10 min to regenerate a 15-cm long 9-mm bore column. The column returns to the original weight, showing no loss of material.

$NaFeCl_4$ can be used as drying agent only when HCl gas does not interfere with the system under investigation. Gases can be dehydrated over this compound, for use in gas chromatographic work with inorganic halides. The compound is a most efficient dehydrating agent and should be usable for determination of water in gases by measurement of the amount of HCl liberated.

4. C. Liteanu and D. Cörmös, *Rev. Roumaine Chim.*, 1965, **10**, 361.
5. P. D. Lark, E. R. Craven and R. C. L. Bosworth, *The Handling of Chemical Data*, p. 177. Pergamon, London, 1968.
6. R. A. Fisher, *Statistical Methods for Research Workers*, 13th Ed., Oliver & Boyd, Edinburgh, 1963.
7. M. A. Kastenbaum, *Biometrics*, 1959, **15**, 323.
8. C. Liteanu and E. Hopîrtean, *Studia Univ. Babeş-Bolyai, Ser. Chem. (1)*, 1966, **11**, 135.
9. D. Ceauşescu and V. Eliu-Ceauşescu, *Rev. Roumaine Chim.*, 1977, **23**, 563.
10. *Idem, Z. Anal. Chem.*, 1976, **282**, 45.

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SODIUM TETRACHLOROFERRATE AS A DEHYDRATING AGENT

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Summary—Fused $NaFeCl_4$ shows a great affinity for moisture, which reacts chemically with it. By passage through a heated column filled with $NaFeCl_4$ coated on bioglass, gases such as nitrogen are found to have retained some moisture when dried over a molecular sieve. The compound also acts as a self-indicator, as the colour changes from yellow to brown after the reaction. It is more efficient than molecular sieves and is regenerated by passing HCl gas through the column.

A number of chemical methods are known for removal of water from liquids and gases. Those of most practical interest in research work are absorption or chemical desiccation and adsorption[1–9] Besides the drying agents mentioned elsewhere[1–9] there are many other compounds such as glycerol, glycol, some polyhydric alcohols, H_2SO_4, CaO, $CuSO_4$, LiBr, $ZnBr_2$, $ZnCl_2$, $CaBr_2$, CaC_2 *etc.* These substances do not remove moisture completely and are only employed when small amounts of moisture are permissable.[7]

In the present work a study has been made of the properties of sodium tetrachloroferrate as a dehydrating agent, especially for gases, and it is compared with the above-mentioned drying agents.

EXPERIMENTAL

$NaFeCl_4$ was prepared from NaCl and $FeCl_3$, which are known to form a 1:1 addition compound.[9] A known amount of anhydrous and resublimed $FeCl_3$ was taken in a glass tube and treated according to the method described earlier.[10,11] $NaFeCl_4$ melts at a fairly low temperature, 158°, and boils at 1060°. It reacts with moisture in gases at room temperature, but is more efficient and reacts completely only in the fused state. Therefore it can only be applied as a drying agent at higher temperatures.

At a temperature of 200° it reacts with moisture completely and its vapour pressure is extremely low, 0.0936 mmHg, calculated from the equation[12]

$$\log P = -(3900/T) + 5.80$$

where T is the absolute temperature. The vapour pressure at 300° is 0.099 mmHg and the compound starts to bleed.

The procedure adopted by Zado and Juvet[13] was used for preparation of the column. Bioglass-2500 (80–100 mesh) dried at 400° and flushed with anhydrous Cl_2 or HCl gas and finally with dry nitrogen to eliminate impurities, if present, was used as solid support for the $NaFeCl_4$ melt. The relatively high density of the melt permits a maximum loading of 45% w/w. The following reaction explains the "absorption" of moisture by the fused melt:

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REFERENCES

1. R. Worthington, *Chem. Ind. (London)*, 1964, 2110.
2. B. K. Beecher, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Ed., Vol. 7, 378–398. Wiley, New York, 1968.
3. *Chemical and Physical Properties of Lithium Compounds*, Foote Mineral Co., Philadelphia, Pennsylvania, Jan., 1957.
4. *Lithium, Gmelins Handbuch der Anorg. Chem.*, p. 114, Verlag Chemie, Berlin, 1927; *Ergänzungsband*, p. 329, Verlag Chemie, Weinheim, 1960.
5. J. M. Dain, *Chem. Weekblad*, 1958, **54**, 277.
6. G. F. Smith, *Talanta*, 1962, **9**, 65.
7. M. Shepherd, in *International Critical Tables*, Vol. III, p. 385. McGraw-Hill, New York, 1928.
8. H. Römpp, *Chemie Lexikon*, 4th Ed., Vol. 2, p. 4525. Franckh'sche Verlag, Stuttgart, 1958.
9. C. M. Cook and W. E. Dunn, Jr., *J. Phys. Chem.*, 1961, **65**, 1505.
10. R. S. Juvet, V. R. Shaw and M. A. Khan, *J. Am. Chem. Soc.*, 1969, **91**, 3788.
11. M. Saleem, M. A. Khan, M. Shahid and K. Iqbal, *Chromatographia*, 1975, **8**, 699.
12. I. S. Morozov and D. Y. Toptygin, *Bull. Acad Sci USSR, Div. Chem. Sci.* 1959, 1832.
13. F. M. Zado and R. S. Juvet, *Proc. 6th Intern. Symp. Gas Chromatog. Rome* 20–23 *Sept.* 1966, p. 283.

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LIQUID–LIQUID EXTRACTION OF A RHENIUM–THIOCYANATE COMPLEX WITH HEXAMETHYLPHOSPHORAMIDE AND DIRECT SPECTROPHOTOMETRIC DETERMINATION IN THE ORGANIC PHASE

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(*Received* 27 *June* 1977. *Revised* 28 *February* 1978. *Accepted* 24 *March* 1978)

Summary—A sensitive and selective method for the extraction of trace rhenium is based on extraction of a Re-thiocyanate complex with hexamethylphosphoramide and chloroform at an acidity of 2–3 *M* hydrochloric acid. Hydrazine sulphate is used as the reducing agent. The system obeys Beer's law at 430 nm, the optimum concentration range is 1.7–8 ppm. The molar absorptivity is calculated to be 2.23×10^4 l.mole^{-1}.cm^{-1}. The colour is stable for at least 48 hr. The method is simple and rapid and is generally free from interference by most of the metals commonly associated with rhenium.

Of the methods[1] that have been proposed for the colorimetric determination of rhenium, that based on the treatment of an acid solution of perrhenate with thiocyanate and stannous chloride[2] has perhaps found the widest application, but tungsten and molybdenum both interfere, and in their presence it is necessary to make a preliminary separation of rhenium by volatilization of the heptoxide, precipitation of the sulphide with a suitable collector and extraction of tetraphenylarsonium perrhenate with chloroform[3] or else removal of molybdenum as Mo(V) thiocyanate with ether.[4] Neutral salts (*e.g.*, chlorides, nitrates) decrease the colour intensity, and the interfering elements include Cu, Se, Te, Au, Pt and V; iron is undesirable except in very small amounts, according to Geilmann and Bode.[2]

Reactions of perrhenates with pyrazoline dithiocarbamates (PDTC) were carried out by Busev *et al.*[5] Although the reactions are highly sensitive (molar absorptivities ranging from 1.0×10^4 to 5.3×10^4 l.mole^{-1}.cm^{-1}) a number of drawbacks make this method less useful. The formation of the rhenium–PDTC complex is slow and chloroform and isoamyl alcohol extract only colourless rhenium compounds immediately after addition of the reagents. The colour appears after at least 35–40 min. If Mo(VI) is present, then it must be converted into the peroxide complex by addition of H_2O_2, as this complex does not interfere. The amount of peroxide is critical, however, as Re(IV) may also be oxidized. Se(IV), Te(IV), Sn(II), iodide, and oxalic, nitric and nitrous acids interfere.

The thiocarbazide derivatives used by Borisova *et al.*[6] are fairly sensitive but the selectivity is rather low. 6-Chloro-8-mercaptoquinoline[7] is claimed to be both sensitive and selective.

Recently, modifications to the thiocyanate method have been suggested, in which a second ligand is added to enhance the colour of the rhenium–thiocyanate complex. Various pyrazolone derivatives[8] have been used for this purpose and molar absorptivities of about 2×10^4 l.mole^{-1}.cm^{-1} have been obtained, but a two-step extraction is necessary, Re(VII) being first extracted with the pyrazolone into chloroform and then the organic phase treated with thiocyanate, hydrochloric acid and tin(II) chloride to give the coloured complex. Molybdenum and tungsten interfere.

In another method, thiourea and thiocyanate are used, in the presence of tin(II) chloride.[9] W(VI), Mo(VI), V(V), Se(IV) and Ni(II) interfere. Another method by Ryabchikov and Lasarev[10] has low sensitivity and low selectivity.

Reviews have been compiled by various authors on the spectrophotometric determination of rhenium.[11–13]

In the method described here, hexamethylphosphoramide (HMPA), which has already been used in the determination of molybdenum with thiocyanate[14] is used to form a mixed complex with rhenium and thiocyanate, which is then extracted with chloroform. Hydrazine sulphate is used as the reducing agent. The colour system is stable for at least 48 hours. The few metals which interfere can be easily masked or separated before the determination

EXPERIMENTAL

Reagents

Rhenium solution. Prepared from Johnson and Matthey "Spec-pure" potassium perrhenate, standardized by the

REFERENCES

1. R. Worthington, *Chem. Ind. (London)*, 1964, 2110.
2. B. K. Beecher, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Ed., Vol. 7, 378–398. Wiley, New York, 1968.
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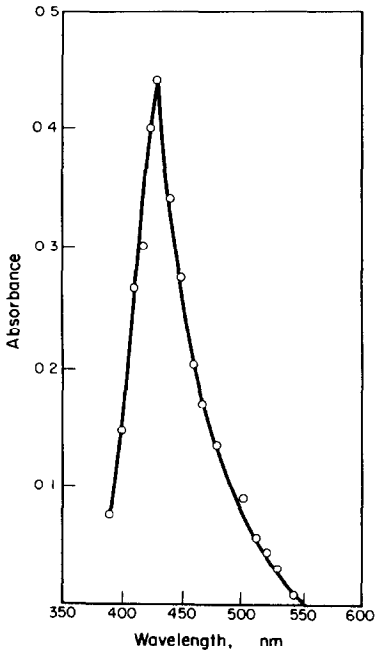


Fig. 1

method of internal electrolysis,[15] and diluted to obtain a rhenium solution of 0.1 mg/ml concentration.

General procedure

A 1-ml aliquot of 0.1-mg/ml rhenium solution was mixed with about 500 mg of ammonium thiocyanate (in aqueous solution) in a 100-ml beaker, and the acidity was adjusted to about 2.5*M* in hydrochloric acid. Then 1 ml of HMPA was added, followed by 3 ml of saturated hydrazine sulphate solution. The solution was heated on a boiling water-bath for about 15 min, cooled, transferred to a separatory-funnel and extracted with three portions of chloroform. The combined organic phases were diluted to volume with chloroform in a 25-ml volumetric flask. A reagent blank was prepared under identical conditions, and the absorbance of the test solution was measured against the blank at 430 nm.

RESULTS AND DISCUSSION

Characteristics of the complex

The absorption spectrum of the amber-coloured system is shown in Fig. 1. The system obeys Beer's law over the range 1.5–8 ppm of rhenium in the final solution. The optimum concentration range, according to Ringbom,[16] is 1.75–8 ppm. The molar absorptivity is 2.23×10^4 l.mole^{-1}.cm^{-1}. The photometric error, calculated according to Ayres,[17] was 2.6%. The relative standard deviation for eight different measurements with 4 ppm of rhenium at 430 nm was 2.4%, the average absorbance being 0.478.

Optimal conditions

Heating for 12–45 min gives the same maximal absorbance, and 15 min was chosen as a convenient heating time.

No colour is produced at acidity below 0.25*M* hydrochloric acid. The colour intensity is maximal at an acidity between 2*M* and 3*M* hydrochloric acid (Fig. 2).

Hydrazine sulphate has been found to be a good reducing agent in the determination of rhenium. Various concentrations were tried but the colour produced always faded with time except when a saturated solution was used, the colour then being stable for 48 hr. A volume of about 3 ml was found satisfactory.

Varying the volume of HMPA from 0.5 to 2 ml had practically no effect on the absorbance, and 1 ml of HMPA was chosen for convenience.

The absorbance is maximal if at least 300 mg of ammonium thiocyanate is added. No colour is produced with less than 50 mg. The amount chosen was 500 mg, but more is necessary if certain other elements are present (see below).

The presence of more than 40 ppm of vanadium or tungsten reduces the absorbance. The effect can be nullified by adding an extra 1.5 g of ammonium thiocyanate before the HMPA and hydrazine sulphate.

Effect of other ions

It was found that no interference was caused by uranium(VI) (1 mg), zirconium (1 mg), vanadium(IV, V) (1 mg), tellurium(IV) (1 mg), tantalum (80 mg), gold (1.2 mg) or manganese(II) (1 g), hydroxylamine hydrochloride (1 g), tartaric acid (500 mg), ascorbic acid (500 mg), EDTA (500 mg) or sodium fluoride (450 mg). Niobium and titanium (1 mg) can be masked with sodium fluoride and copper(II) with thiourea. More than 0.1 mg of platinum(IV) interferes.

Estimation of rhenium in presence of Mo, Fe, Se and Te

The solution containing rhenium and molybdenum or iron is first made 8*M* in hydrochloric acid and then boiled for 15 min with excess of hydrazine hydrochloride. After reduction, the acid concentration is adjusted to 7*M* and the solution equilibrated six times with an equal volume (each time) of isoamyl acetate to remove molybdenum into the organic solvent.[18] The acidity of the aqueous phase is then adjusted to 2.5*M* and the rhenium estimated in the usual way.

Selenium(IV) and tellurium(IV) are both reduced by the hydrazine sulphate. The precipitates coagulate during the

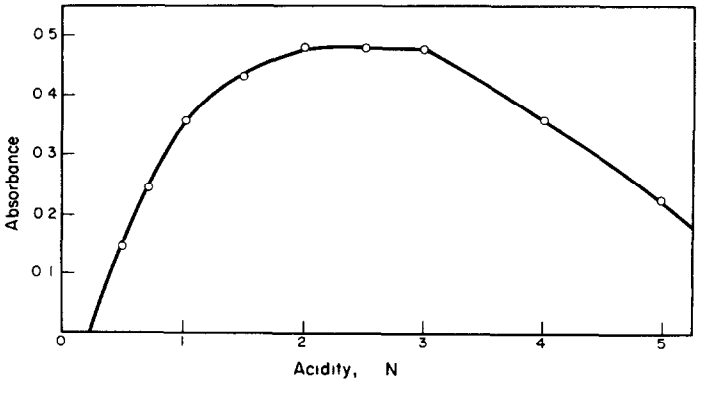


Fig. 2.

heating, and though the finer particles are carried into the chloroform layer they are absorbed on the sodium sulphate in the drying step. When selenium is present it is found that an additional 2 g of ammonium thiocyanate is necessary (but not in the case of tellurium).

Analysis of a complex synthetic mixture

A synthetic mixture was prepared with the following proportions of the elements: 200 ppm of molybdenum, 20 ppm of tungsten, 10 ppm each of iron, selenium and tellurium and 4 ppm of rhenium. The general procedure (modified as outlined above) was applied, and the amounts of rhenium found in three determinations were 3.9, 4.0 and 3.9 ppm.

REFERENCES

1. Z. Marczenco, *Spectrophotometric Determination of Elements*, Horwood, Chichester, 197.
2. W. Geilmann and H. Bode, *Z. Anal. Chem.*, 1948, **128**, 489, 495.
3. S. Tribalat, *Anal Chim. Acta*, 1949, **3**, 113.
4. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957.
5. A. I. Busev, V. M. Bykro and G. K. Kondakova, *Zh. Analit. Khim.*, 1967, 22, 1028.
6. L. V. Borisova, E. I. Plastimna and A. N. Ermakov, *ibid.*, 1974, **29**, 743.
7. J. Bankovskis and E. Lobanova, *Latv. PSR Zinatu Akad. Vestis*, 1960, No. 1 97.
8. V. K. Akimov, A. I. Busev, L. Ya. Kliot, *Zh. Analit. Khim.*, 1973, **28**, 118.
9. C. P. Savarier and T. P. Hariharan, *Mikrochim. Acta*, 1975, 477.
10. D. I. Ryabchikov and A. I. Lazarev, *Zh. Analit. Khim.*, 1955, **10**, 228.
11. Z. Kh. Sultanova, L. K. Chuchalin, B. Z. Iofa and Ya. A. Zolotov, *ibid.*, 1973, **28**, 413.
12. E. N. Pollock and L. P. Zopatti, *Anal. Chim. Acta*, 1965, **32**, 418.
13. L. Rulfs, *CRC Crit. Rev. Anal. Chem.*, 1970, **1**, 335.
14. M. Mitra and B. K. Mitra, *Talanta*, 1977, **24**, 698.
15. A. K. Majumdar and G. Bhowal, *Anal. Chim. Acta*, 1969, **48**, 192.
16. A. Ringbom, *Z. Anal. Chem.*, 1938/39, **115**, 332.
17. G. H. Ayres, *Anal. Chem.*, 1949, **21**, 652.
18. V. Yatirajam and L. R. Kakkar, *Mikrochim. Acta*, 1971, 479.

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ANALYTICAL APPLICATIONS OF A LIQUID ANION-EXCHANGER FOR THE SEPARATION OF URANIUM(IV) IN MALONATE SOLUTION

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(*Received* 31 *December* 1977. *Accepted* 25 *February* 1978)

Summary—Uranium was quantitatively extracted with 4% Amberlite LA-1 in xylene at pH 2.5–4.0 from 0.001 *M* malonic acid. It was stripped from the organic phase with 0.01 *M* sodium hydroxide and determined spectrophotometrically at 530 nm as its complex with 4-(2-pyridylazo) resorcinol. Of various liquid anion-exchangers tested, Amberlite LA-1 was found to be best. Uranium was separated from alkali and alkaline earth metal ions, thallium(I), iron(II), silver, arsenic(III) and tin(IV) by selective extraction, and from zinc, cadmium, nickel, copper(II), cobalt(II), chromium(III), aluminium, iron(III), lead, bismuth, antimony(III) and yttrium by selective stripping. The separation from scandium, zirconium, thorium and vanadium(V) was done by exploiting differences in the stability of chloro-complexes.

Uranium can be extracted with liquid anion-exchangers from several media, *e.g.*, (*a*) hydrochloric acid with tri-n-octylamine,[1,2] tri-iso-octylamine[3,4] and trilaurylamine[5,6] with aromatic hydrocarbons as the diluents, (*b*) nitric acid[7–10] with tri-iso-octylamine[7,8] and Aliquat 336-S[9,10] and (*c*) sulphuric acid with Amberlite LA-1[11] or tri-n-octylamine.[12,13] A few organic acids such as acetic,[14,15] formic and oxalic[16] have also been used in conjunction with tri-n-octylamine or di-n-octylmethylamine, but hitherto no systematic study has been made of the extraction of uranium from malonate media with Amberlite LA-1. This is the subject of this paper, in which it is shown that the extraction is simple, rapid and selective, and permits separation of uranium from elements such as thorium, zirconium, scandium, yttrium and vanadium and many elements which are associated with it in minerals.

EXPERIMENTAL

Reagents

Uranium. A stock solution of uranium was prepared by dissolving 5.70 g of uranyl nitrate in 500 ml of demineralized water containing 1% nitric acid. The solution was standardized gravimetrically with 8-hydroxyquinoline.[17] It was found to contain 5.18 mg of uranium per ml. A solution containing 25.9 mg of uranium was prepared by dilution.

Ion-exchangers. Amberlite LA-1 [*N*-dodecyl-(trialkylmethyl)amine], Amberlite LA-2 [*N*-lauryl(trialkylmethyl)amine], Primene JM-T (mixture of primary amines in the C_{18-22} range) and tri-n-butylamine, were dissolved in suitable diluents in varying proportions. In order to convert liquid exchangers into the malonate form, they were shaken for 10 min with an equal volume of 0.1 *M* malonic acid. A second equilibration, with another 10 ml of 0.1 *M* malonic acid gave no substantial change. The optimum concentration of malonic acid was 0.1 *M*, as at higher concentrations emulsification or turbidity was encountered.

4-(2-Pyridylazo)resorcinol (PAR), 0.1% aqueous solution.

Buffer solution, pH 8. Sodium tetraborate solution (55.9 ml, 0.5*M*) diluted with 0.1*M* hydrochloric acid to 1 litre.

General procedure

A portion of solution containing 51.8 μg of uranium was taken and 5 ml of 0.001 *M* malonic acid were added to it. The pH was adjusted to 3.0 with 0.001 *M* sodium hydroxide or

heating, and though the finer particles are carried into the chloroform layer they are absorbed on the sodium sulphate in the drying step. When selenium is present it is found that an additional 2 g of ammonium thiocyanate is necessary (but not in the case of tellurium).

Analysis of a complex synthetic mixture

A synthetic mixture was prepared with the following proportions of the elements: 200 ppm of molybdenum, 20 ppm of tungsten, 10 ppm each of iron, selenium and tellurium and 4 ppm of rhenium. The general procedure (modified as outlined above) was applied, and the amounts of rhenium found in three determinations were 3.9, 4.0 and 3.9 ppm.

REFERENCES

1. Z. Marczenco, *Spectrophotometric Determination of Elements*, Horwood, Chichester, 197.
2. W. Geilmann and H. Bode, *Z. Anal. Chem.*, 1948, **128**, 489, 495.
3. S. Tribalat, *Anal Chim. Acta*, 1949, **3**, 113.
4. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York, 1957.
5. A. I. Busev, V. M. Bykro and G. K. Kondakova, *Zh. Analit. Khim.*, 1967, 22, 1028.
6. L. V. Borisova, E. I. Plastimna and A. N. Ermakov, *ibid.*, 1974, **29**, 743.
7. J. Bankovskis and E. Lobanova, *Latv. PSR Zinatu Akad. Vestis*, 1960, No. 1 97.
8. V. K. Akimov, A. I. Busev, L. Ya. Kliot, *Zh. Analit. Khim.*, 1973, **28**, 118.
9. C. P. Savarier and T. P. Hariharan, *Mikrochim. Acta*, 1975, 477.
10. D. I. Ryabchikov and A. I. Lazarev, *Zh. Analit. Khim.*, 1955, **10**, 228.
11. Z. Kh. Sultanova, L. K. Chuchalin, B. Z. Iofa and Ya. A. Zolotov, *ibid.*, 1973, **28**, 413.
12. E. N. Pollock and L. P. Zopatti, *Anal. Chim. Acta*, 1965, **32**, 418.
13. L. Rulfs, *CRC Crit. Rev. Anal. Chem.*, 1970, **1**, 335.
14. M. Mitra and B. K. Mitra, *Talanta*, 1977, **24**, 698.
15. A. K. Majumdar and G. Bhowal, *Anal. Chim. Acta*, 1969, **48**, 192.
16. A. Ringbom, *Z. Anal. Chem.*, 1938/39, **115**, 332.
17. G. H. Ayres, *Anal. Chem.*, 1949, **21**, 652.
18. V. Yatirajam and L. R. Kakkar, *Mikrochim. Acta*, 1971, 479.

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ANALYTICAL APPLICATIONS OF A LIQUID ANION-EXCHANGER FOR THE SEPARATION OF URANIUM(IV) IN MALONATE SOLUTION

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Summary—Uranium was quantitatively extracted with 4% Amberlite LA-1 in xylene at pH 2.5–4.0 from 0.001 *M* malonic acid. It was stripped from the organic phase with 0.01 *M* sodium hydroxide and determined spectrophotometrically at 530 nm as its complex with 4-(2-pyridylazo) resorcinol. Of various liquid anion-exchangers tested, Amberlite LA-1 was found to be best. Uranium was separated from alkali and alkaline earth metal ions, thallium(I), iron(II), silver, arsenic(III) and tin(IV) by selective extraction, and from zinc, cadmium, nickel, copper(II), cobalt(II), chromium(III), aluminium, iron(III), lead, bismuth, antimony(III) and yttrium by selective stripping. The separation from scandium, zirconium, thorium and vanadium(V) was done by exploiting differences in the stability of chloro-complexes.

Uranium can be extracted with liquid anion-exchangers from several media, *e.g.*, (*a*) hydrochloric acid with tri-n-octylamine,[1,2] tri-iso-octylamine[3,4] and trilaurylamine[5,6] with aromatic hydrocarbons as the diluents, (*b*) nitric acid[7–10] with tri-iso-octylamine[7,8] and Aliquat 336-S[9,10] and (*c*) sulphuric acid with Amberlite LA-1[11] or tri-n-octylamine.[12,13] A few organic acids such as acetic,[14,15] formic and oxalic[16] have also been used in conjunction with tri-n-octylamine or di-n-octylmethylamine, but hitherto no systematic study has been made of the extraction of uranium from malonate media with Amberlite LA-1. This is the subject of this paper, in which it is shown that the extraction is simple, rapid and selective, and permits separation of uranium from elements such as thorium, zirconium, scandium, yttrium and vanadium and many elements which are associated with it in minerals.

EXPERIMENTAL

Reagents

Uranium. A stock solution of uranium was prepared by dissolving 5.70 g of uranyl nitrate in 500 ml of demineralized water containing 1% nitric acid. The solution was standardized gravimetrically with 8-hydroxyquinoline.[17] It was found to contain 5.18 mg of uranium per ml. A solution containing 25.9 mg of uranium was prepared by dilution.

Ion-exchangers. Amberlite LA-1 [*N*-dodecyl-(trialkylmethyl)amine], Amberlite LA-2 [*N*-lauryl(trialkylmethyl)amine], Primene JM-T (mixture of primary amines in the C_{18-22} range) and tri-n-butylamine, were dissolved in suitable diluents in varying proportions. In order to convert liquid exchangers into the malonate form, they were shaken for 10 min with an equal volume of 0.1 *M* malonic acid. A second equilibration, with another 10 ml of 0.1 *M* malonic acid gave no substantial change. The optimum concentration of malonic acid was 0.1 *M*, as at higher concentrations emulsification or turbidity was encountered.

4-(2-Pyridylazo)resorcinol (PAR), 0.1% aqueous solution.

Buffer solution, pH 8. Sodium tetraborate solution (55.9 ml, 0.5*M*) diluted with 0.1*M* hydrochloric acid to 1 litre.

General procedure

A portion of solution containing 51.8 μg of uranium was taken and 5 ml of 0.001 *M* malonic acid were added to it. The pH was adjusted to 3.0 with 0.001 *M* sodium hydroxide or

Table 1. Effect of malonic acid concentration

Malonic acid concentration, $10^{-4}M$	Extraction, E%	Distribution ratio, D
1.0	64.0	1.78
2.0	88 0	7.40
3.0	96.0	24.0
4.0	97.5	39.0
5.0	98.5	65.7
6.0	99.1	110.0
7.0	99.1	110.0

Table 2. Effect of Amberlite LA-1 concentration

Amberlite LA-1, %	Extraction, E, %	Distribution ratio, D
0.5	70.0	2.34
1 0	89.0	8.09
1.5	94.0	15.7
2.0	96.0	24.0
3.0	98.5	65.7
4.0	99.1	110.0
8.0	99.1	110.0
16.0	99.1	110.0

malonic acid. The total volume was made up to 10 ml. The solution was transferred into a separating funnel and shaken with 10 ml of 4% Amberlite LA-1 in xylene for 10 min. The two layers were allowed to settle and separate. The aqueous layer was discarded and the inside of the stem of the funnel was washed with demineralized water. Then 10 ml of 0.01M sodium hydroxide solution were added to the funnel by pipette, and the mixture was shaken for a further 5 min, then the two phases were allowed to settle and separate. The aqueous layer was carefully withdrawn. It was mixed with 5 ml of buffer solution of pH 8.0 and 2 ml of PAR solution. The volume was made up to 25 ml with demineralized water. After 15 min the absorbance of the complex was measured at 530 nm. The amount of uranium was computed from a calibration curve.[18] For the experiments recorded in Tables 1–5, 51.8 μg of uranium were taken and the procedure above was followed except for the variations indicated

Effect of variables on the extraction

pH. At pH 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 the corresponding degrees of extraction were 0, 0, 60, 90, 99.1 and 99.1% respectively. The optimum pH for complete extraction is therefore 2.5–4.0.

Acid concentration. The effect of malonic acid was ascertained (Table 1). The extraction commenced at a malonic acid concentration of $1 \times 10^{-4}M$, and was quantitative from $5 \times 10^{-4}M$ or higher concentrations of malonic acid. For practical purposes, a concentration of $1 \times 10^{-3}M$ was used.

Amberlite LA-1 concentration. The optimum concentration of Amberlite LA-1 for extraction was investigated (Table 2) and 4% Amberlite LA-1 in xylene was adopted.

Table 3. Effect of various diluents

Diluent	Dielectric constant, ε	Extraction, E%		Distribution ratio, D	
		2% Amine	4% Amine	2% Amine	4% Amine
Benzene	2.3	95.0	98.5	19.0	65.7
Toluene	2.4	94.1	97.0	16.0	32.3
Xylene	2.3	96.0	99.1	24.0	110.0
Chloroform	4.8	54.0	81.5	1.2	4.4
Carbon tetrachloride	2.2	95.0	98.5	19.0	65.7

Table 4. Effect of different types of liquid anion-exchangers

Type of liquid anion-exchanger	Diluent	Extraction, E, %	Distribution ratio, D
Amberlite LA-1 [N-dodecyl (trialkylmethyl)-amine]	Benzene	98.5	65.7
	Xylene	99.1	110.0
	Chloroform	81.5	4.4
Amberlite LA-2 [N-lauryl (trialkylmethyl)-amine]	Benzene	98.5	65.7
	Xylene	99.0	99.0
	Chloroform	80.0	4.0
Primene JM-T (Mixture of primary amines in the C_{18}—C_{22} range)	Benzene	54.0	1.2
	Xylene	—	—
	Chloroform	89.0	8.1
Tri-n-butylamine	Benzene	8.0	0.0
	Xylene	5.0	0.05
	Chloroform	4.3	0.05

Table 5. Effect of metal ion concentration

Amount of U(VI) taken, μg/10 ml	Amount of U(VI) found, μg/10 ml	Extraction, E, %	Distribution ratio, D
6.5	6.4	99.5	199.0
25.9	25.8	99.3	141.9
51.8	51.4	99.2	124.0
103.5	102.8	99.2	124.0
207	205	99.0	99.0
414	410	98.9	89.9
829	817	98.6	70.4
—	1017	98.1	51.6

Various diluents. Uranium was extracted with 2% and 4% Amberlite LA-1 solution in various diluents (Table 3). The ratio of organic to aqueous phase was maintained at 1:1. At other ratios, emulsification took place. There was no emulsion formation at all with xylene as diluent, but diluents such as benzene and toluene rendered the aqueous layer slightly turbid, and with chloroform or carbon tetrachloride there was considerable emulsion formation. Xylene was therefore used as diluent for further work.

Table 6. Effect of diverse ions

Foreign ion	Added as	Tolerance limit, mg
Ag^{+}	$AgNO_3$	0.52
Pb^{2+}	$Pb(NO_3)_2\ 2H_2O$	0.25*
Tl^{+}	Tl_2SO_4	0.26
Cu^{2+}	$CuSO_4.5H_2O$	0.25*
Cd^{2+}	$Cd(NO_3)_2.4H_2O$	0.50*
As^{3+}	$AsCl_3$	0.27
Sb^{3+}	$SbCl_3.3H_2O$	0.13*
Bi^{3+}	$Bi(NO_3)_3.5H_2O$	0.51*
Sn^{4+}	$SnCl_4$	0.50
Au^{3+}	$HAuCl_4.xH_2O$	0.25
Pt^{4+}	H_2PtCl_6	0.26
Fe^{2+}	$FeSO_4.7H_2O$	0.53
Fe^{3+}	$Fe_2(SO_4)_3.7H_2O$	0.13*
Cr^{3+}	$CrCl_3.6H_2O$	0.53*
Al^{3+}	$Al(NO_3)_3.9H_2O$	0.52*
Sc^{3+}	$Sc(NO_3)_3$	0.11†
Y^{3+}	$Y(NO_3)_3$	0.11*
Zr^{4+}	$Zr(NO_3)_4\ 5H_2O$	0.11†
Be^{2+}	$Be(NO_3)_2.4H_2O$	0.53
Th^{4+}	$Th(NO_3)_4.4H_2O$	0.06†
V^{4+}	$VOSO_4.H_2O$	0.11†
Zn^{2+}	$ZnSO_4.7H_2O$	0.53*
Mn^{2+}	$MnSO_4.7H_2O$	0.26
Co^{2+}	$Co(NO_3)_2.6H_2O$	0.52*
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	0.55*
Ca^{2+}	$CaCl_2.6H_2O$	1.20
Sr^{2+}	$Sr(NO_3)_2.2H_2O$	1.20
Ba^{2+}	$Ba(NO_3)_2.4H_2O$	0.51
Li^{+}	$Li_2SO_4.H_2O$	5.20
Na^{+}	NaCl	5.20
K^{+}	KCl	5.18
Rb^{+}	RbCl	1.04
Cs^{+}	CsCl	1.00
SeO_3^{2-}	Na_2SeO_3	0.25†
TeO_3^{2-}	Na_2TeO_3	0.25†
WO_4^{2-}	Na_2WO_4	0.25†
CN^{-}	KCN	0.26†
VO_3^{-}	$NaVO_3.H_2O$	0.10†
$Mo_7O_{24}^{6-}$	$(NH_4)_6Mo_7O_{24}.4H_2O$	0.25†

* Weak complexes scrubbed with water.
† Selectively stripped with 8*M* hydrochloric acid.

Different types of liquid anion-exchanger Uranium was extracted with the four extractants (Table 4). The extraction was quantitative with Amberlite LA-1 and Amberlite LA-2, but Primene JM-T and tri-n-butylamine proved to be poor extractants, hence Amberlite LA-1 was adopted.

Stripping agents. After extraction of uranium into the organic phase, it was stripped with 10 ml of varying concentrations (0.01–4*M*) of sodium hydroxide, sodium carbonate, hydrochloric acid or sulphuric acid. The stripping was complete with 0.01*M* sodium hydroxide. Recovery was incomplete with hydrochloric and sulphuric acid because the stripping agents formed anionic complexes which in turn were re-extracted with the exchanger. Sodium carbonate permitted satisfactory recovery of uranium, but it strongly interfered with the subsequent photometric determination. Higher concentrations of sodium hydroxide were avoided because of emulsification but 10 ml of 0.01*M* sodium hydroxide proved satisfactory for stripping.

Metal ion concentration. Uranium was extracted over the concentration range of 0.6–150 mg (Table 5), the extraction being quantitative up to 100 mg. With 51.8 μg the average recovery was 99.1% and the relative standard deviation 1.2%.

Equilibration times. The time of shaking was varied from 2 to 20 min. The extraction was quantitative within 10 min and the back-extraction was complete within 5 min.

Effect of diverse ions

Uranium was extracted in the presence of a large number of diverse ions. The tolerance limit was set as the amount of foreign ion required to cause ±2% error in the recovery of uranium. The alkali and alkaline earth metal ions, thallium(I), iron(II), silver, arsenic(III) and tin(IV) were incapable of forming any anionic complexes in malonate media and hence were not extracted. Zinc, cadmium, nickel, copper(II), cobalt(II), chromium(III), aluminium, iron(III), lead, bismuth, antimony(III) and yttrium formed weaker complexes than uranium and these could be easily removed by a water wash before the stripping step. However, scandium, zirconium, thorium and vanadium(IV) formed relatively stable complexes, but these could not be easily stripped with 8*M* hydrochloric acid. Uranium, which was not stripped with 8*M* hydrochloric acid because of its re-extraction as its anionic chloro-complex, was subsequently stripped with 1*M* sodium hydroxide.[19,20]

By extending the same methodology, it was possible to separate uranium from anions such as selenite, tellurite, tungstate, cyanide, vanadate and molybdate.

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REFERENCES

1. H. Onishi and Y. Toita, *Bunseki Kagaku*, 1965, **14**, 1141.
2. E. Cerrai and C. Testa, *J. Chromatog.*, 1961, **6**, 443.

3. T. Sato, *Naturwissenschaften*, 1966, **53**, 37.
4. L. Lorenzini, C. Stoppa and W. Barbieri, *Metallurgia*, 1962, **54**, 380.
5. T. Sato, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1461.
6. W. G. Scribner, M. J. Borchers and W. J. Treat, *Anal. Chem.*, 1966, **38**, 1779.
7. M. A. Khattak and R. J. Magee, *Anal. Chim. Acta*, 1966, **35**, 17.
8. W. G. Scribner and A. M. Kotecki, *Anal. Chem.*, 1965, **37**, 1304.
9. G. Koch, *Radiochim. Acta*, 1965, **4**, 128.
10. G. Scibona, *J. Phys. Chem.*, 1966, **70**, 1365.
11. H. Green, *Talanta*, 1964, **11**, 1561.
12. T. Sato, *Bull. Chem. Soc. Japan*, 1968, **41**, 99.
13. C. Deptula and S. Minc, *J. Inorg. Nucl. Chem.*, 1967, **29**, 221.
14. A. A. Lipovskii and M. G. Kuzina, *Zh. Neorgan. Khim.*, 1967, **12**, 1240.
15. F. L. Moore, *Anal. Chem.*, 1960, **32**, 1075.
16. *Idem, ibid.*, 1957, **29**, 1660.
17. A. I. Vogel, *Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 540. Longmans, London, 1962.
18. T. M. Florence and Y. Farrar, *Anal. Chem.*, 1963, **35**, 1613.
19. F. Ichikawa and S. Urono, *Bull. Chem. Soc. Japan*, 1960, **33**, 569.
20. T. Suzuki and T. Sotobayashi, *Bunseki Kagaku*, 1965, **14**, 414.

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ANNOTATIONS

INVESTIGATION ON THE DRYING AND DECOMPOSITION OF SODIUM OXALATE

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Summary—The drying of sodium oxalate at various temperatures was investigated by the microdetermination of the residual water in the heated sample and of the carbon monoxide produced by thermal decomposition. Sodium oxalate heated for 2 hr above 200° and cooled contains less than 20 ppm of water, and may be used as a standard for titrimetry. The decomposition of sodium oxalate into sodium carbonate and carbon monoxide was investigated by non-aqueous titrimetric microdetermination of carbon monoxide. The decomposition begins at 290° and heating between 200° and 250° is recommended for the dehydration of sodium oxalate. The decomposition is complete between 750° and 800° within 20 min and the sodium carbonate obtained begins to decompose at above 810°.

Since 1898, sodium oxalate has been used as a standard reference material (SRM) for standardization of potassium permanganate and acids. Although the reaction is rather complex and is sometimes not recommended,[1] the reagent is still used in many industrial laboratories.

There is a wide difference in the drying temperatures for sodium oxalate reported in the literature,[2] and the temperature at which sodium oxalate begins to decompose into sodium carbonate and carbon monoxide is not precisely defined. The main criticism of the earlier work is that the reactions were followed by measuring the weight loss of the sample at fixed temperatures.

In this investigation, the decomposition temperatures of sodium oxalate and sodium carbonate were identified by measuring the small amounts of carbon monoxide and dioxide evolved. The procedure devised by Jones *et al.*[3,4] and modified by Yoshimori and Katoh,[5,6] was used for the determination of micro amounts of carbon monoxide and dioxide. The water remaining after heating the oxalate was determined by coulometric titration,[7,8] a method already used for investigating the drying conditions for potassium dichromate and sodium carbonate.[9] In this way the optimum conditions for the dehydration of sodium oxalate could be obtained.

The thermal decomposition of sodium carbonate was also investigated by the microdetermination of carbon dioxide, and the optimum temperature for obtaining the carbonate by the thermal decomposition of the oxalate was identified.

EXPERIMENTAL

Determination of carbon monoxide

The apparatus is shown in Fig. 1. Nitrogen at a flow-rate of 100 ml/min was used as carrier gas and was purified by passage over copper(II) oxide at 750°, the carbon dioxide and water being absorbed with soda-asbestos and magnesium perchlorate, respectively. The carbon monoxide produced by the thermal decomposition of sodium oxalate was oxidized with copper(II) oxide at 750°, and the resulting carbon dioxide was absorbed in dimethylformamide (DMF) containing 5% of monoethanolamine. The solution was then titrated with 0.001–0.002*M* tetra-n-butylammonium hydroxide in benzene–methanol solution, which had been previously standardized with pure benzoic acid. The amount of methanol in the standard solution was kept as small as possible in order to prevent fading of the indicator (2 or 3 drops of a 0.05% solution of thymolphthalein in DMF).

Determination of water

The method for the determination of water was reported previously.[7–10] The sodium oxalate was first heated at a fixed temperature for 3 hr in purified argon and cooled for 1 hr in the argon stream, which had been passed through a U-tube containing a desiccant. The sample was then heated at 250° or 270° to remove residual water, the water released being determined coulometrically.

RESULTS AND DISCUSSION

Drying conditions for sodium oxalate

The temperature at which the thermal decomposition of sodium oxalate was initiated was investigated by the present method and the results are shown in Fig. 2. No carbon monoxide could be detected on heating at 280° for 3 hr, but some decomposition at 290° was observed and this increased markedly at higher temperatures. Therefore, the drying temperature for sodium oxalate should be lower than 280°. Considering the heating conditions[2] and the error of temperature measurement in an oven, a drying temperature of 250° is advisable for the dehydration of sodium oxalate. This conclusion is in accord with that reported by Sörensen[11] and Sappenfield *et al.*[12]

The water content of dried sodium oxalate, which had been heated at various temperatures and then cooled in dry argon, was determined and the results are shown in Fig. 3. The temperatures of 250° and 280° were chosen

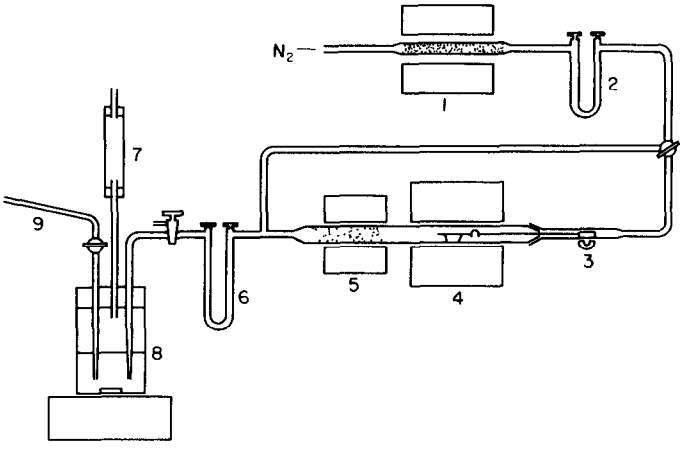


Fig. 1. Apparatus for the determination of micro amounts of carbon monoxide: 1—CuO furnace (750°), 2—soda-asbestos and $Mg(ClO_4)_2$, 3—magnet, 4—sample heater, 5—CuO furnace (750°), 6—$Mg(ClO_4)_2$, 7—NaOH, 8—titration cell, 9—tip of automatic microburette.

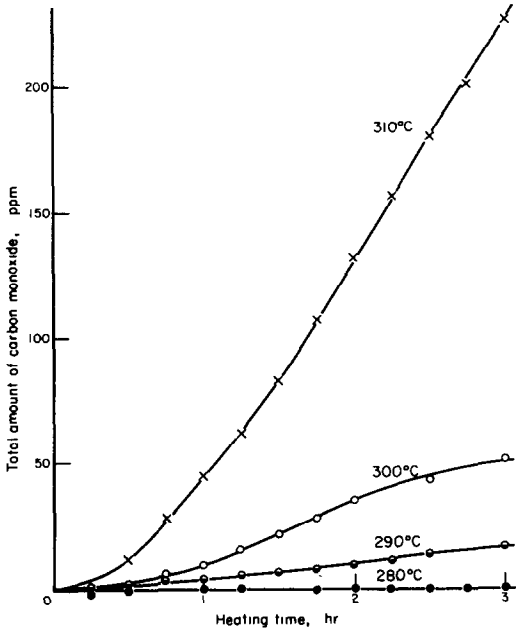


Fig. 2. Amount of carbon monoxide produced by the thermal decomposition of sodium oxalate

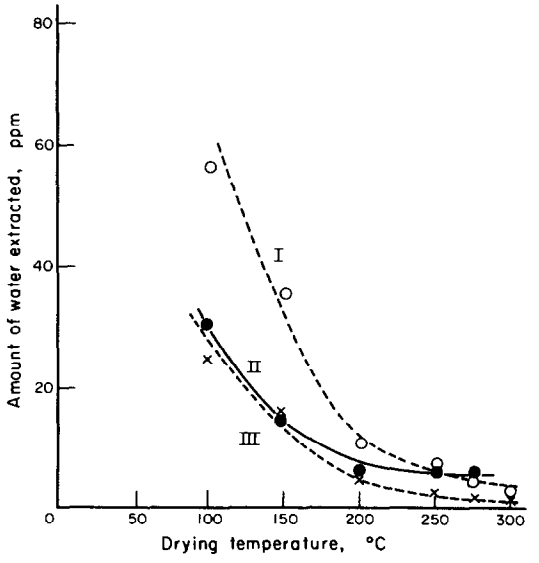


Fig. 3. Amount of water evolved from the "dried" sodium oxalate. Drying time 2 hr: ○—heating temperature 250°, with $CaCl_2$; ●—heating temperature 280°, with $Mg(ClO_4)_2$; ×—heating temperature 250°, with $Mg(ClO_4)_2$.

Table 1. Amount of carbon monoxide produced by the thermal decomposition of sodium oxalate

Temperature, °C	Heating time, *min*	Carbon monoxide recovery, %*
740	30	87.7
750	20	100.1
780	20	100.0
800	15	100.0
820	15	101.7
830	15	107.9

*Above 800°, decomposition products were carbon monoxide and dioxide.

for the removal of water from the "dried" sample. It had been observed previously[9] that the higher temperature is preferable for the complete removal of water from the sample. As shown by curves II and III in Fig. 3, however, the difference in the amounts of water removed at different temperatures was not as great above 250°. From curves I–III it can be inferred that the reagent may be dried completely at temperatures higher than 150°. In a previous review, Yoshimori[2] claimed that the reagent could be dried completely at temperatures higher than 200° and the results shown here confirm his suggestion.

Figure 3 also includes a comparison of some desiccants used in the desiccator in which the sample was cooled. The difference in the efficiency of magnesium perchlorate and calcium chloride was appreciable for samples dried at low temperature, but was much less for samples heated at high temperature. Even calcium chloride was satisfactory when the oxalate was heated at temperatures higher than 200°. Thus, the selection of the drying temperature is more important than the choice of desiccant, although magnesium perchlorate is to be preferred. Strouts *et al.*[13] have stated that the desiccant in the desiccator used for cooling the sample serves no useful purpose. The results shown in Fig. 3 indicate that this is true when the samples are heated to a sufficiently high temperature.

Decomposition of sodium carbonate

Sörensen recommended sodium carbonate (obtained by the thermal decomposition of sodium oxalate at high temperature) as a standard reference material, but the exact temperature is not given in textbooks,[14, 15] although 500° has sometimes been recommended.[16] The carbon monoxide and dioxide produced by the thermal decomposition of the sodium oxalate and carbonate were determined with the apparatus shown in Fig. 1. The results obtained are shown in Table 1 and indicate that the thermal decomposition of sodium oxalate may be incomplete at temperatures up to 740°, while sodium carbonate decomposes above 810°. Pure sodium carbonate may therefore be obtained by heating the sodium oxalate at a temperature between 750° and 800°.

REFERENCES

1. I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, *Quantitative Chemical Analysis*, 4th Ed., p. 827. Macmillan, London, 1969.
2. T. Yoshimori, *Talanta*, 1975, **22**, 827.
3. R. F. Jones, P. Gale, P. Hopkins and L. N. Powell, *Analyst*, 1965, **90**, 623.
4. *Idem, ibid.*, 1966, **91**, 399.
5. T. Yoshimori and N. Katoh, *Bunseki Kagaku*, 1977, **26**, 275, 868.
6. T. Yoshimori, N. Katoh and A. Koike, *J. Japan Inst. Metals*, 1977, **41**, 1236.
7. T. Yoshimori and S. Ishiwari, *Bull. Chem. Soc. Japan*, 1969, **42**, 1282.
8. *Idem, Talanta*, 1970, **17**, 349.
9. T. Yoshimori and N Sakaguchi, *ibid.*, 1975, **22**, 233.
10. T. Yoshimori, S. Ishiwari, Y. Watanabe, T. Harada and S. Yamada, *Trans. Japan Inst. Metals*, 1973, **14**, 396.
11. S. P. L. Sörensen, *Z. Anal. Chem.*, 1905, **44**, 141.
12. K. M. Sappenfield, G. Marinenko and J. L. Hague, *Natl. Bur. Std. Spec. Publ.*, 260–24, 1972, p. 4.
13. C. R. N. Strouts, H. N. Wilson and R. T. Parry-Jones, eds., *Chemical Analysis, The Working Tools*, 2nd Ed.,
14. I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, *op. cit.*, p. 780.
15. I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2nd Ed., Vol. II, p. 77. Interscience, New York, 1947.
16. F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th Ed., Vol. II, p. 500, Wiley, New York, 1935.

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DETERMINATION OF HOD BY INFRARED SPECTROPHOTOMETRY

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Summary—The concentration of HOD in biological fluids is measured by using vacuum distillation, followed by infrared spectrophotometry.

A number of different methods have been proposed for the determination of deuterium oxide in water. One of the earliest was based on the measurement of density,[1,2] but more recent methods have involved instrumental techniques such as cryoscopy,[3] infrared spectrometry, gas chromatography[4] and mass spectrometry.[5]

Thornton and Condon were the first to use infrared spectrometry[6] for the determination of deuterium oxide in water. The simplicity of this method makes it attractive for the rapid determination of large numbers of samples, but problems arise when the samples contain components other than deuterium oxide and water. In particular, samples of biological fluids may contain compounds with an infrared absorption in the region being used for the measurements of deuterium oxide. In this case some form of purification must precede the determination. Wang has attempted to reduce the interference from the additional components in biological fluids by adding activated charcoal,[7] while Turner has used distillation[8] and Stansell[9] has employed sublimation to provide samples which are sufficiently pure for measurement. It must be pointed out that when small quantities of deuterium oxide are mixed with water, the predominant deuterated species existing in solution is HOD and it is the absorption of this species which is actually measured.

The present paper describes a simple method for the determination of HOD in urine or other biological fluids, in which a small volume of pure water–deuterium oxide mixture is removed from the sample by evaporation under reduced pressure and the amount of HOD determined by using the absorption in the infrared region at 2512 cm^{-1}.

EXPERIMENTAL

Materials and apparatus

Deuterium oxide, 99.95 atom%, was obtained from Prochem, BOC Limited. All measurements were made with a Perkin–Elmer Model 180 infrared spectrophotometer. The sample and reference solutions were placed in 0.5-mm path-length liquid cells fitted with calcium fluoride windows.

Procedure

Removal of a sample of the H_2O/HOD mixture from urine. Five ml of a sample of urine containing HOD were placed in a small test-tube fitted with a ground-glass joint, and the tube was connected to a conventional vacuum line. The sample was frozen by immersion in liquid air and the line evacuated. The sample was degassed by alternate melting, pumping and freezing. A second test-tube was connected to the line and cooled in liquid air. The urine sample was melted and the water/HOD mixture distilled into the cooled test-tube by gentle warming.

Measurement of transmittance. The reference and sample cells were filled with distilled water by means of a microsyringe, care being taken to avoid the formation of bubbles which would alter the transmittance. The cells were then placed in the sample and reference beams of the infrared spectrophotometer and the instrument was set to a frequency of 2512 cm^{-1}. The sensitivity was adjusted and the zero and 100% transmission limits set. The sample cell was emptied and refilled with a standard solution of HOD. The instrument was set to record the transmittance of the standard solution and allowed to run for 10 min in order to monitor stability. When a steady trace was obtained the transmittance was measured and the sample solution was removed and replaced by another, having a different concentration of HOD.

RESULTS

Reproducibility of the measurements for standard samples

The day to day reproducibility is summarized in Table 1. The relative standard deviation (coefficient of variation, C.V.), calculated for six measurements over a period of 75 days gives a reproducibility of better than 2%.

The best straight line for the logarithm of the reciprocal of the mean transmittance as a function of concentration was calculated by regression analysis and gave 2.861, −0.0523 and 0.9998 for the slope, intercept and correlation coefficient respectively. The closeness of the correlation coefficient to unity is an indication of a good straight-line relationship.

Reproducibility of the measurements for unknown samples

Two sets of samples were prepared for these studies. In the first set only a fraction of the total water/HOD mixture was distilled from the urine sample. In the second set the urine sample was distilled to dryness.

Partially distilled. A set of samples was prepared containing 0.05, 0.1, 0.15, 0.2 and 0.25 ml of D_2O in 100 ml of urine. Each of these samples was analysed over a period of three days. The data in Table 2 illustrate the reproducibility of the determination, while the recovery data are summarized in Table 3. Estimates of the concentration were made by interpolation of the mean values (shown in Table 2) in the straight-line equation for the standard (Table 1).

Table 1. Reproducibility of the measurement of transmittance (T)

Concentration of D_2O in water, % v/v	Range of transmittance, %	Mean transmittance, %	log $1/T$ (mean)	Standard deviation, %	C.V.,* %
0.05	80.5–82	81.5	$\bar{1}.089$	0.6	0.8
0.1	58–59.5	58.6	$\bar{1}.232$	0.6	1.0
0.15	41–42	41.3	$\bar{1}.384$	0.5	1.2
0.2	30–31	30.3	$\bar{1}.518$	0.5	1.7
0.25	21–22	21.8	$\bar{1}.661$	0.4	1.8

* C.V. = 100 × std. devn./mean.

Table 2. Reproducibility of the measurements of transmittance for urine samples

Concentration of D_2O in urine % v/v	Range of transmittance, %	Mean transmittance, %	log $1/T$ (mean)	Standard deviation, %	C.V %
0.05	83–83.5	83.2	$\bar{1}.080$	0.3	0.3
0.1	59.5–60.5	59.8	$\bar{1}.223$	0.6	1.0
0.15	43–44	43.3	$\bar{1}.363$	0.6	1.3
0.2	31.5–33	32.3	$\bar{1}.491$	0.8	2.4
0.25	23–24	23.3	$\bar{1}.632$	0.6	2.4

Table 3. Recovery of D_2O from urine (partial distillation)

Concentration of D_2O in urine % v/v		
Taken	Found	Recovery, %
0.05	0.046	92.0
0.10	0.096	96.0
0.15	0.145	96.6
0.20	0.190	95.0
0.25	0.239	95.6

Complete distillation. A set of samples of D_2O in urine containing 0.11, 0.15, 0.17 and 0.21 ml of D_2O in 100 ml of urine was prepared. Each sample was distilled to dryness and the distillate analysed over a period of three days. The data in Tables 4 and 5 summarize the reproducibility and recovery as before.

DISCUSSION

There are three problems associated with the determination of HOD in biological fluids by the infrared absorption method. The first is the production of a sample with the same HOD/H_2O ratio as in the biological fluid. The second is the removal of those substances which may have an absorption at the same frequency as that chosen for the measurement of HOD. The third is the measurement of the transmittance at this frequency with sufficient precision to determine the concentration of HOD. Wang[7] has suggested that the first two problems may be solved by the addition of an adsorbent, such as activated charcoal, to the biological fluid. The filtrate, or supernatant liquid, is said to be sufficiently pure to be examined directly in the infrared spectrophotometer. We have not found it possible to measure the concentration of HOD in urine after treatment with activated charcoal, because of a high, varying residual absorption at 2512 cm^{-1} in the filtrate.

Purification of the sample of biological fluid by vacuum distillation is associated with some uncertainty if only a fraction of the original volume is evaporated. This is due to the possibility that segregation of D_2O may occur because of the difference in the vapour pressures of H_2O and D_2O.[10] However, comparison of the results in Tables 3 and 5 suggest that this is overcome by complete evaporation of the sample.

The third problem is probably the most intractable; it consists of the measurement of a low concentration of HOD in the presence of a large concentration of a strong absorber, H_2O. It is necessary to select a frequency at which the ratio of the absorbances of HOD and H_2O is at a maximum, and this is not necessarily an absorption maximum for HOD. The frequency chosen was 2512 cm^{-1} and this required the use of cells with a relatively long path-length. In earlier studies, Turner[8] used a path-length of 0.1 mm, Wang[7] one of 0.4 mm, while Stansell[9] used different path-lengths for reference and sample cells of 0.1 and 0.2 mm, respectively. The cells chosen for this study had a path-length of 0.5 mm. A cell of this path-length filled with water has a low transmittance and this greatly reduces the amount of energy which can reach the detector. As a result the instrument must lose both resolution and precision, so a spectrometer of high sensitivity is required. The instrument chosen for this work was found to be satisfactory both as regards long-term drift and short-term reproducibility. Every determination was checked on 6 occasions over a period of 3 days.

Table 4. Reproducibility of the measurements of transmittance for urine samples (complete distillation)

Concentration of D_2O in urine, % v/v	Range of transmittance, %	Mean transmittance, %	log $1/T$ (mean)	Standard deviation, %	C.V., %
0.11	54.5–55.5	55.0	$\bar{1}.259$	0.5	0.9
0.15	40.5–41	40.7	$\bar{1}.390$	0.3	0.7
0.17	36–36.5	36.3	$\bar{1}.440$	0.3	0.8
0.21	27.5–28 5	28.0	$\bar{1}.553$	0.5	1.8

Table 5. Recovery of D_2O from urine (complete distillation)

Concentration of D_2O in urine, % v/v		
Taken	Found	Recovery, %
0.11	0.109	99.1
0.15	0.155	103.2
0.17	0.172	101.2
0.20	0.211	105.7

Conclusion

Determination of HOD in biological fluids by vacuum distillation and infrared spectrophotometry is simple and rapid: a single measurement may be made in 15 min. An error of 2% is obtained in the concentration range 0.05–0.1%. This is the range of concentration most suitable for the measurement of total body water and results from the application of this method to such measurements are presented elsewhere.

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REFERENCES

1. P. Baertschi and M. Tharkauf, *Helv. Chim. Acta*, 1959, **42**, 282.
2. M. Cohn, in *Preparation and Measurement of Isotopic Tracers*, D. W. Wilson, A. O. C. Nier, S. P. Reimann and J. W. Edwards, eds., p. 51. Ann Arbor, Michigan, 1948.
3. P. B. Reaser and G. E. Burch, *Science*, 1958, **128**, 415.
4. E. M. Arnett, M. Strem, N. Hepfinger, J. Lipowitz and D. McGuire, *ibid.*, 1960, **131**, 1680.
5. I. Friedman, *Geochim. Cosmochim. Acta*, 1953, **4**, 89.
6. V. Thornton and F. E. Condon, *Anal. Chem.*, 1950, **22**, 690.
7. J. Wang, J. R. Pierson and W. G. Kelly, *J. Lab. Clin. Med.*, 1973, **82**, 170.
8. M. D. Turner, W. A. Neely and J. D. Hardy, *J. Appl. Physiol.*, 1960, **15**, 309
9. M. J. Stansell and L. Mojica Jr., *Clin. Chem.*, 1968, **14**, 1112.
10. W. F. Siri, *Isotopic Tracers and Nuclear Radiations*, pp. 263–267. McGraw-Hill, New York, 1949.

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JOSEPH LOUIS GAY-LUSSAC (1778–1850) AND ANALYTICAL CHEMISTRY

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Summary—On the occasion of Joseph Louis Gay-Lussac's 200th anniversary, after a short comprehensive review of his scientific activities and his life, his achievements in the field of analytical chemistry are discussed. Gay-Lussac extensively studied the reaction of hydrogen sulphide with different metals and consequently may be considered the founder of classical qualitative analysis. He developed titrimetry into a scientific method. He designed the first burette that became widespread in use. The terms burette and pipette were created by him. The combustion apparatus designed by him together with Thénard was the starting point for organic elemental carbon–hydrogen analysis.

Science is built brick by brick. By assiduous, meticulous work, innumerable scientists each add a brick to the building. From time to time, however, a person appears who is capable of carrying out some larger part of the work, for instance, digging the whole foundations on which the future building work can then proceed. Gay-Lussac (Fig. 1) was such a person, participating in the foundation of not just one, but several branches of science.

In physics, Gay-Lussac's law states the relationship between the temperature and volume change of gases. The volume of a given mass of gas from 0°C to 100°C increases by 1/266.66 for each degree rise of temperature. The final consequence of this statement is the concept of the absolute zero of temperature (1802). In other experiments he demonstrated that the expansion of gases is connected with heat loss, their compression with heat evolution. This fact had already been noticed earlier, but it was Gay-Lussac who determined quantitative relationships between pressure rise and temperature change (1807). In 1804, he ascended to an altitude of 4000 m in a hydrogen-filled balloon to determine the change in magnetic intensity with height. He repeated this experiment at an altitude of 7000 m, where he took air samples to find out whether their composition was identical with that on the surface of the earth. (This height record was not broken for almost 50 years.)

In general chemistry, Gay-Lussac's law of combining volumes of gases, established in 1808, yielded experimental proof for Dalton's atomic theory. (Actually, the lack of clarity in the concepts of the atom and the molecule still confused matters considerably, and therefore Dalton gave no credit to Gay-Lussac's statements.) In inorganic chemistry, Gay-Lussac was the first to produce elemental boron (1808), and he developed a process to prepare alkali metals by using iron (1808). In an outstanding classic paper he reported studies on the properties and compounds of the recently discovered chemical element iodine (1813). He was the first to study the solubility of salts as a function of temperature (1819). In organic chemistry, he discovered and extensively investigated the cyanide group. He discovered uric acid and stated its identical chemical composition with tartaric acid.

Gay-Lussac was also interested in technology. He experimentally determined optimum chamber temperature in the manufacture of sulphuric acid by the lead chamber process (1807). He invented the Gay-Lussac tower for the recovery of the nitrogen oxides at the end of the process in a coke-packed absorber with counter-current sulphuric acid flow (1827). In fact, the suggestion was primarily meant to prevent air pollution; it was only later that Glover found that the nitrogen oxides absorbed could be set free and recycled.

Such were the most outstanding results of Gay-Lussac's supremely rich scientific activities. Here we only allude to them, since the subject of the present paper is his contribution to analytical chemistry, Gay-Lussac having been one of the greatest creative geniuses in this field too.

Joseph Louis Gay was born on 6 December 1778, in St. Léonard, a small town of the province of Limoges. His father was a judge. Since Gay was a very common family name in Limoges, his father, for distinction, arbitrarily began to use the name Gay-Lussac, after a nearby village where he possessed a small estate, and his son followed suit.

Gay-Lussac began his studies with the priest of the town, and continued them in a Paris boarding school. During the French Revolution his position worsened: his father was arrested and lost his fortune. The young man helped himself by giving private lessons. Then the newly founded Ecole Polytechnique gave access to free higher education for gifted young people. Gay-Lussac successfully passed the entrance examination and became a student of the school in 1797. At that time, Napoleon had not yet turned this institution into a military technical college (which it



Fig. 1.

has remained up to the present). Gay-Lussac completed his studies in 1800 and wished to continue them at the Ecole Nationale des Ponts et Chaussées, the Civil Engineering College. However, Berthollet, professor of the Ecole Polytechnique, turned his attention to the gifted young man and employed him as his private assistant. Berthollet, former physician of the Prince of Orléans, later a Jacobin, just then a good personal friend of the consul Bonaparte, his scientific adviser during his Italian and Egyptian military campaigns, later a senator of Emperor Napoleon, appointed as imperial count, and even later a peer of King Louis XVIII, was a very influential person and remained so, whatever changes took place on the political scene of France (which, in fact, were very frequent and radical at that period). Berthollet's sponsorship was very valuable to Gay-Lussac, who also learned a great deal from him, since it cannot be denied that Berthollet was an excellent chemist, one of the leading scientists of his age. In 1802, Gay-Lussac became assistant in the Ecole Polytechnique, and in this position he often took the place of the very busy Berthollet in giving lectures. In 1804, he was appointed assistant lecturer. In 1805 he became acquainted with Alexander von Humboldt, the versatile German scientist and traveller who stayed in Paris and had at that time a huge (in our view, inordinately so) scientific prestige and influence. Gay-Lussac carried out in his company, the first experiments leading to the law of combining volumes of gases. Then he accompanied him on a long Italian journey down to Naples. During this journey they made magnetic and geological observations. Their tour ended in Berlin. Gay-Lussac had a talent for languages, speaking German and Italian and even some English. This was a rare phenomenon among French scientists of that time. On his return to Paris the academic chair, that is, the membership of the Institut, the successor of the Académie (dissolved during the Revolution) awaited him. In 1808 he became professor of physics at the University of Paris, and two years later—in addition—professor of chemistry at the Ecole Polytechnique (as successor to Fourcroy). He held both chairs for decades, and in addition, some time later, the post of Director of the Mint. He gave up his professorship in physics at the University of Paris in 1832, but only because he was elected professor of chemistry at the Musée d'Histoire Naturelle. Such cumulations of scientific positions were fairly usual in France (and are so, in fact, even in the present). Thus, young Gay-Lussac had good support, but also unusual talent which was duly recognized by his patrons.

He married in 1808. His friend, the pysicist Arago, wrote that he made the acquaintance of a 17-year-old salesgirl in a shop who was reading a textbook on

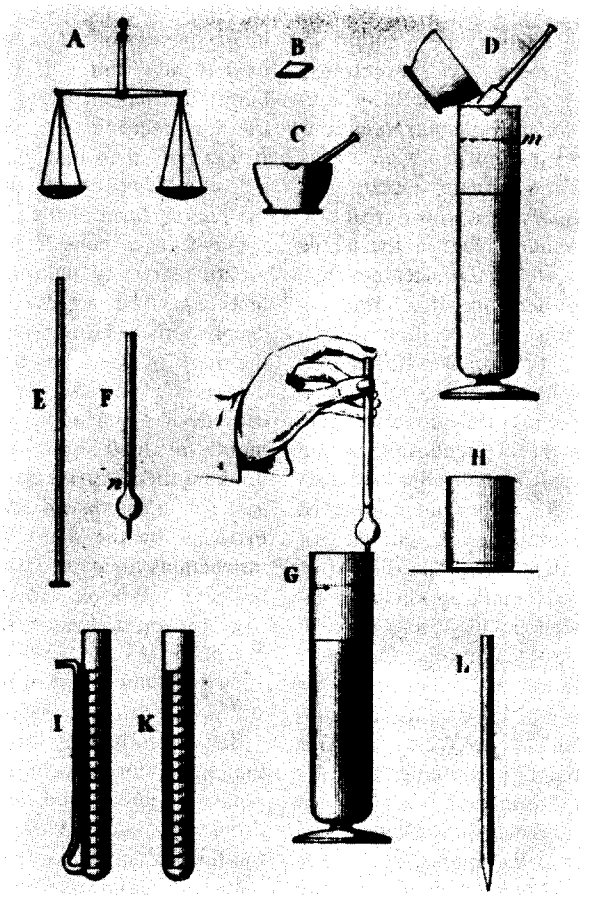


Fig. 2.

chemistry. This fascinated him. He began to teach her and then married her. They lived together for 40 years.

It was also Arago who wrote that Berthollet, at his death, left his peer's buckle to Gay-Lussac, expressing thereby that he considered him his successor in that office. However, it took a long time for Gay-Lussac to be appointed a peer, because he worked manually day by day in the laboratory of the mint, and such work was considered too undignified for a peer of France. Arago's story, however, seems somewhat improbable. According to other sources, Gay-Lussac did not want to be a peer under the rule of the reactionary King Charles X, and accepted this dignity only after the overthrow of Charles's reign, from the hands of the "Bourgois-King" Louis-Philippe, in 1839. Previously, in 1831, 1834 and 1837 he was elected Member of Parliament, but never played any significant role in politics. Actually his only real interest was in science and research, and he was indefatigable in this area. During the last years of his life a painful illness prevented him from practising his passion for research. He died in Paris on 9 May 1850. On his death-bed, he reputedly said "What a pity that I have to leave now when it begins to be so interesting" (namely science).[1,2]

Let us now turn to analytical chemistry which—in many of its branches—owes so much to Gay-Lussac.

In qualitative analysis, the investigation of the reactions of hydrogen sulphide is linked with his name. Boyle had already used hydrogen sulphide to detect arsenic,[3] and other chemists (Bergman, Winterl, Fourcroy and Hahnemann) sporadically also mentioned its use. However, all these experiments were carried out in strong acid media where hydrogen sulphide reacts with relatively few metals. Gay-Lussac investigated its reaction in various media, in strong and weak acids and in ammoniacal solution. He stated the different behaviour of each metal group.[4] These studies were the starting point for hydrogen sulphide becoming the basic class reagent in classical qualitative analysis, as developed by the systematizing work of Rose and Fresenius.

Titrimetry is the most important and most frequently used method of chemical analysis. It was started on its path by Gay-Lussac. Methods that might be considered titrimetric had existed, in fact, from the middle of the 18th century (*e.g.*, the procedures of Geoffroy, Home, Lewis, Descroizilles, Laurens, Welter) to check the "grade" of acids and especially of hypochlorite. All these methods, however, served industrial purposes, and—with some exceptions—did not determine absolute amounts.

"Titration" only indicated whether the solution in question was appropriate, neither too concentrated nor too dilute for practical use, for textile bleaching.

Titration was not in use for scientific purposes, and it was Gay-Lussac who turned it into an exact scientific method. The expressions burette, pipette and titrate, used in all languages, were also his creations.

The most significant auxiliary agent in the textile industry at the beginning of the 19th century was hypochlorite, invented by Berthollet for bleaching cotton. However, its use was not free from risk. If it was too concentrated, it did not bleach, but destroyed the fabric. Descroizilles published a method in 1795 for controlling the appropriate concentration.

He took a sample from the hypochlorite solution with a pipette-like device and added indigo solution to it from a graduated cylinder. If the colour appeared at a defined mark, the solution was suitable for bleaching, if not, the solution had to be diluted or concentrated, according to the mark at which the indigo colour appeared. Welter, in 1817, attempted to render the method exact by determining the active strength of the indigo solution with chlorine. In his first work on titrimetry, in 1824, Gay-Lussac examined Welter's method.[5] Similarly to Welter, he tried to determine the active strength of an indigo solution by using chlorinated water. His method was not much superior to Welter's, but it is worth while to cite a part of his paper and present the figure.

"*F* is a small measure or pipette (petite measure ou pipette) with a volume of 2.5 cm^3...; this is used for the measurement of the chlorinated lime solution. To fill it, it must be immersed in the solution of chlorinated lime, and the solution allowed to rise above the mark *n*, which indicates the volume. When it is filled, the first finger, which should neither be too wet nor too dry, is placed over the pipette which is then placed on the lower part of the cylinder, as shown in *G* in the figure, and by gently lessening the pressure on the finger the solution is caused to flow into the cyclinder. When the lowest part of the concave arc of the solution surface reaches the mark, then the pressure is reapplied with the finger, whereupon the flow of solution ceases. Then the contents of the pipette are run into the beaker *H*.... *I* is a burette, which is used for the measurement of the test pigment (burette destinée à mesurer la teinture d'épreuve), the large marks or degrees correspond to the volume of the small pipette *F*, and these large divisions are further subdivided into five parts."

As may be noticed, the words pipette and burette, in their analytical sense, were created here. (Originally, the word burette means a small jug with spout, and the word pipette a small pipe, in the French language.) The burette shown in Fig. 2 (*J*, *K*) has become known as the Gay-Lussac burette. One hand was used to swirl the solution to be titrated, and the other to hold the burette in a somewhat inclined position. Then the titrating solution left the side capillary drop by drop. I have such a burette in my possession; it is actually true that it can be used to add titrant drop by drop. The Gay-Lussac burette started titrimetry on its triumphal career: its use was practically exclusive for about half a century. It was only then that glass technology became capable of making suitable glass taps, thereby developing the present form of the device.

Gay-Lussac considered sucking the pipette by mouth extremely unhealthy and dangerous. In his first papers he suggested immersing the pipette so deeply in the solution that the latter would rise above the mark by itself. Far too much solution was, however, needed in this case. Later he constructed intricate devices, including taps, to avoid sucking by mouth for the filling of pipettes. Figure 3 is from his book entitled *Instruction sur l'essai des matières d'argent par la voie humide* (Instruction for testing silver materials by the wet way) (1832). I shall omit the instructions for its use, since they take three printed pages in the book. However, chemists also seemed to find it too tricky, for there is no sign that anybody except the inventor ever used it. Also, chemists were apparently not afraid of sucking by mouth, as we all still do up to the present.

Subsequently Gay-Lussac found a better titrant than indigo for hypochlorite: arsenious acid [and also potassium ferrocyanide and mercury(I) nitrate], a few drops of indigo serving only as indicator. This was the first reduction–oxidation indicator.[6]

In 1828 Gay-Lussac published a paper on the testing of commercial potashes.[7] On this subject he had

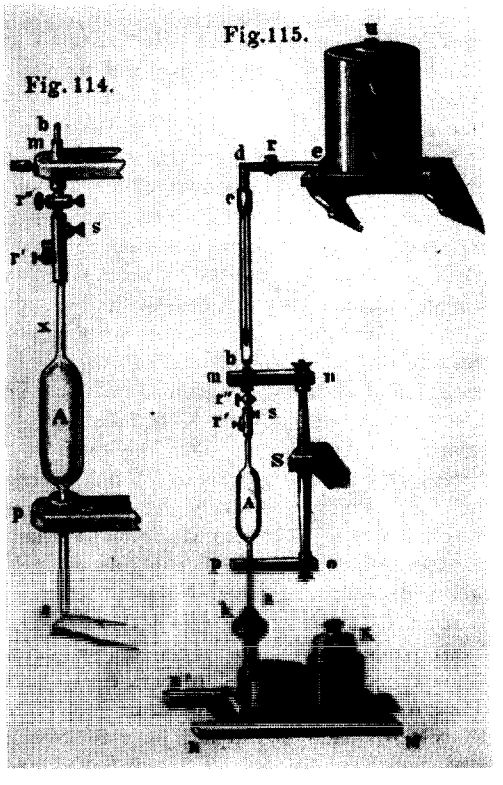


Fig. 3.

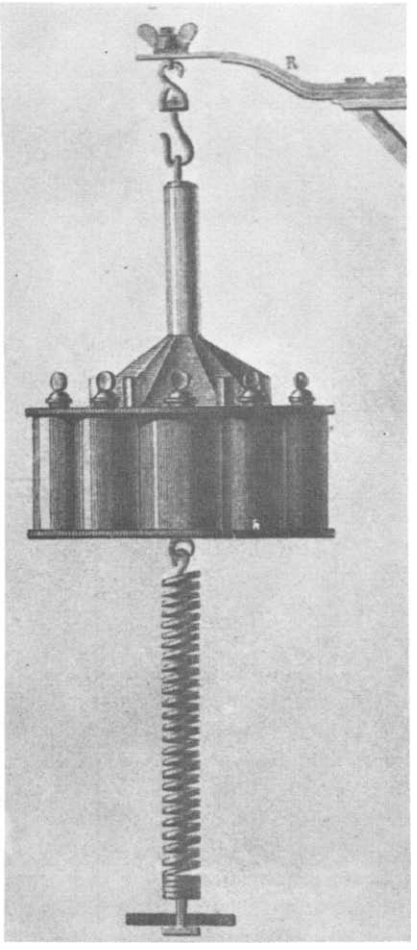


Fig. 4.

many predecessors, from Home's paper in 1756 to Descroizilles's method in 1806. Gay-Lussac based his method on the latter, which, however, was not an absolute method. Gay-Lussac used a standard sulphuric acid solution: he diluted 100 g of concentrated sulphuric acid to 1 litre in a volumetric flask. Thus the 1-litre volumetric flask was also Gay-Lussac's innovation. He was, however, no pioneer in the use of the metric system (litre and gram). Descroizilles having used it 20 years earlier. The expression normal acid (acide normale) appears for the first time in this paper; this was the term he used for the sulphuric acid solution. This expression was not, of course, identical in meaning with the term "normal solution" used since its inception by Ure and Mohr. Gay-Lussac did not arrive at the general concept of measuring solutions. He specified measuring solutions with concentrations which—when an exactly specified sample weight was used—yielded the percentage of the substance to be determined by the amount used to reach the end-point, that is, in the present case, the per cent of alkali metal carbonate when the sample weight of potash was exactly 4.807 g, or, in the case of silver determination, the silver percentage when the sample weighed exactly 1.000 g.

The latter was, in fact, the most celebrated titrimetric procedure developed by Gay-Lussac. It appeared in book form in 1832, and was translated a year later into German by Justus Leibig.[8] In this famous method the end-point was indicated by cessation of the production of turbidity. The concentration of the sodium chloride measuring solution was such that 100 ml precipitated somewhat less than 1 g of silver. These 100 ml were added in one batch to the solution to be titrated. Then, after agitation and sedimentation, titration was continued drop by drop with a solution ten times more dilute, until no further precipitation was observed. The method was extremely accurate, but very time-consuming and required much patience. For agitation Gay-Lussac designed a very ingenious shaking machine, the mode of action of which can be seen from Fig. 4.

Such were Gay-Lussac's most significant contributions to titrimetry, which subsequently was taken up by the chemistry departments of the universities (these being, at that time, the practically exclusive centres of chemical research), developed rapidly and soon became the most important instrument of analysis.

However, we have not yet ended the review of Gay-Lussac's contributions to chemical analysis. There is yet another important field in which his activity was of fundamental importance, namely organic elemental analysis.

The basic criterion for the development of organic chemistry was the determination of the composition of organic compounds. As long as it was not known what a compound consisted of, there was little hope of elucidating its structure, and even less of synthesizing it. The classification of compounds into those of mineral and of vegetable or animal origin is rather old: it can be found as early as the 17th century, in Lemery's work. The basic differences between these classes with respect to combustibility and melting were obviously noticed very soon. For further progress, the development of gas chemistry in the 18th century was necessary, especially the discovery of carbon dioxide and of the fact that this gas was an oxidation product of carbon and the combustion product of organic matter. The discovery of carbon dioxide was Black's contribution, while Lavoisier deserves credit for the other two discoveries. According to Lavoisier, organic compounds were built of carbon, hydrogen and oxygen. Berthollet found that some organic compounds also contain nitrogen. The discovery that other elements—though less commonly—also occur in organic compounds was left to the researchers of the 19th century.

The first attempts to determine the carbon and hydrogen content of organic substances date back to Lavoisier. To determine the composition of oil, he burnt it in a lamp and led the combustion products through a tube filled with calcium chloride into two bulbs filled with alkali. From the decrease in volume of the gas he deduced the amount of carbon dioxide, and from the difference between oxygen lost and car-

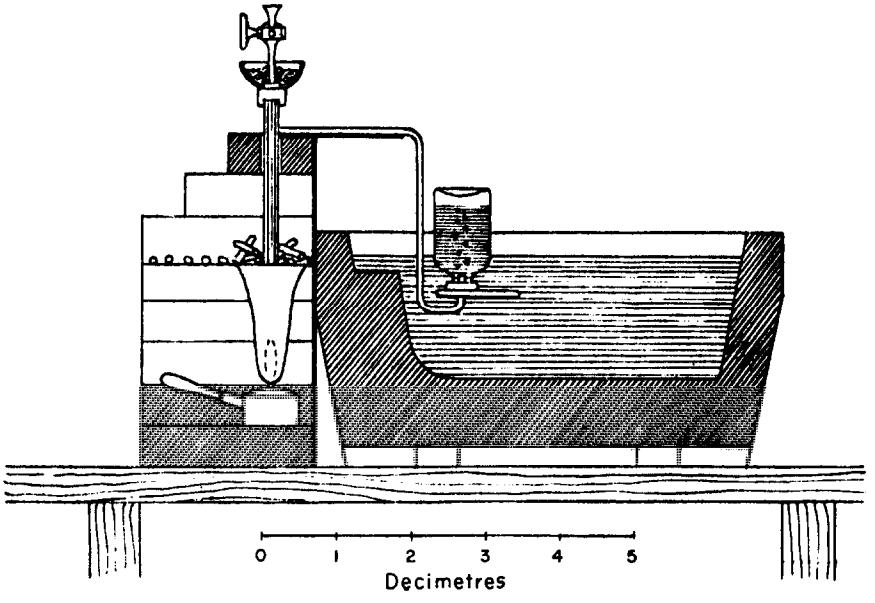


Fig. 5.

bon dioxide produced he attempted to calculate the amount of water formed by the combustion of hydrogen. This technique was rather cumbersome and inaccurate, so Lavoisier himself gave it up and experimented with a simpler method: he burnt the organic substance in a small vessel that floated on mercury under a bulb containing a known volume of oxygen. With this primitive method he carried out only a few experiments, since the results obtained were only very rough approximations. Subsequently Saussure, Berthollet and others studied the combustion analysis of organic substances. Saussure made an important step forward: instead of using a lamp for combustion, he led alcohol through a red-hot porcelain tube.[9]

The first truly practicable method for the determination of carbon and hydrogen in organic compounds was developed by Gay-Lussac and Thénard. Louis-Jacques Thénard (1777–1857) was Gay-Lussac's fellow professor at the Ecole Polytechnique, and professor in chemistry at the Collège de France; they often worked together. Their method was published in 1810 in their book entitled *Recherches physico-chimiques* (Physico-chemical research).[10] Their rather intricate apparatus is shown in Fig. 5.

Combustion was carried out in a vertical glass tube, 20 cm long and 8 mm in diameter, which was heated with a spirit lamp. To the upper end of the tube a tap was attached, which instead of the channel had a small hole drilled in it. The sample, mixed with potassium chlorate, was placed in this hole, and rotation of the tap caused the sample to fall into the heated part of the tube. To remove air from the apparatus a blank combustion was carried out beforehand. The combustion products were led, via a side-tube, through mercury to a sealed vessel. Carbon dioxide was absorbed by potassium hydroxide in the mercury vessel, and the amount determined from the decrease in volume of the gas. After the absorption of carbon dioxide the excess of oxygen was exploded with hydrogen, and the oxygen loss was determined. The original amount of oxygen was known, as in a previous experiment the amount of oxygen formed from potassium chlorate was determined. The decrease in the amount of oxygen was considered to be due to the combustion of the hydrogen content of the substance, and thus the hydrogen content could be determined in this indirect manner.

Their essential contribution was to combust the organic matter not by itself, but mixed with an oxidizing agent in a combustion tube. Explosive potassium chlorate was certainly not the most suitable agent; Gay-Lussac himself soon found a better compound: copper oxide.[11] He proposed this instead of potassium chlorate in 1814, and this agent is in use up to the present, although the combustion apparatus has changed a good deal since. Berzelius (1817) used a horizontal combustion tube and determined the hydrogen content by measurement of the water instead of calculation. The method was further improved by Liebig in 1837 by several modifications, including absorption of carbon dioxide, that is, gravimetric instead of volumetric measurement. The microequipment designed by Pregl in 1912 and still in use is essentially a miniaturized version of the Liebig apparatus.

It should be noted that Gay-Lussac and Thénard also attempted to determine nitrogen in their apparatus. After exploding the excess of oxygen, they assumed the residual gas to be nitrogen. This, however, was incorrect. Nitrogen determination was finally solved by Dumas, in 1831, separately from carbon and hydrogen determination.

In the course of his indefatigable scientific activity Gay-Lussac wrote several books and about 120

papers. He carried out most of the experiments himself. At that time a professor did not have as much assistance at his disposal as nowadays, and was compelled to do much manual experimental work himself. Gay-Lussac's scientific performance is admirable and of permanent value even in the light of 150–180 years. Analytical chemistry deservedly includes him among its greatest representatives.

REFERENCES

1. F. Arago, *Notices biographiques*, in *Oeuvres de F. Arago* III, Paris, 1865.
2. M. P. Crosland, *Dictionary of Scientific Biographies*, pp. 317–327. New York, Vol. V, 1972.
3. F. Szabadváry, *Talanta*, 1958, **2**, 156.
4. J. L. Gay-Lussac, *Ann. Chim.*, 1811, **78**, 86; **80**, 205.
5. *Idem*, *Ann. Chim. Phys.* 1824, **26**, 162.
6. *Idem*, *ibid.*, 1835, **60**, 225.
7. *Idem*, *ibid.*, 1828, **39**, 337.
8. *Idem*, *Instruction sur l'essai des matières d'argent par la voie humide*, Paris, 1832; *Vollständiger Unterricht über das Verfahren Silber auf nassem Weg zu probieren*, Braunschweig, 1833.
9. Th. Saussure, *Ann. Chim.* 1807, **62**, 225; cited by R. Löw, *Pflanzenchemie zwischen Lavoisier und Liebig*, p. 262. München, 1977.
10. J. L. Gay-Lussac and L. J. Thénard, *Recherches physico-chimiques*, Tome 2, p. 265. Paris, 1810.
11. J. L. Gay-Lussac, *Ann. Chim. Phys.* 1814, **95**, 184; 1815, **97**, 53.

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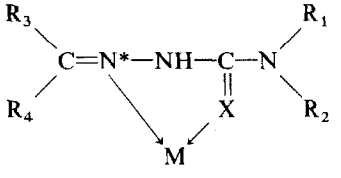
ANALYTICAL APPLICATIONS OF THIOSEMICARBAZONES AND SEMICARBAZONES: A REVIEW

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Summary—The analytical applications of thiosemicarbazones and semicarbazones are reviewed.

Thiosemicarbazones (TSC) and semicarbazones (SC) are a class of compounds obtained by condensing thiosemicarbazide or semicarbazide with suitable aldehydes or ketones. The active grouping for chelation is shown below in structure (I):



(I)

when X = O, semicarbazone
X = S, thiosemicarbazone

Thiosemicarbazones and semicarbazones act as chelating agents for metal ions by bonding through the sulphur or oxygen atom and the hydrazino nitrogen atom marked with an asterisk in (I). In a few cases they behave as unidentate ligands by bonding only through the sulphur or oxygen atom.

Domagk *et al.*[1] reported for the first time the anti-tubercular activities of metal thiosemicarbazones and semicarbazones. Since then a number of papers have appeared on the pharmacology of these compounds. The metal–TSC complexes were found to be active against influenza,[2] protozoa,[3] smallpox[4] and certain kinds of tumours[5] and to be very good pesticides[6] and fungicides.[7] The activity of TSC is thought to be due to their power of chelation with traces of metal ions present in biological systems. The anti-tubercular activity of *p*-acetamidobenzaldehyde thiosemicarbazone is found to be enhanced by the presence of small amounts of copper ions.[8]

Depending upon the type of aldehyde or ketone used for condensation, TSC and SC can act as unidentate, bidentate or multidentate chelating agents for metal ions, producing highly coloured complexes. These coloured complexes are then used in selective and sensitive determination of metal ions. The aim of this review is to summarize these analytical applications.

Preparation of the reagents

Semicarbazones are obtained by condensing semicarbazide hydrochloride with suitable aldehydes or ketones in presence of sodium acetate. Sometimes hydrochloric acid must be present in the preparation of semicarbazones.[9]

Thiosemicarbazones are prepared by condensing thiosemicarbazide with an aldehyde or ketone in the presence of a few drops of glacial acetic acid. Preparation of the mono-derivatives is simple but the di-derivatives are a little difficult and require special treatment. Dipyridylglyoxal dithiosemicarbazone[10] was prepared by cyclizing the mono-derivative with 6*M* hydrochloric acid, for example.

Chemical properties

Just as hydrazones are weaker bases than hydrazines, semicarbazones and thiosemicarbazones are weaker bases than semicarbazides and thiosemicarbazides respectively. Hydrolysis of these compounds yields first the hydrazones, hence these compounds resemble hydrazones in many of their reactions.

Mild reductions of semicarbazones and thiosemicarbazones yield 1-substituted semicarbazide and thiosemicarbazide, respectively. Catalytic reduction of these compounds yields hydrazides are further hydrolysed to hydrazines. Reaction with alkoxides such as sodium ethoxide converts semicarbazones into hydrazones, and with a strong base, hydrocarbons are obtained. This reaction may be applied for replacement of the carbonyl group by a CH_2-group.

The reagents can be readily hydrolysed to give the original carbonyl compound and hence are often useful for identification and isolation of carbonyl compounds. A method of obtaining the equivalent weight of the parent carbonyl compound is to hydrolyse the semicarbazone with aqueous hydrochloric acid and titrate with standard iodate solution.[11]

ANALYTICAL APPLICATIONS

The various thiosemicarbazones and semicarbazones which have been used as analytical reagents are summarized in Table 1.

Applications in spectrophotometry

Semicarbazones and thiosemicarbazones form coloured metal complexes in conditions ranging from moderately acidic to moderately alkaline. Only a few are used to determine metal ions in highly acidic medium. 3-Hydroxypicolinaldehyde thiosemicarbazone is used to determine Co(II) in highly acidic medium.[27] Similarly glyoxal dithiosemicarbazone reacts with Ag(I) and Hg(II) at pH 1.1.[28] Salicylaldehyde thiosemicarbazone has been used to determine Mo(VI) in presence of iron in highly acidic medium.[52]

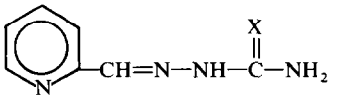
Extraction of the complexes not only increases the sensitivity but is also helpful in simultaneous determination of metal ions. Dipyridylglyoxal dithiosemicarbazone[19] reacts with Ni(II) and Co(II) at pH 5.2, but only the Ni(II) complex is extractable into chloroform, and hence allows the determination of both metals when present together. Biacetyl monoxime thiosemicarbazone has been used to determine Bi(III) in presence of Cu(II), by extraction of the complex into isobutyl methyl ketone.[38] Presence of EDTA[15,18,28] is sometimes necessary for completion. Cyclohexane-1,2-dione dithiosemicarbazone has been used to determine Cu(II) in alkaline medium, alkaline tartrate medium and

Table 1.

Abbreviation	Structure	Systematic name	References
PAT	II	Picolinaldehyde thiosemicarbazone	12–16
PAS	II	Picolinaldehyde semicarbazone	17
DPGT	III	Dipyridyl glyoxal dithiosemicarbazone	10, 18, 19
DPKT	IV	Di-2-pyridyl ketone thiosemicarbazone	20
MPKT	V	Methyl-2-pyridyl ketone thiosemicarbazone	21
PAPT	VI	Picolinaldehyde-4-phenyl-3-thiosemicarbazone	22, 23
APPT	VII	2-Acetylpyridine-4-phenyl-3-thiosemicarbazone	24
MPAT	VIII	6-Methylpicolinaldehyde thiosemicarbazone	25, 26
HPAT	IX	3-Hydroxypicolinaldehyde thiosemicarbazone	27
GDT	X	Glyoxal dithiosemicarbazone	28
APT	XI	Acetophenone thiosemicarbazone	29
HMAPS	XII	2-Hydroxy-5-methylacetophenone semicarbazone	30, 31
HMAPT	XII	2-Hydroxy-5-methylacetophenone thiosemicarbazone	30, 32, 33
DAPT	XIII	2,4-Dihydroxyacetophenone thiosemicarbazone	34
BAMOS	XIV	Biacetyl monoxime semicarbazone	17
BAMOT	XIV	Biacetyl monoxime thiosemicarbazone	35–39
BAMOPT	XV	Biacetyl monoxime 4-phenyl-3-thiosemicarbazone	40
BAMT	XVI	Biacetyl monothiosemicarbazone	41
DBAS	XVII	2,4-Dihydroxybenzaldehyde semicarbazone	42
DBAT	XVII	2,4-Dihydroxybenzaldehyde thiosemicarbazone	43–45
NBAT	XVIII	4-Nitrobenzaldehyde thiosemicarbazone	46
AMBAT	XVIII	4-Acetamidobenzaldehyde thiosemicarbazone	46
DABAT	XVIII	4-Dimethylaminobenzaldehyde thiosemicarbazone	47
ESBAT	XVIII	*p*-Ethylsulphonylbenzaldehyde thiosemicarbazone	48–50
SAS	XIX	Salicylaldehyde semicarbazone	51
SAT	XIX	Salicylaldehyde thiosemicarbazone	52–54
HNAT	XX	2-Hydroxy-1-naphthaldehyde thiosemicarbazone	55, 56
TAS	XXI	*o*-Thymolaldosemicarbazone	57
TAT	XXII	Thiophene-2-aldehyde thiosemicarbazone	58
PADT	XXIII	*o*-Phthalaldehyde dithiosemicarbazone	59
PIDT	XXIV	Phthalimide dithiosemicarbazone	60–62
FAT	XXV	2-Furaldehyde thiosemicarbazone	63
NFAS	XXVI	5-Nitro-2-furaldehyde semicarbazone	64, 65
PTFA	XXVII	4-Phenyl-3-thiosemicarbazone of 2-furaldehyde	66
NQT-4S	XXVIII	1,2-Naphthoquinone-2-thiosemicarbazone-4-sulphonic acid	9, 67–70
NQS-4S	XXVIII	1,2-Naphthoquinone-2-semicarbazone-4-sulphonic acid	67, 68, 69, 71
PQMT	XXIX	Phenanthrequinone monothiosemicarbazone	72
SAPT	XXX	Salicylaldehyde-4-phenyl-3-thiosemicarbazone	73
1,2 CDDT	XXXI	1,2-Cyclohexanedione dithiosemicarbazone	74, 75
1,3 CDDT	XXXII	1,3-Cyclohexanedione dithiosemicarbazone	76
FAcT	XXXIII	Furylacrolein thiosemicarbazone when R = 2-furyl and R′ = H, R = Ph, 2-furyl, 5-methyl-2-furyl, 5-nitro-2-furyl and R′ = H, Et	77, 78
TBPK	XXXIV	2-Benzothiazolylphenyl ketone thiosemicarbazone	79
IT	XXXV	*β*-Ionone thiosemicarbazone	80
BTDD	XXXVI	Bisthiosemicarbazone of diethyl-3,4-dioxadioate	81
LS	XXXVII	Lawsone semicarbazone	82
FPDT	XXXVIII	Furylpentadienal thiosemicarbazone	83

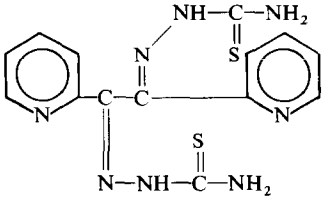
Structures in Table 1

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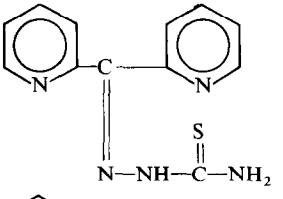


when X = S, PAT
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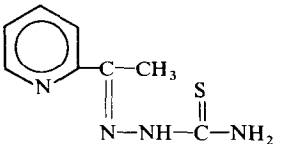
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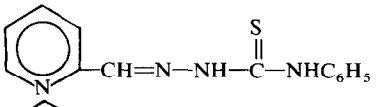
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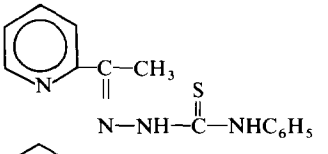
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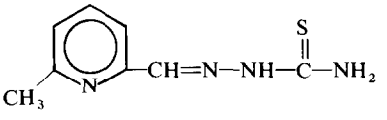
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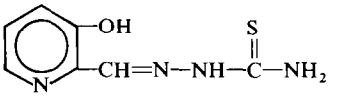
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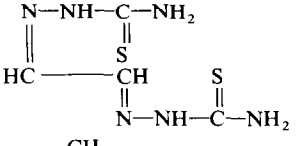
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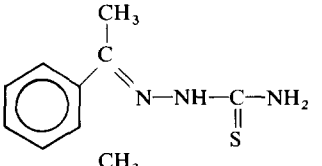
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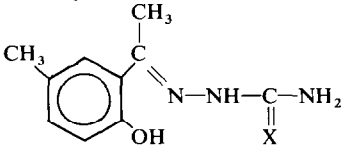
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XI

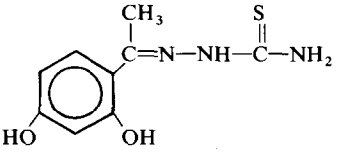


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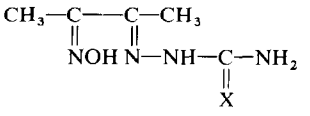
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X = S, HMAPT

XIII



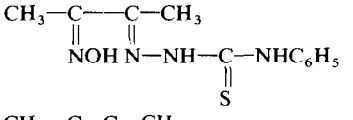
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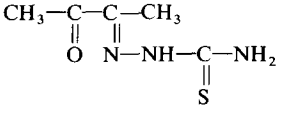


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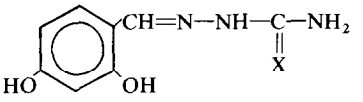
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XVI

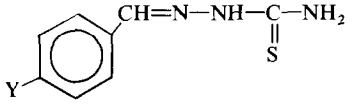


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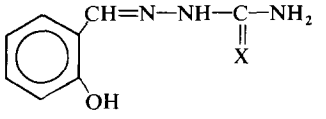
when X = O, DBAS
X = S, DBAT

XVIII



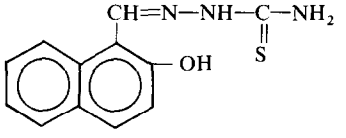
when Y = NO_2, NBAT
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Y = $N(Me)_2$, DABAT
Y = SO_2Et, ESBAT

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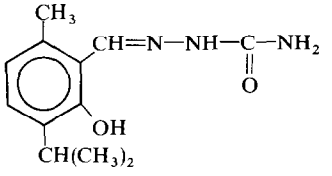


when X = O, SAS
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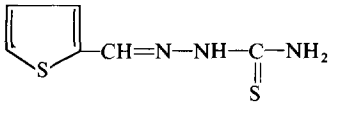
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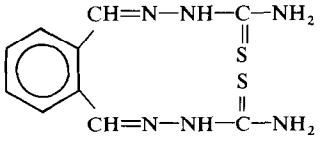
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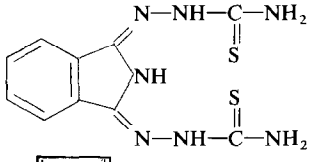
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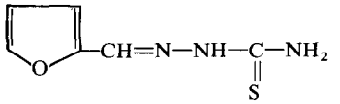
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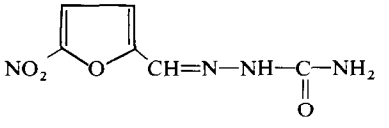
XXIV



XXV

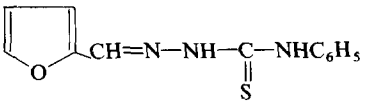


XXVI

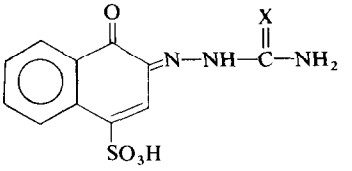


Structures in Table 1 (*contd.*)

XXVII

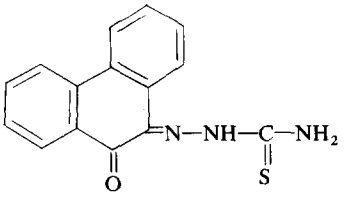


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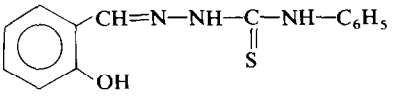


when X = S, NQT-4S
X = O, NQS-4S

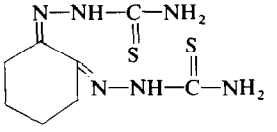
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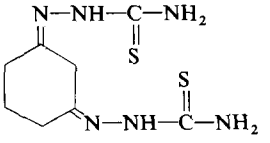
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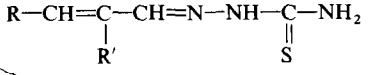
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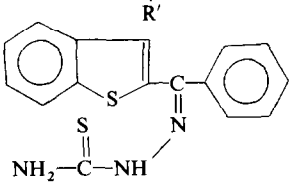
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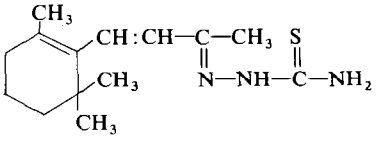
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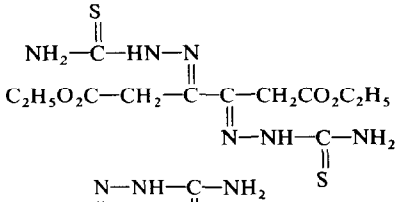
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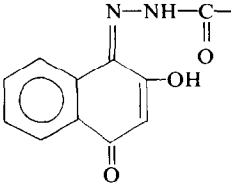
XXXV



XXXVI



XXXVII



XXXVIII

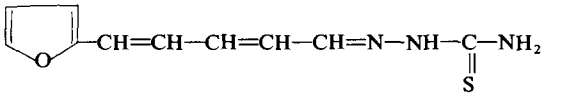


Table 2. Spectrophotometric data

Compound	Ion	λ_{max}, *nm*	ε, $10^4\ l.mole^{-1}.cm^{-1}$	pH*	Limit of determination, *ppm**	Extraction	M : L	Remarks	Refs.
PAT	Co(II)	356	1.40	5.6–9.5			1 : 2		12
		410	0.74						
	Ni(II)	385	1.90	7.2–10.7			1 : 2		13
	Fe(II)	610	0.58	9.4–12.3			1 : 3		14
	Fe(III)	360	1.40	3.9–7.9			1 : 2		14
	Cu(II)	360	2.20	8.9–10.7			1 : 1		13
	Ag(I)	316					1 : 1	In presence of EDTA	15
	Ni, Cu, Fe, Co in mixtures							Binary, ternary and quarternary mixtures analysed	16
PAS	Cu(II)	350		9.5	0.3–1.5				17
	Ni(II)	350		10.0	0.2–1.2				17
	Co(II)	345		10.0	0.5–2.2				17
DPGT	Fe(III)	400					1 : 1	In presence of EDTA	18
	Fe(II)	550	0.56	2.5	2–9		1 : 2		18
		590–610	0.71	5–10.0	2–7.5		1 : 1		18
	Fe(II)	630	0.66	10.0	2–8	$CHCl_3$	1 : 1		18
	Ni(II)	410	1.17	5.2	1–5	$CHCl_3$	1 : 1	Simult. detn. of both Ni and	19
	Co(II)	410	0.91	5.2	1–7		1 : 2	Co by extn. of one complex at pH 5.2. Also used for anal. of mixt. of Co and Ni and industrial catalysts	19
DPKT	Fe(II)	620	0.93	2.5–7.5	1–4		1 : 2	Ascorbic acid present	20
	Ni(II)	395	1.96	6.0–6.9 7.5–9.5	0.5–2.5		1 : 2	6.0–6.9 pH range is more sensitive	20
	Co(II)	415	1.00	3.8–6.0	1–5		1 : 2		20
	Cu(II)	395	1.13	3.9–4.2 5.5–9.0	1–5		1 : 1		20
MPAT	Os(IV)	420	0.94	1.5			1 : 2		25
		460	1.30	1.5			1 : 2		25
	Os(VI)	480				$C_6H_5 \cdot CH_2OH$	1 : 2		25
	Pd(II)	420		2.0	150–800 μg			Heating is necessary	26
	Rh(III)	430		2.0	50–500 μg				26

Table 2. (*contd.*)

Compound	Ion	λ_{max}, *nm*	ε, $10^4\ l.mole^{-1}.cm^{-1}$	pH*	Limit of determination, *ppm**	Extraction	M : L	Remarks	Refs.
HPAT	Co(II)	450	2.35	7.0–9.0	0.3–3.5		1 : 2	pK_1, pK_2, pK_3 reported as	27
			0.78	1.0–3.0	1.0–6.0		1 : 2	3.48, 6.76 and 10.75 respectively	
MPKT	Re(V)	430	0.46	2.4–6*M* HCl	36–38.8μ*M*		1 : 1	Redn. of Re(VII) to Re(V) with $SnCl_2$ in 2.4–6*M* HCl	21
PAPT	Co(II)	390	2.99	1.0	0.2–2	$CHCl_3$	1 : 2	Detn. of Ni and Co in mixture	22
	Ni(II)	390		8–9	0.8–1.5		1 : 2		23
		400		8–9	0.8–2.0	$CHCl_3$	1 : 2		
GDT	Ag(I)	335	4.30	1.0–7.0			1 : 1	In presence of EDTA	28
	Hg(II)	335	4.40	1.01–7.0			1 : 1	In presence of EDTA	28
APPT	Fe(II)	650	0.68	4.9–11.0	2–9	C_6H_6	1 : 2		24
	Fe(II)	610		5.6–9.8			1 : 2	Homogeneous medium	24
	Fe(III)	395	2.40	5.0–6.0	0.2–2		1 : 2		24
APT	Cu(II)	418	0.83	Alk. med.	up to 5μ*M*	CH_2Cl_2	1 : 2		29
		490	0.37	Alk. med.					
	Cu(I)	590	0.37				1 : 1		29
DAPT	Co(II)	390	1.40	7.9	0.024–2.4 mg		1 : 1	pK_1, pK_2 and pK_3 were 9.6, 11.2 and 12.4	34
	Cu(II)	400	2.00	3.6	0.025–2.5 mg		1 : 2		34
HMAPT	Fe(II)	645		2.2	0.5–8.0 μg		1 : 1	Stability const. $\log\beta = 4.0 \pm 1$	32
HMAPS	Fe(III)	600					1 : 1	In presence of Na_2EDTA/ $(NH_4)_2C_2O_4$, $\log\beta = 5.3 \pm 0.1$	31
BAMOT	Co(II)	325	0.49	5.0					35
	Ni(II)	356	0.88	9.5					36
	Fe(II)	335	1.45	5.3	1–4.5		1 : 2		37
		410	1.45	5.3	1–8.0		1 : 2		37
	Cu(II)	345	1.06	8.5–9.5			1 : 1		38
	Bi(III)	335		2.5–3.5	8–22	IBMK	1 : 2		38
	Mn(III)	545	0.27	9.2–10.3					39
BAMOPT	Co(II)	345	1.77	3.8–8.0			1 : 2		40
	Ni(II)	375	1.71	5.2–10.0			Variable		40
	Fe(II)	350	1.76	4.0–9.3			1 : 2		40
	Cu(II)	360	1.27	8.5–9.7			1 : 1		40
	Mn(III)	550	0.36	10.0	2–12	Amyl alc.	1 : 2		40

Table 2. (*contd.*)

Compound	Ion	λ_{max}, *nm*	ε, $10^4\ l.mole^{-1}.cm^{-1}$	pH*	Limit of determination *ppm**	Extraction	M : L	Remarks	Refs.
BAMOS	Cu(II)	335		10.0	1–5				17
	Ni(II)	340		11.4	0.5–2.5				17
	Co(II)	330		8.6	1–8				17
DBAT	Cu(II)	300			2.5–3.85 μg		1 : 1		43
AMBAT	Os	436		Acidic	1.2–14.7 μg				46
NBAT	Os	436		Acidic	0.5–8.6 μg				46
DABAT	Os	430			0.6–12 μg				47
ESBAT	Pd(II)	420			1–7.0 μg			30% ethanol	48
BAMT	Cu(II)	410			2–9		1 : 1		41
	Ni(II)	400			1–3.5		1 : 2		41
FAcT	Pd(II)	390	3.95		3.4–53 μg				77
	Pt(II)	390	6.25		6.2–78 μg				77
	Pd(II)	390	0.41	2–10				Simultaneous detn. is	78
	Pt(IV)	390	0.57	2.5–3.5				possible at two different	
		460						wavelengths	78
TAT	Cu(II)	372	3.90	4.7	0.2–1.2	$CHCl_3$		$pK_1 = 10.6$	58
1,2, CDDT	Zn(II)	415			1.1–6.6				74
	Co(II)	450		5.5	2.2–8.7				75
		500							
	Ni(II)	400		2.4–3.4	2.2–5.6				75
	Fe(II)	640	0.47		1.5–9.0			Water–DMF 9 : 1	75
	Fe(III)	400		2.5–4.2	1.0–3.2				75
	Cu(II)	467		4.5–6.0				Can be detd. in alk. med.,	84
								alk. tart. or EDTA soln.	
1,3 CDDT	Cu(II)	350	2.32	6.3				pK_1, 4.7; pK_2, 10.05	76
	Co(II)	370	2.80	6.3					76
	Zn(II)	510	1.42	6.3					76
	Ni(II)	410	1.32	6.3					76
	Pd(II)	370	1.92	6.3					76
	Pt(IV)	360	2.27	6.3					76
SAT	Mn(II)		0.40	conc. HCl	0.74–6.0 μg	TBP			53
	Mo(VI)	520	0.48	1.5	1–18		1 : 1	Mo and Fe can be detd. in	52
								presence of each other;	
								also used in analysis of	
								Ni–Cr and Mo–Fe alloys	
	Fe(III)	590	0.17	10.0	1–28		1 : 2		52
SAS	Cu(II)	685		3–5					51

Table 2. (*contd.*)

Compound	Ion	λ_{max}, *nm*	ε, $10^4\ l.mole^{-1}.cm^{-1}$	pH*	Limit of determination, *ppm**	Extraction	M : L	Remarks	Refs.
PADT	Co(II)	385	0.56	8–10.5	1–11		1 : 1		59
	Ni(II)	400	0.81	7.5–9.0			1 : 1		59
		450		8.8	up to 4.5	$CHCl_3$	1 : 1		
NFAS	Hg(II)	420–480		3.5–7.5	up to 0.2m*M*			Also appl. to ores containing 0.5% Cu(II), 2% Zn(II), 0.4% Pb(II) and 5.6% Fe(III)	65
FPDT	Pd(II)	413 420	0.62	3–10	2–10μ*M*			Used for detn. of Pd(II) in catalysts and simult. detn. of Pd(II) and Pt(IV) in a mixt., at pH 3.75 and 413 and 480 nm	83
NQS-4S	Zr(IV)	510–520	2.70	2–3	up to 3.9		1 : 2		67
	Th(IV)	490–500	2.44	2.8–4.5	up to 13		1 : 2		67
	UO_2(II)	500	1.78	4.8–6.2	1–21		1 : 2		67
	Sc(III)	500	3.71	5–7.3	up to 1.35		1 : 2		67
	Y(III)	490	3.13	6.7–8.3	up to 2.9		1 : 2		67
	Pb(II)	500	1.72	5.5–7.3	up to 8.5		1 : 1		67
	Bi(III)	515		Acidic	16–133 μg		1 : 1	HNO_3/KNO_3 buffer	71
NQT-4S	Cu(II)	555		Acidic	2–20 μg		1 : 2		9
	Zn(II)	520	2.00	6–7			1 : 2	Formation constant detd.	70
	Cd(II)	520	1.90	6–7			1 : 2		70
	Cu(II)	550	1.33	3–7			1 : 2		70
	Pb(II)	540	1.56	6–7			1 : 1		70
IT	Cu(II)	380 400		4.7	1–6 μg	$CHCl_3$	1 : 2		80
BTDD	Cu(II)	490			0.7–7 μg		1 : 1		81
TBPK	Cu(II)	446		6.5	0.2–15 μg				79
PIDT	Os	450	1.30	3.3–4.5	1–12 μg		1 : 1	50% DMF	60
	Rh(III)	410	3.10	6–7	0.6–2.7			DMF–acetate buffer	61
	Pd(II)	420	2.80	4.5	1.0–3.5				61
	Pt(IV)	450 or 480		5.0	1–10		1 : 1	Can be detd. in presence of eq. amount of Au by addn. of 10% NaCN	62
LS	Th(IV)	560	0.38	2–3	0.3–3.7		1 : 1	80% alc. medium; stability constant 2.4×10^4	82

* Unless otherwise indicated.

Table 3. Use as indicators

Compound	Ion	pH	Limit of determination	Colour change	Remark	Refs.
NFAS	Hg(II)		1 mg	Orange to yellow	EDTA direct	64
HMAPS	Fe(III)	2.0	up to 100 mg	Green to colourless	EDTA direct	30
HMAPT						
PQMT	Cu(II)	0.5–4.0	1 μg–30 mg	Red to colourless	EDTA direct, also used for Cu in brass and gun metal	72
	Zn(II)	4.4–7.5	65 μg–65 mg	Red to colourless	and Ni in monel K and Brightway G	72
	Cd(II)	4.8–6.0	20 μg–110 mg	Red to colourless		72
	Hg(II)	5.3–6.8	40 μg–100 mg	Red to colourless		72
	Ni(II)	4.5–7.0	12 μg–60 mg	Red to colourless		72
TAS	Fe(II)	Addition		Deep red to colourless	EDTA direct	57
	Fe(III)	of		Deep violet to colourless	EDTA direct	57
	Ni(II)	NaOH		Yellowish green to colourless	EDTA direct	57
	Cu(II)	or HCl		Deep green to blue	EDTA direct	57
	Co(II)	has no		Yellow to colourless	EDTA direct	57
	UO_2(II)	effect on		Blood red to light yellow	EDTA direct	57
	V(V)	complex		Deep mustard to greenish yellow	EDTA direct	57
NQS-4S	Pb(II)	5.5–6.8	0.1–207 mg	Purple to greenish yellow	Hexamine/HNO_3 buffer, EDTA	67
	Bi(III)	1.7–2.8	0.1–20 mg	Purple to greenish yellow	Dil. NH_3/HNO_3 buffer, EDTA	67
	PO_4^{3-}	6.0–7.3	0.5–28.5 mg	Greenish yellow to pink	Pyridine/HNO_3 or hexamine/HNO_3	68
	MoO_4^{2-}	6.0–7.0	1–80 mg	Greenish yellow to pink	Pyridine/HNO_3 or hexamine/HNO_3	68
	WO_4^{2-}	6.0–7.0	12–50 mg	Greenish yellow to pink	Titration with $Pb(NO_3)_2$	68
	SO_4^{2-}	4.8–5.5	1.7–6.9 mg	Greenish yellow to pink	Titration with $Pb(NO_3)_2$ in 30% methanol medium	68
	I^-	2.5–4.5	0.6–4 mg	Purple to yellow	Titration with $Hg(NO_3)_2$ in isopropyl alc. medium	67
NQT-4S	Ni(II)	5.0–6.5	0.6–30 mg	Yellow to purple	EDTA direct, non-reversible AcOH/HAc	67
	Cu(II)	3.7–6.8	0.6–15.8 mg	Yellow to purple	EDTA direct, non-reversible AcOH/HAc	67
	Zn(II)	5.5–6.8	0.6 65 mg	Yellow to purple	EDTA direct, non-reversible AcOH/HAc	67
	Cd(II)	5.5–6.8	1–56 mg	Yellow to purple	EDTA direct, non-reversible AcOH/HAc	67
	In(III)	4.0–6.0	0.2–36 mg	Purple to yellow	NaAC/HAC, EDTA direct	69
	Pb(II)	5.5–6.8	0.1–207 mg	Purple to yellow	Hexamine/HNO_3, direct	67
	Bi(III)	1.7–2.8	0.1–105 mg	Purple to yellow	Hexamine/HNO_3, direct	69
	Al(III)				Detd. by back-titration with Zn(II)	69

Table 3. (*contd.*)

Compound	Ion	pH	Limit of determination	Colour change	Remark	Refs.
	Ga(III)				Detd. by back-titration with Zn(II)	69
	Fe(III)				Detd. by back-titration with Zn(II)	69
	Al + Cu				Al-EDTA complex broken by NaF; and released EDTA titrated with Zn(II). Also Al in bauxite	69
	Al + Fe					69
	Al + Ga				Al-EDTA complex broken by NaF; and released EDTA titrated with Zn(II). Also Al in bauxite	69
	PO_4^{3-}	5.0–7.0	0.5–28.5 mg	Yellow to purple	Hexamine/HNO_3, titn. with $Pb(NO_3)_2$	68
	MoO_4^{2-}	5.0–6.0	1–80 mg	Yellow to purple	Hexamine/HNO_3, titn. with $Pb(NO_3)_2$	68
	WO_4^{2-}	6.0–7.0	12–50 mg	Yellow to purple	Hexamine/HNO_3, titn. with $Pb(NO_3)_2$	68
	I^-	2.5–4.0	0.6–4 mg	Yellow to purple	Isopropyl alc., titn. of I^- with Hg(II)	67
	$Fe(CN)_6^{4-}$	0.3–2 ml of 0.2*M* hexamine	2–42 mg	Purple to yellow	$(NH_2)_4SO_4$ or KCl or K_2SO_4 necessary, titn. of std. Zn(II) soln. with ferrocyanide	67
		2–6 ml of 0.2*M* hexamine	1.6–159 mg	Purple to yellow	NH_4Cl or $(NH_4)_2SO_4$ necessary; titn. of std. Cd(II) soln. with ferrocyanide	

Table 4. Fluorimetric applications

Compound	Metal	pH	Excitation max., *nm*	Fluorescence max., *nm*	Range of determination	M : L	Remarks	Refs.
SAS	Sc		370	455	0.002–0.02 ppm	1 : 1		
	Zn	6.15–6.4			up to 3 μg	1 : 1	Also appl. to det. 0.002–0.004% of Zn(II) in $CdSO_4$ and $CdCl_2$, after sepn. of Zn(II) as thiocyanate into isoamyl alc.	51
	Ga	3.5			2.5–65 μg	1 : 2		51
	Al	5.4			3.5–17 μg	1 : 2		51
	Y	6.9			15–125 μg	1 : 2		51
HNAT	Ga	3.2	412	472	1 μ*M*	1 : 1		56
DBAS	Sc	6.0	360	425			0.002–0.3% of Sc detd. in allanite, mica, *etc.*	31

EDTA medium.[84] It was generally observed that semicarbazones containing hydroxy groups *ortho* to the aldehyde group gave good colour reactions. Thiosemicarbazones are rather selective and sensitive for copper.

Applications of these compounds for spectrophotometric investigations are summarized in Table 2.

Applications as visual indicators

The most common application is the direct titration of the metal against EDTA solution with thiosemicarbazones and semicarbazones as indicators. With *o*-thymolaldosemicarbazone,[57] addition of acid or alkali has no effect on the complex formed. Phenanthraquinone monothiosemicarbazone[72] was used to determine Cu in brass and gun metal, and Ni in monel K and Brightway G. Phosphate, molybdate, tungstate and sulphate were titrated with lead nitrate, with 1,2-naphthoquinone-2-semicarbazone as indicator.[68] Aluminium was determined by EDTA back-titration, with 1,2-naphthaquinone-2-thiosemicarbazone-4-sulphonic acid as indicator and zinc solution as titrant.[69] Aluminium and copper were determined together by breaking the Al–EDTA complex by addition of sodium fluoride and titrating the released EDTA with zinc.[69] Iodide has been determined by mercurimetric titration in isopropyl alcohol, with the same indicator.[67]

Uses of these compounds as indicators are summarized in Table 3.

Applications as gravimetric reagents

Only a very few semicarbazones and thiosemicarbazones are used in the gravimetric determination of metal ions. Komatsu and Hiroaki used a 0.1% ethanolic solution of *p*-ethylsulphonylbenzaldehyde thiosemicarbazone for gravimetric determination of Hg^{2+} in acidic medium ($<2.5N$).[49] It gives a yellow precipitate which is washed with 1*M* hydrochloric acid and dried at 110–120°. It is also used for estimation of Pd(II),[50] giving an orange-yellow precipitate in 5*M* hydrochloric acid, which is washed with 1% hydrochloric acid and water, and dried at 110–120°.

Hovorka and Holzbecker[54] used salicylaldehyde thiosemicarbazone to precipitate the yellow crystalline $Cd(C_8H_8ON_3S)_2$ (containing 22.4% Cd) from cadmium nitrate or sulphate solution; the method is not applicable to solutions containing chloride, fluoride or oxalate.

2,4-Dihydroxybenzaldehyde thiosemicarbazone has also been employed for estimation of cadmium[44] and nickel.[45] In the cadmium estimation at pH 6.5–8.5, Fe^{3+}, Al^{3+}, $Cr,^{3+}$, CN^-, citrate, traces of F^- and >2.5 mg/ml of other halides interfere. In the estimation of nickel, the green complex $(C_8H_8N_3O_2S)_2Ni \cdot 6H_2O$ was precipitated in the pH range 5.0–6.5.

2-Furaldehyde thiosemicarbazone has been used by Pavon and Pino[63] as a gravimetric reagent for palladium at pH 2.0–6.0. The orange precipitate is washed with 10% aqueous ethanol and dried at 60–120°. The reagent is said to have advantages over dimethylglyoxime and 2-furaldioxime.

The same authors[66] used a 2% ethanolic solution of the 4-phenyl-3-thiosemicarbazone of 2-furaldehyde for gravimetric estimation of palladium in the pH range 3.0–5.0.

Potentiometric studies

Bhatt *et al.*[55] studied the complexes of 2-hydroxy-1-naphthaldehyde-4-phenyl-3-thiosemicarbazone with Cu^{2+}, Ni^{2+}, Co^{2+} and VO^{2+} by pH-titration. The proton–ligand stability constant is 1.43×10^{10}. The stability constants were determined by several methods in 70% dioxan medium. All four metals formed 1:2 complexes. The order of the stability constants is $VO^{2+} > Cu^{2+} \simeq Co^{2+} > Ni^{2+}$.

Complexation by salicylaldehyde-4-phenyl-3-thiosemicarbazone has also been studied potentiometrically by Bhatt *et al.*[73] at 25° and ionic strength 0.1 in 50% aqueous dioxan. The proton-ligand stability constant is 7.94×10^9 and the $\log \beta$ values for the complexes are 9.44, 10.28, 9.84 and 8.94 for VO^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+} respectively.

Similar studies were done on the 2-hydroxy-5-methylacetophenone thiosemicarbazone complexes[33] of Cu(II), Mn(II), Co(II), Zn(II) and Ni(II), at 40° in water–dioxan (1:3). The order of the stability constants is Zn < Cu > Co > Ni > Mn.

Fluorimetric determination

Salicylaldehyde semicarbazone, 2-hydroxy-1-naphthaldehyde thiosemicarbazone and 2,4-dihydroxybenzaldehyde semicarbazone have also been used for the spectrofluorimetric determination of a number of metal ions, the information for which is summarized in Table 4.

Other uses

In the presence of cyanide and tartrate, manganese can be detected by a spot-test on paper even when Ag, Pb, Cu, Cd, Bi, Ni, Zn and Fe(III) are present, by use of an ethanolic solution of dimethylglyoxime thiosemicarbazone.[85] Complexes of Cu(II), Hg(II), Cd(II) and Zn(II) with the 4,4′-diphenylthiosemicarbazones of 1,2-diketones can be separated by thin-layer chromatography on alumina with ethyl acetate as solvent.[86]

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REFERENCES

1. G. Domagk, R. Behnisch, F. Mietzsch and H. Schmidt, *Naturwissenschaften*, 1946, **33**, 315.

2. N. N. Orlova, V. A. Aksevova, D. A. Selidovkin, N. S. Bogdanova and G. N. Pershin, *Russ. Pharm. Toxic.*, 1968, 348.
3. K. Butler, *U.S. Patent No.* 3,382,266, 7 May 1968.
4. D. J. Bauer, L. St. Vincent, C. H. Kempe and A. W. Downe, *Lancet*, 1963, **2,** 494.
5. H. G. Petering, H. H. Buskirk and G. E. Underwood, *Cancer Res.*, 1964, **64,** 367.
6. C. W. Johnson, J. W. Joyner and R. P. Perry, *Antibiotics Chemotherapy*, 1952, **2,** 636.
7. H. W. Gansman, C. I. Rhykerd and H. R. Hinderliter, E. S. Scott and L. F. Audrieth, *Botan. Gaz.*, 1953, **114,** 292.
8. K. Libermeister, *Z. Naturforsch. B*, 1950, **5,** 79.
9. T. Ueda, A. Takada and K. Kosugi, *Yakugaku Zasshi*, 1971, **91,** 1244.
10. J. L. Bahamonde, D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 1972, **26,** 7.
11. S. Patai, *The Chemistry of Carbonyl Groups*, Interscience, New York, 1966.
12. J. M. Cano Pavon, D. P. Bendito and F. Pino, *An. Quim.*, 1969, **65,** 667.
13. J. M. Cano Pavon, J. Vazquez Aller, D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 1971, **25,** 149.
14. J. M. Cano Pavon, D. P. Bendito and F. Pino, *An. Quim.*, 1971, **67,** 299.
15. D. J. Leggett and B. W. Budesinsky, *Microchem., J.*, 1971, **16,** 87.
16. J. M. Cano Pavon and D. P. Bendito, *Inform. Quim. Anal.*, 1973, **27,** 20.
17. M. P. Martinez, D. P. Bendito and F. Pino, An. Quim., 1973, **69,** 747.
18. J. L. Bahamonde, D. P. Bendito and F. Pino, *Talanta*, 1973, **20,** 694.
19. *Idem, Analyst*, 1974, **99,** 355.
20. M. P. Martinez, M. Valcarcel and F. Pino, *Anal. Chim. Acta*, 1976, **81,** 157.
21. L. V. Borisova, E. I. Plastiniva and A. N. Ermakov, *Zh. Analit. Khim.*, 1974, **29,** 1362.
22. J. L. Gomez Ariza, J. M. Cano Pavon and F. Pino, *Talanta*, 1976, **23,** 460.
23. J. L. Gomez Ariza and J. M. Cano Pavon, *Anal. Lett.*, 1976, **9,** 677.
24. M. T. Martinez Aguilar, J. M. Cano Pavon and F. Pino, *Anal. Chim. Acta*, 1977, **90,** 335.
25. J. M. Lopez Fernandez, M. Valcarcel and F. Pino, *An. Quim.*, 1975, **71,** 789.
26. *Idem, Quim. Anal.*, 1976, **30,** 8.
27. J. M. Cano Pavon, A. Levado and F. Pino, *Mikrochim. Acta*, 1976, **II,** 233.
28. B. W. Budesinsky and J. Svec, *Anal. Chim. Acta*, 1971, **55,** 115.
29. L. C. Calzolari, L. L. Coassini, P. Benci and L. Favretto, *Ann. Chim.*, 1973, **63,** 363.
30. G. S. Manku, *Curr. Sci. (India)*, 1976, **45,** 294.
31. J. R. Shah and R. P. Patel, *J. Indian Chem. Soc.*, 1973, **8,** 562.
32. M. C. Patel, J. R. Shah and R. P. Patel, *ibid.*, 1973, **50,** 560.
33. B. H. Patel, J. R. Shah and R. P. Patel, *ibid.*, 1976, **53,** 9.
34. A. Aydin and F. Baykut, *Chim. Acta Turc.*, 1975, **3,** 51.
35. D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 1967, **21,** 31.
36. *Idem, ibid.*, 1968, **22,** 1.
37. *Idem, ibid.*, 1968, **22,** 277.
38. M. Valcarcel and D. P. Bendito, *ibid.*, 1970, **24,** 49.
39. T. Naito, S. Una and S. Suguira, *Nagoya Shiritsu Daigaku Yakugakubu Kiyo*, 1957, **5,** 57.
40. J. M. Cano Pavon, J. C. J. Sanchez and F. Pino, *Anal. Chim. Acta*, 1975, **75,** 335.
41. F. B. Sanchez, M. P. Martinez and F. Pino, *Inform. Quim. Anal.*, 1969, **23,** 17.
42. K. Morisige, S. Sasaki, K. Hiraki and Y. Nishikawa, *Bunseki Kagaku*, 1975, **24,** 321.
43. S. Stankoviansky, A. Beňo, J. Čársky and E. Kominaková, *Chem. Zvesti*, 1971, **25,** 123.
44. S. Stankoviansky, J. Čársky, A. Beňo and E. Dolniková, *ibid.*, 1968, **22,** 50.
45. S. Stankoviansky, J. Čársky and A. Beňo, *ibid.*, 1969, **23,** 589.
46. G. Baiulescu, C. Lazar and C. Cristescu, *Zh. Analit. Khim.*, 1960, **15,** 505.
47. G. Popa, C. Lazar, I. C. Ciurea and C. Cristescu, *Analale Univ. "C.I. Parhon", Ser. Stiint. Nat. Chim.*, 1963, **12,** 95.
48. S. Komatsu, H. Nishimura and Z. Hiroaki, *Nippon Kagaku Zasshi*, 1958, **79,** 895.
49. S. Komatsu and Z. Hiroaki, *ibid.*, 1957, **78,** 715.
50. S. Komatsu, T. Kida and Z. Hiroaki, *ibid.*, 1956, **77,** 1437.
51. I. Kiyoharu, *ibid.*, 1966, **87,** 570.
52. D. P. Bendito and F. Pino, *Mikrochim. Acta*, 1976 **I,** 613.
53. F. Vláčil and D. Valentová, *Sb. Vys. Sk. Chem-Technol. Praze, Anal. Chem.*, 1968, **H3,** 43.
54. V. Hovorka and Z. Holzbecker, *Bull. Intern. Acad., Tech'que, Sci. Cl. Math. Natur. Med.*, 1953, **51,** 43; *Ref. Zh. Khim.*, 1954, Abstr. No. 20, 357.
55. Y. N. Bhatt, K. K. Patel, K. J. Shah and R. S. Patel, *J. Indian Chem. Soc.*, 1975, **52,** 1035.
56. K. Harumi, B. Norikagu, K. Satoshi and O. Takeo, *Bunseki Kagaku*, 1971, **20,** 1315.
57. S. L. Garg and K. K. Panda, *Indian J. Appl. Chem.*, 1972, **35,** 149.
58. J. A. Munoz Leyva, J. M. Cano Pavon and F. Pino, *An. Quim.*, 1973, **69,** 251.
59. M. R. Rueda, J. A. Munoz Leyva and J. Antonio, *Quim. Anal.*, 1975, **29,** 122.
60. M. Guzman, D. P. Bendito and F. Pino, *Anal. Chim. Acta*, 1976, **83,** 259.
61. *Idem, An. Quim.*, 1976, **72,** 651.
62. *Idem, ibid.*, 1974, **70,** 828.
63. J. M. Cano Pavon and F. Pino, *Talanta*, 1973, **20,** 339.
64. K. G. Anisimova and O. A. Tataev, *Zh. Analit. Khim.*, 1971, **26,** 180.
65. K. N. Bagdasarov, L. G. Anisimova and O. A. Tataev, *Zavodsk. Lab.*, 1968, **34,** 390.
66. J. M. Cano Pavo and F. Pino, *Anal. Lett.*, 1974, **7,** 159.
67. S. Kesavan, *Thesis*, University of Delhi, 1977.
68. S. Kesavan, B. S. Garg and R. P. Singh, *Talanta*, 1977, **24,** 51.
69. *Idem, J. Chinese Chem. Soc.*, 1977, **24,** 32.
70. V. Vajgand and M. Jaredic, *Chem. Anal. (Warsaw)*, 1975, **20,** 1125.
71. T. Ueda, A. Takada and K. Kosugi, *Yakugaku Zasshi*, 1972, **92,** 332.
72. A. K. Singh, K. C. Trikha, R. P. Singh and M. Katyal, *Talanta*, 1975, **22,** 551.
73. Y. N. Bhatt, K. K. Patel, K. J. Shah and R. S. Patel, *J. Indian Chem. Soc.*, 1975, **52,** 1214.
74. J. A. Munoz Leyva, J. M. Cano Pavon and F. Pino, *Inform. Quim. Anal.*, 1972, **26,** 226.
75. *Idem, Quim. Anal.*, 1974, **28,** 90.
76. J. J. B. Nevado, J. A. Munoz Leyva and M. R. Ceba, *Talanta*, 1976, **23,** 257.
77. V. P. Kerentseva, M. D. Lipanova and I. S. Mustafin, *Zh. Analit. Khim.*, 1971, **26,** 1144.
78. V. P. Kerentseva, M. D. Lipanova and L. I. Mas'ko, *ibid.*, 1972, **27,** 1561.
79. U. Toyozo and A. Sumiyuki, *Bunseki Kagaku*, 1961, **10,** 941.
80. M. Guzman, D. P. Bendito and F. Pino, *Inform. Quim. Anal.*, 1973, **27,** 209.
81. W. Gorski and S. Podlasin-Paradowska, *Acta, Pol., Pharm.*, 1972, **29,** 31.

82. A. D. Nejkar, S. B. Padhye and B. A. Kulkarni, *J. Univ. Poona, Sci. Technol.*, 1976, **48,** 285.
83. L. I. Mas'ko, V. P. Kerentseva and H. Lipanova, *Zh. Analit. Khim.*, 1975, **30,** 315.
84. J. A. Munoz Leyva, J. M. Cano Pavon and F. Pino, *An. Quim.*, 1976, **72,** 392.
85. V. Hovorka and Z. Holzbecker, *Bull. Intern. Acad. Tech'que. Sci. Cl. Sci. Math., Natur. Med.*, 1953, **51,** 125; *Ref. Zh. Khim.*, 1954, Abstr. No. 20, 372.
86. U. Niederschulte and K. Ballschmiter, *Z. Anal. Chem.*, 1972, **261,** 191.

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ACIDITES ET COMPLEXES DES ACIDES (ALKYL- ET AMINOALKYL-) PHOSPHONIQUES—I

DETERMINATION POTENTIOMETRIQUE DES CONSTANTES D'ACIDITE PAR AFFINEMENT MULTIPARAMETRIQUE: PRISE EN COMPTE DE L'IMPURETE CARBONATE

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Résumé—Les déterminations utilisent les données (volume de réactif, potentiel) des neutralisations suivies par potentiométrie. Pour éviter toute erreur systématique, les constantes d'acidité sont affinées conjointement avec tous les autres paramètres influents (concentration totale du protolyte, concentrations des impuretés, caractéristiques de la chaîne de mesure...) à l'aide du programme MUPROT. La comparaison des résultats de l'ajustement multiparamétrique avec ceux des méthodes habituelles fait apparaître des divergences importantes. Une attention particulière est portée à l'impureté carbonate; pour en tenir compte, des expressions modifiées du volume de réactif sont établies. Le courant d'azote utilisé dans les neutralisations classiques déplace l'équilibre liquide–gaz auquel participe l'acide carbonique: dans ce cas, seules des expressions approchées sont envisageables. Un procédé plus rigoureux, qui consiste à travailler en enceinte fermée, est proposé.

La courbe de neutralisation d'un protolyte suivie par potentiométrie ou pH-métrie est fonction de nombreux paramètres. Lors d'une détermination, la valeur calculée d'un paramètre quelconque dépend plus ou moins fortement des autres: si une incertitude les affecte ou s'ils sont omis (impuretés, déréglage de l'ensemble de mesure...) ils transmettent une erreur systématique sur le paramètre à calculer. Pour atténuer les incertitudes il est donc nécessaire d'effectuer un calcul simultané de toutes les grandeurs influentes, même quand un seul paramètre est désiré. Un affinement multiparamétrique, basé sur une expression générale du volume de réactif, a été réalisé dans cet esprit puis testé sur de nombreux exemples:[1] parmi ceux-ci, le dosage d'un mélange de polyacides de constantes de stabilité inconnues, par une soude carbonatée, en utilisant une chaîne de mesure non standardisée, a été mené à bien.[2]

Nous nous intéresserons ici essentiellement à l'utilisation de cet affinement pour l'obtention des constantes d'acidité, toutes les améliorations attendues pouvant aussi s'appliquer à l'analyse.

Nos observations lors de l'interprétation de quantité de courbes de neutralisation d'acides alkylphosphoniques et aminoalkylphosphoniques nous ont amené à nous faire une idée du rôle fâcheux du carbonate souvent introduit par la base forte titrante. Il participe à un équilibre liquide–gaz:

$$H_2CO_3 \rightleftharpoons CO_2(g) + H_2O$$

qui perturbe les équilibres en solution. Malheureusement, comme nous sommes dans le cas classique des manipulations effectuées avec passage d'un courant d'azote dans la cellule de mesure, l'équilibre précédent se trouve déplacé vers la droite ce qui modifie l'équation de conservation des masses en solution. Il faut donc retoucher les équations de base utilisées précédemment.[1,2] Au vu des inconvénients de cette technique, d'autres moyens expérimentaux, capables d'aboutir à une prise en compte rigoureuse du carbonate, seront proposés. Aucune méthode existante n'est satisfaisante en ce qui concerne le carbonate.

Outre l'affinement des constantes d'acidité et de la concentration du carbonate, rappelons que nous nous donnons la possibilité de déterminer conjointement:

—la concentration totale du protolyte; son obtention devient primordiale quand les volumes équivalents sont peu marqués (notons que cette notion de volume équivalent devient assez floue en présence de carbonate). De plus, certains des acides étudiés, facilement dégradables, doivent être préparés par pesée de faibles quantités juste avant l'emploi: seul le calcul permet d'avoir une précision suffisante sur la concentration totale. Quelques méthodes particulières, applicables aux monoacides, ont été proposées par Benet et Goyan,[3] Metzger *et al.*,[4] Binder et Ebel,[5] pour tenir compte de cette concentration.

—les concentrations des impuretés autres que le carbonate: sous-produits de la préparation des composés, écarts à la composition formelle, impuretés du sel de fond... Plusieurs méthodes décrivent l'analyse de mélanges binaires d'acides de concentrations du même ordre de grandeur et de constantes d'acidité connues;[6–11] Ingman *et al.*[12] envisagent, de surcroît, l'affinement des constantes d'acidité.

—les caractéristiques de la chaîne de mesure (potentiel

normal ou décalage d'origine, défauts de réponse, etc....) qui permettent d'obtenir la concentration de H^+ à partir de l'indication du potentiomètre. La majeure partie des procédés existants proposent un étalonnage préalable de l'ensemble de mesure à partir d'un dosage acide fort–base forte qui aboutit au calcul plus ou moins complet des paramètres caractéristiques.[13-17] Pour des milieux suffisamment acides, Kankare réalise une méthode potentiostatique de détermination des constantes d'acidité sans standardisation préalable des électrodes;[18] ces constantes étant connues, le calcul est adapté pour l'analyse des mélanges.[19] Bos et Lengton,[20] avec une pile de mesure non étalonnée, procèdent par élimination pour obtenir la constante d'un monoacide de concentration totale connue et éventuellement le potentiel normal.

L'augmentation du nombre de paramètres ajustables améliore l'interprétation des données: Meites *et al.*[21,22] déterminent la concentration totale d'un protolyte, celle du réactif titrant, la constante d'acidité et le coefficient d'activité tandis que Briggs et Stuehr[23] affinent simultanément la constante d'acidité, la concentration de l'acide et celle d'une impureté totalement dissociée. Pehrsson *et al.*,[24,25] dans des cas simples (diacide, mélange de monoacides...), calculent les constantes d'acidité, les concentrations totales et retouchent le potentiel normal E'_0. Le caractère multiparamétrique est encore accru par Mønsted et Mønsted[26] qui, pour un polyacide, effectuent un ajustement complet des caractéristiques de la chaîne de mesure en envisageant la présence d'impuretés fortement acides ou basiques. Le programme LETAGROP[27,28] va encore plus loin en affinant les constantes de stabilité, la concentration du protolyte et de certaines impuretés, les potentiels normal et de jonction. C'est le seul travail où le rôle du carbonate est envisagé. Par contre ce programme est très lourd d'utilisation. Signalons que dans ces traitements multiparamétriques la réponse de l'électrode de verre est toujours supposée idéale (référence 26 exceptée).

Après avoir établi les expressions du volume de réactif qui tiennent compte de façon satisfaisante du comportement du carbonate, nous appliquons les affinements aux neutralisations d'acides *N*-alkylaminométhylphosphoniques effectuées sous azote, en examinant la répercussion de la variable carbonate sur les valeurs des autres paramètres.

PRINCIPAUX SYMBOLES

B	Nombre de protolytes présents dans la solution ajoutée
C	Concentration totale
C_x^0, C_{x1}^*, C_{x2}^*	Concentrations totales en carbonate ajouté
D	Nombre de protolytes présents dans la solution de départ
G	$=(v_g-v)/(v_0+v)/RTK_p$
H	Concentration totale en acide fort ($H>0$) ou en base forte ($H<0$)
$\bar{H}$	Titre moyen d'un réactif fort obtenu en négligeant le carbonate
h	Concentration en H^+ libre
I	Forme totalement ionisée d'un protolyte initial
i	Indice relatif aux espèces présentes dans la solution de départ
J	Nombre de constantes de stabilité d'un acide donné
j	Nombre de protons entrant dans H_jI ou H_jX
K_w	Produit ionique de l'eau
k_j	β_j/β_{j-1}
N	Nombre de protons initialement fixés à I, X
$\bar{n}_{H_o}$	Nombre moyen de H liés
	Exposant relatif à une concentration totale initiale
P	Pente des électrodes
pH	Indication du potentiomètre
S	Somme des carrés des résidus
v	Volume du réactif ajouté
v_g	Volume initial de la phase gaz
v_0	Volume initial de solution
W	Terme de pondération
X	Forme totalement ionisée d'un protolyte présent dans la solution ajoutée
x	Indice relatif aux espèces présentes dans la solution ajoutée
β	Constante globale de stabilité
β_1, β_2	Constantes globales de l'acide carbonique
ε	Décalage d'origine [expression (1)]
σ_v	Ecart-type sur le volume, calculé en fin d'affinement
σ_{0v}^2, σ_{0pH}^2	Variances expérimentales estimées sur le volume et le pH
$3\sigma_i$	Estimation de l'incertitude sur un paramètre affiné
[ ]	Concentration

ELEMENTS THEORIQUES

Les équations suivantes rattachent les paramètres caractérisant les constituants chimiques aux variables expérimentales: volume de réactif et potentiel. Elles ne sont valables qu'à force ionique et température constantes.

Concentration de H^+

La concentration h de H^+ est calculée à partir de:

$$-\log h = \varepsilon + \varepsilon_{ja} h + \varepsilon_{jb} K_w h^{-1} + Py \qquad (1)$$

où y est l'indication de l'appareillage (E ou pH). Pour les expressions des différents symboles, nous renvoyons à notre travail antérieur.[2] Notons qu'en pHmétrie, dans le cas d'une chaîne de mesure standardisée, ε et P sont proches respectivement de $\log \gamma_H$ et de l'unité; ε_{ja} et ε_{jb} permettent de tenir compte des potentiels de jonction.

Comme ε_{ja}, ε_{jb}, mais surtout ε et P, sont des grandeurs ajustables, la standardisation préalable des électrodes n'est plus indispensable.[2]

Volume de réactif

Pour pouvoir les appliquer également à l'analyse des mélanges, les expressions seront établies sous leur forme la plus générale. L'équation classique de conservation des concentrations en protons, appliquée à un volume initial v_0 de protolytes à neutraliser (indice i) auquel un volume v de réactif est ajouté (indice x),

s'écrit:

$$\frac{v_0}{v_0+v}\left(H_i^0+\sum_{i=1}^{i=D} N_i C_i^0\right)+\frac{v}{v_0+v}\left(H_x^0+\sum_{x=1}^{x=B} N_x C_x^0\right)$$
$$=\sum_{i=1}^{i=D}\sum_{j=0}^{j=J_i} j[\mathrm{H}_j\mathrm{I}]+\sum_{x=1}^{x=B}\sum_{j=0}^{j=J_x} j[\mathrm{H}_j\mathrm{X}]+h-[\mathrm{OH}]. \quad (2)$$

H_i^0 et H_x^0 représentent—à un facteur multiplicatif près—la concentration totale de l'anion d'acide fort (H_i^0, $H_x^0 > 0$) ou du cation d'une base forte (H_i^0, $H_x^0 < 0$).

Cette équation, point de départ des démonstrations habituelles, n'est valide que pour des espèces exclusivement présentes en solution. En développant les concentrations des H liés au carbonate figurerait alors dans cette relation:

$$2[\mathrm{H_2CO_3}]+[\mathrm{HCO_3^-}].$$

Or l'acide carbonique participe à un équilibre liquide–gaz:

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{CO_2(g)+H_2O} \quad \begin{cases} K_p = \dfrac{[\mathrm{H_2CO_3}]}{P_{\mathrm{CO_2}}} \\ [\mathrm{H_2CO_3}] = [\mathrm{H_2CO_3}]_{\text{réel}} \\ \qquad +[\mathrm{CO_2}]_{\text{sol.}} \end{cases}$$

Etant donné la possibilité de déplacement de l'équilibre par l'intermédiaire de la phase gaz, l'équation protonique n'est plus directement applicable à l'acide carbonique. Il faut donc retoucher les équations habituelles en tenant compte de la technique expérimentale puisque celle-ci peut influer différemment sur ce dernier équilibre.

Deux cas importants sont à distinguer:
—d'une part les manipulations en système fermé
—d'autre part les neutralisations réalisées en système ouvert—qui correspondent au cas classique du passage d'un courant d'azote dans la cellule de mesure—et auxquelles nous nous intéresserons tout particulièrement.

Système fermé

L'évidence, qui nous est apparue assez tardivement et qui n'avait jamais été envisagée précédemment, est d'imposer la conservation des masses. Pour cela, il faut travailler en système fermé. L'équation protonique s'applique au nombre de moles et comprend CO_2(g), sans oublier que celui-ci est un diacide en solution ($j = 2$).

La conservation du nombre de protons fixés au carbonate s'écrit alors:

$$2n_{\mathrm{CO_2}}+2(v_0+v)[\mathrm{H_2CO_3}]\cdot 10^{-3}+(v_0+v)[\mathrm{HCO_3^-}]\cdot 10^{-3}.$$

Pour ce type de manipulation, un vase de titrage classique avec couvercle, rendu hermétiquement clos, est utilisé. Dans ces conditions le volume initial de la phase gaz est v_g et devient $(v_g - v)$ lors de l'addition de réactif.

La somme γ des termes relatifs au carbonate, à introduire dans l'équation (2) devient, en appliquant la loi des gaz parfaits à n_{CO_2}:

$$\gamma = 2G[\mathrm{H_2CO_3}]+2[\mathrm{H_2CO_3}]+[\mathrm{HCO_3^-}]$$
$$\text{avec } G=\left(\frac{v_g-v}{v_0+v}\right)\frac{1}{RTK_p}.$$

Si le carbonate existe dans la solution initiale (C_i^0) et est introduit par le réactif (C_x^0), on obtient en appliquant la conservation en carbonate:

$$\gamma=\left(\frac{v_0}{v_0+v}C_i^0+\frac{v}{v_0+v}C_x^0\right)\frac{2(G+1)\beta_2 h^2+\beta_1 h}{(G+1)\beta_2 h^2+\beta_1 h+1}$$

où β_1 et β_2 sont les constantes globales de stabilité de HCO_3^- et H_2CO_3. Par extension de la définition classique des $\bar{n}_H$, on peut dire que

$$\{2(G+1)\beta_2 h^2+\beta_1 h\}\{(G+1)\beta_2 h^2+\beta_1 h+1\}^{-1}$$

représente le nombre moyen de H liés au carbonate.

En rappelant que les concentrations des H liés aux espèces en solution se calculent toujours[1,2] par:

$$\sum_0^{J_i} j[\mathrm{H}_j\mathrm{I}]=\frac{v_0}{v_0+v}C_i^0\bar{n}_{\mathrm{H}_i}$$
$$\sum_0^{J_x} j[\mathrm{H}_j\mathrm{X}]=\frac{v}{v_0+v}C_x^0\bar{n}_{\mathrm{H}_x}$$

et en reportant dans (2), on obtient l'expression générale suivante, qui pour chaque valeur de h permet de calculer le volume de réactif v_c:

$$v_c = v_0\frac{H_i^0+\sum_{i=1}^{D} C_i^0(N_i-\bar{n}_{\mathrm{H}_i})-h+\dfrac{K_w}{h}}{-H_x^0-\sum_{x=1}^{B} C_x^0(N_x-\bar{n}_{\mathrm{H}_x})+h-\dfrac{K_w}{h}} \quad (3)$$

avec

$$\begin{cases} \bar{n}_{\mathrm{H}_i}=\dfrac{\sum_0^{J_i} j\beta_{ij}h^j}{\sum_0^{J_i}\beta_{ij}h^j} \\ \bar{n}_{\mathrm{H}_x}=\dfrac{\sum_0^{J_x} j\beta_{xj}h^j}{\sum_0^{J_x}\beta_{xj}h^j} \\ \bar{n}_{\mathrm{H}}=\dfrac{2(G+1)\beta_2 h^2+\beta_1 h}{(G+1)\beta_2 h^2+\beta_1 h+1} \quad \text{pour le carbonate.} \end{cases}$$

Cette nouvelle expression de v_c nous permet de proposer une technique universelle et rigoureuse pour la prise en compte du carbonate: il suffit, contrairement aux techniques habituelles, de travailler en système fermé. Ce procédé a été éprouvé avec succès dans le cas le plus difficile qui est le dosage d'un acide fort par le carbonate de sodium: ont ainsi été obtenus β_1, β_2, K_p, ainsi que la concentration du carbonate ajouté.[29]

Un cas limite du $\bar{n}_H$ relatif au carbonate est celui

correspondant à $(v_g - v) = 0$, ce qui nous ramène à l'expression classique de v_c,[1,2] où H_2CO_3 ne se distingue pas des autres acides. Expérimentalement, cela consiste à isoler la solution de la phase gaz par une couche non miscible (huile de vaseline par exemple). Ce procédé que nous avions introduit empiriquement s'en trouve justifié.[2] Il est malheureusement plus délicat à mettre en oeuvre: en effet les électrodes risquent d'être souillées lors de leur retrait de la solution; de plus il est difficilement compatible avec l'utilisation d'un passeur d'échantillons et par suite il se prête mal à l'automatisation des dosages.

Système ouvert

Les techniques expérimentales et les équations précédentes ont été introduites trop tardivement pour que nous puissions en bénéficier. En effet, nous disposons de quantité de données (v, pH) de neutralisation d'acides phosphoniques et aminophosphoniques, prélevées en utilisant la technique classique de passage d'un courant d'azote au dessus de la solution. Il faut donc retoucher les équations de base pour traduire de façon satisfaisante le comportement du carbonate.

Le passage du courant d'azote provoque une diminution de H_2CO_3 par déplacement d'équilibre. Pour une neutralisation effectuée par une base forte carbonatée, cela revient à dire, que lorsqu'elle est ajoutée à un milieu suffisamment acide elle se comporte comme si elle ne contenait pas de carbonate; à l'inverse le CO_3^{2-} est conservé en milieu basique. Les cas intermédiaires sont envisageables: la concentration en carbonate étant alors plus faible que celle attendue. Précisons que le titre de la base à introduire dans les calculs est obligatoirement la concentration totale en ion alcalin $|H_x^0| = [M^+]_T = [OH^-]_T + 2[CO_3^{2-}]_T$, qui seule est constante.

Avec ce type de neutralisation, il n'est plus possible de proposer une interprétation rigoureuse. Les deux méthodes approchées suivantes ont été utilisées, pour simplifier nous ne traiterons que le cas du carbonate présent dans le réactif ajouté.

Hypothèse d'une discontinuité. Soit une courbe de neutralisation présentant deux zones tampon nettement distinctes. Nous supposons que dans chacune de ces régions le comportement du carbonate ajouté est homogène, mais qu'il existe une discontinuité entre celles-ci (Fig. 1).

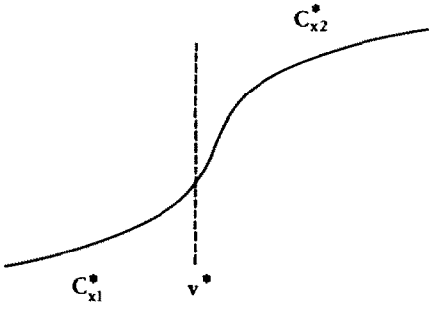


Fig. 1.

Dans le premier domaine de pH, le carbonate se comporte comme si sa concentration était C^*_{x1}, à partir du volume v^* de réactif celle-ci devenant C^*_{x2}. L'expression de v_c devient, en sortant le terme relatif au carbonate ajouté de la somme globale

$$v_c = v_0 \frac{H_i^0 + \sum_{i=1}^{D} C_i^0(N_i - \bar{n}_{H_i}) + \frac{v^*}{v_0}(C^*_{x1} - C^*_{x2})(2 - \bar{n}_H) - h + \frac{K_w}{h}}{-H_x^0 - \sum_{x=1}^{B-1} C_x^0(N_x - \bar{n}_{H_x}) - C^*_{x2}(2 - \bar{n}_H) + h - \frac{K_w}{h}} \quad (4)$$

$$\bar{n}_H = \frac{2\beta_2 h^2 + \beta_1 h}{\beta_2 h^2 + \beta_1 h + 1} = \text{nombre moyen de H liés au carbonate.}$$

Conventions:

$$\begin{cases} \text{lorsque } v < v^* & C^*_{x2} = C^*_{x1} \\ \text{lorsque } v > v^* & C^*_{x2} \neq C^*_{x1} \\ H_x^0 \text{ titre total en ion alcalin.} \end{cases}$$

Ce type de calcul peut être élargi à un plus grand nombre de régions tampons en augmentant les discontinuités. La recherche du volume v^* est possible. Pour que cette méthode soit envisageable il faut disposer de données de grande précision pour atténuer les corrélations entre paramètres.

Fonction semi-empirique de dégagement de CO_2. Toute fonction est envisageable. Nous avons choisi tout à la fois la plus simple et la plus extrême en supposant que le CO_2 dégagé est égal au H_2CO_3 qui se serait formé en milieu fermé. Ceci revient à modifier l'expression de v_c en y introduisant une concentration variable C_x^* en carbonate ajouté. v_c s'obtient alors à partir de l'expression (4) en faisant

$$C^*_{x1} = C^*_{x2} = C_x^0\left(1 - \frac{\beta_2 h^2}{\beta_2 h^2 + \beta_1 h + 1}\right)$$

C_x^0 est la concentration réelle du carbonate ajouté, β_1 et β_2 étant les constantes de formation de H_2CO_3.

Obtention des paramètres inconnus

En schématisant, l'obtention des inconnues des expressions (1), (3) ou (4) revient à corriger les valeurs des paramètres jusqu'à aboutir à la meilleure coïncidence entre points expérimentaux (v, pH) et les courbes faisant intervenir les variables recalculées: $v_c = f(\text{pH})$ et $v = f(\text{pH}_c)$. Cette coïncidence est jugée correcte lorsque la somme des carrés des résidus S est minimale.

Pour les développements concernant cet affinement par moindres carrés nous renvoyons aux publications antérieures;[1,2,29] notons les points essentiels.

(a) Pour être en mesure de minimiser une somme S qui tient compte des incertitudes sur les deux variables expérimentales (v, pH), une réduction du nombre de variables est effectuée. Elle conduit à minimiser,

comme l'ont fait d'autres auteurs,[26,30-32] la somme

$$S = \sum_n \frac{(v_n - v_{nc})^2}{\sigma_{0v}^2 + \sigma_{0pH}^2 \left(\frac{\partial v_{nc}}{\partial pH_n}\right)^2} = \sum_n W_n (v_n - v_{nc})^2.$$

Les résidus correspondent aux distances des points expérimentaux à la courbe $pH/\sigma_{0pH} = f(v_c/\sigma_{0v})$. Il est évident que le fait de multiplier les variances estimées σ_{0v}^2 et σ_{0pH}^2 par un même facteur ne modifie en rien les résultats de l'affinement: on peut donc tout aussi bien utiliser les variances relatives.[30]

Le terme W_n apparaît comme un terme de pondération. Les deux affinements limites, fréquemment rencontrés, deviennent des cas particuliers: l'affinement sur le volume correspond à $\sigma_{0pH}^2 = 0$, celui sur le pH à $\sigma_{0v}^2 = 0$; pour obtenir alors des résidus "réels" il faut introduire respectivement $\sigma_{0v}^2 = 1$ et $\sigma_{0pH}^2 = 1$.

(*b*) Pour calculer les corrections à apporter aux paramètres α, il faut avoir recours aux dérivées partielles $\partial v_c/\partial\alpha$. Elles sont obtenues à partir de leurs expressions analytiques. Remarquons que les programmes habituels utilisent souvent des dérivations numériques rendant ainsi l'affinement multiparamétrique moins rigoureux.

Le programme MUPROT (Affinement MUltiparamétrique appliqué aux neutralisations de PROTolytes) correspondant est écrit en ALGOL 60 pour ordinateur CII 10070; il est en cours de transcription pour calculateur de laboratoire (Hewlett–Packard 9825). Une version en FORTRAN IV est également disponible.

PARTIE EXPERIMENTALE

Seules les manipulations effectuées en système ouvert sont envisagées ici. Pour avoir une idée du comportement moyen du carbonate, douze courbes de neutralisation de quatre acides différents (acides *N*-méthylaminométhylphosphonique, *N*,*N*-diméthylaminométhylphosphonique, *N*-éthylaminométhylphosphonique et *N*,*N*-éthylaminométhylphosphonique) sont utilisées à raison de trois courbes par composé. Pour cela des solutions de ces acides (v_0 = 50,00 ml) en milieu KNO_3 0,100*M* sont neutralisées par la potasse, à une température de 25 ± 0,05° et avec passage d'un courant d'azote au-dessus de la solution. L'allure d'une courbe type est représentée par la figure 2. La base forte est ajoutée avec une microburette de 1 ml, le volume pouvant être apprécié à 0,001 ml près; un pH-mètre Radiometer PHM 64 permet une résolution de 0,001 unité de pH. La chaîne de mesure, constituée d'une électrode de verre (Schott, type U) et d'une électrode de référence au calomel (Ingold, type 303), est standardisée à l'aide des tampons phtalate [pH(S) = 4,008] et borax [pH(S) = 9,180]; dans ces conditions, la pente *P* des électrodes peut être fixée égale à l'unité dans les calculs.

Le terme ε, proche alors de $\log\gamma_H$, est déterminé pour le même couple d'électrodes; à partir d'un dosage acide fort–base forte [expressions (1), (4)] on obtient:

$$\varepsilon = -0{,}077 \pm 0{,}001$$

soit

$$\gamma_H \sim 0{,}838.$$

La potasse est dosée par le phtalate acide de potassium, le titre total $H_x^0 = -[K^+]_T = -0{,}1006 \pm 0{,}001$, qui seul reste constant, est retenu pour les calculs ultérieurs.

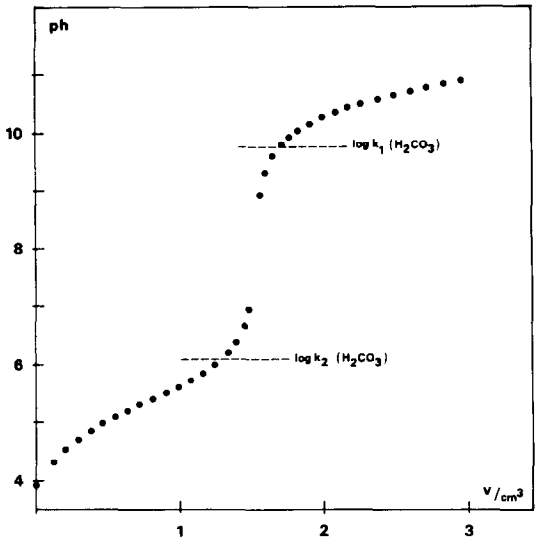


Fig. 2.

RESULTATS ET DISCUSSION

Pour un affinement donné, les valeurs des paramètres et des incertitudes ($3\sigma_i$) portées dans les tableaux 1 et 2 sont les moyennes des résultats relatifs à chacune des douze courbes de neutralisation.

Choix de la pondération

Libérons nous d'abord du rôle de la pondération. D'après la résolution de l'appareillage (pH-mètre, burette) la pondération correcte correspond à $\sigma_{0v}/\sigma_{0pH} = 1$. Le tableau 1 permet de comparer les valeurs moyennes des résultats obtenus avec $\sigma_{0v}/\sigma_{0pH} = 1$ ainsi qu'avec les poids extrêmes ($\sigma_{0v} = 1$, $\sigma_{0pH} = 0$) et ($\sigma_{0v} = 0$, $\sigma_{0pH} = 1$), dans le cas d'un affinement typique de C_1^0, β_{11}, β_{12} du protolyte initial ainsi que de la concentration du carbonate ajouté.

Il a été vérifié à l'aide de tous les affinements décrits par la suite (voir tableau 2), que la pondération influait toujours de la même façon sur les résultats, principalement en ce qui concerne les domaines d'incertitude.

L'examen de ces résultats permet de choisir entre les différentes pondérations. Bien qu'il soit plus rigoureux de tenir compte des incertitudes sur v et pH par l'intermédiaire de σ_{0v} et σ_{0pH} appropriés, on constate:

—que l'affinement sur le pH atténue particulièrement la précision sur les constantes de stabilité: des observations faites par ailleurs[29] ont montré qu'il favorisait plutôt les concentrations car les poids W_n augmentent considérablement dans les zones d'équivalence où $\partial v_c/\partial pH$ diminue. En règle générale il sera préférable d'utiliser cette pondération lorsque les courbes de neutralisation sont utilisées à des fins d'analyse. Il faut alors s'assurer que la réponse de l'électrode est stable vers l'équivalence: l'écart-type σ élevé du tableau 1 semble indiquer qu'il y subsistait un défaut d'équilibre. Pour terminer, signalons que la convergence de l'affinement est généralement beaucoup plus difficile,

Tableau 1. Influence de la pondération
$H_x^0 = -[K^+]_T = -0{,}1006$
$\varepsilon = -0{,}077$
H_2CO_3: $\log\beta_1 = 9{,}78$; $\log\beta_2 = 15{,}9$
Nombre de points moyen par courbe: 38

	Affinement sur le pH $\sigma_{0pH} = 1 \quad \sigma_{0v} = 0$	Affinement pondéré $\sigma_{0pH} = \sigma_{0v} = 1$	Affinement sur le volume $\sigma_{0v} = 1 \quad \sigma_{0pH} = 0$
C_1^0 $(\pm 3\sigma_i)$	$2{,}990(\pm 0{,}009)\cdot 10^{-3}$	$3{,}002(\pm 0{,}006)\cdot 10^{-3}$	$3{,}002(\pm 0{,}007)\cdot 10^{-3}$
$\log\beta_{11}$ $(\pm 3\sigma_i)$	$11{,}181(\pm 0{,}064)$	$11{,}147(\pm 0{,}016)$	$11{,}149(\pm 0{,}013)$
$\log k_{12}$ $(\pm 3\sigma_i)$	$5{,}271(\pm 0{,}005)$	$5{,}275(\pm 0{,}002)$	$5{,}275(\pm 0{,}002)$
carbonate ajouté $(\pm 3\sigma_i)$	$2{,}3(\pm 0{,}3)\cdot 10^{-3}$	$1{,}9(\pm 0{,}2)\cdot 10^{-3}$	$1{,}9(\pm 0{,}2)\cdot 10^{-3}$
$\log K_w$ $(\pm 3\sigma_i)$	$-13{,}843(\pm 0{,}023)$	$-13{,}843(\pm 0{,}005)$	$-13{,}843(\pm 0{,}003)$
écart-type σ	$3{,}1\cdot 10^{-3}$	$0{,}67\cdot 10^{-3}$	$0{,}85\cdot 10^{-3}$

les valeurs à ajuster devant être assez proches des valeurs finales.

—la réponse des électrodes n'étant pas toujours satisfaisante dans les régions de forte pente, il est préférable de ne pas leur donner d'importance particulière lors de la détermination des constantes de stabilité. Ceci revient donc à utiliser l'affinement sur le seul volume ($\sigma_{0pH} = 0$) où le poids des régions tampons est renforcé. L'amélioration des domaines de confiance sur β_{11}, k_{12} et K_w conforte ce choix (voir tableau 1). Notons d'ailleurs que $\sigma_{0pH} = 0$ ne veut pas dire que les erreurs sur le pH sont nulles mais qu'elles sont considérées comme des erreurs sur le volume par l'intermédiaire des expressions de v_c [(3), (4)]. Par la suite, seule la pondération $W_n = 1$ sera utilisée puisqu'elle semble la mieux adaptée à la détermination des constantes de stabilité, les autres paramètres étant considérés ici comme secondaires.

Evidemment tous les résultats se rejoindront pour les courbes ne présentant pas de saut de pH prononcé, c'est à dire lorsque les $\partial v_c/\partial$pH restent du même ordre de grandeur.

Affinements multiparamétriques

Les calculs sont maintenant menés en utilisant différentes stratégies de complexité variable, certaines d'entre elles rejoignent les méthodes habituelles de détermination des constantes d'acidité. Les en-têtes des colonnes du tableau 2 décrivent les expressions utilisées ainsi que les conditions du calcul: celles-ci diffèrent principalement dans les procédés utilisés pour tenir compte du carbonate et dans le nombre de paramètres obtenus. Seules les valeurs affinées sont affectées de trois fois leur écart-type.

Nous ne détaillerons ici que le mode d'obtention des paramètres lorsque la concentration du carbonate est supposée différente dans les deux zones tampon (tableau 2, colonne 1). Le calcul est conduit de manière particulière à partir de l'expression (4):

—tout d'abord il faut choisir le volume v^* (ou le pH*) pour lequel la discontinuité dans le comportement du carbonate est la plus probable. Ce choix est guidé en effectuant différents affinements avec des v^* différents: le tracé de $v^* = f$(écart-type σ_v) présente un minimum pour le volume v^* le plus favorable. Nous obtenons v^* = 1,47 ml qui est légèrement inférieur au volume équivalent (~1,52 ml), le pH* correspondant est voisin de 6,9.

—un affinement global de C_1^0, β_{11}, k_{12}, C_{x1}^*, C_{x2}^* et K_w montre une corrélation importante entre C_1^0, C_{x1}^*, C_{x2}^* et K_w qui gène la convergence. Cet inconvénient ne peut être évité, dans le cas présent, car la précision des données expérimentales est insuffisante: il faudrait travailler avec des volumes de la qualité de ceux délivrés par une seringue micrométrique ($\sigma_{0v} = 2\cdot 10^{-4}$ ml).

Une solution consisterait à fixer K_w qui est calculable dans une autre manipulation (neutralisation d'un acide fort par une base forte). Nous préférons utiliser une technique différente. Nous séparons les paramètres fortement corrélés en deux groupes: en partant des valeurs obtenues lorsque la concentration du carbonate est supposée constante (tableau 2, colonne 4) nous affinons alternativement C_1^0, C_{x1}^*, C_{x2}^*) et (β_{11}, k_{12}, K_w) jusqu'à convergence. La valeur la plus probable de K_w est ainsi obtenue, elle est d'ailleurs très proche de la valeur attendue; celle-ci est alors fixée dans l'affinement des autres paramètres C_1^0, β_{11}, k_{12}, C_{x1}^*, C_{x2}^* (il est vérifié alors que les composés à étudier ne contiennent pas d'impureté totalement dissociée: $H_i^0 = 0$).

Une autre possibilité applicable aux cas difficiles consiste à alléger l'expression (4) en y introduisant le rapport C_{x1}^*/C_{x2}^* comme nouveau paramètre: celui-ci est alors déterminé par ailleurs pour des acides de force équivalente. Signalons qu'il est également possible de fixer C_{x1}^* ou C_{x2}^* dans les calculs: par exemple dans le traitement des données d'une dosage acide fort–base forte, $C_{x1}^* = 0$ tant que le pH est suffisamment acide; la concentration totale en carbonate C_{x2}^* est ainsi obtenue et pourra éventuellement être utilisée par la suite.

L'examen de l'ensemble des résultats montre dans tous les cas que la prise en compte du carbonate réduit l'écart-type σ_v, traduisant une nette amélioration de l'interprétation des données. D'après ce qui a été dit lors de l'établissement de l'expression (4), il est normal de trouver dans la zone la plus acide ($v < v^*$) une concentration en carbonate C_{x1}^* inférieure à celle obtenue dans la seconde (tableau 2, colonne 1);

Tableau 2. Influence du type d'affinement sur les constantes d'acidité ($\log\beta_{11}$, $\log k_{12}$) d'acides aminophosphoniques

$\sigma_{0_V} = 1, \sigma_{0pH} = 0$

$H_x^0 = -[K^+]_T = -0{,}1006$ (①②③④)

$\overline{H_x^0} = -[K^+]_T + C_x^0 = -0{,}0987$ (⑤⑥⑦)

$\varepsilon = -0{,}077$; $P = 1$

Nombre moyen de points par courbe: 38

		①	②	③	④	⑤	⑥	⑦
Solution initiale	C_1^0 ($\pm 3\sigma_i$)	$3{,}010(\pm 0{,}007)\cdot 10^{-3}$	$3{,}022(\pm 0{,}005)\cdot 10^{-3}$	$3{,}012(\pm 0{,}015)\cdot 10^{-3}$	$3{,}002(\pm 0{,}007)\cdot 10^{-3}$	$3{,}002(\pm 0{,}008)\cdot 10^{-3}$	$3{,}013(\pm 0{,}017)\cdot 10^{-3}$	$3{,}002\cdot 10^{-3}$
	$\log\beta_{11}$ ($\pm 3\sigma_i$)	11,140(±0,013)	11,133(±0,013)	11,138(±0,017)	11,149(±0,013)	11,067(±0,026)	11,205(±0,025)	11,190(±0,015)
	$\log k_{12}$ ($\pm 3\sigma_i$)	5,278(±0,002)	5,279(±0,002)	5,277(±0,003)	5,275(±0,002)	5,291(±0,005)	5,296(±0,012)	5,292(±0,010)
Solution ajoutée	Base forte H_x^0	−0,1006	−0,1006	−0,1006	−0,1006	−0,0987	−0,0987	−0,0987
	carbonate C_x^0 ($\pm 3\sigma_i$)	0	$1{,}4(\pm 0{,}2)\cdot 10^{-3}$	$1{,}6(\pm 0{,}5)\cdot 10^{-3}$	$1{,}9(\pm 0{,}2)\cdot 10^{-3}$	0	0	0
	carbonate C_{x1}^* ($\pm 3\sigma_i$)	$1{,}6(\pm 0{,}3)\cdot 10^{-3}$	0	0	0	0	0	0
	carbonate C_{x2}^* ($\pm 3\sigma_i$)	$2{,}0(\pm 0{,}3)\cdot 10^{-3}$	0	0	0	0	0	0
	$\log\beta_1$ de H_2CO_3 ($\pm 3\sigma_i$)	9,78	9,78	9,6(±0,3)	9,78	0	0	0
	$\log\beta_2$ de H_2CO_3 ($\pm 3\sigma_i$)	15,9	15,9	15,8(±0,4)	15,9	0	0	0
	$\log K_w$ ($\pm 3\sigma_i$)	−13,848*	−13,839(±0,004)	−13,840(±0,005)	−13,843(±0,003)	−13,845(±0,012)	−13,794	−13,794
	écart-type σ_y ml	$0{,}86\cdot 10^{-3}$	$0{,}99\cdot 10^{-3}$	$0{,}74\cdot 10^{-3}$	$0{,}85\cdot 10^{-3}$	$3{,}9\cdot 10^{-3}$	$8{,}6\cdot 10^{-3}$	$9{,}0\cdot 10^{-3}$

① Concentration en carbonate différente dans les deux zones tampons, expression (4)
Volume de réactif où se produit la discontinuité $v^* = 1{,}47$, $pH^* = 6{,}9$
(*) $3\sigma_i$ n'a pas de signification, car $\log K_w$ provient d'un affinement alterné

② Concentration en carbonate variant suivant une loi empirique, expression (4) modifiée

③ Concentration en carbonate C_x^0 constante: affinement des constantes de stabilité de H_2CO_3

④ Concentration en carbonate C_x^0 constante

} avec affinement de C_1^0, β_{11}, k_{12}, K_w

⑤ Concentration en carbonate supposée nulle, la concentration en base forte est fixée à une valeur moyenne $\overline{H_x^0} = -0{,}1006 + C_x^0$ (C_x^0 étant la valeur obtenue en ④)

⑥ K_w fixé

⑦ Fixation de la concentration totale de l'acide à étudier C_1^0 déterminée par la méthode des trois tangentes

} réduction du nombre de paramètres à affiner

Tableau 3. Constantes ($\log\beta_1$; $\log k_2$) d'acides aminoalkylphosphoniques

Acide	Méthode graphique		Affinement multiparamétrique	
aminométhylphosphonique	10,00	$5,38^{33}$	10,05	5,39
amino-1 éthylphosphonique	10,15	$5,56^{33}$	$10,19_5$	$5,58_5$
amino-1 propylphosphonique	$10,21_5$	$5,63_5{}^{33}$	$10,25_5$	$5,65_5$
amino-1 butylphosphonique	10,24	$5,66^{33}$	$10,28_5$	$5,67_5$
amino-1 pentylphosphonique	10,25	$5,68_5{}^{33}$	10,29	5,70
amino-1 méthyl-2 propylphosphonique	10,31	$5,77_5{}^{33}$	$10,35_5$	$5,79_5$
amino-1 méthyl-1 éthylphosphonique	$10,28_5$	$5,79^{33}$	10,31	$5,80_5$
amino-2 éthylphosphonique	10,92	$6,22^{34}$	11,05	$6,24_5$
amino-3 propylphosphonique	11,00	$6,87^{35}$	$11,06_5$	$6,88_5$

cependant le courant d'azote n'y déplace pas totalement l'équilibre $H_2CO_3 \rightleftharpoons CO_2(g)+H_2O$. Pour des concentrations faibles en carbonate, pour des temps courts nécessaires à une manipulation et lorsque le domaine de pH recouvre en partie le $\log k_2$ de H_2CO_3 (6,1), il subsiste donc une certaine quantité de carbonate. Nous pouvons retenir les résultats de ce type de calcul, car bien qu'il n'améliore pas l'écart-type, il est plus satisfaisant d'un point de vue chimique. L'utilisation d'une loi empirique de dégagement de CO_2 (tableau 2, colonne 2), bien qu'imparfaite, traduit le même phénomène, les résultats se rapprochant assez des précédents. L'affinement des constantes de stabilité de H_2CO_3, à C_x^0 constant, (tableau 2, colonne 3) en donne des estimations grossières qui recoupent les valeurs attendues: un glissement de celles-ci est cependant observable ce qui est une manière de traduire la variation du comportement du carbonate. Lorsque la concentration en carbonate est supposée constante (tableau 2, colonne 4), les résultats commencent à s'écarter des précédents, mais ils sont encore très acceptables malgré un C_x^0 manifestement trop important.

Il serait concevable d'ajuster de surcroît la pente P des électrodes. Mais les paramètres deviennent trop fortement corrélés ce qui augmente leur incertitude. Il est alors préférable, pour chaque manipulation, d'effectuer une standardisation préalable. Dans ces conditions, nous avons vérifié, à l'aide de dosage acide fort–base forte, que la réponse du couple d'électrodes correspond à une pente égale à l'unité.

Intéressons nous maintenant aux constantes β_{11} et $k_{12} = \beta_{12}/\beta_{11}$. Lorsqu'il est tenu compte du carbonate, les valeurs diffèrent très peu, au plus de quelques millièmes: on peut donc, à la rigueur, choisir indifféremment parmi ces affinements. Dans un contexte différent (zone de pH plus étendue, précision accrue sur les données, concentration en carbonate plus élevée) il faudrait obligatoirement utiliser les équations introduisant un départ de CO_2.

Les méthodes plus classiques (tableau 2, colonnes 5, 6, 7) où le carbonate est négligé, puis K_w fixé... font dévier d'une façon importante les constantes de stabilité. Ceci est particulièrement net en milieu basique: suivant l'hypothèse de calcul, $\log\beta_{11}$ fluctue entre 11,067 et 11,205, soit un domaine de 0,14 unité! L'introduction de la valeur théorique $\varepsilon = -\log\gamma_H$ aurait fait dériver encore plus les constantes d'acidité. Les valeurs de $\log k_{12}$ sont plus cohérentes puisque le milieu est tamponné, d'où une influence moindre des autres paramètres.

Avec ces méthodes classiques, l'écart-type $3\sigma_i$ sur les constantes de stabilité est moins significatif car il ne tient pas compte des omissions ou des erreurs introduites par les paramètres fixés (tableau 2, colonne 7 par exemple). L'écart-type global σ_v indique d'ailleurs que l'interprétation est de moins en moins bonne lorsque le nombre de paramètres fixés croît.

Les considérations précédentes expliquent les divergences constatées dans la bibliographie: les constantes d'acidité calculées sans précautions vont dépendre fortement des conditions expérimentales locales (présence de carbonate, non vérification de la réponse des électrodes ou autre erreur systématique) et ne seront donc valables qu'à un moment donné, pour un réactif donné... Ainsi, nous-mêmes avons dû avoir recours, dans nos premiers travaux relatifs aux acides aminoalkylphosphoniques, aux méthodes graphiques habituelles de détermination des constantes d'acidité: malheureusement, elles accumulent les incertitudes provenant des paramètres fixés ou omis. Des écarts, souvent importants, sont observés lorsque l'on passe de ces méthodes graphiques aux affinements multiparamétriques (tableau 3).

La méthode que nous proposons, en tenant compte d'un maximum de paramètres aboutit à des constantes de stabilité réellement reproductibles. Nous l'avons vérifié pour l'acide aminométhylphosphonique ($NH_2CH_2PO_3H_2$) qui a été étudié à cinq périodes différentes, de 1968 à 1972, avec électrodes et réactifs différents: la reproductibilité entre les $\log\beta_{11}$ et $\log k_{12}$—que l'on peut chiffrer par le calcul de l'écart-type existant entre ces valeurs—est excellente puisqu'elle est de 0,005 unité sur $\log\beta$ (ce qui correspond à la résolution de l'appareil utilisé!).

CONCLUSION

Ce travail montre, s'il en était besoin, que l'affinement multiparamétrique est indispensable pour la détermination des constantes d'acidité car en éliminant toutes les erreurs systématiques il est garant de la fiabilité des résultats.

En plus des paramètres influants déjà envisagés par

ailleurs[1,2] (concentrations totales, impuretés, réponse des électrodes...) nous nous sommes tout particulièrement intéressés aux moyens de prise en compte de l'impureté carbonate, inévitable lorsque le réactif titrant est une base.

Il est possible d'exploiter les manipulations effectuées sous courant d'azote, malgré les altérations de la conservation du carbonate, il est alors nécessaire d'adapter la stratégie à chaque problème particulier:

—lorsque la concentration totale en carbonate est faible (inférieure à 1% du réactif titrant) elle peut être maintenue constante (C_x^0);

—lorsque celle-ci est plus élevée, il est préférable d'utiliser les équations qui introduisent des discontinuités dans la concentration totale en carbonate. Par exemple, pour les acides aminophosphoniques, dont les courbes de neutralisation possèdent deux régions tampons distinctes, il est logique de n'envisager qu'une discontinuité. La base forte se comporte alors comme si, dans une première région elle contenait une concentration C_{x1}^* en carbonate qui devient ensuite C_{x2}^*. Cette discontinuité peut être atténuée en introduisant une fonction semi-empirique qui rendra la variation de concentration plus progressive.

—la cinétique de dégagement de CO_2 se superpose aux équilibres en solution. Il en résulte que les moyens de calcul ne peuvent être qu'approchés, vu l'impossibilité dans laquelle nous sommes d'introduire des relations exactes. La concentration en carbonate doit être considérée comme un terme correctif qui assure cependant une excellente reproductibilité des constantes de stabilité.

Devant ces inconvénients inévitables en milieu ouvert nous proposons une nouvelle technique, qui consiste à travailler en milieu fermé, et dont les fondements sont rigoureux. Les expressions de calcul sont alors appliquées à l'ensemble phase liquide–phase gaz. Le phénomène cinétique subsiste toujours, mais aboutit à un état d'équilibre; si on se donne la peine de l'atteindre, la concentration du carbonate correspondra à sa concentration réelle, sinon elle jouera comme précédemment le rôle d'un terme correctif. Nous utiliserons systématiquement dans l'avenir ce type de procédé, en espérant qu'il se généralisera au détriment de la technique utilisant le passage d'un courant d'azote.

Pour les déterminations de constantes de stabilité, les corrections relatives au carbonate que nous proposons doivent évidemment intervenir en complément des précautions à prendre pour l'obtention de bases fortes aussi peu carbonatées que possible, une concentration faible en carbonate ne pouvant être qu'un élément favorable.

Remarquons que l'analyse des mélanges de protolytes bénéficiera des améliorations apportées ici. En effet, lorsque l'on désire accroître la précision sur les concentrations des différents constituants, il faut être capable de maitriser l'influence du carbonate.

LITTERATURE

1. G. Nowogrocki, J. Canonne et M. Wozniak, *Bull. Soc. Chim. France*, 1976, 5.
2. *Idem, ibid.*, 1976, 1369.
3. L. Z. Benet et J. E. Goyan, *J. Pharm. Sci.*, 1967, **56,** 665.
4. R. Phan-Tan-Luu, J. M. Surzur, J. Metzger, J. P. Aune et C. Dupuy, *Bull. Soc. Chim. France*, 1967, 3274.
5. A. Binder et S. Ebel, *Z. Anal. Chem.*, 1975, **274,** 359.
6. F. Auerbach et E. Smolczyk, *Z. Phys. Chem.*, 1924, **110,** 65.
7. A. Frisque et V. W. Meloche, *Anal. Chem.*, 1954, **26,** 468.
8. F. Ingman et E. Still, *Talanta*, 1966, **13,** 1431.
9. N. Purdie, M. B. Tomson et G. K. Cook, *Anal. Chem.*, 1972, **44,** 1525.
10. A. Ivaska, *Thèse*, Åbo, 1975.
11. C. McCallum et D. Midgley, *Anal. Chim. Acta*, 1975, **78,** 171.
12. F. Ingman, A. Johansson, S. Johansson et R. Karlsson, *ibid.*, 1973, **64,** 113.
13. H. M. Irving, M. G. Miles et L. D. Pettit, *ibid.*, 1967, **38,** 475.
14. G. Carpeni, E. Boitard, R. Pilard, S. Poize et N. Sabiani, *J. Chim. Phys.*, 1972, **69,** 1445.
15. C. Rossi et S. Combet, *Compt. Rend.* 1972, **274C,** 120.
16. V. V. Tsibanov, I. O. Bogatyrev et K. B. Zaborenko, *Zh. Fiz. Khim.*, 1974, **48,** 1613.
17. C. Rossi et S. Combet, *Anal. Chim. Acta*, 1977, **89,** 189.
18. J. J. Kankare, *Anal. Chem.*, 1972, **44,** 2376.
19. *Idem, ibid.*, 1973, **76,** 149.
20. M. Bos et W. Lengton, *Anal. Chim. Acta*, 1975, **76,** 149.
21. D. M. Barry et L. Meites, *ibid.*, 1974, **68,** 435.
22. D. M. Barry, L. Meites et B. H. Campbell, *ibid.*, 1974, **69,** 143.
23. T. N. Briggs et J. E. Stuehr, *Anal. Chem.*, 1974, **46,** 1517.
24. L. Pehrsson, F. Ingman et S. Johansson, *Talanta*, 1976, **23,** 769.
25. *Idem, ibid.*, 1976, **23,** 781.
26. L. Mønsted et O. Mønsted, *Acta Chem. Scand.*, 1976, **A30,** 203.
27. P. Brauner, L. G. Sillén et R. Whiteker, *Arkiv Kemi*, 1969, **31,** 365.
28. G. Baldwin et L. G. Sillén, *ibid.*, 1969, **31,** 391.
29. M. Wozniak, *Thèse*, Lille, 1977.
30. W. E. Wentworth, *J. Chem. Educ.*, 1965, **42,** 96.
31. H. G. Mendelbaum, F. Madaule et M. Desgranges, *Bull. Soc. Chim. France*, 1973, 1619.
32. I. Nagypál, *Acta Chim. Acad. Sci. Hung.*, 1974, **82,** 29.
33. M. Wozniak, J. Nicole et G. Tridot, *Bull. Soc. Chim. France*, 1972, 4445.
34. *Idem, Chim. Anal. Paris*, 1972, **54,** 147.
35. *Idem, Analusis*, 1972, **1,** 498.

Summary—The determinations are based on potentiometric titration data (volume of reagent, potential). To avoid any systematic error, the acidity constants are refined together with every other significant parameter (initial protolyte concentration, concentration of impurities, electrode chain characteristics...) with the program MUPROT. Comparison of the multiparametrically adjusted results with those obtained by the usual methods reveals noticeable discrepancies. Particular attention is paid to carbonate as impurity; to take it into account, modified expressions for the titrant volume are established. The current of nitrogen used in the classical methods shifts the liquid-gas equilibrium of carbonic acid; in that case, only the approximate equations are to be considered. Working with a closed system is proposed as a more rigorous procedure.

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ACIDITES ET COMPLEXES DES ACIDES (ALKYL- ET AMINOALKYL-) PHOSPHONIQUES—II

AFFINEMENT MULTIPARAMETRIQUE APPLIQUE AUX COMPLEXATIONS SUIVIES PAR POTENTIOMETRIE

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Résumé—Le programme d'affinement multiparamétrique MUCOMP ajuste les constantes globales de stabilité des complexes $M_qH_jA_p$ (M: atome central, H: proton et A: coordinat) avec recherche des espèces mineures et compensation des erreurs systématiques (concentrations totales du complexant, du cation, des impuretés; caractéristiques des électrodes). Les données traitées (volume de réactif, potentiel) sont celles des neutralisations du protolyte complexant en présence de cation. Il constitue le dernier élément d'une chaîne de programmes originaux applicables à l'étude des complexations par potentiométrie. Il est testé à partir de l'exemple des complexes cuivriques de l'acide *N,N*-diméthylaminométhylphosphonique. Les résultats obtenus permettent d'envisager son extension à l'analyse des mélanges de cations ou de protolytes.

Lorsque la complexation s'effectue par des centres coordinants qui ont des propriétés acido-basiques, la technique de choix est la protométrie puisqu'elle permet de suivre aisément les neutralisations des protolytes en présence de cations. L'affinement des constantes de stabilité des complexes, que nous décrivons ici, constitue le dernier élément d'une chaîne de programmes adaptée aux études potentiométriques. La stratégie qui y est utilisée peut se résumer ainsi.

—Tout d'abord la neutralisation des protolytes seuls permet, grâce à un ajustement multiparamétrique (programme MUPROT[1–3]) de caractériser correctement les solutions à étudier (concentration totale du coordinat, constantes d'acidité, présence d'impuretés); de plus, elle fournit des renseignements sur le réactif titrant (concentration totale et en carbonate) et la chaîne de mesure (pente des électrodes, décalage d'origine...).

—Il faut ensuite rechercher les espèces en solution. Alors que cette étape est éludée par un grand nombre d'auteurs, nous avons développé une méthode de détection des espèces[4] qui approfondit les travaux existants. A partir des données de neutralisation de mélanges coordinat–métal, elle permet d'obtenir, sans hypothèse initiale, la composition moyenne des complexes et leurs constantes de stabilité approximatives (programmes CONCEA, CONCEM, COMP[5]).

—La dernière étape est l'affinement de ces constantes de stabilité. Comme dans le cas des protolytes seuls, il est nécessaire d'effectuer un ajustement multiparamétrique pour éliminer toutes les erreurs systématiques. A partir des données précédentes, il doit donc permettre:

—d'affiner les constantes de stabilité
—de détecter les espèces mineures
—de retoucher les concentrations totales
—de tenir compte des impuretés et des caractéristiques de la chaîne de mesure avec possibilité de les ajuster.

Rappelons qu'une version simplifiée a d'abord été utilisée au laboratoire: elle a permis de tester les méthodes de détection des espèces[4] puis d'étudier les complexes des acides α-aminophosphonocarboxyliques et α, ω-diaminophosphoniques.[6]

Après avoir établi les équations théoriques et décrit leur traitement, nous relaterons les tests réalisés sur les complexes cuivriques de l'acide *N,N*-diméthylaminométhylphosphonique. Les débouchés importants de ce programme pour l'analyse des solutions seront évoqués.

Travaux antérieurs

Il n'est pas dans notre intention de faire une revue exhaustive des programmes d'affinement des constantes de stabilité des complexes, pour cela nous renvoyons aux mises au point de Childs *et al.*[7] et de Rossotti *et al.*[8] Nous ne parlerons ici que des programmes de traitement des données de la potentiométrie, suffisamment généraux pour s'appliquer au moins au cas des complexes mixtes $M_qH_jA_p$. Le tableau suivant amorce une comparaison; parmi ceux-ci, les programmes les plus utilisés sont le LETAGROP et le SCOGS.

L'évolution des programmes étant constante, il se pourrait qu'à l'heure où nous écrivons, d'autres versions nouvelles ou améliorées aient été réalisées. Tous les programmes, LETAGROP excepté, n'affinent que les constantes de stabilité, les autres

Programmes	Programmes apparentés	Variable choisie pour le calcul des résidus	Méthode de minimisation	Type de dérivation	Paramètres calculés	Pondération	Remarques
LETAGROP[11–19]		E, v, $\bar{n}$, C_H... suivant le bloc utilisé	"Pit mapping"	Numérique	β_{qjp} Ajustement d'autres paramètres dans de "faibles limites" (C_A^0, "dirt acid", E_0, *etc.*...)	Apparemment non utilisée dans les applications	Programme très général applicable à d'autres techniques que la potentiométrie[18,19] Très lourd d'utilisation Surtout appliqué, comme les suivants, au calcul des constantes de stabilité
	MAP[20]	C_H, $\bar{n}$			β_{qjp}	oui, avec la variable C_H	
	LS/2[21]	v			β_{qjp}	non	
	ACREF 3A[22,23]	j			$\beta_{qj\ldots p}$	non	
GAUSS[20]		C_H	Gauss		β_{qjp}	oui	Des programmes du même type ont été utilisés par Perrin *et al.*[24,25]
	SCOSUS[26]	C_H			$\beta_{qj\ldots p}$		Calcul d'une seule constante de stabilité
SCOGS[27]		v			$\beta_{qj\ldots p}$	non	Nagypál propose des extensions à ce programme[28]
	VARIAT[29]	Taux de neutralisation			$\beta_{qj\ldots p}$	non	
MINIQUAD[10]		C_A et C_M et C_H, *etc.*		Analytique	$\beta_{qj\ldots p}$	non	Les concentrations libres manquantes sont obtenues dans la même étape que les constantes de stabilité Accepte les indications de plusieurs électrodes LEAST WGN[9], moins général que MINIQUAD, introduit une pondération

paramètres étant supposés exactement connus et irrémédiablement fixés.

D'abord, le calcul des concentrations libres manquantes est généralement effectué par la méthode de Newton–Raphson, qui éventuellement est simultanée à la détermination des β_{qjp}.[9,10] Ensuite les constantes de stabilité approximatives vont être progressivement améliorées en leur appliquant des corrections: ces dernières sont calculées en utilisant la méthode de Gauss ou la technique du "pit-mapping".[11–18] Le calcul des dérivées partielles est alors nécessaire. Malheureusement la presque totalité des auteurs utilisent une dérivation numérique par incrémentation des constantes à affiner

$$\frac{\partial f}{\partial a} = \frac{f(a+\Delta)-f(a-\Delta)}{2\Delta}$$

Celle-ci, très simple à mettre en oeuvre, présente l'inconvénient d'être lente et d'aboutir à des dérivées, donc à des corrections erronnées, si les incréments Δ sont mal choisis. La simplicité de ce calcul explique d'ailleurs la généralité impressionnante de certains programmes: en effet la dérivation étant toujours la même, quel que soit le paramètre, il est plus facile de traiter d'emblée les cas les plus compliqués, même lorsque les fonctions ne sont pas explicites. Nous avons opté pour la dérivation analytique, qui nécessite des expressions différentes suivant le paramètre, mais qui est plus rigoureuse.

Le choix de la variable à partir de laquelle vont être calculés les résidus est très important: la méthode des moindres carrés est basée sur le caractère aléatoire de l'erreur, il faudra éviter d'utiliser des variables essentiellement sujettes aux erreurs systématiques ou fonctions auxiliaires des autres variables ($\bar{n}, Z, \bar{q}\ldots$) qui accumulent les incertitudes. Si plusieurs variables sont entachées d'erreur et s'il est impossible d'en tenir compte, il est alors préférable de choisir celle qui comporte la plus grande incertitude. Les résidus doivent avoir une signification directement interprétable sur la courbe expérimentale.

Pour ces diverses raisons, nous pensons qu'il est souhaitable d'utiliser directement les données de la potentiométrie (volume de réactif v ou potentiel E). En effet les résidus relatifs aux concentrations totales (C_A, C_M, C_H), qui peuvent englober erreurs systématiques et erreurs aléatoires, sont déjà moins tangibles que les précédents, ceux qui correspondent aux fonctions auxiliaires l'étant encore moins. Avec ce dernier type de variables, les données expérimentales de départ et recalculées peuvent s'éloigner notablement. Lorsque la variable utilisée dans l'affinement varie trop fortement ($[H^+]$ par exemple), sa variance σ^2 n'est plus constante: il faut alors effectuer une pondération du type $1/\sigma^2$. L'introduction de tels poids est souvent superflue.[8]

L'originalité de notre programme réside dans les deux points suivants.

—A la différence des méthodes d'affinement habituelles où l'erreur expérimentale est reportée sur une seule variable, nous minimisons une somme de résidus où les erreurs sur les deux variables (volume et potentiel) sont prises en compte.

—Les erreurs systématiques peuvent être éliminées car nous nous donnons la possibilité d'affiner, outre les constantes de stabilité, tous les autres paramètres influents (concentrations totales, caractéristiques de la chaîne de mesure). Jusqu'à présent, seul LETAGROP était capable de compenser partiellement ce type d'erreur. Ceci permettra d'ailleurs d'appliquer ce programme à l'analyse des solutions (dosage de mélanges de cations, de complexants, *etc.*...).

PRINCIPAUX SYMBOLES

Cette liste de symboles complète ou modifie celle de l'article précédent.[3]

A	Forme totalement ionisée du coordinat
a, m, h	Concentrations de A, M, H libres
C_A	Concentration totale en A ; $C_A = \sum p\beta_{qjp} m^q h^j a^p$
C_H	Concentration totale des H liés
C_M	Concentration totale en M ; $C_M = \sum q\beta_{qjp} m^q h^j a^p$
L	Nombre de paramètres à affiner
M	Atome central
NP	Nombre de points expérimentaux
$\bar{n}$	Nombre moyen de coordinats par atome central
q, j, p	Coefficients des complexes $M_qH_jA_p$
y	Indication du potentiomètre (pH ou E)
α	Paramètre à affiner
β_{qjp}	Constante globale de stabilité $\beta_{qjp} = [M_qH_jA_p](m^p h^j a^p)^{-1}$
Δ	Correction
$\{x\}$	Valeur de x au début ou en cours d'affinement

Pour simplifier, les charges sont omises.

EXPRESSION DU VOLUME DE REACTIF CALCUL DE LA CONCENTRATION EN H^+

Comme pour les protolytes seuls, c'est l'équation de conservation en protons qui est utilisée. Cette fois nous nous limitons volontairement au cas d'un seul protolyte, susceptible de former des complexes $M_qH_jA_p$, de concentration totale initiale C_A^0. La seule impureté envisagée, outre l'acidité forte H_i^0, est le carbonate (concentration initiale C_i^0, ajoutée C_x^0); la solution est neutralisée par une base forte de titre H_x^0 ($H_x^0 < 0$). Vu l'écriture des expressions suivantes, il faut introduire le titre total en base forte dans les calculs ($H_x^0 = -[K^+]_T$).

Etant donné que l'acide carbonique participe à un équilibre liquide–gaz, il est nécessaire, pour satisfaire à la conservation des masses, de travailler en système fermé:[3] le nombre de moles de CO_2 dans la phase gaz (n_{CO_2}) est alors introduit dans l'équation suivante:

$$\frac{v_0}{v_0+v}(H_i^0 + N_A C_A^0 + 2C_i^0) + \frac{v}{v_0+v}(H_x^0 + 2C_x^0)$$
$$= \sum j[M_qH_jA_p] + 2\left\{\frac{n_{CO_2}\cdot 10^3}{v_0+v} + [H_2CO_3]\right\}$$
$$+ [HCO_3^-] + [H^+]$$

Le terme $\sum j[M_qH_jA_p]$ englobe les espèces complexées (q, H, $p \neq 0$), les formes acides du coordinat ($q = 0$, $p = 1$), les complexes hydroxylés du cation ($p = 0$, $j < 0$) et également la concentration libre en OH^- ($q = p = 0$, $j = -1$, $\beta_{0-10} \equiv K_w$). En posant $\bar{n}_H$, nombre moyen de H liés au carbonate, nous aboutissons à:

$$v_c = v_0 \frac{H_i^0 + N_A C_A^0 - \sum j\beta_{qjp} m^q h^j a^p + (2 - \bar{n}_H) C_i^0 - h}{-H_x^0 + \sum j\beta_{qjp} m^q h^j a^p - (2 - \bar{n}_H) C_x^0 + h} \quad (1)$$

avec

$$\bar{n}_H = \frac{2(G+1)\beta_2 h^2 + \beta_1 h}{(G+1)\beta_2 h^2 + \beta_1 h + 1} \text{ où } G = \left(\frac{v_g - v}{v_0 + v}\right) \frac{1}{RTK_p}.$$

Cette expression est rigoureuse. Cependant, comme nous l'avons vu lors de l'établissement des équations relatives aux protolytes seuls,[3] il est possible d'utiliser des expressions approchées pour traiter les neutralisations effectuées avec passage d'un courant d'azote. Pour simplifier, nous nous limitons alors au cas où le carbonate n'est présent que dans la base forte titrante. En milieu ouvert, la base se comporte comme si elle contenait plus ou moins de carbonate, cette quantité dépendant surtout du pH de la solution en cours de neutralisation.

—On peut supposer une discontinuité dans la concentration totale en carbonate: la base se comporte alors comme si elle contenait une concentration C_{x1}^* en carbonate qui devient C_{x2}^* à partir du point (v^*, pH*). Le volume calculé v_c est obtenu en retouchant l'expression (1) où

$$\begin{cases} n_H = \{2\beta_2 h^2 + \beta_1 h\}\{\beta_2 h^2 + \beta_1 h + 1\}^{-1} \\ \text{pour } v < v^* \quad C_i^0 = 0 \quad C_x^0 = C_{x1}^* \\ \text{pour } v > v^* \quad C_i^0 = \dfrac{v^*}{v_0}(C_{x1}^* - C_{x2}^*) \quad (C_x^0 = C_{x2}^*) \end{cases}$$

—Il est également possible d'utiliser une fonction empirique de dégagement de CO_2 (f); il suffit dans l'expression (1) de faire:

$$\begin{cases} C_i^0 = 0 \\ C_x^0 = C_x^0 \times f \end{cases}$$

Il est évidemment concevable d'élargir l'expression (1) en y introduisant d'autres paramètres (acidités et complexes mixtes $M_qH_jA_pB_r$ faisant intervenir un autre complexant, complexation de deux cations par un même protolyte, *etc.*...).

Rappelons que la concentration en H^+ est obtenue à partir de l'indication du potentiomètre et des caractéristiques de la chaîne de mesure.[2,3]

TRAITEMENT MATHEMATIQUE

Determination de a *et* m *libres* (*méthode de Newton–Raphson*)

Les concentrations libres a et m sont calculées par la méthode de Newton–Raphson, à partir des expressions de C_A et C_M. Les corrections $\Delta a/\{a\}$ et $\Delta m/\{m\}$ ainsi obtenues donnent de nouvelles valeurs $\{a\}'$ et $\{m\}'$, avec

$$\{a\}' = \{a\}\left(1 + \frac{\Delta a}{\{a\}}\right), \quad \{m\}' = \{m\}\left(1 + \frac{\Delta m}{\{m\}}\right)$$

Pour freiner les corrections qui risquent d'être exagérées lorsque les valeurs initiales $\{a\}$, $\{m\}$ sont fortement erronées, on assimile $\Delta a/\{a\}$ à $\Delta(\ln a)$, la nouvelle valeur est alors:

$$\{a\}' = \{a\}\, e^{\Delta a/\{a\}}$$

Ce frein évite aux concentrations de devenir négatives et permet ainsi la poursuite du calcul.

Cette approximation est licite en fin de calcul où $\Delta a/\{a\} \to 0$ et $e^{\Delta a/\{a\}} \sim 1 + \Delta a/\{a\}$. Ce type de correction est également employé dans le calcul des constantes de stabilité, il y est même indispensable car certaines estimations initiales peuvent être très éloignées des valeurs finales.

Au premier cycle, à partir de h, v, C_A, C_M, des valeurs approximatives de $\{\beta_{qjp}\}$ et d'estimations grossières $\{a\}$ et $\{m\}$, de meilleures valeurs $\{a\}'\{m\}'$ sont obtenues. Les itérations sont poursuivies tant que $\Delta a/\{a\}$ et $\Delta m/\{m\}$ dépassent un seuil de précision fixé (ici 10^{-6}). Pour accélérer le calcul dans le cycle suivant, ces valeurs de a et m sont utilisées comme estimations initiales $\{a\}$, $\{m\}$.

Affinement des paramètres par la méthode des moindres carrés

Les paramètres à déterminer sont affinés par la méthode classique des moindres carrés. Les éléments les plus marquants du programme que nous proposons sont les suivants.

(*a*) Il est basé sur une expression générale du volume de réactif.

(*b*) Rappelons qu'une réduction du nombre de variables aboutit à un coefficient de pondération[3]

$$W_n = \frac{1}{\sigma_{0v}^2 + \sigma_{0y}^2 \left(\dfrac{\partial v_{nc}}{\partial y_n}\right)^2}$$

où σ_{0v}^2 et σ_{0y}^2 sont les variances relatives estimées, sur le volume de réactif v et sur le potentiel y, ce terme introduit dans

$$S = \sum W_n (v_n - v_{nc})^2$$

permet de tenir compte dans l'affinement des incertitudes sur les deux variables expérimentales.

(*c*) De plus, c'est un affinement multiparamétrique. Comme nous disposons des données de courbes de neutralisation pour divers C_A^0, C_M^0, il est nécessaire pour éliminer les erreurs systématiques, d'utiliser la stratégie suivante où les paramètres sont divisés en deux classes:

—la première concerne les constantes de stabilité β_{qjp} qui sont affinées sur l'ensemble des données (NP $= NP_1 + NP_2 + \ldots$).

—tandis que les paramètres affectés d'erreurs systématiques (concentrations totales, caractéristiques de la chaîne de mesure) sont ajustés à partir

des groupes de points (NP_1, NP_2,...) que constituent les différentes courbes de neutralisation.

Dans ce cas, les valeurs des paramètres qui minimisent S ($\partial S/\partial\alpha_l = 0$; $\partial S/\partial\beta_l = 0$) sont obtenues à partir d'un système de L équations dont la représentation matricielle est celle de la figure 1, que l'on peut noter:

$$A = B \times \Delta$$

Le vecteur Δ, dont les éléments aboutissent aux corrections à apporter aux paramètres, est obtenu en multipliant par la matrice de covariance B^{-1}, soit:

$$B^{-1} \times A = \Delta$$

Notons que ce sont les corrections relatives ($\Delta\alpha_l/\alpha_l$ et $\Delta\beta_l/\beta_l$) qui sont introduites pour les mêmes raisons que dans le calcul des concentrations libres a et m.

(*d*) Les dérivées partielles ($\partial v_c/\partial \ln\alpha_l$ et $\partial v_c/\partial \ln\beta_l$) nécessaires à l'obtention de ces corrections, sont calculées à partir de leurs expressions analytiques.

Programme MUCOMP

Le programme MUCOMP (affinement MUltiparamétrique appliqué à la COMplexation par les Protolytes) est écrit en ALGOL 60 pour ordinateur CII 10070; une nouvelle version est en cours d'adaptation pour calculateur Hewlett–Packard 9825.

Les entrées principales en sont:

—les données (v, y) relatives à différentes courbes de neutralisation,

—les coefficients entrant dans l'expression de v_c; la formule des complexes,

—les valeurs des paramètres (constantes de stabilité, concentrations, caractéristiques de la chaîne de mesure): elles peuvent être très approximatives pour les paramètres que l'on a choisi d'affiner,

—les variances relatives σ^2_{0v} et σ^2_{0y} qui sont habituellement estimées à partir de la résolution des appareils.

Ces différentes valeurs permettent de calculer successivement $[H^+]$, a et m, v_c, $\partial v_c/\partial \ln\alpha_l$ et $\partial v_c/\partial \ln\beta_l$, ce qui aboutit aux corrections à apporter aux paramètres à affiner; les cycles de calcul sont repris jusqu'a convergence satisfaisante.

La sortie des résultats comprend:

—un tableau y, $-\log[H^+]$, a, m, v, v_c, résidu, $\bar{n}$

—les écarts-types correspondant aux différentes courbes; l'écart-type global σ

—les valeurs des paramètres affinés, les domaines de confiance $3\sigma_i$, les coefficients de corrélation entre paramètres

—accessoirement la répartition des différentes espèces.

Remarques

L'expression de v_c (1) a été volontairement établie en la limitant aux paramètres qui, dans notre cas, interprètent au mieux les courbes de neutralisation. La contribution des complexes des ions du sel de fond (ici K^+ et NO_3^-), insignifiante, n'a pas été introduite dans les expressions de C_A et C_M. Donc, dans l'état actuel du programme, les paramètres affinables sont:

β_{qjp}, C^0_A, C^0_M, H^0_i, concentrations du carbonate, ε, P

Le calcul des corrections est réitéré jusqu'à atteindre un critère d'arrêt qui est basé sur le calcul matriciel; celui-ci permet de calculer la somme:

$$S^* = \sum (v_n - v_{nc}) \frac{\partial v_{nc}}{\partial \alpha_l} \Delta\alpha_l$$

qui s'annule lorsque les corrections deviennent négligeables. Dans le programme, nous introduisons donc un nouvel écart-type $\sigma^* = \sqrt{(S-S^*)/(NP-L)}$

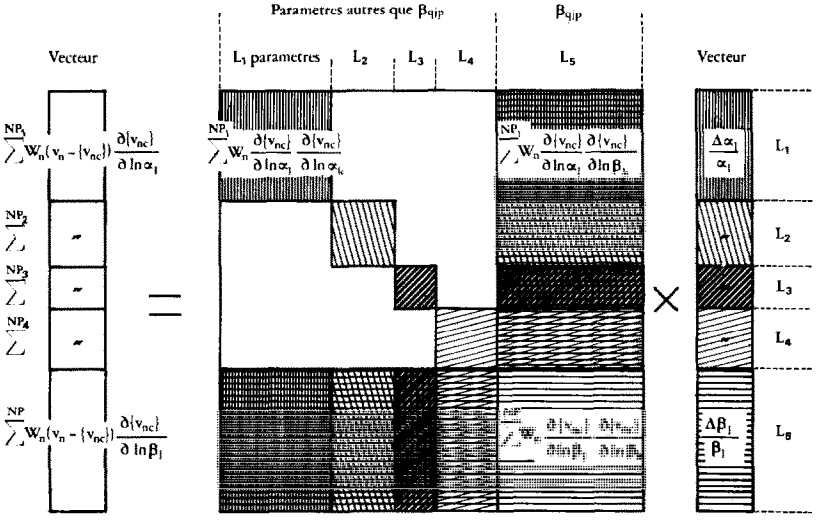


Fig. 1.

qui tend vers le précédent lorsque l'affinement converge.

Les termes diagonaux $B^{-1}(i,i)$ de la matrice de covariance fournissent une estimation des écarts-types σ_i sur les valeurs affinées

$$\frac{\sigma_i}{\alpha_i} = \sigma\sqrt{B^{-1}(i,i)}$$

Nous prendrons $3\sigma_i$ comme erreur sur un paramètre; lorsqu'une constante de stabilité β_{qjp} devient inférieure ou de l'ordre de $3\sigma_i$, l'espèce correspondante est considérée comme inexistante. L'erreur sur les $\log\beta_{qjp}$ n'est égale à $(\sigma_i/\beta_{qjp}/\ln 10)$ que lorsque $\sigma_i \ll \beta_{qjp}$; calculé de cette manière, l'écart-type sur les "log" est d'autant plus erroné que σ_i/β_{qjp} est grand.

Il est possible, dans les cas compliqués traitant un grand nombre d'inconnues ou lorsque la convergence est difficile, d'effectuer des affinements alternés. Le calcul est alors mené sur une partie des paramètres jusqu'à minimisation des résidus, puis certains d'entre eux sont fixés et de nouveaux paramètres sont affinés et ainsi de suite... De très bonnes estimations sont ainsi obtenues, cependant il est indispensable de terminer par un affinement global.

Il est envisageable de supposer qu'un paramètre à affiner—parmi C_A^0, C_M^0, H_i^0, concentrations du carbonate, ε, P—est commun à toutes les neutralisations: des formes matricielles plus classiques sont alors retrouvées où ces paramètres communs figurent, comme les β_{qjp}, pour toutes les données (Fig. 1).

Exemple

Ici, une seule application de ce programme, concernant les complexes cuivriques de l'acide *N*,*N*-diméthylaminométhylphosphonique $(CH_3)_2N^+HCH_2PO_3H^-$ est décrite. Elle permet de comparer les résultats obtenus en effectuant différents types d'affinements (introduction de différentes pondérations, essais d'espèces mineures...). La recherche des erreurs systématiques est réalisée en retouchant les paramètres autres que les constantes de stabilité (C_A^0, C_M^0, C_x^0,...).

PARTIE EXPERIMENTALE

Les neutralisations des mélanges C_A^0, C_M^0 (Fig. 2) sont conduites de la même façon que pour les protolytes seuls (à 25°, force ionique 0,100*M* en KNO_3, réactif titrant identique, chaîne de mesure standardisée, passage d'un courant d'azote au dessus de la solution,...).[3]

Pour atténuer les erreurs, la solution de Cu^{2+} est dosée, après échange sur résine cationique sous forme H^+, par la base forte précédente, d'où C_M^0.

Les données expérimentales (v, pH) correspondent aux rapports $C_A^0/C_M^0 \sim 2$ ($v_0 = 50{,}00$ ml) et $C_A^0/C_M^0 \sim 3$ ($v_0 = 33{,}35$ ml) avec $C_M^0 = 1{,}512\cdot10^{-3}M$.

Neutralisation du protolyte seul

La neutralisation de l'acide seul aboutit aux paramètres qui sont généralement maintenus constants dans les calculs ultérieurs: constantes d'acidité β_{0j1}, K_w, C_A^0, concentration(s) du carbonate, H_i^0, ε et éventuellement la pente P des électrodes.

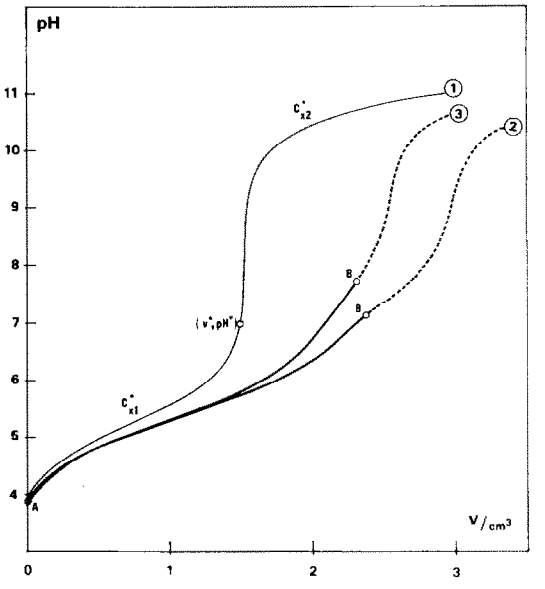


Fig. 2.

Comme les neutralisations sont effectuées avec passage d'un courant d'azote il est préférable d'envisager les équations qui supposent une discontinuité dans la concentration du carbonate [équation (4) de la partie I[3]].

Les valeurs moyennes suivantes sont ainsi obtenues:

$\log\beta_{011} = 11{,}063$ ($\pm 0{,}009$)
$\log\beta_{021} = 16{,}247$ ($\pm 0{,}01$) ou $\log k_{021} = 5{,}184$ ($\pm 0{,}004$)
$\log K_w = -13{,}848$
$\{C_A^0 = 3{,}019\cdot10^{-3}$ ($\pm 0{,}014\cdot10^{-3}$) pour $v_0 = 50{,}00$ ml
$(C_A^0/C_M^0 \sim 2)$
$\{C_A^0 = 4{,}526\cdot10^{-3}$ ($\pm 0{,}014\cdot10^{-3}$) pour $v_0 = 33{,}35$ ml
$(C_A^0/C_M^0 \sim 3)$
$C_{x1}^* = 1{,}4\cdot10^{-3}$ ($\pm 0{,}4\cdot10^{-3}$)
$C_{x2}^* = 1{,}8\cdot10^{-3}$ ($\pm 0{,}3\cdot10^{-3}$)

Le protolyte de départ est exempt de carbonate ($C_i^0 = 0$) ou d'impureté totalement dissociée ($H_i^0 = 0$). Les termes ε et P n'étant déterminés conjointement qu'avec une précision médiocre, sont obtenus dans les mêmes conditions opératoires par dosage acide fort–base forte ($\varepsilon = -0{,}077$; $P = 1{,}00$).

Remarque

Fortuitement, le point (v^*, pH*) qui limite, dans la neutralisation de l'acide seul, le premier domaine où la concentration en carbonate est C_{x1}^* (Fig. 2), est proche du pH supérieur d'étude des complexes (point B, Fig. 2). On peut donc directement utiliser l'expression (1) de v_c où $C_x^0 = C_{x1}^* = 1{,}4\cdot10^{-3}$.

Sinon il faudrait introduire dans v_c les valeurs de C_{x1}^* et C_{x2}^*. Lorsque le pH final d'étude des complexes est assez proche de pH*, il est possible, pour simplifier, de traiter les courbes de neutralisation de l'acide seul en choisissant comme pH*, le pH final d'étude des complexes.

Avec ces précautions, les perturbations provoquées par l'acide carbonique sont compensées au mieux: son influence dans l'expression de v_c a alors toute chance d'être reproductible d'une neutralisation à l'autre.

Neutralisation du cation seul

Différentes solutions de Cu^{2+} de concentration totale initiale C_M^0 sont neutralisées par la potasse. Dans nos conditions expérimentales ($\mu = 0{,}1$ en KNO_3 à 25°) l'espèce

prédominante détectée est $Cu_2(OH)_2^{2+}$, avec:

$$\log \beta_{2\,-2\,0} = -10{,}7_2\ (\pm 0{,}1)$$

Contrairement aux travaux d'Achenza,[30,31] la présence de $CuOH^+$ s'avère ici improbable.

Affinements et recherche des espèces mineures

L'étude des variations de fonctions non explicites[4] aboutit à la détection des formes complexées prédominantes et à l'obtention de leurs constantes de stabilité approximatives (programmes CONCEA, CONCEM, COMP[5]).

Dans le cas de l'acide $(CH_3)_2N^+HCH_2PO_3H^-$ (abréviation H_2A) nous écourtons cette étape en nous basant sur les résultats obtenus pour un grand nombre d'acides analogues où les formes détectées sont:

$$CuHA,\quad CuA,\quad CuH_2A_2,\quad CuHA_2,\quad CuA_2$$

Les constantes β_{qjp} à affiner sont estimées à partir de celles d'un acide comparable, ici l'acide aminométhylphosphonique. Pour dégrossir le problème une seule pondération est utilisée ($\sigma_{0v} = 1$, $\sigma_{0y} = 0$). Les données de pH supérieur à 7,13 ($C_A^0/C_M^0 \sim 2$) et 7,74 ($C_A^0/C_M^0 \sim 3$) ne sont pas utilisées car le pH dérive alors légèrement, indiquant une précipitation imperceptible, qui comme nous le verrons, peut être celle d'un phosphonate basique de cuivre.

Avec les hypothèses précédentes l'affinement converge mais n'est pas satisfaisant:

—l'écart-type qui est de $6 \cdot 10^{-3}$ ml est trop élevé compte tenu de la précision de l'appareillage: il devrait être proche de 10^{-3} ml pour un affinement correct

—l'aspect des résidus en fin de courbe est anormal et indique que l'interprétation n'y est pas correcte: il faut donc introduire un complexe plausible en milieu basique. Nous pensons immédiatement à Cu(OH)A ou $Cu_2(OH)_2A_2$ car le complexe hydroxylé de Cu^{2+} est condensé. Les calculs sont repris en ajoutant ces espèces: l'introduction de β_{1-11} améliore nettement l'écart-type ($\sigma_v = 0{,}8 \cdot 10^{-3}$ ml), alors que celle de β_{2-22} ne le modifie pas ($\sigma_v = 6{,}0 \cdot 10^{-3}$ ml) rendant improbable l'existence de $Cu_2(OH)_2A_2$.

Influence de la pondération

Le tableau 1 regroupe les résultats relatifs à l'utilisation de quelques pondérations ($\sigma_{0y} = 1$, $\sigma_{0v} = 0$) ($\sigma_{0y} = 1$, $\sigma_{0v} = 1$) ($\sigma_{0y} = 0$, $\sigma_{0v} = 1$), la pondération statistique ($\sigma_{0y} = 1$, $\sigma_{0v} = 1$) devrait, théoriquement, traduire au mieux les incertitudes expérimentales. Tous les paramètres autres que les β_{qjp} sont maintenus constants aux valeurs obtenues par neutralisation de l'acide seul. Pour une comparaison plus aisée, les valeurs comportent un excès de chiffres significatifs.

La pondération statistique implique que les variances σ_{0v}^2 et σ_{0y}^2 restent constantes. Alors que cette condition est réalisée pour σ_{0v}^2, il est bien connu que les défauts de réponse de l'électrode de verre s'accentuent dans les zones de forte pente ($\partial y/\partial v$): il est donc concevable d'admettre que la variance expérimentale sur l'indication y de la chaîne de mesure est une fonction croissante de ($\partial y/\partial v$), impossible à expliciter. L'utilisation d'un terme de la forme $\sigma_{0y} \cdot f(\partial y/\partial v)$ au lieu de σ_{0y} dans l'expression de W_n atténuera, annulera ou même inversera l'influence de ($\partial v/\partial y$) dans le terme de la pondération. Nous avons choisi un juste milieu dans la prise en compte de la variance réelle sur y ce qui nous amène à préférer une pondération où W_n reste constant. En d'autres termes, alors que les calculs statistiques nous conduisent à accorder une grande confiance aux points où ($\partial y/\partial v$) est élevé, les constatations expérimentales (défauts d'équilibre) nous obligent à être plus modestes dans l'utilisation des zones correspondantes. Cependant, si en améliorant la saisie des données (contrôle rigoureux de la dérive) on arrive à s'assurer que la variance σ_{0y}^2 est la même pour tous les points, il faudra rétablir la pondération statistique.

Un autre argument consiste à dire, comme dans l'étude d'acides seuls, qu'il est préférable d'ajuster les constantes de stabilité dans les domaines de pH où leur influence est prédominante: il n'est donc pas anormal d'utiliser un poids constant car celui-ci ne donne pas d'importance particulière aux données relatives aux sauts de potentiels.

A l'inverse, les affinements utilisant la seule variable y (pH ou E), en donnant une précision illusoire aux points des zones de forte pente, risquent d'altérer les résultats, essentiellement ceux concernant les constantes de stabilité.

Ces observations ont été avancées par souci de rigueur, car, d'un point de vue plus pratique, comme les ($\partial y/\partial v$) varient ici dans des limites raisonnables, la pondération affecte peu les résultats (voir tableau 1).

Calcul des autres paramètres et recherche des erreurs systématiques

L'affinement des autres paramètres, outre l'intérêt qu'il présente dans l'analyse des solutions permet également la recherche et la compensation des erreurs systématiques; cette possibilité intervient en complément des moyens indiqués précédemment (répartition non aléatoire des résidus, écart-type global élevé) qui avaient permis de détecter les erreurs systématiques dues à l'omission des espèces mineures.

Le tableau 2 regroupe quelques exemples d'affinements multiparamétriques. Seules les valeurs affinées comportent une incertitude, l'erreur sur les "log" est systématiquement égale à $3(\sigma_i/\beta_{qjp}/\ln 10)$.

Les concentrations totales C_A^0, C_M^0 et C_x^0 sont correctement retrouvées (tableau 2, b, c, d): si ce n'était pas le cas, il faudrait reconsidérer le problème en recherchant d'autres espèces mineures jusqu'à se rapprocher des C_A^0, C_M^0 et C_x^0 attendus. L'écart-type global est inchangé indiquant l'inexistence d'erreurs systématiques rattachées à ces concentrations. Seuls les affinements de C_A^0 et éventuellement de C_x^0 nous semblant ici réalistes: en effet, la précision sur C_M^0 est faible et il vaut mieux se fier alors aux résultats d'une autre méthode de dosage.

Dans certaines déterminations, dont nous reparlerons dans une publication ultérieure, le calcul de C_A^0 s'avère indispensable: certains acides aminophosphoniques se dégradent en solution ce qui interdit le passage par

Tableau 1. Influence de la pondération

	$\sigma_{0v} = 0$, $\sigma_{0y} = 1$	$\sigma_{0v} = 1$, $\sigma_{0y} = 1$	$\sigma_{0v} = 1$, $\sigma_{0y} = 0$
$\log \beta_{111}(3\sigma_i)$	13,369(0,016)	13,367(0,011)	13,366(0,011)
$\log \beta_{101}(3\sigma_i)$	7,993(0,007)	7,992(0,005)	7,992(0,005)
$\log \beta_{1-11}(3\sigma_i)$	0,208(0,018)	0,211(0,018)	0,211(0,019)
$\log \beta_{122}(3\sigma_i)$	26,02(0,18)	26,06(0,11)	26,06(0,10)
$\log \beta_{112}(3\sigma_i)$	20,839(0,060)	20,842(0,040)	20,843(0,037)
$\log \beta_{102}(3\sigma_i)$	13,862(0,023)	13,858(0,024)	13,857(0,026)
σ	$1{,}7 \cdot 10^{-3}$	$0{,}7 \cdot 10^{-3}$	$0{,}8 \cdot 10^{-3}$

Tableau 2. Affinements multiparamétriques

	a	b	c	d	e	f
$\log \beta_{2\text{-}20}(3\sigma_i)$	−10,72	−10,72	−10,72	−10,72	−10,72	−10,8(0,5)
$\log \beta_{111}(3\sigma_i)$	$13{,}36_6$(0,01)	13,36(0,02)	$13{,}36_5$(0,01)	$13{,}36_6$(0,01)	$13{,}3_9$(0,14)	$13{,}36_6$(0,01)
$\log \beta_{101}(3\sigma_i)$	7,992(0,005)	7,99(0,03)	7,99(0,03)	$7{,}99_0$(0,01)	8,00(0,08)	$7{,}99_4$(0,01)
$\log \beta_{1-11}(3\sigma_i)$	0,21(0,02)	0,20(0,07)	$0{,}1_8$(0,13)	0,20(0,09)	0,23(0,12)	0,21(0,02)
$\log \beta_{122}(3\sigma_i)$	$26{,}0_6$(0,1)	$26{,}0_8$(0,13)	$26{,}0_8$(0,12)	$26{,}0_8$(0,11)	26,1(0,6)	$26{,}0_6$(0,10)
$\log \beta_{112}(3\sigma_i)$	20,84(0,04)	$20{,}8_4$(0,13)	$20{,}8_7$(0,14)	20,85(0,08)	20,9(0,6)	20,83(0,06)
$\log \beta_{102}(3\sigma_i)$	13,86(0,03)	13,84(0,06)	$13{,}8_9$(0,13)	$13{,}8_7$(0,15)	13,9(0,3)	13,85(0,03)
$C_A^0(3\sigma) \times 10^3$	3,019	$3{,}02_2$(0,015)	3,019	3,019	3,019	3,019
$C_M^0(3\sigma) \times 10^3$	1,512	1,512	$1{,}51_7$(0,02)	1,512	1,512	1,512
$C_x^0(3\sigma) \times 10^3$	1,4	1,4	1,4	1,5(0,2)	1,4	1,4
$P(3\sigma)$	1,000	1,000	1,000	1,000	0,999(0,007)	1,000
$C_A^0(3\sigma) \times 10^3$	4,526	$4{,}53_1$(0,012H)	4,526	4,526	4,526	4,526
$C_M^0(3\sigma) \times 10^3$	1,512	1,512	$1{,}51_3$(0,01)	1,512	1,512	1,512
$C_x^0(3\sigma) \times 10^3$	1,4	1,4	1,4	1,5(0,3)	1,4	1,4
$P(3\sigma)$	1,000	1,000	1,000	1,000	0,999(0,007)	1,000
$\sigma_v \times 10^3$ ml	0,760	0,762	0,768	0,766	0,769	0,763

75 points expérimentaux
$\sigma_{0r} = 1 \quad \sigma_{0y} = 0$
$\log \beta_{011} = 11{,}063$
$\log \beta_{021} = 16{,}247$
$\log K_w = -13{,}848$
$\varepsilon = -0{,}077$

l'intermédiaire d'une solution stock. Le mélange (C_A^0, C_M^0) est alors préparé juste avant la manipulation par pesée d'acide. Malheureusement l'erreur sur C_A^0 risque alors d'être importante car les masses utilisées sont faibles. Le recours à l'affinement de C_A^0 compensera ce type d'erreur systématique. La concentration C_x^0 du carbonate (tableau 2, d) correspond à celle obtenue pour le protolyte seul (C_{x1}^*) ce qui valide la stratégie adoptée à ce sujet. Les constantes β_{qjp} sont peu altérées, mais comme il fallait s'y attendre leur domaine d'incertitude augmente.

Le calcul de la pente (tableau 2, e) dans ce domaine de pH restreint, est à la limite de la méthode. D'ailleurs l'affinement de P ne peut être retenu car il provoque de forte corrélations entre paramètres ce qui se traduit par des écarts-types σ_i inacceptables. L'affinement du décalage d'origine ε mène aux mêmes constatations. Il est alors préférable de fixer ces paramètres par standardisation de la chaîne de mesure (P et ε reproductibles). Une autre solution serait d'élargir dans la mesure du possible la zone de pH de calcul.

L'obtention de $Cu_2(OH)_2$ (tableau 2, f) confirme l'existence de CuAOH: en effet, les β_{2-20} et β_{1-11} étant corrélés ($U_{ij} = 0{,}9$), il aurait été concevable qu'une valeur erronée de β_{2-20} (tableau 2, a) provoque par compensation l'apparition de l'espèce mineure CuAOH. L'introduction de CuOH à la place de $Cu_2(OH)_2$ augmente les résidus sur le volume; ceux-ci sont encore accrus si ce type de complexe hydroxylé est négligé.

L'affinement simultané des constantes d'acidité β_{0j1} ne donne pas de convergence satisfaisante, vu leur forte corrélation avec les constantes β_{qjp}. Pour terminer indiquons que les limites de la méthode ont été testées en affinant un nombre encore plus grand de paramètres. Certains calculs convergent mais les paramètres deviennent de plus en plus reliés, ce qui accroît les incertitudes.

CONCLUSION

Pour ce qui est du calcul des constantes de stabilité de complexes protonés $M_qH_jA_p$ l'affinement multiparamétrique que nous proposons présente l'originalité

—de tenir compte, en cas de nécessité, des incertitudes sur les deux variables expérimentales (v, pH ou E) par une pondération appropriée

—d'introduire les termes relatifs aux impuretés

—de rechercher et de compenser les erreurs systématiques

—d'employer, pour faciliter l'affinement, un calcul plus rigoureux des dérivées partielles ainsi qu'une stratégie particulière d'obtention des paramètres autres que les constantes de stabilité.

Les constantes de stabilité obtenues sont alors indépendantes des paramètres expérimentaux locaux, ce qui n'était pas réalisé jusqu'à présent.

En outre, des perspectives intéressantes s'offrent pour l'analyse des solutions. En effet, malgré l'absence de saut de potentiel prononcé sur les courbes de neutralisation du protolyte en présence de cation, il a été possible d'obtenir leurs concentrations totales. En utilisant un complexant approprié on pourra doser aisément tout cation; de plus, en élargissant ce programme, le dosage direct de mélanges de cations devient envisageable. Le choix des complexants sélectifs sera grandement facilité par les très nombreuses constantes de stabilité publiées jusqu'à présent.

Nous espérons également analyser ainsi des mélanges de protolytes de force égale qui, avec un cation donné, donnent des complexes de stabilités différentes.

Pour terminer, signalons que des programmes de ce genre, facilement adaptables pour de petits calculateurs de laboratoire, peuvent rendre de grands services dans l'exploitation des dosages potentiométriques à des fins d'analyse.

REFERENCES

1. G. Nowogrocki, J. Canonne et M. Wozniak, *Bull. Soc. Chim. France*, 1976, 5.
2. *Idem, ibid.*, 1976, 1369.
3. M. Wozniak et G. Nowogrocki, *Talanta*, 1978, **25,** 138.
4. *Idem, Bull. Soc. Chim. France*, 1974, 435.
5. M. Wozniak, *Thèse*, Lille, 1977.
6. A. Verbert, *Thèse 3ème cycle*, Lille, 1973.
7. C. N. Childs, P. S. Hallman et D. D. Perrin, *Talanta*, 1969, **16,** 1119.
8. F. J. C. Rossotti, H. S. Rossotti et R. J. Whewell, *J. Inorg. Nucl. Chem.*, 1971, **33,** 2051.
9. A. Sabatani et A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1972, 1693.
10. A. Sabatani, A. Vacca et P. Gans, *Talanta*, 1974, **21,** 53.
11. L. G. Sillén, *Acta Chem. Scand.*, 1962, **16,** 159.
12. *Idem, ibid.*, 1964, **18,** 1085.
13. N. Ingri et L. G. Sillén, *Arkiv Kemi*, 1964, **23,** 97.
14. L. G. Sillén et B. Warnqvist, *ibid.*, 1969, **31,** 315.
15. *Idem, ibid.*, 1969, **31,** 341.
16. R. Arneck, L. G. Sillén et O. Wahlberg, *ibid.*, 1969, **31,** 353.
17. P. Brauner, L. G. Sillén et R. Whiteker, *ibid.*, 1969, **31,** 365.
18. L. G. Sillén et B. Warnqvist, *ibid.*, 1969, **31,** 377.
19. D. H. Liem, *Acta Chem. Scand.*, 1971, **25,** 1521.
20. R. S. Tobias et M. Yasuda, *Inorg. Chem.*, 1963, **2,** 1307.
21. A. Dei, P. Paoletti et A. Vacca, *ibid.*, 1968, **7,** 865.
22. R. P. Martin et M. Blanc, *Bull. Soc. Chim. France*, 1969, 1866.
23. R. P. Martin et J. P. Scharff, *Compt. Rend.*, 1973, **277C,** 1339.
24. D. D. Perrin et I. G. Sayce, *J. Chem. Soc.* A, 1967, 82.
25. *Idem, ibid.*, 1968, 53.
26. D. D. Perrin, I. G. Sayce et V. S. Sharma, *ibid.*, 1967, 1755.
27. I. G. Sayce, *Talanta*, 1968, **15,** 1397.
28. I. Nagypál, *Acta Chim. Acad. Sci. Hung.*, 1974, **82,** 29.
29. T. Kaden et A. Zuberbühler, *Talanta*, 1971, **18,** 61.
30. F. Achenza, *Ann. Chim. (Rome)*, 1958, **48,** 565.
31. *Idem, ibid.*, 1964, **54,** 240.

Summary—The multiparametric refinement program MUCOMP fits the overall stability constants of complexes $M_qH_jA_p$ (M: metal ion, H: proton, A: ligand) and permits simultaneously the detection of the minor species and the compensation of systematic errors (total concentrations of ligands, cation, impurities and electrode cell characteristics). The processed data (reagent volume, potential) are collected from base titrations of complexant–cation mixtures. It is the last element of a chain of original programs intended for the study of complex formation by potentiometry. It was tested on the copper complexes of *N*,*N*-dimethylaminomethylphosphonic acid. The method will be extended, in the future, to allow analysis of mixtures of cations or protolytes.

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CO-CRYSTALLIZATION WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL, AND X-RAY FLUORESCENCE, FOR TRACE METAL ANALYSIS OF WATER

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Summary—Adding 20 mg of 1-(2-pyridylazo)-2-naphthol (PAN) to a water sample at 70°, and filtering off the precipitate after cooling, gives efficient preconcentration prior to X-ray fluorescence analysis of water. Up to the capacity of about 100 μeq of PAN used, the trace metal recoveries are around 90% or higher for Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Eu^{3+}, and above 70% for many other ions. The recovery yields usually do not vary critically with pH in the neutral pH-range, and are practically independent of the sample salinity, sample volume and trace-metal concentration. Enrichment factors as high as 2×10^5 can be achieved. Counting statistics would then allow detection limits of 0.03 ppM. The blank levels in commercial PAN, however, lead to typical detection limits of about 1 ppM. The coefficient of variation is typically in the 5–10% range at the 10-ppM level. The accuracy and applicability of the procedure are illustrated by comparative analyses on samples of synthetic solutions, river and drinking water.

In spite of its many inherent attractive characteristics, X-ray fluorescence is seldomly used for multi-element trace analysis of aqueous samples, because of the enrichment step that is required prior to the analysis. This preconcentration may consist in, *e.g.*, filtration through suitable ion-exchange resin columns and compressing the resin into a pellet, or solvent extraction followed by spotting of the extract onto a carrier. Only for low salinity matrices is preconcentration by evaporation or freeze-drying applicable.

Precipitation of the trace elements with a non-specific organic reagent and subsequent collection on a filter results in a strongly enriched thin uniform sample of a low atomic-number matrix. Such a target can be presented directly to the X-ray machine and guarantees analysis with optimal sensitivities and minimal matrix effects. Several authors have recommended sodium diethyldithiocarbamate (DDTC)[1–3] or ammonium pyrrolidinedithiocarbamate (APDC)[4] for this purpose, and 1-(2-pyridylazo-)-2-naphthol (PAN), has been introduced by Püschel[5] and applied by Watanabe *et al.*[2] in combination with wavelength-dispersive X-ray fluorescence. Earlier, PAN had been used extensively in analytical chemistry as an indicator and an extractant.[6] The yellow undissociated form of PAN ($pK_{a_1} = 2.9$ and $pK_{a_2} = 11.5$), existing in neutral solutions, forms insoluble and usually red chelates with many transition metals.[7] PAN is practically insoluble in water. When a small volume of alcoholic PAN-solution is added to an aqueous sample, the PAN crystallizes out and carries with it all strong colloidal metal–PAN chelates by co-crystallization. Addition of a carrier metal can thus be avoided. This report evaluates the analytical characteristics of co-crystallization enrichments on PAN, from water samples of any salinity, in combination with energy-dispersive X-ray fluorescence.

EXPERIMENTAL

Reagents

The water used was demineralized and doubly distilled in quartz apparatus. Batches of PAN were purchased from Aldrich (No. 10103-6), Baker (No. 1156) and Merck (No. 7351) to compare their characteristics. The Merck product was subsequently used, as a 0.5% solution in ethanol. Test solutions of metals were prepared by dissolving weighed quantities of dried analytical-grade salts or from "Titrisol" standards, and stored in polyethylene bottles. An artificial sea-water matrix was prepared by dissolving 239.4 g of sodium chloride, 50.8 g of magnesium chloride, 39.9 g of sodium sulphate, 11.2 g of calcium chloride and 6.7 g of potassium chloride in 10 litres of doubly distilled water. If necessary, pH adjustments were done with "suprapur" sodium hydroxide and hydrochloric acid. The experiments were carried out in glass apparatus because polyethylene appeared to adsorb some PAN from the solution. The filtration unit included a Gelman No. 4200 "polysulfon" filter-funnel, sealed by means of a "Teflon"-coated magnet, with a plastic filter-support screen. The radioactive tracers ^{54}Mn, ^{65}Zn, ^{152}Eu and ^{203}Hg were all of high specific activity and in chloride solution.

Instrumentation

For the X-ray fluorescence analyses a Kevex 0810 system was used, including a 60-kV, 4-kW, water-cooled Röntgen-tube with tungsten anode and an interchangeable secondary target. The characteristic X-rays were measured, after collimation, by a 30-mm² Si(Li) detector with 170-eV resolution at 5.9 keV. The voltage pulses, proportional to the X-ray energy, were led through an amplifier into an analogue-to-digital converter and pulse-height analyser (4096 channels). The X-ray spectra were stored on magnetic tape and afterwards analysed by a PDP 11/45 computer. By using molybdenum as a secondary target with the Röntgen-tube always operating at 40 kV and 40 mA, it was possible to determine elements with $Z < 50$ through their K_α radiation and those with $Z > 50$ though their L_α and L_β emission. The data-reduction was based on an iterative least-squares peak-fitting program, correcting for energy-calibration shifts, and relying on experimentally determined K_α/K_β ratios for the elements with $Z < 50$.[8] Atomic-absorption spectrometry was done

with a Perkin–Elmer 503 Flameless Atomic Absorption Spectrometer with Massmann oven. The microsamples were injected into the graphite rod of the oven with Eppendorf micropipettes. Spectrophotometric measurements for the PAN determinations were performed with a Beckman Cecil 202 double-beam ultraviolet-spectrophotometer. Gamma-spectrometry for tracer experiments was performed on a 63-cm^3 coaxial Ge(Li) detector (Philips APY 45 A/N), connected to a 4000-channel analyser. All chemical manipulations were carried out at a laminar-flow clean-air bench.

Procedure

To each 0.5–4-litre water sample, 4 ml of PAN-solution (containing 20 mg of PAN) were added. The sample was heated at 70–80° for about 10 min, allowed to cool, then filtered under suction through a preweighed 47-mm diameter 0.4-μm pore-size Nuclepore N 040 CPR 04700 filter. The loaded filter containing the precipitate in a 9.62-cm^2 area was dried at 100°, weighed, stretched on a "Teflon" ring and presented to the X-ray unit. The counting usually lasted for 5000 sec.

RESULTS AND DISCUSSION

Blank effects

Some 30 blank analyses were carried out by applying the experimental procedure to 1-litre portions of doubly distilled water and using the three brands of PAN. The average results showed similar impurity levels in each batch of PAN (except for a higher Ti and Fe-content in the Baker product) namely approximately 200 ng/cm^2 for Fe, 80 ng/cm^2 for Zn, 30 ng/cm^2 for Cr, Ni and Cu and 10 ng/cm^2 for Ti, Mn and Br (referred to filter area and corresponding to about 100, 30, 15 and 5 ppm, respectively, in the PAN itself). In view of its lower price and satisfactory characteristics, the Merck product was preferred and used exclusively for further work.

Except for Zn, the contribution of the doubly distilled water to these blank values was practically negligible, as the apparent blanks remained nearly constant for water volumes varying between 0.1 and 1 litre. Only for Cr and Cu was the contribution of the Nuclepore filter substrate to the overall blank relatively important. Nuclepore membranes were previously[9] selected as a substrate for the collection of precipitates prior to X-ray analysis, because they are very thin (0.92 mg/cm^2) and pure, and exhibit good mechanical characteristics.

Effect of equilibration time

After addition of PAN and heating to about 70°, different 1-litre water samples at pH 9.5, spiked with 50 ppM* of Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, were set aside to equilibrate and cool for periods from 3 hr up to 3 days. Filtering off the PAN-precipitates after this yielded identical and maximum collection yields in all cases.

Effect of pH

In order to determine the optimal pH for the enrichment, the experimental procedure was applied to 500-ml doubly distilled water-samples at various pH-values, containing 25 ppM of Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. Afterwards the experiments were repeated on a synthetic sea-water matrix spiked with the same trace metals. The results were corrected for blanks, and for X-ray absorption effects by using mass-absorption coefficients determined by transmission experiments (the absorption correction amounts to only, *e.g.*, 3% for Cr and 1.2% for Zn for a typical 2 mg/cm^2 load of PAN on the filter). The results were not significantly different for the two series of experiments, hence the collection yields are independent of the sample salinity (see also below). The average values are plotted in Fig. 1. The collection of Ni^{2+}, Cu^{2+} and

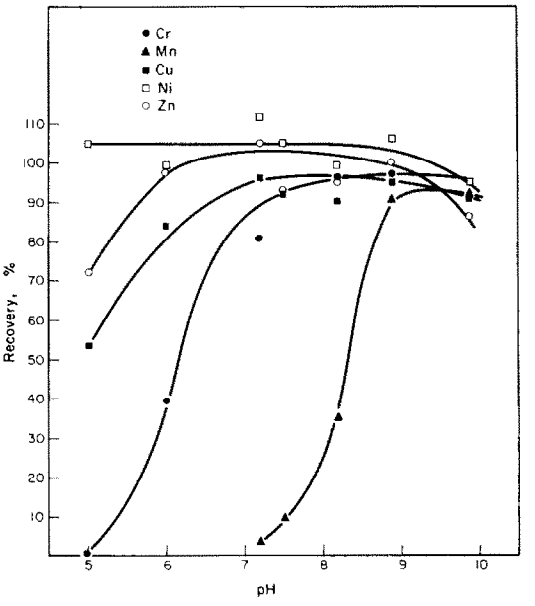


Fig. 1. Influence of pH on the recovery of Cr^{3+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}

Zn^{2+} appears to be constant in the pH-range 6.5–10. Cr^{3+} and Mn^{2+} can be satisfactorily collected only at high pH. Working with acetate or ammonium buffers, Püschel *et al.*[7] found similar results for Mn, Ni and Zn but a slightly stronger pH-dependence below pH 8.5 for Cu. They also observed a quantitative recovery of Fe but low values for Ti (except around pH 6.5), V (except around pH 4.5) and Pb. Watanabe *et al.*[2] recommended working with a pH-10 buffer to obtain optimal co-precipitation of Mn, Fe, Cu, Zn and Cd with PAN and a nickel carrier. However, Van Landschoot[10] observed that at pH 9.8 considerable amounts of Ca co-crystallize with PAN from an artificial sea-water matrix, resulting in lower enrichment factors.

In view of the available results, a pH of 9 was preferred. It allows high recoveries of many trace ions and does not necessitate the addition of large amounts of

*ppM = parts per milliard (10^9).

acids or bases to natural water samples with pH near 7 (which would increase the contamination risk). Also, near the natural pH of water, DDTC[2] is very effective as a co-precipitation agent, whereas APDC has been used at pH 2.[4]

Recovery of PAN

In nine blank experiments with 500-ml portions of doubly distilled water at pH 8 to which 20 mg of PAN had been added, the quantity of PAN recovered on the filter was weighed and the concentration of PAN remaining in solution was determined by ultraviolet-spectrometry at 465 nm after extraction into diethyl ether. Also the quantity of PAN adhering to the beaker walls was determined by dissolution in ethanol and ultraviolet-spectrometry.

We found that $86 \pm 2\%$ of the PAN is recovered on the filter and $11.5 \pm 0.8\%$ remains in solution, indicating the solubility of PAN in water to be 4.6 ppm. Only $3.0 \pm 0.3\%$ adhered to the beaker walls, ruling out the necessity to add a surfactant as suggested by Watanabe *et al.*[2] The fraction of PAN recovered on the filter decreased to 70% and 50% for a 2-litre and a 4-litre sample respectively. The trace metal recoveries, however, are quite independent of the sample volume (see below).

Effect of sample volume

To several doubly distilled water samples (0.5-, 1- and 2-litre volumes), spiked with 50 μg of Cr^{3+}, Mn^{2+}, Cu^{2+} and Zn^{2+}, 20-mg of PAN were added and the precipitates were filtered off, weighed and analysed. The results, included in Table 1, show that the influence of sample volume on the trace ion recoveries is insignificant. The apparent recoveries of over 100% for Zn^{2+} might be due to inaccurate corrections for blanks and to some contamination effects. Working with sample volumes larger than 2.5 litres appeared to be too time-consuming to be practical.

Effect of salinity

Parallel experiments were carried out on 500-ml samples of synthetic sea-water, a 1:2 dilution of the synthetic sea-water and a 30% sodium chloride solution. Five hundred ppM of Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} had been added to these samples. Table 1 compares the recoveries with the averages found for all experiments on 500-ml doubly distilled water-samples. It appears that high concentrations of alkali and alkaline earth metal ions do not interfere strongly with the trace metal collection on PAN.

Under similar experimental conditions, Van Landschoot[10] found that only 0.0002, 0.004 and less than 0.001% respectively was co-crystallized of the Na, Ca and Mg present in an artificial sea-water sample.

The enrichment technique described seems applicable to a wide range of aqueous samples, including brines. Also, DDTC can be used in highly saline matrices.[11]

Proportionality between X-ray response and concentration

From a standard solution containing Cr^{3+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, ten 1-litre samples at different dilutions were prepared, with concentrations varying between 1 ppM and 0.5 ppM. The average analysis results are plotted in Fig. 2. In the central region perfect linearity is observed between the amount of trace metal added and the resulting X-ray response of the final target, with correlation coefficients of 0.994, 0.9993, 0.9993, 0.9996 and 0.9978 for Cr, Mn, Ni, Cu and Zn respectively. This implies that the recovery is independent of the ion concentration. A similar conclusion was drawn by Püschel[5] for Mn, Fe, Ni and Cu. At the higher-concentration end the results in Fig. 2 deviate from linearity because the co-crystallization capacity of PAN is exceeded. Moreover, with a total transition-metal load of 5 ppm the PAN targets became brittle and burst upon drying. Extrapolations of the curves in Fig. 2 seem to indicate a total capacity of about 100 μeq/20 mg of PAN. The significant deviations at low concentrations are due to some contamination effects, and to inaccurate blank corrections which become important at this concentration level (see below).

Filter load homogeneity

The homogeneity of the filter load was tested by X-ray analysis of several filters at their centre and at four

Table 1. Effect of sample volume and salinity on trace metal recoveries

Ion	Recovery ± standard deviation, %					
	Doubly distilled water			1:2 dilution of synthetic sea-water	Synthetic sea-water	30%NaCl solution
	2 litres	1 litre	500 ml	500 ml	500 ml	500 ml
Cr^{3+}	83 ± 24(2)*	92 ± 5(4)*	89 ± 4(11)*	83 ± 11(2)*	86 ± 6(3)*	97(1)*
Mn^{2+}	90 ± 9(2)	87 ± 3(3)	99 ± 7(9)	96 (1)	86 (1)	97(1)
Ni^{2+}	96 ± 8(2)	102 ± 5(4)	92 ± 4(10)	95 ± 3(2)	97 ± 5(3)	100(1)
Cu^{2+}	89 ± 11(2)	95 ± 4(4)	90 ± 3(11)	89 ± 2(2)	89 ± 4(3)	89(1)
Zn^{2+}	108 (1)	102 ± 3(3)	98 ± 5(8)	109 (1)	109 ± 4(2)	104(1)

* ( ) = number of determinations.

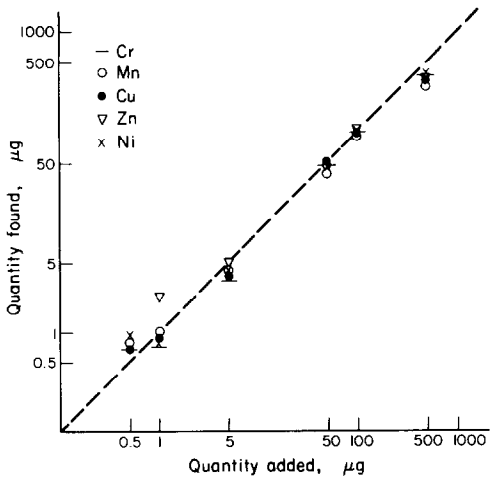


Fig. 2. Proportionality between the quantity found and the quantity added, for Cr^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}.

random locations. It appeared that the target inhomogeneity should be responsible for a coefficient of variation of less than 5%, to be added by the usual root-sum-of-squares method to other contributions to the uncertainty. Experiments involving radioactive tracers were also carried out for some elements. Spikes of ^{54}Mn, ^{65}Zn, ^{152}Eu and ^{203}Hg were added to a 1-litre water sample, and from the filter containing the PAN-precipitate 16 discs (3 mm in diameter) were punched out at random and measured by Ge(Li) spectrometry. The measured count-rate varied by an average of 3.1% among the different discs. It thus appears that the loaded filters are sufficiently homogeneous to be analysed by a narrow exciting X-ray beam.

Influence of natural dissolved organic matter

Solutions containing 2.5 ppm of Mn^{2+}, Co^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+} and Eu^{3+}, spiked with radioactive tracers, were equilibrated for a week with 0.5–10 ppM of humic substances typical of fresh water. It appeared that the recoveries were reduced by an average of 15% for the 2-ppm concentration of humic material that is typical of many surface waters. The reduction in recovery was somewhat more severe for Eu^{3+} than for the other ions, and this might be related to the particularly high strength and non-ionic character of humic complexes of tervalent ions.[12] No further reduction in recovery was noted at humic substance concentration levels above 5 ppm. Detailed conclusions and well founded interpretations are not yet possible on this point. A more complete separate study is now being undertaken to investigate the influence of humic substances on this and other analysis procedures.

Enrichment factors and detection limits

Enrichment factors are defined as the weight ratio in the sample before and after the preconcentration step. Of 20 mg of PAN added to a 0.5- or 2.5-litre water sample, some 18 or 13 mg of PAN, respectively, crystallizes out, and the trace metal ions are nearly quantitatively recovered with this precipitate while the usually abundant alkali metal ions remain in solution. Hence enrichment factors of approximately 2×10^5 and 3×10^4 for the 2.5-litre and 0.5-litre water samples, respectively, are obtained. This compares very favourably with most other enrichment techniques.

Taking into account the blank impurities (assumed constant) of the Nuclepore filter and PAN, and the contribution to the background by the X-ray scatter by the filter and precipitate, the conventional criterion of three times the square root of the background will lead to theoretical interference-free detection limits, for this simple analysis technique, of about 0.2 ppM Cr, Mn and Zn and 0.1 ppM Ni and Cu for 0.5-litre water-samples and 0.04 ppM Cr, Mn and Zn and 0.02 ppM Ni and Cu for 2.5-litre samples. Of course, as is obvious in Fig. 2, not only counting statistics contribute to the uncertainty at low concentration levels, and the blank values are not constant in practice. For 1-litre water-samples, the typical PAN blank levels correspond to 2 ppM Fe, 0.8 ppM Zn, 0.3 ppM Cr, Ni, Cu and 0.1 ppM Ti and Mn. Realistic detection limits would be at the 1 ppM level, but depend strongly on the element. A separate study is presently being carried out to investigate the possibility of reducing the blank levels of commercially available PAN by a sublimation procedure.

Collection yields and elemental range

The average collection yields, for all the experiments in this work, were $90 \pm 3\%$ for Cr, $96 \pm 4\%$ for Mn, 95 $\pm 3\%$ for Ni, $91 \pm 3\%$ for Cu, $100 \pm 3\%$ for Zn, 88% for Hg and 89% for Eu.

In addition it was found that under the experimental conditions used, recoveries greater than 70% were obtained for Zr, Ag, Cd, Sn, lanthanides, Hf, U and Th but nor for Ga, Te, Sb, W, Tl and Pb. In sea-water of pH 8 Van Landschoot[10] found comparable recoveries for Cr, Cu, Zn and Hg, and also measured satisfactorily high and constant recoveries for Sc, Fe, Co, Cd and In but not for As, Mo, and Sb. Püschel[13] stated that in addition PAN can form strong chelates with Ti, Vi, Ga, Y, Nb, Ru, Rh, Pd, Os, Ir, Pt, Au and Bi. It can thus be

Table 2. Precision when 6 filters, containing 5 μg of each metal, are analysed

	Recoveries, μg	Average, μg	Coefficient of variation, %
Cr	4.1; 4.5; 4.0; 4.3; 4.4 4.0	4.2	5
Mn	4.9; 5.4; 4.9; 5.4; 4.7 5.0	5.0	6
Ni	4.2; 4.8; 4.4; 4.4; 3.9 4.6	4.4	7
Cu	4.2; 4.0; 4.6; 4.4; 4.4 5.1	4.4	9

Table 3. Analysis of IAEA intercomparison sample W-3

	Result of co-crystallization with PAN, *ppM*	Certified value, *ppM*	Overall intercomparison average, *ppM*
Cr	10.7	12.0	11.0
Mn	10.8	12.0	10.8
Fe	42.5	32.0	49.6
Co*	9.4	12.1	11.9
Ni	11.0	12.0	10.7
Cu	11.2	12.0	12.5
Zn	15.0	12.0	13.6
Pb	24.8	16.0	30.3

* Inaccurate owing to important Fe-K_β interference.

expected that, in certain conditions, these metals also can be enriched by co-crystallization on PAN.

Precision

Table 2 gives recovery results for replicate analyses on 500-ml artificial sea-water samples containing 10 ppM each of Mn, Cr, Ni, Cu and Zn. An average coefficient of variation of only 7% is noted. From Table 1, for results of experiments carried out in completely different circumstances, an average overall coefficient of variation of 12% is calculated. These data suggest a reproducibility of 5–10% for the enrichment step.

Accuracy

The overall reliability of the proposed method was illustrated in several tests. The procedure was applied to a fraction of intercomparison sample W3, distributed by the International Atomic Energy Agency as an acidified concentrate to simulate, after dilution, "a fresh water sample". The sample had previously been analysed by many laboratories in an intercomparison run.[14] Table 3 compares the present results with the concentrations given by the organizers and the averages found by the participating laboratories. The data indicate a very satisfactory agreement between our results and the averages from the analyses included in the intercomparison run.

Samples from four rather polluted small rivers were analysed both by direct flameless atomic-absorption spectrometry (accuracy estimated to be in the 10–20% range) and by the present technique. After collection the samples were acidified to pH 1 and then filtered. The data given in Table 4 for 50 ml of the filtrates compare favourably. Tap-water samples were analysed by X-ray fluorescence, using both this technique and an enrichment step involving trace metal chelation by oxine and adsorption on activated carbon.[15] The results, assuming quantitative recoveries in both cases, are listed in Table 5. The experiments using activated carbon yield a somewhat higher result, maybe because of a more effective collection of the naturally occuring metal–humic acid complexes.[16]

Table 5. Analyses of tap water by X-ray fluorescence after co-crystallization with PAN, and after chelation and adsorption on activated carbon[15]

	Average results ± standard deviation, *ppM*	
	PAN (4 replicates)	Activated carbon (7 replicates)
Mn	0.42 ± 0.17	0.87 ± 0.05
Fe	3.3 ± 0.5	4.5 ± 0.3
Ni	2.2 ± 0.2	2.4 ± 0.1
Cu	1.4 ± 0.14	2.2 ± 0.1
Zn	2.4 ± 0.2	3.5 ± 0.2

In conclusion, it can be stated that the procedure combines simplicity, versatility, good precision and accuracy, and offers excellent perspectives for trace analysis from the ppM-level up to a total transition metal content of a few ppm, independent of the water-sample salinity.

Table 4. Analyses by the present technique (PAN) and atomic-absorption spectrometry (AAS) of typical river-water samples collected in Flanders (*ppm*)

Element	River							
	Aa		Kleine Nete		Grote Nete		Mark	
	PAN	AAS	PAN	AAS	PAN	AAS	PAN	AAS
Cr	0.026	—	—	—	—	—	0.006	—
Mn	0.32	—	0.27	—	0.39	—	0.6	—
Fe	3.9	4.5	5.0	5.6	6.0	7.2	2.4	2.5
Ni	0.11	—	0.026	—	0.015	—	0.013	—
Cu	0.12	0.10	0.050	0.046	0.016	0.009	0.012	0.008
Zn	0.35	0.36	0.24	0.26	1.47	1.43	0.18	0.16

REFERENCES

1. C. W. Luke, *Anal. Chem.*, 1964, **36**, 318.
2. H. Watanabe, S. Berman and D. S. Russell, *Talanta*, 1972, **19**, 1363.
3. T. Florkowski, B. Holynska and S. Piorik, p. 213, in

Measurement, Detection and Control of Environmental Pollutants, International Atomic Energy Agency, Vienna, 1976.
4. J. F. Elder, S. K. Perry and F. P. Brady, *Environ. Sci. Technol.*, 1975, **9,** 1039.
5. R. Püschel, *Talanta,* 1969, **16,** 351.
6. N. Desai and H. Gandhi, *Chim. Anal. Paris,* 1968, **50,** 297.
7. R. Püschel, E. Lassner, W. Martin and D. Martin, *Mikrochim. Acta,* 1969, 145.
8. P. Van Espen, H. Nullens and F. Adams, *Nucl. Instr. Meth.,* 1977, **142,** 243.
9. M. Vanderstappen and R. Van Grieken, *Z. Anal. Chem.,* 1976, **282,** 25.
10. A. Van Landschoot, *M.Sc. Thesis,* Rijksuniversiteit Gent, 1974.
11. B. Holynska and K. Bisinek, *Determination of Amounts of Metals in Saline Water by XRF with NaDDTC Preconcentration Report* INT 74/I Krakow, 1975.
12. B. Kribek, J. Kaigl and V. Oruzinsky, *Chem. Geol.*, 1977, **19,** 73.
13. R. Püschel, *Mikrochim. Acta,* 1965, **4,** 772.
14. R. Dybczynski, A. Zugsavul and O. Suschny, *Report on the Intercomparison of Determinations of Selected Radionuclides and Trace Elements in Water,* Report IAEA/RL/40, December 1976.
15. B. Vanderborght, J. Verbeeck and R. Van Grieken, *Bull. Soc. Chem. Belg.*, 1977, **86,** 23.
16. B. M. Vanderborght and R. E. Van Grieken, *Envir. Anal. Chem.*, 1978, **5,** 221.

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CONCENTRATION AND DETERMINATION OF TRACE ORGANIC POLLUTANTS IN WATER

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Summary—Organic pollutants in water are isolated on a mini-sampler tube containing a macroporous resin. The sorbed pollutants are next thermally transferred to a second sorption tube and then to an analytical column where they are separated and determined by temperature-programmed gas chromatography. Excellent recoveries were obtained for tests in which model organic compounds of various classes were added to water. The water sample is much smaller than that required with previous analytical methods.

The nature and concentrations of organic pollutants in drinking water are matters of great concern. It is vital that reliable methods of water analysis be developed. Because of the extremely low concentration (usually < 1 ppM*) of those organic contaminants in drinking water that are amenable to gas-chromatographic separation an efficient concentration method is required. Gas-stripping techniques have been used successfully for volatile compounds and for highly insoluble compounds such as alkanes.[1, 2] Solvent extraction works well for many pesticides and certain other compounds, but the degree of extraction of many classes of organic compounds is low.[3] Other disadvantages of solvent extraction include the necessity to use very pure solvent, general inconvenience of handling large samples, and the loss of volatiles during evaporation. Activated carbon is an efficient sorbent but desorption from it with organic solvents is often slow and incomplete.

The XAD-2 resin sorption method[4] is probably the most reliable and thoroughly tested method for determining trace organic pollutants in drinking water. However, the solvent evaporation step in this procedure results in a partial or complete loss of volatile compounds. In addition, the volume (2 μl) of the ether concentrate taken for gas-chromatographic analysis is only a small fraction (1/500) of the total.

To avoid these drawbacks a procedure has been developed in which organic compounds that are sorbed on a resin are thermally desorbed directly onto a gas-chromatographic column for analysis. A thermal desorption method was proposed earlier by Mieure and Dietrich[3] but they did not develop the method very much. They found that interstitial water often caused the FID flame to be extinguished. In the present method this difficulty is avoided by first desorbing onto a Tenax tube the sorbed organic compounds from a tube containing XAD-2. This eliminates virtually all of the water entrained in the XAD-2 tube. Then the organics are thermally desorbed from the Tenax tube directly onto the gas-chromatograph column.

* Parts per milliard (10^9).

EXPERIMENTAL

Resins

XAD-2 resin from Rohm and Haas was ground and sieved in the dry state. The 60–80 mesh resin was used after purification according to the procedure of Junk *et al.*[4]

Tenax-GC, 60–80 mesh, was used without further purification.

Apparatus and equipment

A Hewlett-Packard 5756 B gas chromatograph equipped with a linear temperature programmer and FID detector was used. Stainless-steel tubing was used for all columns and injection-port liners. The injection port was enlarged by drilling to accommodate the glass sorption tubes. The column for separations was either 6 ft × 1/8 in. o.d. packed with 5% OV-17 on Chromosorb W AW DMCS (80–100 mesh) or 4 ft × 1/8 in. packed with Tenax-GC (60–80 mesh).

Sorption tubes were 2 mm i.d., 10 cm in length. They were filled with 7 cm of either XAD-2 or Tenax-GC, held in place with a plug of glass wool at either end. The XAD-2 tubes were conditioned by thermal desorption at 240° and repetitive blanks were run until a low, tolerable background was achieved. A blank run involved wetting the resin with triply-distilled water and following steps 2 and 3 of the analytical procedure. The Tenax-GC tube required only a simple conditioning by heating for 1 hr at 275° to achieve a tolerable blank level.

A mini-sampler for water was devised in which a 20-ml glass syringe is connected to an XAD-2 sorption tube (Fig. 1). The connection is made with the special Kel-F coupler shown in Fig. 2.

Samples

Water samples containing 3–100 ppM (μg/l.) of model organic compounds were prepared by adding 2–5 μl of standard solution in methanol to a 15-ml (or larger) water sample and mixing well.

Procedure

1. (*Sampling*). Pass a 15-ml (or larger) sample through the XAD-2 sorption tube by using the mini-sampler with hand pressure to force the water through (about 1–2 min). Then force as much residual water as possible from the tube, using 20 ml of air. Cap the sorption tube at both ends unless the analysis is to continue without delay.

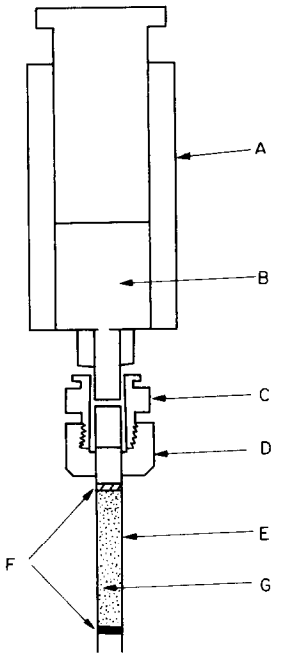


Fig. 1. Mini-sampler for small water volumes: (A) 20-ml glass hypodermic syringe; (B) water sample; (C) coupler for attaching mini-column (E) to the syringe; (D) 1/4-in. Swagelok nut; (E) 2-mm i.d. Pyrex tube; (F) glass-wool plugs; (G) 80 mg of 60–80 mesh resin.

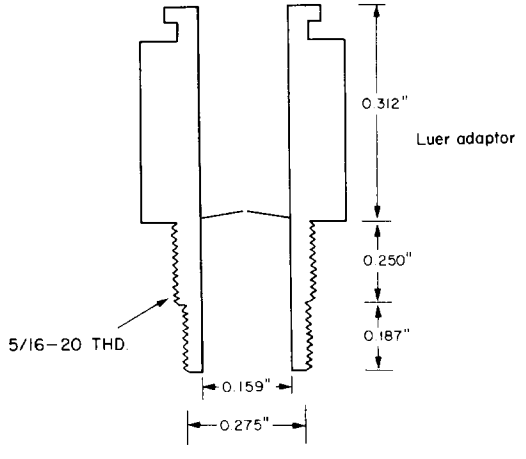


Fig. 2. Kel-F coupler.

2. (*Thermal desorption*). Connect the XAD-2 tube to a Tenax sorption tube. Place the XAD-2 tube in a heated zone maintained at 220° with helium flowing at 50 ml/min into the XAD-2 tube and out of the Tenax tube. (The Tenax tube is held at approximately 45°.) Continue desorption from the XAD-2 onto the Tenax tube for ~15 min or until the Tenax is visibly dry.

3. (*Separation*). Disconnect the two tubes and place the Tenax tube in the modified GC injection port, held at 220°, and apply a helium carrier-gas flow of 20 ml/min. (The oven section of the chromatograph is at approximately room temperature.) Allow 10 min for transfer of organic solutes from the Tenax tube to the column, then separate by raising the temperature at 20°/min up to 200°, finally holding this temperature for 10 min.

4. (*Measurement*). Inject 2–5 µl of standard organic solution in methanol through a zone heated to 220° onto a Tenax tube at room temperature (or slightly above). Desorb and chromatograph the organic compounds as in step 3. Compare the heights of the sample and standard peaks to calculate the amounts of sample constituents.

RESULTS AND DISCUSSION

Recovery

Organic compounds representing eight different classes and covering a wide volatility range were added to water (at 3–200 ppM levels) and used to test the resin extraction–thermal desorption procedure. The recovery was calculated by comparing the peak height with that for a known standard solution (in methanol) injected directly onto the Tenax tube and thermally desorbed into the GC column at 220°. The recoveries are summarized in Table 1. The average recovery was 83%. However, if the results from three polar compounds known to be incompletely retained by the XAD-2 (acetone, butanol, pentanol) are discarded, the average is 88%. The overall reproducibility is 5–8%. These recoveries compare well with those obtained by other procedures. However, no other single procedure will give satisfactory results for water samples containing both volatile compounds (chloroform, benzene, *etc.*) and less volatile substances such as naphthalene and acetophenone.

The recoveries of carboxylic acids were not reproducible. This is believed to be due to the difficulty of direct determination of acids by gas chromatography. A selective method for concentration of the acids with subsequent gas chromatography of their derivatives would be more desirable. The recoveries for phenols varied from 4 to 90%. These inconsistent results are probably due to the high affinity of Tenax-GC for phenols. All attempts to improve the yield for phenols failed, and the method is not satisfactory for these compounds.

Some natural water samples were analysed by the proposed method. A typical chromatogram is shown in Fig. 3, but represents only a general profile of the contaminants in the water sample, since no identification was attempted.

Method parameters

Choice of sorbents. In our first experiments water was passed through a small column of XAD-2 and the organic compounds were thermally desorbed onto an 18 × 1/4 in. GC column at room temperature and packed with Tenax-GC. A switching valve in the gas chromatograph allowed water to pass through the column to vent while organic solutes were concentrated on the Tenax. After a few minutes the valve was switched to connect the Tenax column to a second

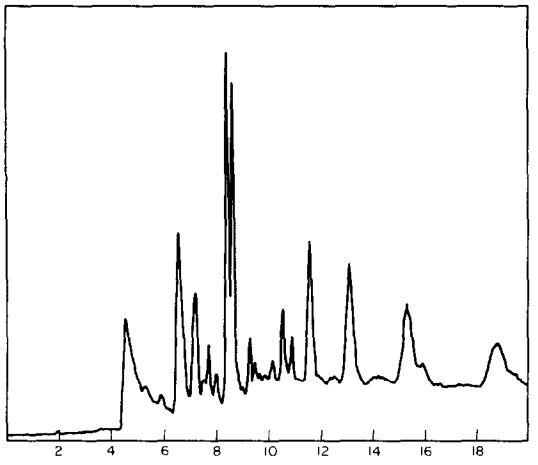


Fig. 3. Gas chromatogram of organic compounds extracted from the drinking water of Slater, Iowa.

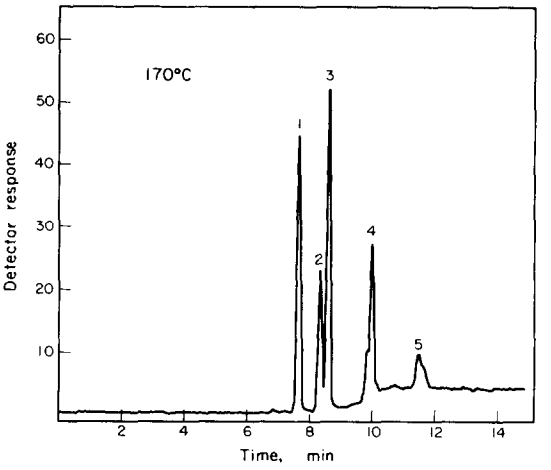


Fig. 4. Gas chromatogram of model compounds injected as a solution in methanol: (1) benzene; (2) octane; (3) toluene; (4) 2-octanone and (5) acetophenone. Desorption temperature: 170°.

16 × 1/8 in. Tenax column. The oven temperature programme was started and the organic substances were separated.

This procedure was partly successful but had two important limitations: (1) The recovery of less volatile compounds (*e.g.*, napthalene) was not reproducible, and (2) the stationary phase of the second GC column was limited to Tenax or some similar hydrophobic material.

Several experiments were performed in which Tenax-GC was used instead of XAD-2 in the mini-sampler tube, but recoveries were consistently low (10–20%). The combination of both XAD-2 and Tenax-GC sorption tubes outlined in the procedure was the only method tried that gave satisfactory results for a variety of organic compounds.

Desorption temperature. The good recoveries shown in Table 1 indicate that 220° is adequate for total thermal desorption from XAD-2 onto Tenax-GC. Temperatures much above this lead to bigger blanks, apparently because of some decomposition of the XAD-2. However, whether the second desorption, from Tenax-GC onto the gas chromatographic column, is complete or not is unknown, because the peaks of the organic sample solutes (from the XAD-2 desorption) are compared with peaks of standards which are simply injected as their methanol solutions into the Tenax column. The effect of Tenax-column desorption temperature on the final chromatogram was therefore examined by injecting into the Tenax

Table 1. Overall recovery efficiency of resin extraction and thermal desorption method of analysis on XAD-2 for organics in water at the 3–100 ppM level

Compounds	Recovery efficiency, %	Compounds	Recovery efficiency, %
Alkanes		*Polynuclear aromatics*	
Octane	88	Naphthalene	98
Heptane	81	2-Methylnaphthalene	97
Tridecane	90	*Chlorobenzenes*	
Alkylbenzenes		Chlorobenzene	90
Benzene	90	*o*-Dichlorobenzene	82
Toluene	97	*Ketones*	
o-Xylene	90	Acetone	55
Cumene	82	2-Octanone	83
Ethers		Undecanone	86
Hexyl	80	Acetophenone	92
Benzyl	70	*Alcohols*	
Esters		l-Butanol	<40
Benzyl acetate	95	l-Pentanol	<40
Methyl decanoate	88	l-Octanol	85
Methyl hexanoate	86	l-Decanol	84
*Haloforms**		*Phenols and acids*	
Chloroform	87	No quantitative results	
Bromodichloromethane	95		

* Chlorinated methanes were tested at a concentration of 200 ppM in water (*i.e.*, 200 μg/l.).

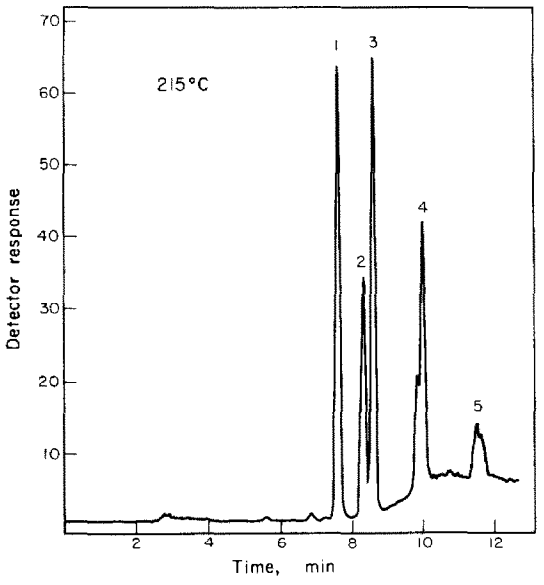


Fig. 5. Same conditions as for Fig. 4 except desorption temperature: 215°.

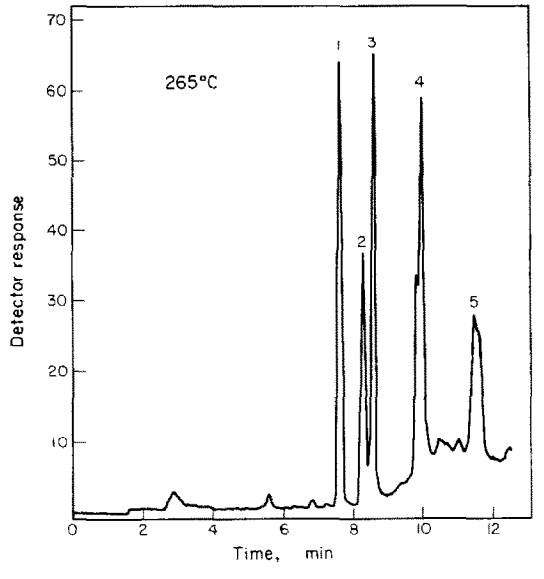


Fig. 6. Same as for Fig. 4 except desorption temperature: 265°.

tube 2 μl of methanol solution containing 0.8 μg each of benzene, octane, toluene, 2-octanone and acetophenone. The solutes were desorbed from the Tenax tube at three different temperatures and the results compared. The chromatograms from these tests are shown in Figs. 4–6. These chromatograms show that lowering the temperature has little effect on desorption of volatile compounds such as octane, benzene and toluene, but retention of the higher-boiling compounds on the Tenax is more serious. In our procedure (step 3) it was convenient to desorb at 220° because this temperature was used for desorption of the XAD-2 tube in the other GC injection port. However, the results in Fig. 6 indicate that a higher temperature (265°, for example) would be advantageous. Any material not desorbed from the Tenax at 220° will be removed in the conditioning treatment at 275°, and will not affect subsequent performance.

Desorption time. The time needed for desorption of organic solutes from the Tenax tube was also studied. Figure 7 shows that benzene is desorbed much more quickly than naphthalene, which is less volatile. However, desorption of naphthalene is complete in 10 min, so this desorption time was regarded as adequate, as naphthalene was the most difficult (of the compounds tested) to desorb. No attempt was made to optimize the desorption times for the wide variety of compounds tested. However, desorption times in excess of 30 min may adversely affect the peak shape for compounds such as n-octane and chloroform.

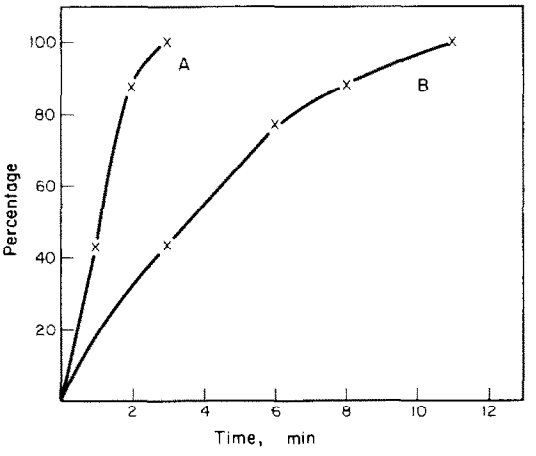


Fig. 7. Effect of the desorption time for the Tenax tube. A benzene, B naphthalene.

Sample size and sensitivity. The ability of the XAD-2 mini-sampler tubes to retain organic compounds from water samples larger than 15 ml was checked in two ways. In the first, injection of a standard sample of benzene and toluene (in 2 μl of methanol) followed by washing the tube with 100 ml of distilled water, there was no measurable loss of organic solutes. The second method was to analyse two different water samples, one of 15 ml and the other of 60 ml. The recoveries were similar (Table 2).

The larger XAD-2 sampler used earlier[4] contained 2000 mg of resin and effectively removed organic impurities from at least 50 l. of water. The mini-sampler contains 80 mg of XAD-2 and would be expected to be effective with water samples as large as 1

Table 2. Effect of water sample size

	Recovery, %	
Compound	15-ml sample	60-ml sample
Acetone	49	60
Benzene	90	90
Toluene	97	102

litre. In one instance a 1-litre sample was successfully analysed for chloroform and other halocarbons.

The method is capable of detecting 0.1 ppM of organic compound in a 15-ml water sampler, given a detector sensitivity (FID) of 1 ng. The sensitivity can be improved by using a larger sample size.

Storage of sorbed compounds. To test the applicability of the mini-sampler for field sampling, water samples spiked with five volatile halocarbons (chloroform, carbon tetrachloride, bromodichloromethane, dibromochloromethane, and bromoform) were chosen for testing. After the synthetic water samples had been forced through the mini-samplers, these were stored in screw-capped test-tubes for a specific period of time before analysis. There was no measurable loss of the halocarbons in four days of storage. Although more results are needed, it does appear that organic compounds sorbed on the mini-sampler tubes are quantitatively retained for several days.

Conclusion

The method proposed can be used to determine low concentrations of a wide variety of organic compounds in water. Since all of the organic pollutants removed from the water are used for chromatographic analysis, a much smaller water sample can be used than before. This means that field sampling with immediate sorption onto a mini-sampler is now feasible.

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REFERENCES

1. K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatog.*, 1975, **106**, 299.
2. W. Bertsch, E. Anderson and G. Holzer, *ibid.*, 1975, **112**, 701.
3. J. P. Mieure and M. W. Dietrich, *J. Chromatog. Sci.*, 1973, **11**, 559.
4. G. A. Junk, J. J. Richard, M. D. Grieser, M. D. Witiak, J. J. L. Witiak, M. D. Arguello, R. V., H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatog.*, 1974, **99**, 745.

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DETERMINATION OF REFRACTORY ELEMENTS IN U_3O_8 BY CARRIER DISTILLATION EMISSION SPECTROGRAPHY

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Summary—An emission spectrographic method using carrier distillation for the determination of the refractory impurities Ta, Hf, Nb, Th, and W in uranium is described. Different carriers, such as Ga_2O_3, AgCl, AgCl + LiF, and AgCl + NaF in various proportions, were investigated: a 1% NaF + 9% AgCl mixture as carrier at 10% of total charge arced was found to be the most suitable. Spectra were excited in a d.c. arc at 12 A and were photographed with 35-sec exposures. Palladium was used as an internal standard. The lowest limits of determination lie in the range 1–10 ppm for a 100-mg charge. The precision of the method is about 16% or better.

The need for high-purity uranium materials for use in nuclear reactors has been responsible for the development of methods of analysis capable of detecting and estimating ppm or less of those metallic impurities having large absorption cross-sections for neutrons. Emission spectrography is widely used in quality control of nuclear fuels, for the determination of trace metal impurities in uranium. Common impurities[1,2] which have medium or high volatility may be determined by the technique of carrier distillation, originally developed by Scribner and Mullin.[3] Less volatile or refractory impurities, however, such as Ta, Hf, Nb, W *etc.*, and the rare earths, are generally estimated[4–9] after their chemical separation from the matrix, but carrier distillation with proper choice of carrier and of the proportion of carrier to sample has been shown to be suitable for the determination of some refractory elements.[10–12] Though the limits of determination obtained by the methods involving chemical separation are lower than those for the carrier distillation technique, chemical separation has some disadvantages such as the possibility of contaminating the sample, and a longer analysis time. This paper describes a carrier distillation method for the determination of the refractory impurities Hf, Ta, Nb, W and Th in uranium metal. Different carriers in varying amounts were investigated with the aim of achieving the optimum sensitivity: a mixture of silver chloride and sodium fluoride in the ratio 9:1 at 10% of total charge arced was found to be most suitable. Palladium (0.01%) was used as an internal standard.

EXPERIMENTAL

Apparatus

Spectrograph: Hilger E-546, 3.4 m Ebert plane grating.
Grating: 1200 grooves/mm, blazed at 3000 Å in the first order, giving reciprocal linear dispersion of 2.5 Å/mm in the first order.
Power supply: Hilger source unit FS 131 with timer FS 106.
Microphotometer: Hilger non-recording microphotometer L-503 with galvoscale FR-333.
Electrodes: anode—standard "carrier distillation" type electrode, ASTM designation E-130-66 type S-2, used on type S-1 pedestal; cathode—0.120-in. diameter preformed pointed electrode, ASTM designation E-130-66 type C-1.
Plate calibration: Hilger seven-step sector (ratio 2:1) with iron spectrum.

Preparation of carriers and standards

High-purity uranium metal was converted into the oxide U_3O_8 by heating in air in a muffle furnace for about an hour at 850°. The oxide was then ground to pass a 200-mesh nylon sieve (Spex Industries No. 3542) which was used for preparation of standards to ensure reproducibility of particle size, as the intensity ratio tends to depend upon particle size.[13]

A mixture of all the impurity elements to be determined was prepared by weighing out their oxides and thoroughly grinding the mixture with a mortar and pestle. A portion of this impurity mixture was then mixed with U_3O_8 to make the master standard (A). Silver chloride, sodium fluoride and palladium [weighed in the form of $(NH_4)_2PdCl_4$] were ground together to make a homogeneous carrier–internal standard mixture (B). Silver chloride and sodium fluoride were added in the ratio of 9:1.

A series of seven standards was then prepared by mixing varying amounts of master standard (A) with fixed amounts of carrier internal standard mixture (B), and U_3O_8 to give the concentration range of 1–1000 ppm for different elements. The concentration of palladium in all the standards was 0.01% whereas that of silver chloride plus sodium fluoride carrier was 10%.

For the investigation of the effect of carrier composition on the intensity ratios of different elements, synthetic samples with a fixed concentration of each element in the estimation range were prepared with different carriers. Fixed amounts of impurity mixture and internal standard were ground and thoroughly mixed in the mortar with different amounts of carrier and uranium oxide.

Preparation of samples

Uranium samples in the form of UO_2, U_3O_8, $UO_2(NO_3)_2$ *etc.* were taken as received and heated in platinum crucibles in the furnace at 850° for an hour; uranium metal samples were first cleaned with carbon tetrachloride, water, dilute nitric acid and again finally with quartz-distilled water before being heated to 850° in the furnace. Each sample was then ground to a fine powder and 450 mg of it were mixed with 50 mg of carrier–internal stan-

dard mixture by grinding together for about an half an hour to ensure homogeneity.

Spectrographic procedure

Duplicate standards and samples (100 mg) were loaded into the electrode crater. The electrodes were dried under an infrared lamp to remove traces of moisture, and tapped, then a tool was used to make a vent hole in the charge and to pack the charge uniformly. These operations facilitated the smooth release of the minute amounts of impurities into the arc and also minimized the amount of uranium coming into the arc. The samples and standards were excited in a glass chamber[4] inside the glove box. The spectra of the samples and standards were photographed on the same plates in duplicate under the following conditions:

Region: 2400–3600 Å.
Arc current: 12 A, d.c.
Slit-width: 15 μm.
Analytical gap: 5 mm (not kept constant during arcing).
Exposure time: 35 sec.
Photographic emulsion: Kodak Spectrum Analysis No. 1; two plates 25·4 × 10.2 cm.
Plate development: 3 min at 25° in Kodak D-19 developer; fixed in Kodak acid fixing salt solution for 3 min.

Intensity ratios were calculated for all the lines and working curves were plotted (log intensity ratio *vs.* log concentration) to evaluate the concentration in the samples. The precision of the method, expressed as coefficient of variation, was determined from ten replicate determinations on synthetic U_3O_8 samples.

RESULTS AND DISCUSSION

While theoretical considerations are helpful in providing general guide lines for the choice of carrier for the determination of different elements in refractory matrices, it is still necessary to carry out extensive experimental work if the optimum sensitivity of the final method is to be achieved. Figure 1 shows the plot of intensity ratios of Ta, Hf, W, Th and Nb for different carriers and their concentrations. It can be seen from the graph that 5% gallium oxide as carrier, which is widely used for common metallic impurities, could produce a detectable line only for W at 20 ppm while Ta, Hf, Nb and Th could not be detected even at 20–100 ppm concentrations. This could possibly be due to the relatively high volatility of tungstic oxide compared to that of other refractory oxides. With 5% silver chloride as carrier, analytical lines of all the refractory impurities could be photographed, and the intensity ratio for W was higher than when gallium oxide was used.

This could be ascribable to the higher arc temperature with silver chloride, due to the higher ionization potential of silver (7.57 eV) compared to that of gallium (6.0 eV), or to the probability of forming relatively volatile chlorides of the refractory metals by reaction with the silver chloride. Systematic study revealed that Hf, W and Th did not show much variation in intensity ratio with 10–30% of silver chloride, while Ta and Nb showed a large variation over this range. However, favourable intensity ratios were obtained for all the elements with 10% silver chloride added as carrier. At higher concentrations of silver chloride the background increased, thereby decreasing the intensity ratio.

When lithium fluoride was added to the silver chloride carrier the intensity ratios for all the elements were found to be higher than those with silver chloride alone, but the arc was not very stable. Intensity ratios for all the elements were found to be slightly higher when sodium fluoride was added instead of lithium fluoride, and in addition, the mixtures of silver chloride and sodium fluoride were then prepared, with different proportions of the two salts, such that the sodium fluoride constituted from 0.5 to 5% of the final sample mixture. It can be seen from Fig. 1 that the intensity ratios of all the analytical lines were highest for 1% of sodium fluoride in the prepared samples, and the emission spectrographic method using carrier distillation technique was therefore standardized with use of the 9:1 silver chloride–sodium fluoride carrier.

The effect of other impurities in uranium on the intensity ratios was also investigated. The intensity ratios of the lines from Hf, Ta, Nb and Th were calculated from measurements made on samples containing 21 common impurities, *viz.* Al, B, Be, Ca, Cd, Co, Cr, Cu, Fe, In, Li, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti, V and Zn, with the total concentration varying from 100 to 1000 ppm. It was observed that the intensity ratios for Hf, Ta, Nb and Th lines showed a maximum variation of about 20% with increasing amounts of impurities, which is only slightly more than the coefficient of variation (16%). This indicates that the determination of these refractory impurities will not be significantly affected by the presence of the common impurities mentioned, up to a total concentration of 1000 ppm.

Analytical lines for the elements studied, along with concentration ranges covered, are given in Table 1. The palladium lines at 2447.9 and 3027.9 Å were used as internal standard lines. The working curves were drawn as a graph of log (intensity of element line/intensity of Pd line) vs. log (concentration) and were linear over the ranges studied. The equations for the working curves for all the elements are also given in Table 1. Table 2 shows detection limits reported in the literature for the carrier distillation technique, along with those obtained here. It can be seen that the limit of detection for hafnium by this method is the lowest, those for W and Ta are comparable with the lowest reported values, while that for Nb is a little higher than the previous lowest. Results for the determination of thorium by carrier distillation have not been reported previously.

The precision of estimation of the impurities, expressed as the coefficient of variation based on ten replicate samples with duplicate determinations is shown in Table 3. The precision of the method lies in the range 8–16% for different elements, and the recoveries are quantitative within the experimental error.

This method has been used for the analysis of

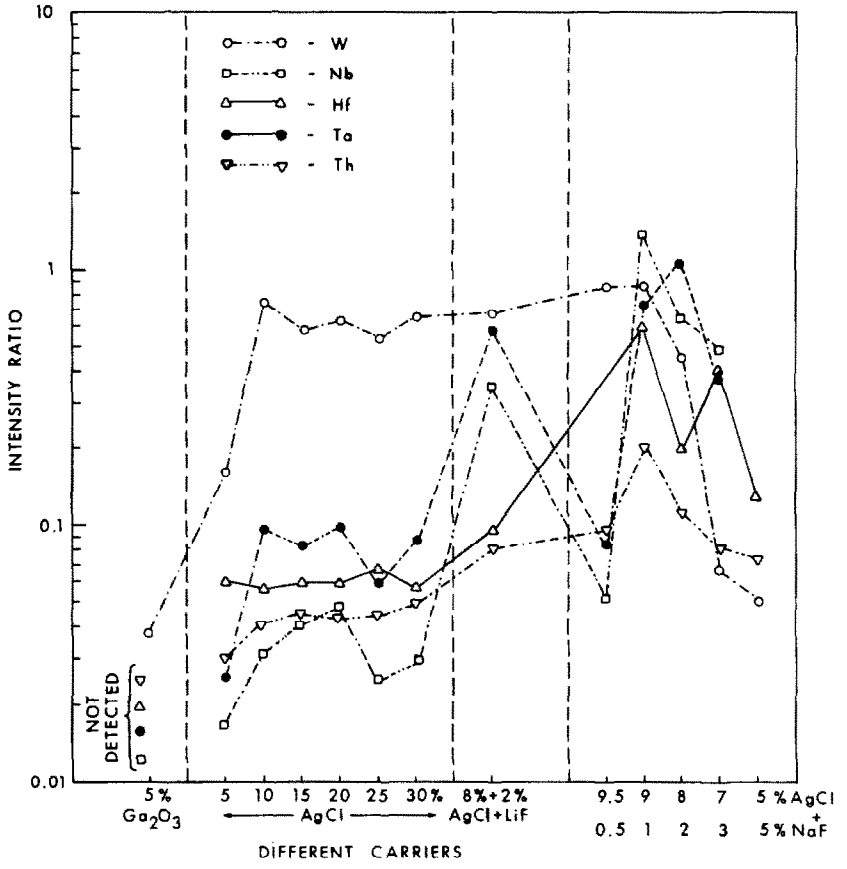


Fig. 1. Effect of carriers on intensity ratios.

Table 1. Analytical lines, estimation ranges, and equations for the working curves

Element	Analytical line, Å	Internal std. line, Å	Working range, *ppm*	Equation for working curve*
Hf	2940.7	Pd 3027.9	5–500	$\log Y = 0.89 \log x - 2.30$
Hf	2638.7	Pd 2448	5–500	$\log Y = 0.54 \log x - 1.72$
Nb	2733	Pd 2448	10–1000	$\log Y = 0.80 \log x - 2.20$
Nb	2716	Pd 2448	10–1000	$\log Y = 0.75 \log x - 1.76$
Nb	2899	Pd 3027.9	10–1000	$\log Y = 0.73 \log x - 2.2$
Ta	2646.4	Pd 2448	4–200	$\log Y = 0.62 \log x - 1.78$
Ta	2653	Pd 2448	2–200	$\log Y = 0.91 \log x - 2.60$
Th	2688	Pd 2448	10–500	$\log Y = 0.83 \log x - 2.51$
W	2681.4	Pd 2448	1–100	$\log Y = 0.59 \log x - 1.68$
W	2946.98	Pd 3027.9	5–100	$\log Y = 0.59 \log x - 1.61$

* Here x and y represent concentration and intensity ratio respectively.

Table 2. Comparison of detection limits

Element	Estimation limit, *ppm* Pepper[8]*	Feldman[9]* (LASL)	Feldman[9]* (UCY)	Pepper[12]	Present method *
Hf	100	300	100	—	5
Nb	4	25	4	—	10
Ta	10	30	10	1	2
Th	—	—	—	—	10
W	10	100	100	1	1

* Charge 100 mg.
† Charge 600 mg.

Table 3. Precision and accuracy

Element (analysis line, Å)	Amount added, *ppm*	Amount found, *ppm**	Coeff. of variation, %
Hf (2940.7)	50	51	15
Hf (2638.7)	50	53	12
Nb (2733)	100	104	14
Nb (2716)	100	104	16
Nb (2899)	100	96	15
Ta (2646.4)	20	21	14
Ta (2653)	20	21	14
Th (2688)	50	52	15
W (2681.4)	10	10	8
W (2946.98)	10	10	12

* Average for ten replicate samples.

several samples of high-purity uranium oxide and has been found to be suitable for the determination of these refractory elements at ppm levels.

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REFERENCES

1. J. E. Rein, G. M. Matlack, G. R. Waterbury, R. T. Phelps and C. F. Metz, *U.S. At. Energy Comm. Rept.*, LA-4622, 1971. *Chem. Abstr.*, 1971, **75**, 94309.
2. A. G. Page, S. V. Godbole, K. S. B. Deshkar and B. D. Joshi, *Bhabha At. Res. Centre Rept.*, BARC-862, 1976.
3. B. F. Scribner and H. R. Mullin, *J. Res. Natl. Bur. Stds.*, 1946, **37**, 379.
4. A. G. I. Dalvi, C. S. Deodhar and B. D. Joshi, *Talanta*, 1977, **24**, 143.
5. C. J. Rodden, *U.S. At. Energy Comm. Rept.*, TID-7003, 1956.
6. R. Ko, *U.S. At. Energy Comm. Rept.*, WHAN-SA-44, 1970. *Chem. Abstr.*, 1971, **75**, 71004.
7. J. C. Janvier, *Comm. Energie At. France Rapport*, No. 4433, 1973.
8. C. E. Pepper, *U.S. At. Energy Comm. Rept.*, NLCO-999, 1967. *Chem. Abstr.*, 1968, **68**, 45258.
9. C. Feldman, *U.S. At. Energy Comm. Rept.*, ORNL-TM-1590, 1966. *Chem. Abstr.*, 1967, **66**, 90933.
10. I. Schoenfeld, *Israel At. Energy Comm. Rept.*, IA-925, 1964. *Chem. Abstr.*, 1965, **62**, 11146.
11. R. S. Vogel, *U.S. At. Energy Comm. Rept.*, MCW-1471, 1962.
12. C. E. Pepper, *U.S. At. Energy Comm. Rept.*, NLCO-1105, 1973. *Anal. Abstr.*, 1974, **27**, 3179.
13. C. J. Martell, *U.S. At. Energy Comm. Rept.*, LA-5454, 1974. *Chem. Abstr.*, 1974, **81**, 85696.

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SPECTROPHOTOMETRIC TITRATION OF ZIRCONIUM IN SILICEOUS MATERIALS

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Summary—An accurate and selective complexometric titration procedure based upon a spectrophotometrically detected end-point has been developed for the determination of zirconium in glasses, glass-ceramics and refractories. A *p*-bromomandelic acid separation step for zirconium imparts excellent selectivity to the procedure. The method is particularly important for the 1–5% concentration range where a simple, accurate and selective method for the determination of zirconium has been lacking.

Although several methods are available for the determination of zirconium, *e.g.*, spectrophotometry (Pyrocatechol Violet), gravimetry (*p*-bromomandelic acid) and complexometry (EDTA), none has proven satisfactory for the precise determination of low levels (1–5%) of zirconium in complex glasses, glass-ceramics and refractories. Spectrophotometry is sensitive but lacks the necessary precision for the accurate determination of zirconium.[1–3] Gravimetry generally exhibits good precision and accuracy, but is tedious, and our studies have shown that co-precipitation of contaminants from solutions of complex glass compositions is a problem.[4–7] Although complexometry is rapid, it suffers from a variable end-point (sharp to sluggish) depending upon the glass composition.[8,9] The major goal of this study was to improve the sensitivity, precision and accuracy of the EDTA complexometric method of Su *et al.*[9] by incorporating a *p*-bromomandelic acid separation step and using a spectrophotometrically detected end-point for the titration. The principles and practical applications of spectrophotometric titrations have been described by several authors.[10–12] Sweetser and Brickler[13] and Milner and Edwards[14] have reported methods for the complexometric determination of zirconium with absorptiometric end-point detection, but neither of these methods has proved suitable for the analysis of glass. One[13] lacked the necessary selectivity, the other[14] utilized sulphuric acid, which precludes the analysis of glasses containing lead and barium.

EXPERIMENTAL

Reagents

Standard zirconium solution, 0.0125*M*. Exactly 0.1540 g of ZrO_2 (ignited at 1100°) was weighed, and fused in a platinum dish with 4 g of anhydrous 1:1 sodium carbonate–sodium borate mixture in a muffle furnace set at 1000°. When cooling, the melt was dissolved by warming with 40 ml of perchloric acid (1 + 1) and 10–15 ml of distilled water. The solution was then cooled and diluted to 100 ml in a standard flask.

Standard EDTA solution, 0.014*M*. Make a 0.5% EDTA solution. Evaporate a 10.00-ml aliquot of the 0.01250*M* zirconium solution to dryness and then ignite at 1000°. Fuse the residue with 2–3 g of 1:1 sodium carbonate–sodium borate mixture, cool the dissolved melt in 10–15 ml of distilled water and 25 ml of perchloric acid (1 + 1) dilute to 100 ml, heat to 95°, add 3 drops of Xylenol Orange indicator solution and titrate immediately with the EDTA, detecting the end-point spectrophotometrically (520 nm). Alternatively weigh 10–15 mg of ignited ZrO_2 on a microbalance and apply the fusion procedure *etc.*

Spectrophotometric titrations

Spectrophotometric titrations were conveniently done with a Brinkman Probe Colorimeter coupled to a Metrohm Potentiograph–Titrator. The absorbance measurements (at 520 nm) were unaffected by ambient light and the end-points and were readily determined from the sharp break in the titration curve.

Procedure for sample analysis

Mix the sample with 1:1 anhydrous sodium carbonate–sodium borate mixture in a platinum dish and fuse in a muffle furnace (1000°). The ratio of flux to sample weight must be at least 10:1. Allow to cool, then add 20 ml of perchloric acid (1 + 1) and 10–20 ml of distilled water and allow the solution to digest for 2–3 hr. Filter off the silica by suction and set aside the filtrate which contains nearly all of the zirconium, and wash well with warm distilled water. Transfer to a platinum dish, char the paper, then ignite at 700–800°. Treat the silica with hydrofluoric and perchloric acids, evaporate to dryness, then treat the residue with 70% perchloric acid, heat to dryness and ignite at 1000°. Fuse the ignited residue with 1 g of 1:1 sodium carbonate–sodium borate mixture and dissolve the cooled melt with 5 ml of perchloric acid (1 + 1) and 5 ml of distilled water. Combine this solution with the zirconium filtrate previously set aside, and reduce the volume to about 75 ml by evaporation. Precipitate zirconium from the hot solution by addition of 25 ml of 0.1*M* *p*-bromomandelic acid solution with stirring. Digest the precipitate on a steam bath, then filter off by suction, wash well with distilled water and ignite at 1000°. Determine the zirconium in the residue by the procedure described above for the standardization of EDTA.

DISCUSSION

Zirconium is often a very significant part of complex matrices for glasses and ceramics comprised of major and minor levels of silicon, barium, lead, lanthanum, aluminium, titanium, iron, antimony, silver and other elements. Hence an accurate knowledge of its concentration, at both the major and minor levels, is necessary for correlating specific physical properties with chemical composition. Owing to inherent characteristics of the methods, the various procedures for zirconium, particularly at low concentration levels (<5%), have never been fully satisfactory. The gravimetric method (*p*-bromomandelic acid) is tedious in that three precipitations are required to preclude serious contamination, and the EDTA complexometric method often suffers from a sluggish end-point. By combining the two methods and utilizing spectrophotometric end-point detection, a very reliable method has been developed for determining zirconium levels as low as 1% in siliceous materials. Some essential features encompassed in the new procedure are described. No hydrofluoric acid treatment is used for sample dissolution, thus precluding interference from fluoride retention. Su and Campbell[7] established that fluoride retained from hydrofluoric acid sample decomposition is very difficult to eliminate by fuming with perchloric acid. Sulphuric acid is not admissible at low zirconium concentration levels in the presence of barium and lead. However, hydrofluoric acid treatment of the filtered silica followed by evaporation and ignition at 1000° presents no problem of residual fluorides. The inclusion of a simple *p*-bromomandelic acid separational step for zirconium ensures a sharp end-point for titrations despite complexity of the glass compositions. The separational step is unnecessary for simple compositions involving alkali metals, calcium, magnesium, boron, silica and aluminium. The spectrophotometric end-point detection gives better sensitivity, precision, and accuracy than the current visual end-point detection techniques. Because zirconia standards in siliceous materials are not commercially available, the results by the proposed method were compared with those from the standard p-bromomandelic acid procedure.

Diverse ion study

A study of the effect of diverse ions on the titration was completed for those elements commonly found in glass compositions. A specific amount of each salt (10 or 100 mg) was added to a zirconium solution (15.4 mg of ZrO_2) before EDTA titration, and the results were compared with those in the absence of the added ion. Antimony, titanium and lanthanum were added at the 10-mg level. Of these three elements, only antimony appeared to interfere, causing a 1.5% negative bias. Zinc, cadmium, iron, calcium, magnesium, barium, vanadium, cobalt, lead, aluminium and bismuth were added at the 100-mg level. Of these elements, only bismuth interfered by being titrated with zirconium, imparting a large positive bias to the titration. The effect of antimony, barium and lead was examined more critically by applying the whole procedure. Barium and lead were included because their concentrations in some of the glass compositions were particularly high. The resulting data from the titrations revealed that antimony was indeed a major interference, causing a negative bias of approxinately 25%. Barium and lead did not interfere. The interfering effect from antimony was evidently intensified by the fusion step and acid dissolution. Perhaps the formation of an anionic complex between antimony and oxygen[15] complexed the zirconium to the extent of causing the negative bias for the titration. The *p*-bromomandelic acid separation step precluded interference from bismuth but not from antimony. Hence, of the elements examined, only antimony interfered.

Extent of co-precipitation in the gravimetric method for zirconia

Before using the *p*-bromomandelic acid procedure as a reference method, it was necessary to examine it with respect to the extent of co-precipitation. Two approaches were used. First, zirconium was precipitated from solutions repetitively until the weights of the ignited zirconium oxide residues were essentially constant. Secondly, the zirconiim oxide residues were examined spectrographically to determine the degree to which specific contaminants were present. The results in Table 1 for a high-aluminium glass indicate that the constant weight was attained after the third precipitation. Spectrographic examination of several ignited zirconium oxide residues from high-aluminium glasses, glass-ceramics and refractories indicated that the amount of co-precipitation from aluminium varied. Generally, three precipitations provided spectrographically clean residues. The data in Table 2 indicate that constant weight is more difficult to obtain for lead glasses than high-aluminium glasses, probably because of co-precipitation of lead. This is supported by the spectrographic data (Table 3) which showed a lead to be detectable in the zirconium oxide after the third precipitation but not the fourth. No losses due to the solubility of zirconium *p*-bromomandelate were detected in our study. This is in

Table 1. Extent of co-precipitation in high-aluminium glasses

Sample	Precipitation with *p*-bromomandelic acid	ZrO_2 on ignition *mg*
1	Second	15.47
	Third	14.43
	Fourth	14.40
2	Second	15.96
	Third	15.25
3	Fourth	15.18

Table 2. Extent of co-precipitation in high-lead glass

Sample	Precipitation with *p*-bromomandelic acid	ZrO_2, ignited *mg*	ZrO_2 %
1	Second	22.02	7.08
	Third	21.19	6.66
	Fourth	21.03	6.61
2	Second	21.35	6.88
	Third	20.90	6.74
	Fourth	20.50	6.61
3	Second	21.26	6.88
	Third	20.88	6.76
	Fourth	20.68	6.69
	Fifth	20.66	6.68
4	Second	22.03	7.08
	Third	21.02	6.75
	Fourth	20.80	6.68
	Fifth	20.74	6.66

Table 3. Spectrographic examination of ignited ZrO_2 residues from high-lead glasses

Concentration range, %	High-lead glass residue 3rd precipitation	High-lead glass residue 4th precipitation
>30	Zr	Zr
10–30	—	—
3.0–10	—	—
1.0–3.0	Hf	Hf
0.3–1.0	Pb	—
0.1–0.3	—	—
0.03–0.1	B, Ba	Al
0.01–0.03	Bi, Fe, Al	B, Si, Fe

agreement with other investigators[5,16,17] who found the *p*-bromomandelic acid method to be quantitative at the 0.1–20 mg level.

Estimate of precision

The precision of the titrimetric portion of the procedure was estimated by titrating on five successive days aliquots of standard zirconium solution with EDTA (fusion not included). The mean and 95% confidence limits were $0.01419 \pm 0.00003M$. An estimate of the precision for the overall procedure was obtained on a glass sample of high lead composition (Table 4).

Effect of hafnium

Spectrographic examination established that zirconium oxide residues from the gravimetric analysis of glasses contain approximately 2% hafnium. Since the atomic weight for hafnium is nearly double that of zirconium, calculations show that a measurable error results in the complexometric method when the EDTA is standardized with hafnium-free zirconium

Table 4. Zirconium determination in typical glass and refractory matrices

Sample	ZrO_2, %			
Oxide composition*	Complexometric	Mean	Gravimetric	Mean
Ba-Si-B-La, Zr†	0.88, 0.87, 0.89, 0.93	0.89	0.90, 0.88	0.89
Si-Al-Mg-Ti-Zr	3.67, 3.53, 3.66, 3.56	3.60	3.65, 3.51, 3.51	3.56
Pb-Si-B-Li-Ti-Cd-Zr§	6.67, 6.70, 6.70, 6.77, 6.61	6.69	6.58, 6.70, 6.61, 6.61, 6.68	6.64
Si-Pb-Li-Zr	6.37, 6.31	6.34	6.32	—
Si-Pb-Li-Zr	6.51, 6.56	6.53	6.60	—
Al-Zr	45.6	—	46.6, 45.7	46.1
Al-Zr	59.9	—	60.8, 59.9	60.3

* Major components.
† Colorimetric procedure: 0.84% ZrO_2.
§ 95% Confidence limits for the mean:
Complexometric method: 6.69 ± 0.072
Gravimetric method: 6.64 ± 0.059.

and used for the titration of zirconium in hafnium-containing samples. When the results are compared with those obtained gravimetrically, the error at the 6% ZrO_2 level is insignificant, but becomes increasingly important at concentration levels greater than 10% ZrO_2. Hence to preclude an error of this type, purified hafnium-containing zirconium oxide used for batching of glass melts was used to standardize the EDTA solution. The material was purified by precipitation with *p*-bromomandelic acid followed by ignition to the oxide. Although this practice is somewhat empirical in nature, it results in a more accurate analysis relative to total zirconium and hafnium.

REFERENCES

1. J. P. Young and J. C. White, *Talanta*, 1958, **1**, 263.
2. D. F. Wood and J. T. Jones, *Analyst*, 1965, **90**, 125.
3. J. O. Hibbits, A. F. Rosenberg, R. T. Williams and S. Kallman, *Talanta*, 1965, **11**, 1509.
4. R. B. Hahn, *Anal. Chem.*, 1951, **23**, 1259.
5. R. A. Papucci, D. M. Fleishman and J. J. Klingenberg, *ibid.*, 1953, **25**, 1758.
6. R. A. Papucci and J. J. Klingenberg, *ibid.*, 1955, **27**, 835.
7. Y. S. Su and D. E. Campbell, *Anal. Chim. Acta*, 1971, **55**, 265.
8. Y. S. Su, *Anal. Chem.*, 1965, **37**, 1067.
9. Y. S. Su, W. R. Strzegowski, A. R. Kacyon and I. E. Lichtenstein *Anal. Chim. Acta*, 1976, **81**, 167.
10. J. M. Fortuin, P. Karsten and H. L. Kies, *ibid.*, 1954, **10**, 356.
11. R. F. Goddu and D. N. Hume, *Anal. Chem.*, 1954, **26**, 1740.
12. J. B. Headridge, *Photometric Titrations*, Pergamon, New York, 1961.
13. P. B. Sweetser and C. E. Bricker, *Anal. Chem.*, 1954, **26**, 195.
14. G. W. C. Milner and J. W. Edwards, *Analyst*, 1955, **80**, 879.
15. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry, 3rd Ed.*, p. 392. Interscience, New York, 1972.
16. C. E. Bricker and G. R. Waterbury, *Anal. Chem.*, 1957, **29**, 558.
17. R. Belcher, A. Sykes and J. C. Tatlow, *Anal. Chim. Acta*, 1954, **10**, 34.

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DETERMINATION OF ZINC IN BLAST FURNACE FLUE DUSTS*

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Summary—Two methods for the determination of zinc in blast-furnace flue dusts are described. One involves a solvent extraction step using methyl isobutyl ketone to separate the zinc from the bulk of the interfering elements, followed by a complexometric titration of the zinc with EDTA, using Eriochrome Black T as indicator. The other employs differential pulse polarography with a hydrochloric acid + pyridine supporting electrolyte. In this method, the interference of iron is prevented by reducing it with hydroxylamine hydrochloride; aluminium is complexed with potassium fluoride. Other elements, with the exception of cobalt, do not interfere. Excellent agreement between the two methods is obtained in the range 0.01–0.6% zinc.

Because of difficulties encountered in determining zinc in blast-furnace flue dust by an atomic-absorption spectrophotometric technique, it was necessary to determine the zinc by other methods. In these samples the zinc was estimated to be in the range 0.05–1.0%.

A previous series of reports has outlined procedures for the determination of relatively large amounts of zinc in zinc ores, concentrates and tailings by solvent extraction followed by EDTA titration or polarographic and amperometric methods.[1,2] It appeared that two of the procedures described,[1] a polarographic method and a solvent extraction–EDTA titration method, were the most applicable to the determination of the small amounts of zinc in the blast-furnace gas dust samples. The polarographic method is subject to interference by cobalt, and the solvent extraction–EDTA titration method is subject to interference by cadmium. Neither cadmium nor cobalt was believed to be present in the flue dust samples in amounts sufficient to warrant concern, but by employing the two methods, the results could be compared to ascertain if a serious interference occurred in either method. For example, if cadmium were present in significant amounts its presence would be detected in the polarographic method, because it gives a wave at -0.61 V *vs.* the SCE. This wave appears well in advance of the zinc wave and does not interfere with the determination of zinc. On the other hand, cobalt and other interfering elements that may be extracted in trace amounts by the solvent extraction step are prevented from interfering in the titration with EDTA by the addition of potassium cyanide.

This paper describes the successful application of each of these two methods to the determination of zinc in blast-furnace flue dusts. Slight modifications to the solvent extraction–EDTA titration method were necessary because of the presence of large amounts of iron and other extractable impurities. The polarographic method did not require modification other than ignition of the samples to remove the large amounts of carbon present. The zinc was determined by differential pulse polarography, a technique useful for determining small amount amounts of an element in the presence of elements that are polarographically reducible before the element sought.[3,4]

EXPERIMENTAL

Apparatus

A Princeton Applied Research Model 174 Polarographic Analyzer with PAR Model 174A Mercury Drop Timer and Houston Omnigraphic Model 2000 X-Y Recorder was used, with Sargent-Welch capillary tubing (S-29417) and H-type polarographic cell (S-29400).

Dissolution procedure

Ignite the sample in a porcelain crucible at dull red heat to remove carbon. Take 0.5–2 g of sample if the titrimetric method is to be used, otherwise a 0.2-g sample will suffice for the polarographic method. Treat the residue in the crucible with 5 ml of 12*M* hydrochloric acid and 1–2 ml of 72% perchloric acid. Warm the sample to dissolve the soluble salts and transfer to a 100-ml beaker. Add 5 ml of 9*M* sulphuric acid and evaporate to fumes to remove the excess of hydrochloric and perchloric acids. Add 20 ml of water plus 2 or 3 drops of 12*M* hydrochloric acid and boil to dissolve the soluble salts. Cool to room temperature.

Titrimetric method

Transfer the solution to a separatory funnel (fitted with a Teflon stop-cock), using a minimum of water to rinse the beaker. Add ammonia solution dropwise to neutralize the excess of acid, until a faint precipitate of iron hydroxide appears, then clear the solution with a few drops of hydrochloric acid. Note the volume of solution, which should be between 25 and 40 ml. Add in succession, with mixing after each addition, 6–10 g of ammonium hydrogen fluoride, 5 ml of saturated thiourea solution and 30 ml of 50% ammonium thiocyanate solution. If the solution at this point is deep red, insufficient ammonium hydrogen fluoride

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is present and more should be added until the solution is pale yellow. The red colour will also appear if the solution is too acid and in that case, add ammonia solution dropwise to reduce the acidity, but do not allow the solution to become basic or the zinc will not be extracted. If the volume of the sample solution exceeds 25 ml, add 3 g of solid ammonium thiocyanate for each 5 ml of solution in excess of 25 ml and dissolve it. Add 40 ml of methyl isobutyl ketone and shake for 2 or 3 min to extract the zinc. Allow the phases to separate and discard the lower, aqueous layer. Wash the organic layer by shaking with 25 ml of the wash-solution (25% ammonium thiocyanate, 7.5% ammonium hydrogen fluoride, 75 ml of saturated thiourea solution per litre) to reduce the amount of impurities, especially iron, co-extracted with the zinc. Drain and discard the aqueous layer. Drain the organic layer into an 800-ml beaker and rinse the separatory funnel several times with water, adding the rinsings to the beaker. Add 30 ml of pH-10 ammonia buffer solution (350 ml of concentrated ammonia solution and 54 g of ammonium chloride per litre), 50–100 ml of acetone and dilute to 400 ml with water. Add 2–3 ml of 20% potassium cyanide solution and about 100 mg of Eriochrome Black T indicator mixture (0.2 g of indicator mixed with 100 g of potassium chloride). The solution at this point will be orange-red in colour owing to the zinc that is liberated from its cyanide complex by the acetone. Titrate the zinc with 0.01*M* EDTA solution until the solution turns greenish-blue. Add 4% formaldehyde solution in small amounts and continue to titrate until further addition of formaldehyde has no effect on the colour. Further addition of Eriochrome Black T may be necessary if blocking of the indicator is evident. The end-point will be green in colour rather than blue, as is the case with pure zinc solutions, because of the presence of impurities co-extracted with the zinc.

Polarographic method

Transfer the solution to a 100-ml volumetric flask and dilute to about 50 ml with water. Add ammonia solution dropwise to neutralize the excess of acid, until a faint precipitate of iron hydroxide appears, then clear with 1 or 2 drops of hydrochloric acid. Add 2.0 ml of 12*M* hydrochloric acid and 20 ml of 10% hydroxylamine hydrochloride solution. Bring the solution to the boil* and when the reduction of iron is complete, cool to room temperature and add 0.3 g of potassium fluoride to complex any aluminium present. Add 5.0 ml of pure pyridine (by pipette), 2 ml of 0.1% Triton X-100 solution as maximum suppressor, dilute to the mark with water and mix. Transfer a portion of the solution to a polarographic cell maintained at 25.0 ± 0.1° in a water-bath and deaerate the solution with nitrogen. Immerse a dropping mercury electrode in the solution and record a polarogram, using differential pulse polarography, at a potential from −0.8 to −1.2 V *vs.* the SCE. Calculate the zinc content by reference to a calibration chart prepared from pure zinc solutions.

RESULTS AND DISCUSSION

Titration method

The solvent extraction–EDTA titrimetric method described in a previous report[1] is basically the method proposed by Kinnunen and Wennerstrand.[5] The zinc is extracted as its thiocyanate complex, into methyl isobutyl ketone. Ammonium fluoride is added to prevent the extraction of iron, and thiourea is added to prevent the extraction of copper and silver. The zinc is titrated with standard EDTA solution, with Eriochrome Black T as indicator. Potassium cyanide is added to mask any interferents that may be co-extracted with the zinc, acetone and formaldehyde are added to demask the zinc from its cyanide complex. This method had previously been used only for the separation and determination of macro-amounts of zinc, *i.e.*, 20–150 mg of zinc in samples of zinc concentrates, ores and tailings; the behaviour of smaller amounts of zinc was not investigated. Because of the different composition of the blast-furnace flue dusts (see Table 1), and the fact that very large amounts of iron were present, a few preliminary experiments were carried out to see whether relatively small amounts of zinc, *e.g.*, 1–5 mg, could be extracted quantitatively from solutions containing large amounts of iron and quantities of copper and nickel about the same as those of zinc. The results of these tests are shown in Table 2 and indicate that they can. The titration method was applied to the determination of zinc in several samples of blast-furnace flue dusts. In preliminary experiments, treatment of the samples with mixtures of hydrochloric, nitric and perchloric acid failed to remove the carbon expeditiously and it was found easier and less time-consuming to ignite the samples to remove the carbon. Treatment of the residue with hydrochloric and perchloric acid readily dissolved the sample, leaving only a residue of silica which did not interfere with the determination of zinc. In these experiments, some erratic results were obtained, but it was found that this was due to the samples being inhomogeneous rather than to volatilization or loss of zinc in the ignition step. In subsequent work, all the samples were reground and mixed in a mechanical grinder to ensure homogeneity. The results of these analyses are given in Table 3, together with the results obtained by the polarographic procedure.

The extraction procedure is essentially identical to that used for the analysis of zinc concentrates, except that much larger amounts of ammonium hydrogen fluoride are necessary to mask the amount of iron present in the flue dust. In addition, the organic phase containing the zinc must be washed with thiocyanate–fluoride–thiourea solution to reduce further the amount of impurities co-extracted with the zinc. In spite of this washing, a significant amount of iron and possibly other impurities was found to accompany the zinc. These impurities were masked to a great extent by the potassium cyanide added before the titration but the end-point was not as distinct

Table 1. Average composition of blast-furnace dusts

Total Fe (5–10% metallic Fe) 55%
Carbon 5–10%
CaO 2–5%
MgO 1–3%
SiO_2 3–10%
K_2O, Na_2O, Al_2O_3, 0.5% each
Zn 0.05–1.0%

* This is convenient for rapid control work, but because of possible hysteresis effects in the volume of the flasks, it is better to use conical flasks for this step.

Table 2. Extraction of small amounts of zinc from synthetic solutions containing iron, copper and nickel

Metals present	Zinc present, *mg*	Zinc found, *mg*
Fe^{3+} 300 mg, Cu 5 mg, Ni 5 mg	5.18	5.19
Fe^{3+} 300 mg, Cu 5 mg, Ni 5 mg	1.04	1.04

Table 3. Determination of zinc in blast furnace gas dusts by solvent extraction—EDTA titration and polarographic methods

Sample	Zinc, %*			
	EDTA titration		Polarography	
EMT-1704	0.63,	0.63	0.61,	0.58
EMT-1705	0.49,	0.49	0.49,	0.48
EMT-1706	0.15,	0.15	0.16,	0.16
EMT-1707	0.097,	0.090	0.087,	0.090
EMT-1708	0.020,	0.010	0.010,	0.007
EMT-1710	0.34,	0.34	0.33,	0.33

* Individually weighed samples.

as in the titration of pure zinc solutions. The initial ketone extract was colourless, but on standing it became yellow and the colour at the end-point was green rather than pure blue. Some blocking of the Eriochrome Black T occurred and addition of more indicator was necessary during the titration. For 2–5 mg of zinc the end-point was satisfactory, but for less than 1 mg, the end-point was more uncertain. The method appears to be satisfactory for flue dust samples containing more than 0.05% of zinc.

Polarographic method

The procedure used was essentially the same as described for the determination of zinc in zinc ores,[1] but again, because of the nature of the sample, it was preferred to remove the carbon by ignition and use the same dissolution procedure as before.

The polarographic procedure was applied to the determination of zinc in several samples of blast-furnace flue dust. The results of these analyses are shown in Table 3 and may be compared with those obtained by the titration method, with which they are in excellent agreement. The polarographic method is more rapid than the titration method because an extraction step is unnecessary. Moreover, especially if differential pulse polarography is employed, the method is capable of determining much smaller amounts of zinc and a smaller sample weight can be taken. An additional advantage is that the polarographic method may be used to determine copper and nickel simultaneously with the zinc, if desired, although this aspect was not pursued. The polarograms of the samples showed the presence of copper, lead and nickel and although not determined, they were estimated to be in the range 0.02% Cu, 0.02% Pb and from 0.02 to 0.1% Ni. In most samples, the copper and nickel contents were lower than the zinc content, but in a few samples the nickel exceeded the zinc content, e.g. samples EMT-1707 and 1708. Cadmium was not detectable. Cobalt was not present in significant amounts; if it had been, the polarographic results would have been higher than the titrimetric results.

REFERENCES

1. A. Hitchen and G. Zechanowitsch, *CANMET Rept.* MRP/MSL 77-275 (TR), Department of Energy, Mines and Resources, Ottawa, Canada, 1977.
2. *Idem, CANMET Rept.* MRP/MSL 77-48 (TR), Department of Energy, Mines and Resources, Ottawa, Canada, 1977.
3. L. Meites, *Polarographic Techniques*, 2nd Ed., Interscience, New York, 1965.
4. E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, 1964 **36,** 1366.
5. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1953 **42,** 80.

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GAS CHROMATOGRAPHIC STUDY OF VOLATILE OXIDES AND HYDROXIDES OF Re, Tc, Os, Ru AND Ir—II

THERMOCHROMATOGRAPHIC INVESTIGATIONS

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Summary—The enthalpies and entropies of absorption on quartz granules of the oxides and hydroxides of Re, Tc, Os, Ru and Ir have been determined by thermochromatography. The separations of these elements have been achieved with dry and moist oxygen as reactive and carrier gas.

Thermochromatography (TC) is a form of gas chromatography in which compounds are separated in a column with a negative temperature gradient. Each compound has a characteristic deposition temperature, so that a compound is not characterized by a retention volume or a retention time, but by a certain deposition position in the column or a characteristic temperature. Since the only possibility for direct measurement of the deposited compounds is the use of radioactivity, the method is restricted to the separation of radioactive compounds.[1–14] Thermochromatography can also be used for the determination of thermodynamic values[15–17] such as the enthalpy and entropy of adsorption.

The aim of the present work was the determination of enthalpies and entropies of adsorption of oxides and hydroxides of some transition elements, with quartz as stationary phase.

EXPERIMENTAL

Apparatus

Figure 1 shows the experimental arrangement for the thermochromatographic experiments with a temperature gradient. The oven consisted of 11 separate heating coils wound on a ceramic tube, inner diameter 25 mm and length 100 cm. The first two coils were 3 and 7 cm long, the other nine 10 cm long. The temperatures of the different heating circuits were controlled by a potentiometer. The oven was wrapped with asbestos and embedded in a container filled with mica. Between the coils Ni–Ni/Cr thermocouples were installed so that the temperature gradient could be checked continuously. The solid line in Fig. 1 shows the gradient when the carrier gas was dry; the dotted line shows the gradient with moist carrier gas.

The separation column was a quartz tube, bore 8 mm, packed with annealed quartz granules (315–630 μm diam.). A cooling trap at 0° was also packed with quartz granules. When moist carrier gas was used the trap was left empty and its temperature was 25°. The quartz column was

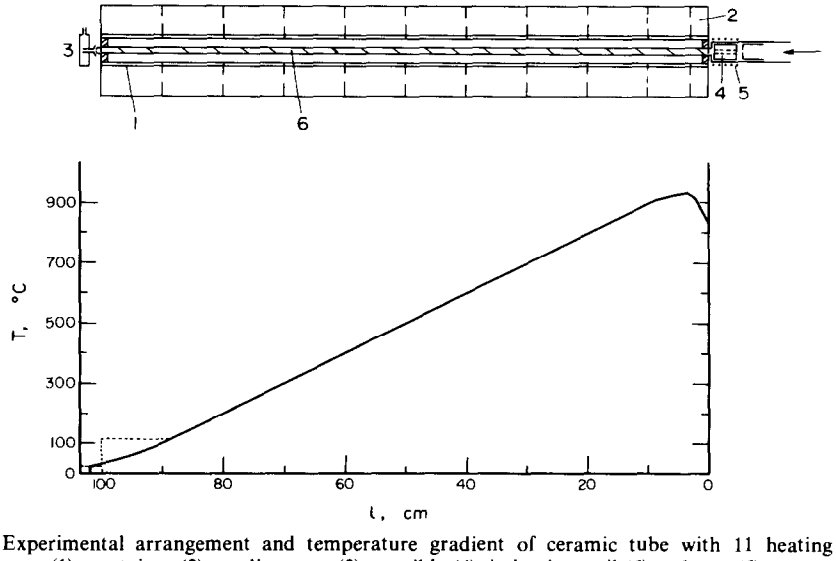


Fig. 1. Experimental arrangement and temperature gradient of ceramic tube with 11 heating coils (1), container (2), cooling trap (3), crucible (4), induction coil (5), column (5).

annealed before each experiment for about 1 hr at 850° to remove adsorbed water and other compounds.

Materials

The elements investigated were produced by nuclear reactions resulting from the irradiation of uranium foils (93%^{235} U) with thermal neutrons and of gold foils with 600 MeV-protons. The irradiated metal foils were heated in a graphite crucible (with a boron nitride wrapping) by high-frequency induction heating to a temperature of about 1500°. The nuclear reaction products were volatilized as oxides in an oxygen atmosphere, or as oxides and hydroxides in an oxygen/water atmosphere. The volatile products were either separated directly in the column or before separation were condensed at the beginning of the column by a cooling jacket and revolatilized at 950°. The latter method gives a precise starting point for the separation. At the completion of the experiment the quartz column was removed from the oven and the compounds which had been transported and deposited were determined by γ-spectrometry. This was achieved by passing the quartz column in front of a Ge(Li)-detector in steps of 2 cm with a measuring time of 15 min.

All experiments were carried out at atmospheric pressure with a gas flow-rate of 6 ml/min at room temperature. The partial pressure of water vapour in experiments with moist oxygen was 150 mmHg. The time for one experiment varied between 5 and 120 min.

RESULTS AND DISCUSSION

Determination of enthalpies and entropies of adsorption

The migration velocity of a compound in a gas chromatographic column is determined by the velocity of the carrier gas and the distribution of the compound between the mobile and stationary phases or in the case of gas adsorption chromatography, between the gas phase and the solid phase. The following equation has been derived for linear ideal gas chromatography,[18]

$$\frac{dl}{dt} = \frac{u_T}{K_i + 1} \tag{1}$$

where l is the distance of the peak maximum from the starting point, t is the time, u_T the carrier gas velocity at the temperature of the column and K_i the distribution coefficient of species i.

The following assumptions are inherent in this equation: the distribution coefficient is independent of concentration, diffusion processes can be neglected, adsorption equilibrium is reached instantaneously and the velocity of the carrier gas is constant at every point along the column. In this study the first assumption is justified, since nuclear reaction products were used so that measurements were carried out in the linear range of the Langmuir adsorption isotherm. The other conditions were only partly fulfilled.

For the special case of migration in a thermochromatographic column the velocity u_T, the distance l and the distribution coefficient K_i must be expressed as a function of temperature.

$$u_T = u_0 \frac{T}{T_0} \tag{2}$$

where u_0 is the velocity of the carrier gas at temperature T_0;

$$\frac{dT}{dl} = -a \tag{3}$$

where a is the temperature gradient; K_i can be expressed in terms of K_c, the concentration equilibrium adsorption constant, by the equation

$$K_i = \frac{s}{V_g} K_c \tag{4}$$

where s is the surface area of the solid phase and V_g the gas volume of the column (dead volume).

The calculation of K_p from K_c can be done by using the following equation assuming ideal gas properties:

$$K_p = K_c(RT)^{\Delta\nu} \tag{5}$$

The change $\Delta\nu$ in the number of moles in the gas phase by adsorption on a solid phase is -1. From equations (4) and (5) equation (6) can easily be derived:

$$K_i = \frac{s}{V_g} RT \exp\left(\frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}\right) \tag{6}$$

where ΔH^0 is the standard adsorption enthalpy and ΔS^0 the standard adsorption entropy.

From equations (1), (2), (3) and (6) it follows that,

$$dt = \frac{T_0}{aTu_0}\left[1 + \frac{s}{V_g} RT \exp\left(\frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}\right)\right] dT \tag{7}$$

For the movement of a compound in the temperature gradient from the starting temperature T_s to the characteristic deposition temperature T_a in time t_a, the following equations are obtained,

$$\int_0^{t_a} dt = \frac{T_0}{-au_0} \int_{T_s}^{T_a} \left[\frac{1}{T} + \frac{s}{V_g} R \exp\left(\frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}\right)\right] dT \tag{8}$$

$$t_a = \frac{T_0}{u_0 a}\left[\ln\frac{T_s}{T_a} + \frac{s}{V_g} R \exp\left(\frac{\Delta S^0}{R}\right) \int_{T_a}^{T_s} \exp\left(\frac{-\Delta H^0}{RT}\right) dT\right] \tag{9}$$

The integral

$$\int_{T_a}^{T_s} \exp\left(\frac{-\Delta H^0}{RT}\right) dT = Z \tag{10}$$

cannot be solved and has to be calculated numerically. In Fig. 2 $\ln Z$ is plotted against $1/T_a$ for different values of ΔH^0. To a first approximation linear curves of the form

$$\ln Z = \frac{-\Delta H^0}{RT_a} \tag{11}$$

are obtained. From equations (9) and (10) the expression

$$\frac{t_a a u_0}{T_0} = \ln\frac{T_s}{T_a} + \frac{s}{V_g} R \exp\left(\frac{\Delta S^0}{R}\right) Z \tag{12}$$

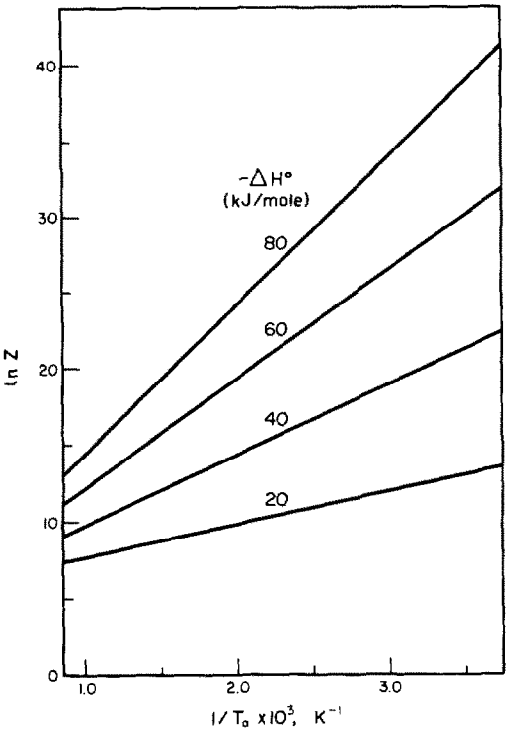


Fig. 2. Variation of ln Z with $1/T_a$ (T_s = 1173 K).

is derived and when ln (T_s/T_a) is neglected,

$$\ln Z = \ln \frac{t_a a u_0 V_g}{T_0 R s} - \frac{\Delta S^0}{R}. \tag{13}$$

The error obtained when ln (T_s/T_a) is neglected is dependent on the time t_a and the deposition temperature T_a. This error is at a maximum of 15% when t_a = 5 min and 1% when t_a = 120 min.

When ln (T_s/T_a) is neglected the error is comparable to (sR/V_g) exp $(\Delta S^0/R)$ Z and is dependent on ΔS^0, ΔH^0 and T_a and is less than 10%. Equation (13)

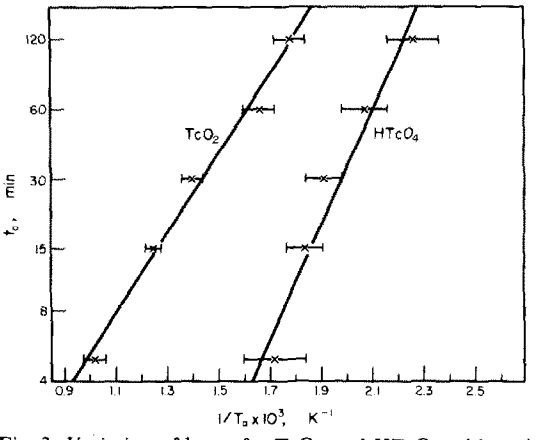


Fig. 3. Variation of log t_a for TcO_2 and $HTcO_4$ with reciprocal deposition temperature.

can be solved for ln t_a:

$$\ln t_a = \ln Z + \frac{\Delta S^0}{R} + \ln \frac{R T_0 s}{a u_0 V_g}. \tag{14}$$

From equation (11) the expression

$$\log t_a = \frac{-\Delta H^0}{2.3 R T_a} + \frac{\Delta S^0}{2.3R} + \log \frac{R T_0 s}{a u_0 V_g} \tag{15}$$

is obtained.

Merinis and Boussières obtained, for the movement of a compound in a logarithmic temperature gradient $dT/dl = -\alpha T$, a similar relation, which, however, cannot be used for the determination of entropy values.[8] In Figs. 3–5 log t_a values are plotted against $1/T_a$. The enthalpies of adsorption can be calculated from the slopes and the entropies from the intercepts of the linear curves (Figs. 3–5) when the constant log $(RT_0 s/au_0 V_g)$ is known. The calculated values are summarized in Table 1, the errors being calculated by regression analysis. The constant has been evaluated by using the following values, R = 8.314 J. deg^{-1}. mole^{-1}, T_0 = 273 K, s = 4000 cm^2, a = 10

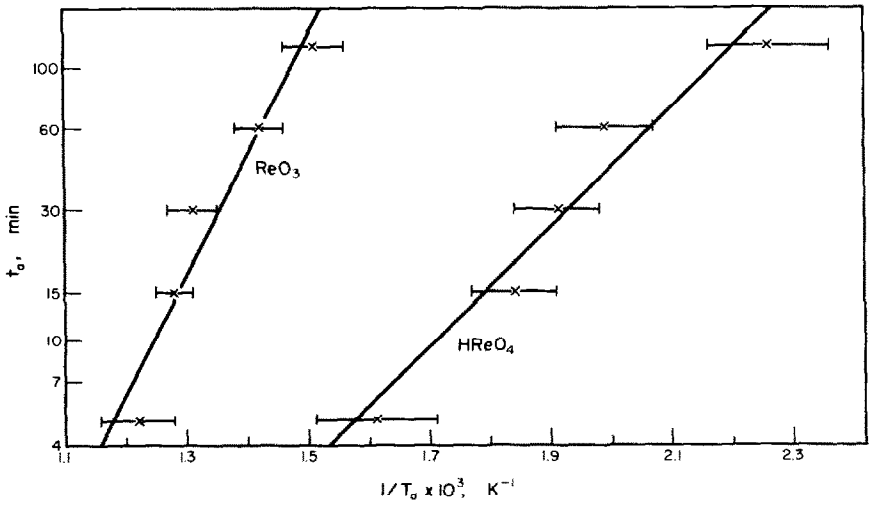


Fig. 4. Variation of log t_a for ReO_3 and $HReO_4$ with reciprocal of deposition temperature.

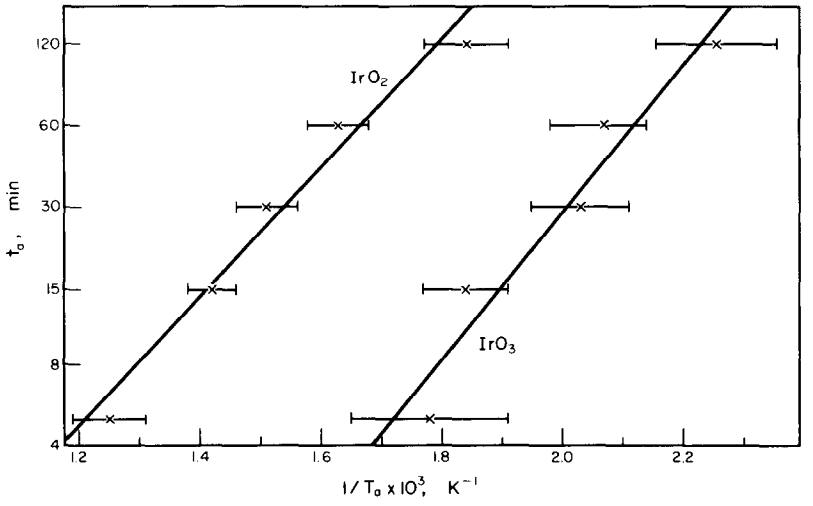


Fig. 5. Variation of log t_a for IrO_2 and IrO_3 with reciprocal of deposition temperature.

Table 1. Enthalpies and entropies of adsorption evaluated from isothermal and thermochromatographic experiments

Compound	Isothermal experiments $-\Delta N^\circ$, *kJ/mole*	$-\Delta S^\circ$, *J.mole*$^{-1}$ *deg*$^{-1}$	Thermochromatographic experiments $-\Delta H^\circ$, *kJ/mole*	$-\Delta S^\circ$ *J.mole*$^{-1}$.*deg*$^{-1}$
TcO_2	20.2 ± 1.4	128.2 ± 1.6	33.1 ± 2.1	81.0 ± 3.0
TcO_3	64.2 ± 2.9	227.0 ± 4.7		
$HTcO_4$	51.9 ± 5.4	188.3 ± 8.2	47.4 ± 6.3	126.8 ± 12.3
ReO_3	67.1 ± 5.1	187.0 ± 5.0	84.2 ± 12.6	147.3 ± 17.0
$HReO_4$	68.7 ± 2.3	206.4 ± 3.4	42.1 ± 5.7	114.8 ± 11.0
RuO_3	40.4 ± 2.0	189.4 ± 3.4		
RuO_4	10.2 ± 1.7	139.9 ± 3.1		
OsO_4	9.8 ± 2.0	157.5 ± 6.8		
IrO_2			45.0 ± 4.4	102.8 ± 6.8
IrO_3	42.6 ± 3.8	191.0 ± 6.2	51.6 ± 7.7	137.0 ± 15.3

deg/cm, $u_0 = 26.2$ cm/min at T_0 and $V_g = 21$ ml. The enthalpies and entropies of adsorption obtained from isothermal experiments[17] are listed for comparison purposes.

A comparison of the enthalpy values obtained from isothermal and thermochromatographic experiments reveals no significant difference. The values determined from the movement of molecular species in the temperature gradient are subject to larger errors than those listed in Table 1, especially in those cases where a species gives only small differences in deposition temperature with different times. For example, the deposition temperature of IrO_3 differs only by 120°C when t_a is changed from 5 to 120 min.

When comparing the entropy values determined by isothermal gas chromatography and by thermochromatography significant systematic differences are found, the thermochromatographic values being too low. This may be due to the simplication of the theoretical relation [Eq. (15)] or to experimental error.

Behaviour of the elements and chemical composition of the transported species

Rhenium. In gas chromatographic separations with oxygen, ReO_3 was formed, whereas in separations using an oxygen/water mixture, $HReO_4$ was formed.[17] There were no indications of the decomposition of these compounds. Figure 4 shows the migration of ReO_3 and $HReO_4$ in a temperature gradient.

Technetium. The gas chromatographic separations with oxygen as reactive gas show that two different technetium oxides contribute to the transportation process (Fig. 6).[17,19] During reaction in the crucible at 1500° TcO_3 is formed. In experiments without condensation TcO_3 is transported through the column and decomposes continuously to TcO_2. In experiments with condensation before separation the decomposition takes place during the condensation. On revolatilization at 950° TcO_3 is not reformed in an oxygen atmosphere and only TcO_2 is transported (Fig. 6). An indication of the decomposition of TcO_3 during transportation is a long tailing of the peak in the thermochromatogram (Fig. 6). The migration velocity of TcO_3 in the gradient could not be followed, because after 5 min the deposition temperature of 250° was reached, and TcO_2 was formed and continued to migrate. Thermochromatographic separations with short experimental times are necessary to differentiate between the two technetium oxides and to observe the decomposition of TcO_3. In experi-

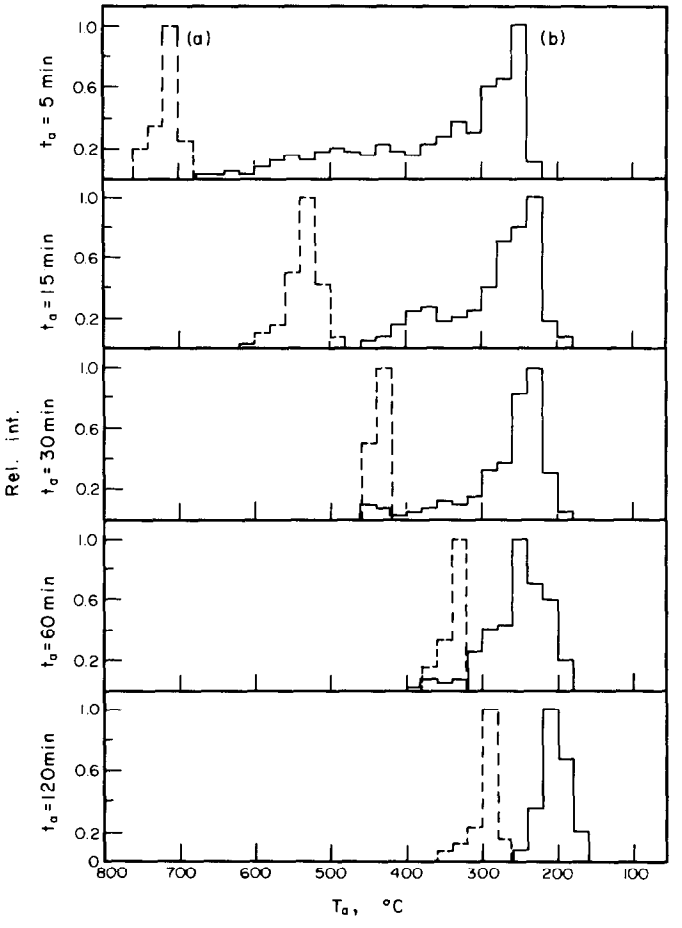


Fig. 6. Migration of TcO_2 and TcO_3 in a temperature gradient, (*a*) experiments with condensation, (*b*) experiments without condensation before separation.

ments with an oxygen/water mixture as carrier gas, $HTcO_4$ could be identified[17] and Fig. 3 shows its migration in the gradient.

Osmium. OsO_4 was identified in separations with oxygen and oxygen/water mixtures as carrier gas. In the latter case the yield was only about 50%.[17] It was not possible to determine the enthalpy or entropy of adsorption of OsO_4 on quartz because migration in the temperature gradient could not be investigated. After 5 min OsO_4 had already been deposited at 25°.

Ruthenium. The transportation of two ruthenium oxides could be identified in separations with oxygen. They are RuO_3 and RuO_4 and decompose continuously during condensation and transportation below 350°, into non-volatile RuO_2.[17] In the thermochromatogram two peaks could be identified at 180 ± 40° and at 290 ± 40° (Fig. 7). It was not possible to relate the peaks to the oxides. The deposition temperature was independent of time so it was not possible to investigate the migration rate in the temperature gradient. Peak area ratios were not reproducible. When an oxygen/water mixture was used the same two ruthenium oxides were transported but the yield was only about 10%, possibly because of reduction of RuO_3 and RuO_4 by water vapour.

Iridium. Two iridium oxides were identified when oxygen was used as carrier gas. They were probably IrO_2 and IrO_3.[17] Figures 5 and 8 show the migration of IrO_2 and IrO_3 in a temperature gradient. The ratios of the peak areas were not reproducible. In Fig. 8 an advantage of thermochromatography over isothermal and temperature-programmed gas chromatography is demonstrated, because the behaviour of IrO_2 can be investigated, even if the formation and transportation yields are quite low.[17] The yield of iridium decreases to about 5% when an oxygen/water mixture carrier gas.

Separations

Figure 7 shows a thermochromatogram of an experiment without condensation before separation, with oxygen as reactive and carrier gas, after 30 min. The elements rhenium and osmium are separated, whereas the peaks of technetium, iridium and ruthenium overlap.

Figure 9 shows a thermochromatogram of an experiment without condensation before separation, when an oxygen/water mixture is used as reactive and carrier gas. The elements technetium and rhenium are deposited at the same temperature and must be separ-

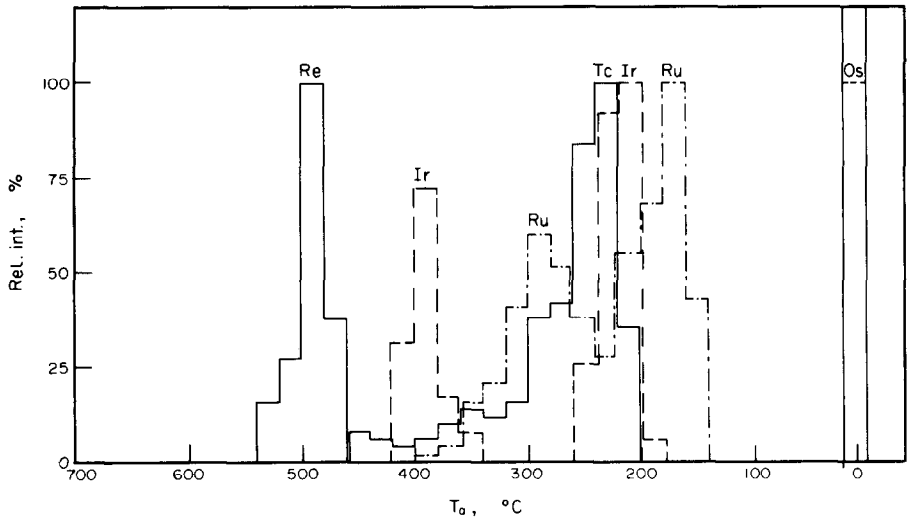


Fig. 7. Thermochromatogram of an experiment without condensation before separation. Reactive gas O_2, experimental time 30 min.

ated in some other way. Osmium can be found in the cooling trap but transportation of iridium and ruthenium does not occur.

Separation of technetium from iridium and ruthenium. With an oxygen/water mixture technetium can be separated, but iridium and ruthenium are only partly volatilized. The technetium yield is decreased in comparison with that when oxygen is used as reactive gas. In cases where at the start of the column a potassium chromate filter is used (Fig. 10), ruthenium is partly retained, whereas technetium is completely deposited. This method gives a separation of technetium from iridium and with a longer experimental period, an additional separation from ruthenium.

Separation of iridium and ruthenium. A complete separation of iridium and ruthenium as oxides is not possible. It can only be achieved when ruthenium is not transported. For example, when the reaction products which have been formed at 1500° are condensed before separation, and the products volatilized with argon as carrier gas, only IrO_3 and IrO_2 are revolatilized and ruthenium is not transported. This is due to the decomposition of RuO_4 and RuO_3 to the non-volatile RuO_2 which cannot be reoxidized in an argon atmosphere.

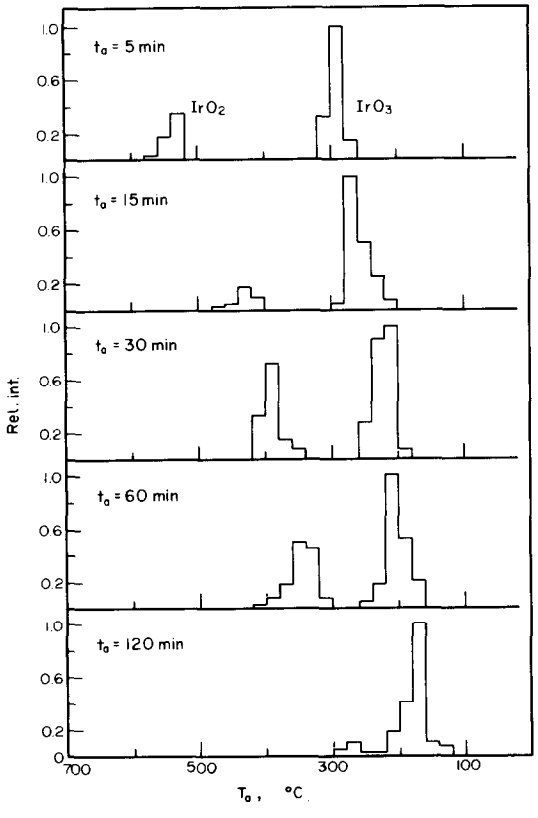


Fig. 8. Migration of IrO_2 and IrO_3 in a temperature gradient.

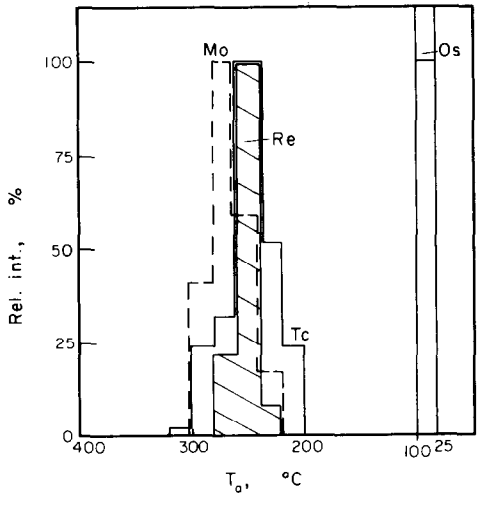


Fig. 9. Thermochromatogram of an experiment without condensation before separation. Reactive gas O_2/H_2O, experimental time 30 min.

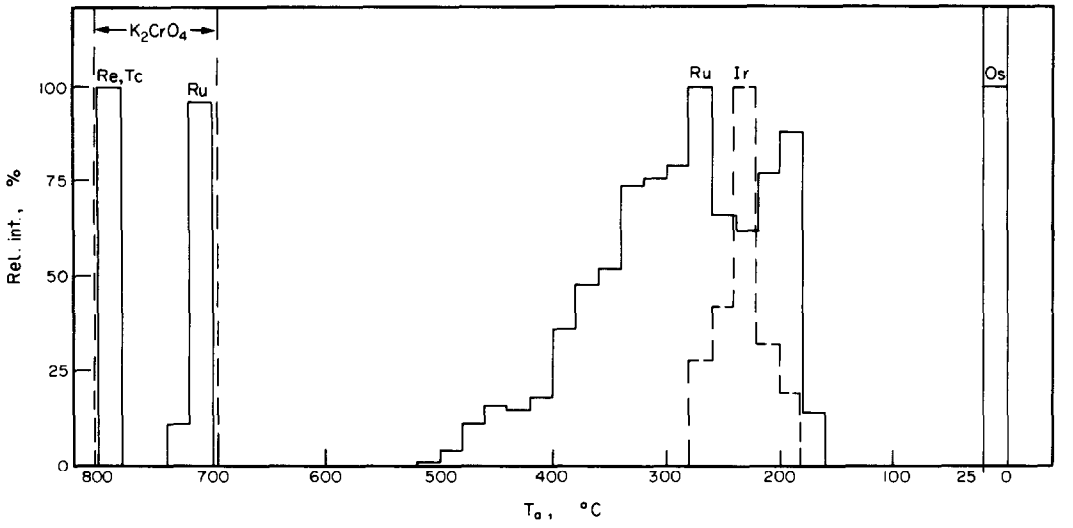


Fig. 10 Thermochromatogram of an experiment without condensation before separation, with a K_2CrO_4-filter. Reactive gas O_2, experimental time 30 min.

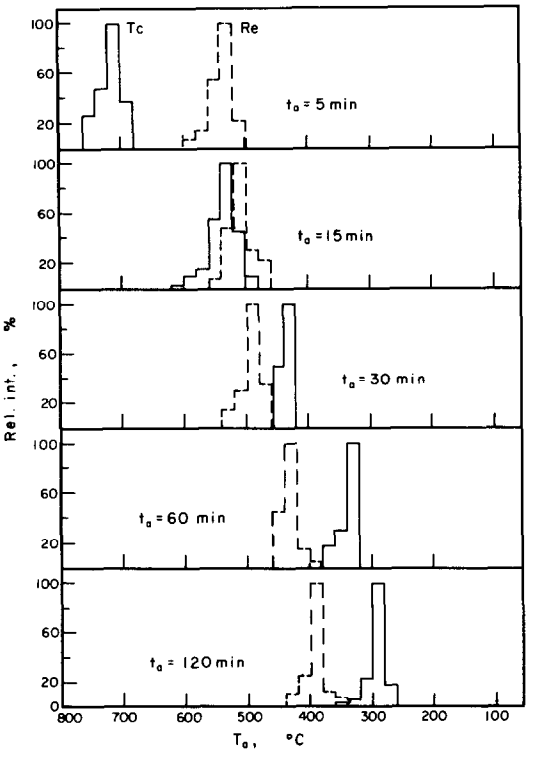


Fig. 11. Separation of Tc and Re in a temperature gradient.

Separation of rhenium and technetium. Rhenium and technetium can be separated in an oxygen stream (Fig. 7), but it is necessary to know the optimal time in experiments with condensation before separation. This is demonstrated in Fig. 11, which shows the efficiency of separation of Re and Tc as a function of time. At t_a = 5 min the two peaks are resolved, at t_a = 15 min they overlap, and after longer periods they are again resolved.

CONCLUSION

The results show that thermochromatography is a method which can be used for the evaluation of thermodynamic data. It is also an elegant method for the preconcentration of trace elements in analysis.

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REFERENCES

1. B. Bayar, N. G. Zaitseva and A. F. Novgorodov, *Radiochem. Radioanal. Lett.*, 1973 **15**, 231.
2. B. Bayar, I. Votsilka, N. G. Zaitseva and A. F. Novgorodov, *JINR* P 12-7164, Dubna, 1973.
3. *Idem, Radiochem. Radioanal. Lett.* 1975, **22**, 53.
4. *Idem, JINR* P 12-7340, Dubna, 1973.
5. *Idem, Soviet Radiochem*, 1974, **16**, 871.
6. B. Bayar, N. G. Zaitseva and A. F. Novgorodov, *ibid.*, 1974, **16**, 877.
7. J. Merinis and G. Boussières, *Anal. Chim. Acta*, 1961, **25**, 498.
8. *Idem, Radiochim. Acta*, 1969, **12**, 140.
9. J. Merinis, Y. Legoux and G. Boussières, *Radiochem. Radioanal. Lett.*, 1970, **3**, 255.
10. *Idem, ibid.*, 1972, **11**, 59.
11. B. Eichler and V. P. Domanov, *GSI—tr*—17/74.
12. B. Eichler, *ibid.*,—73/4.
13. *Idem, Radiochem. Radioanal. Lett.*, 1975, **22**, 147.
14. B. Eichler and V. P. Domanov, *J. Radioanal. Chem.*, 1975, **28**, 143.
15. B. Eichler and I. Zvara, *GSI—tr*—6/75.
16. B. Eichler, V. P. Domanov and I. Zvara, *ibid.*,—4/76.
17. A. Steffen and K. Bächmann, *Talanta*, 1978, **25**, 551.
18. E. Leibnitz and H. G. Struppe, *Handbuch der Gaschromatographie*, Verlag Chemie, Weinheim, 1970.
19. K. Bächmann, V. Matschoß, J. Rudolph, A. Steffen and S. Tsalas, *Nucl. Instr. Methods*, 1976, **139**, 343.

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STUDIES ON EXTRACTION OF Cu(II), Ga(III), In(III) AND Tl(III) WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOL-5-ONE

SEPARATION AND SPECTROPHOTOMETRIC DETERMINATION OF COPPER AND GALLIUM

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Summary—The extraction of Cu(II), Ga(III), In(III) and Tl(III) with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (HPMBzP) from aqueous solutions has been investigated. The mechanism of extraction and the composition of the species extracted has been determined. The effect of equilibration time, various organic solvents and salting-out agents on the extraction of copper and gallium has also been investigated. The green $Cu(PMBzP)_2$ chelate has absorption maxima at 298 and 670 nm, and PMBzP has maximum absorbance at 290 nm. A new and sensitive spectrophotometric method for copper has been devised, based on the absorbance at 670 nm. The presence of excess of reagent does not interfere and no special treatment is necessary to destroy it. The proposed method has some advantages and has been applied for the determination of copper in various soil samples. Gallium has been separated from indium, thallium, copper, iron and many other elements. The recovery of gallium and copper was 100 ± 0.2%.

β-Diketones are widely used for the extraction of metals. Acetylacetone and thenoyltrifluoroacetone (TTA) have been most widely applied,[1,2] and benzoylacetone less often.[3] The separation of gallium from indium with acetylacetone has been reported[4] but the several steps involved are a serious drawback. Gas chromatography has been used for the separation of the TTA complexes of aluminium, gallium and indium.[5] Another class of extractants that has received some attention in the last decade is that of the acylpyrazolones.[6,7] These are characterized by good chemical stability and reasonable solubility in organic solvents, and they are simple to prepare from readily accessible chemicals, but only the caproyl[8,9] and benzoyl[10,11] derivatives have been studied.

The present work was undertaken to study the liquid–liquid extraction of copper and group IIIB elements. Gallium can be separated from indium and thallium and determined in the presence of many elements, and the light green $Cu(PMBzP)_2$ complex, which absorbs at 670 nm, can serve as the basis for a new spectrophotometric method for the determination of copper in soils. The results are reproducible and the recovery of both copper and gallium is 100 ± 0.2%.

EXPERIMENTAL

Reagents

All the reagents were of analytical-reagent grade and used without further purification. Stock solutions of copper, gallium, indium and thallium were prepared by dissolving appropriate quantities of their salts in 250 ml of 0.1*N* nitric acid. The solutions were standardized by titration with EDTA or gravimetrically. 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one was synthesized according to the standard method.[6,7] Standard buffers (potassium chloride/hydrochloric acid, hydrochloric acid/potassium phthalate, sodium hydroxide/potassium phthalate, sodium hydroxide/boric acid) were used to cover the pH range 1–10.

Measurement of distribution ratio

Equal volumes (3 ml) of the aqueous and organic phases were shaken mechanically for 1 min in glass-stoppered bottles at room temperature. Preliminary studies showed that equilibrium was established in 1–2 min. The phases were centrifuged and separated. The distribution ratio was calculated as the ratio between the concentrations in the organic phase and the aqueous phase.

Preparation of pyrazolonates

Copper pyrazolonate. To a warm solution of 1.9 g of copper nitrate trihydrate in 100 ml of water, 4.75 g of HPMBzp dissolved in 100 ml of methanol were added slowly with constant stirring. The mixture was heated on a water-bath for 1 hr. The green precipitate was filtered off, washed with water and methanol and dried in a vacuum desiccator. Found: Cu 10.2%, C = 65.7%, H = 4.3%; $Cu(C_{17}H_{13}N_2O_2)_2$ requires Cu = 10.17%, C = 65.8%, H = 4.2%. Thermogravimetric study showed the absence of water in the complex.

Gallium pyrazolonate. To a warm solution of 1 g of gallium chloride in 50 ml of water, 4.5 g of HPMBzp dissolved in 100 ml of methanol were added. The mixture was heated on a water-bath for 30 min. The light yellow gallium pyrazolonate was filtered off and recrystallized from 95% alcohol. Found, Ga 7.65%, C 67.8%, H 4.3%; $Ga(C_{17}H_{13}N_2O_2)_3$ requires Ga 7.72%, C 67.7%, H 4.35%.

Indium pyrazolonate. To 0.96 g of indium chloride dissolved in 50 ml of warm water, 3.6 g of HPMBzP dissolved in 100 ml of methanol were added. The solution was

heated for 30 min. Light yellow crystals separated out and were recrystallized from 95% alcohol. Found: In 11.55%, C 62.0%; H 4.1%; $In(C_{17}H_{13}N_2O_2)_3$ requires In 11.6%, C 62.1%, H 4.1%.

Thallium pyrazolonate. To 1.9 g of thallium nitrate dissolved in 100 ml of warm water, 4.1 g of HPMBzP dissolved in 100 ml of methanol were added and the solution was heated for 45 min. Light yellow crystals separated out and were recrystallized from 95% alcohol. Found: Tl 19.5%, C 59.0%, H 3.65%; $Tl(C_{17}H_{13}N_2O_2)_3$ requires Tl 19.6%, C 58.9%, H 3.7%.

Determination of gallium, indium and thallium

Gallium. A portion of gallium nitrate solution in an appropriate buffer of pH 3.5–5.0 was shaken with 0.3*M* HPMBzP solution in xylene for 1 min in a 25-ml separatory funnel. The phases were centrifiged and separated. The yellowish organic layer was shaken for 5 min with 10 ml of 6*M* hydrochloric acid containing 0.5 ml of 0.5% Rhodamine B solution. The two layers were allowed to separate. The reddish violet gallium complex was measured photometrically at 565 nm against a reagent blank.

Indium. A portion of indium chloride solution was diluted and the pH adjusted to 3–3.5 with an appropriate buffer. Then 10 ml of 0.03*M* HPMBzP solution in xylene were added and the mixture was shaken for 1 min. The phases were centrifuged and separated. Indium was stripped from the organic phase with 0.1*M* hydrochloric acid. The pH of the acid extract was raised from 3 to 11 with ammonia solutions and 2 ml of 1% oxine solution in ethanol were added. The yellow indium oxinate complex was measured photometrically at 400 nm against a reagent blank.

Thallium. A portion of thallium solution was quantitatively extracted at pH 2.0–5.5 with 0.03*M* HPMBzP solution in xylene. The organic layer was shaken with 2*M* hydrochloric acid containing 2 ml of 1% Rhodamine B solution in ethanol. The reddish violet complex was measured photometrically at 560 nm against a reagent blank.

Separation of gallium from indium and thallium

A portion of a mixture containing gallium, indium and thallium was adjusted to pH 1.2 and shaken for 1 min with 10 ml of 0.03*M* HPMBzP solution in xylene. The phase were centrifuged and separated. The extraction cycle was repeated. The organic layers were combined and thallium was stripped with 2*M* hydrochloric acid. To the aqueous phase free from thallium, 1 ml of water containing 0.5 mg of potassium thiocyanate was added and the pH raised to 5.5 with ammonia solution. Then 10 ml of 0.03*M* PMBzP solution in xylene were added and the mixture was shaken for 1 min. The phases were centrifuged and separated. From the organic phase gallium was stripped with dilute hydrochloric acid.

Recommended procedure for copper

A portion of sample solution containing not less than 3 μg of copper was transferred to a 25-ml separatory funnel, followed by addition of 5 ml of 4% potassium dihydrogen phosphate solution. The pH was adjusted to 3.0–6.0 with an appropriate buffer and the aqueous phase was shaken for 2 min with 10 ml of 0.03*M* HPMBzP solution in chloroform. The phases were centrifuged and separated and the absorbance of the organic phase was measured at 670 nm against a reagent blank.

RESULTS AND DISCUSSION

The results reported here are the means of two or three runs.

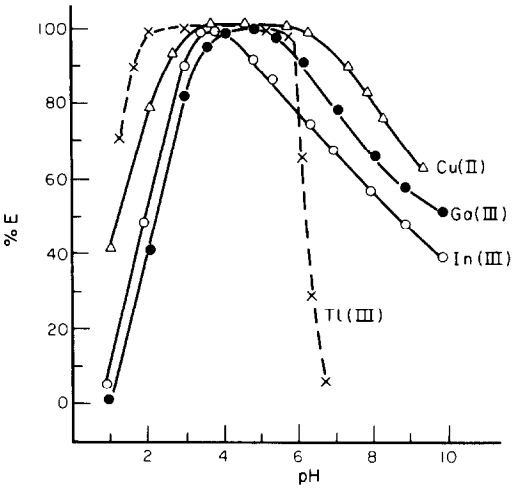


Fig. 1. Extraction as a function of pH.

Figure 1 shows the extractions, as a function of pH. With the HPMBzP concentration kept constant at 0.03*M* there is negligible extraction of copper, gallium and indium below pH 1.0, but thallium is 70% extracted. Plots of log $[D_m]$ *vs.* log [HPMBzP] at constant ionic strength 0.15 and pH 3.8–5.5 are linear with slopes of 3 for Ga, In and Tl, and 2 for copper, indicating that the complexes formed are ML_3 and ML_2 respectively. Increasing the ionic strength to 2.0 does not change the slope. The slopes of plots of log $[D_m]$ *vs.* pH indicate the liberation of three moles of hydrogen ions per mode of metal in the extraction of gallium, indium and thallium and two in the extraction of copper. Hence the extraction process may be represented as

$$M^{n+} + x\text{HPMBzP} \overset{K_1}{\rightleftharpoons} M(\text{PMBzP})_x + nH^+$$

$$K_1 = \frac{[M(\text{PMBzP})_x]\,[H^+]^n}{[M^{n+}]\,[\text{HPMBzP}]^x}$$

The terms in brackets should be the activities, but the concentrations may be used if they are low enough. Since the ratio of $[M(PMBzP)_x]$ to $[M^{n+}]$ is the distribution coefficient D we have $D = K_1\,[\text{HPMBzP}]^x/[H^+]^n$. Hence $\log D = \log K_1 + x \log [\text{HPMBzP}] + n$ pH. The K_1 values found in this way are 1.2×10^{-5}, 0.012, 0.07 and 0.17 for Ga(III), In(III), Tl(III) and Cu(II) respectively. The corresponding values for gallium,[2] indium[5] and copper[12] with TTA are 4.0×10^{-6}, 2.1×10^{-4} and 4×10^{-2} respectively, indicating the superiority of HPMBzP over TTA.

Absorption spectra

Figure 2 shows the absorption spectra of the Ga–Rhodamine B, In–oxinate, Tl–Rhodamine B and copper–pyrazolone complexes. The effect of reagent concentration on the absorbance of copper is given in Table 1. The extraction of 10 μg of copper is com-

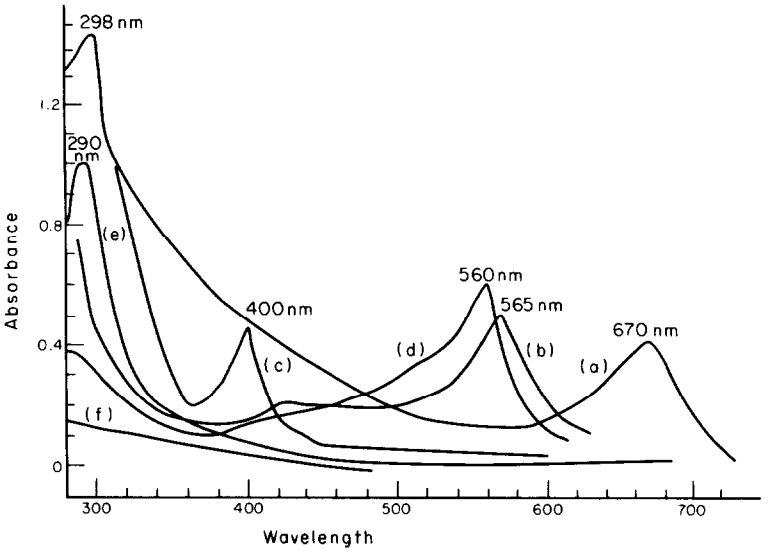


Fig. 2. Absorption spectra of (a) copper–pyrazolone complex; [Cu] = 0.1 × $10^{-3}M$: [PMBzP] = 3 × $10^{-2}M$: (b) gallium–Rhodamine B complex; [Ga] = 2.79 × $10^{-4}M$: (c) indium–oxine complex; [In] = 7 × $10^{-5}M$: (d) thallium–Rhodamine B complex; [Tl] = 5 × $10^{-5}M$: (e) PMBzP: (f) ethanol.

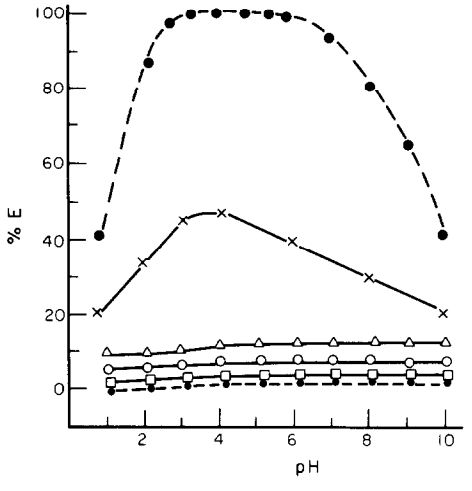


Fig. 3. Efficiency of various solvents for the extraction of copper. ●–●–●—Chloroform. ×–×–×—Carbon tetrachloride. △–△–△—Benzene. ○–○–○—Toluene. □–□–□—Xylene. ·–·–·—Amyl alcohol, ethyl acetate or methyl iso butylketone.

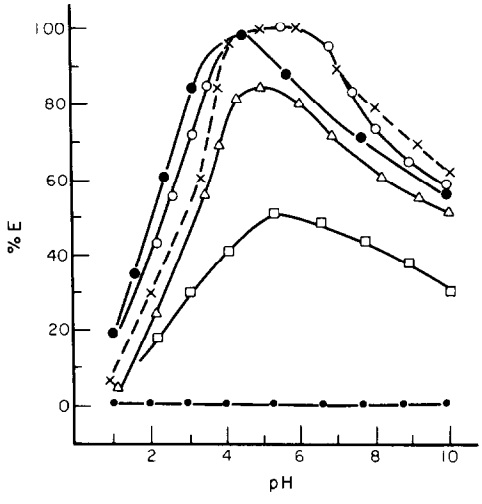


Fig. 4. Efficiency of various solvents for the extraction of gallium. ×–×–×—Xylene. ○–○–○—Ethyl acetate. ●–●–●—Methyl isobutyl ketone. △–△–△—Toluene. □–□–□—Benzene. ·–·–·—Amyl alcohol, chloroform or carbon tetrachloride.

Table 1. Effect of reagent volume and concentration on extraction of 10 μg of copper at pH 4.0

[HPMBzP], *M*	HPMBzP solution added, ml	Absorbance at 670 nm	Extraction, %
0.01	3	0.32	30
0.015	3	0.36	45
0.02	3	0.50	60
0.025	3	0.65	80
0.030	3	0.705	100
0.035	3	0.705	100
0.040	1	0.705	100
0.045	2	0.705	100
0.050	1	0.705	100

plete with 3 ml of 0.03*M* HPMBzP in chloroform but incomplete with the same volume at lower concentrations. There is no significant increase in the absorbance when the concentration of the reagent is increased from 0.03 to 0.05*M*, even when the volume is decreased to 1 ml.

The absorbance is stable for at least a week. Beer's law is obeyed over the range 2–30 μg of metal ion.

Choice of organic solvent

Figure 3 shows the extraction of copper, which is quantitative with chloroform at pH 3.0–6.0 in 2 minutes; 40% extraction is obtained with carbon tetrachloride. There is no extraction into amyl alcohol, ethyl acetate or methyl isobutyl ketone, and extraction into benzene, toluene and xylene is negligible. Figure 4 shows the extraction of gallium, which is quantitative with ethyl acetate, methyl isobutyl ketone and xylene. Carbon tetrachloride, chloroform and amyl alcohol do not dissolve the complex, and in other solvents the degree of extraction is in the order xylene > toluene > benzene.

Effect of equilibration time

Extraction of copper is quantitative in 1.5 min and that of gallium in 1 min. Longer shaking produces no effect on the degree of extraction. It is therefore, recommended that the shaking-time should be 2 min.

Interferences

Tables 2 and 3 show the effect of various cations on the recovery of copper and gallium. Several ions were examined for their effect on the extraction of copper. The tolerance limit was taken as the amount required to cause a ±2% error in the recovery. The ions showing strong interference for copper were

Table 2. Effect of diverse ions on the determination of copper(II) (100 μg) with 0.03*M* HPMBzP in $CHCl_3$ at pH 5.0

Foreign ions	Added as	Tolerance limit, μg
Li	LiCl	10
K	KCl	10
Sr	$SrCl_2.2H_2O$	5
Fe	$FeSO_4.7H_2O$	4*
Cr	$CrCl_3.6H_2O$	10
Al	$Al(NO_3)_3.9H_2O$	4*
Ga	$GaCl_3$	5†
In	$InCl_3$	5†
Ge	$GeCl_4$	10
Sn	$SnCl_2.2H_2O$	5
Pb	$Pb(NO_3)_2$	4.5§
Sc	$ScCl_3$	0.5
Y	$YCl_3.6H_2O$	0.5
Ti	$Ti(SO_4)_2$	10
Zr	$Zr(NO_3)_4$	10
Co	$Co(NO_3)_2.6H_2O$	3
Ni	$NiSO_4.6H_2O$	4
Mn	$MnCl_2.4H_2O$	3
Zn	$ZnSO_4.7H_2O$	3
Cd	$CdCl_2.H_2O$	3
Tl	$Tl(NO_3)_3$	5†
F^-	KF	10
Cl^-	KCl	10
Br^-	KBr	10
NO_3^-	KNO_3	10
NO_2^-	$NaNO_2$	10
I^-	KI	none
CN^-	KCN	none
SCN^-	KSCN	10
SO_4^{-}	Na_2SO_4	10
SO_3^-	Na_2SO_3	10
$S_2O_3^{2-}$	$Na_2S_2O_3.5H_2O$	none
Citrate	Potassium citrate	5
Oxalate	Ammonium oxalate	4.5
Tartrate	Potassium hydrogen tartrate	5
EDTA	EDTA (disodium salt)	2
Phthalate	Potassium hydrogen phthalate	8
Acetate	Sodium acetate	10
Phosphate	KH_2PO_4	5.5
Borate	Sodium borate	10

* Masking with 4% potassium hydrogen phosphate.
† Masking with KSCN.
§ Masking with H_2O_2.

Table 3. Determination of gallium with Rhodamine B after extraction with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one

Foreign ion (amount, *g*)	Gallium added, μg	Gallium found, μg
Cu (0.5)*	100	99.9
Fe (0.5)†	100	99.9
In (0.5)§	100	99.9
Ni (0.2)	50	49.8
Co (0.2)	50	49.9
Tl(III) 0.1)	50	49.9
Zn (0.2)	50	49.9
Cd (0.2)	50	49.9
Hg (0.1)	50	49.9
Pb (0.2)	50	49.9
Bi (0.2)	50	50.0
Sb(V) (0.1)	50	49.9
Zr(IV) (0.2)	50	50.0
Ca (0.2)	50	49.9
Na (0.5)	50	50.0
Mn(II) (0.2)	50	49.9
Cr(III) (0.2)	50	50.0
Ru(III) (0.05)	50	49.8
Rh(III) (0.05)	50	49.9
Pd(II) (0.1)	50	49.9
Ti(IV) (0.1)	50	50
Pt(IV) (0.02)	50	49.9
Na_2 EDTA (0.5)	50	none
Lactic acid (0.5)	50	none
Citric acid (0.5)	50	none
Ascorbic acid (0.5)	50	none
Tartaric acid (0.5)	50	49.9
Phthalic acid (potassium salt 0.5)	50	49.9
Acetate (0.5)	50	50
Borate (0.5)	50	50
Phosphate (0.5)	50	49.8
CN^- (0.5)	50	49.9
SCN^- (0.0005)	50	49.9
SO_4^{-2} (0.5)	50	50
$S_2O_3^{-2}$ (0.5)	50	49.9
SO_3^{-2} (0.5)	50	49.9

iodide and cyanide, while EDTA slowed down the extraction. Several masking agents were used to eliminate interferences. Rare earths, group III elements and iron were extracted along with copper and were masked with tartrate, thiocyanate and sodium phosphate respectively. Ga, In and Tl, which are extracted under the same conditions, did not interfere photometrically as their PMBzP complexes all have maximum absorption at about 280 nm. The interference of Pb and Hg was overcome with hydrogen peroxide. Many ions such as those of Ti, Zr, Hf, Mo, Al, Cr, alkali metals, Ag, Sn [Sn(IV)], Te, Se were not extracted at all under the conditions used and hence did not interfere. Ions of elements such as Ca, Cd, Zn, Co and Ni, which were extracted wholly or partially under the conditions used, did not interfere photometrically. Similarly no interference in the determination of 100 μg of gallium was observed for 500 mg of Cu, Fe and In, while 200 mg of Co, Ni, Cd, Zn, Ca and many other cations did not interfere in the determination of 50 μg of gallium. EDTA, citric acid, ascorbic acid and lactic acid seriously interfered in the extraction of gallium. Tl(III) was removed by extracting at low pH prior to the determination of gallium, while Fe, Cu and In (which were also extracted at pH 5.0 or above) were masked with potassium phosphate, potassium cyanide and potassium thiocyanate respectively.

The recommended procedures possess many advantages. It is possible to separate copper and gallium from indium and thallium and also from many other elements. The methods are very rapid as the extraction requires only two minutes. The results are reproducible and the recovery of both copper and gallium is $100 \pm 0.2\%$.

REFERENCES

1. A. Krishen and H. Freiser, *Anal. Chem.* 1959, **31**, 923.
2. P. V. Dhond and S. M. Khopkar, *Talanta*, 1976, **23**, 51.
3. J. Starý and El Hladky, *Anal. Chim. Acta*, 1963, **28**, 227.
4. H. Jaskolska and J. Minczewski, *Chem. Anal. (Warsaw)*, 1967, **12**, 697.
5. G. P. Morie and T. R. Sweet, *Anal. Chem.*, 1965, **37**, 1552.
6. B. S. Jensen, *Acta Chem. Scand.*, 1959, **13**, 1668.
7. *Idem*, *ibid.*, 1959, **13**, 1890.
8. M. Y. Mirza, *Talanta*, 1968, **15**, 137.
9. *Idem*, *Anal. Chim. Acta*, 1968, **40**, 229, 235.
10. L. I. Moseev and B. V. Monakhov, *Radiokhimiya*, 1966, **10**, 309.
11. O. Navratil and B. S. Jensen, *J. Radioanal. Chem.*, 1970, **5**, 313.
12. H. Akaiwa, H. Kawamoto and F. Izumi, *Talanta*, 1976, **23**, 403.

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SHORT COMMUNICATIONS

SPECTROPHOTOMETRIC DETERMINATION OF BISMUTH WITH DIETHYLENETRIAMINEPENTA-ACETIC ACID

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(*Received* 21 *October* 1977. *Revised* 22 *May* 1978. *Accepted* 2 *June* 1978)

Summary—Diethylenetriaminepenta-acetic acid is used for spectrophotometric determination of bismuth (at 270 nm) in 1.6 *M* perchloric acid. The system obeys Beer's law in the range 1–40 μg/ml. The method has been tested for the determination of bismuth in pure lead and polymetallic ores.

It is well known that Bi(III) forms stable complexes with many aminopolycarboxylic acids, some of which have been used for the spectrophotometric determination of bismuth, *e.g.*, EDTA,[1–4] DCTA[4,5] and hydroxyethylethylenediaminetriacetic acid (HEDTA).[6]

The formation, composition and stability of complexes of bismuth with diethylenetriaminepenta-acetic acid (DTPA) have been thoroughly studied.[5,7–9] The complex obtained can be used for the spectrophotometric determination of bismuth in the presence of various ions. A method has been published for spectrophotometric determination of Bi(III) with DTPA in pig lead[8] but a preliminary separation of Pb(II) is said to be required.

The aim of this work was to investigate further the spectrophotometric determination of bismuth with DTPA.

EXPERIMENTAL

Solutions of DTPA and the perchlorates of Bi(III), Fe(III), Cu(II) and Pb(II) were prepared and standardized. Sodium hydroxide solution and perchloric acid were used to adjust the pH.

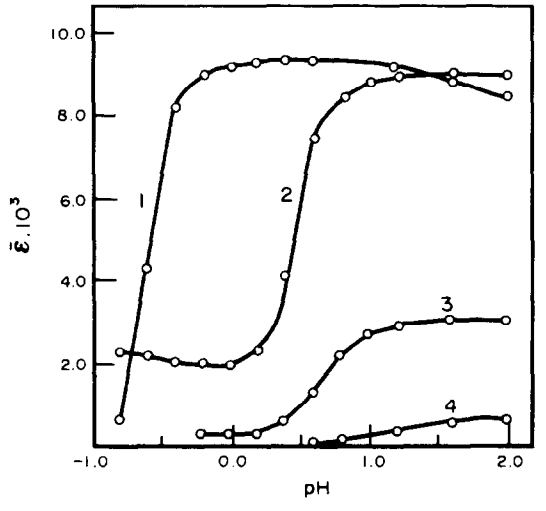


Fig. 1. Apparent molar absorptivities at 270 nm of the DTPA complexes of 1–Bi(III); 2–Fe(III); 3–Cu(II); 4–Pb(II), as a function of pH.

Preliminary investigation

From the stability of the Bi(III) complex with DTPA[5,8,9] and the data in Fig. 1, we concluded that the selectivity of the determination increases with concentration of perchloric acid, the optimum being 1–1.6 *M*.

It was found that the alkali and alkaline earth metals, Zn, Cd, Ni, Co(II), Al, Cr(III), Mn(II), Sn(IV), Sb(V), Ga and In do not interfere. The presence of Fe(III), Cu(II) and Pb, however, must be taken into consideration. Figure 2 shows that Fe(III) and Cu(II) interfere most strongly. This is because the Fe(III), Cu(II) and Bi(III) DTPA complexes all absorb at 270 nm (the wavelength of choice) (Fig. 2). However, the iron and copper complexes are less stable than the bismuth complex and can be destroyed by adding enough acid. Iron(III) in perchloric acid medium still absorbs at 270 nm, however, and this makes it necessary to use a compensation method, the absorbance of the Bi–DTPA complex being measured against a solution identical with it except for omission of the DTPA. In the absence of iron(III), water can be used as the reference

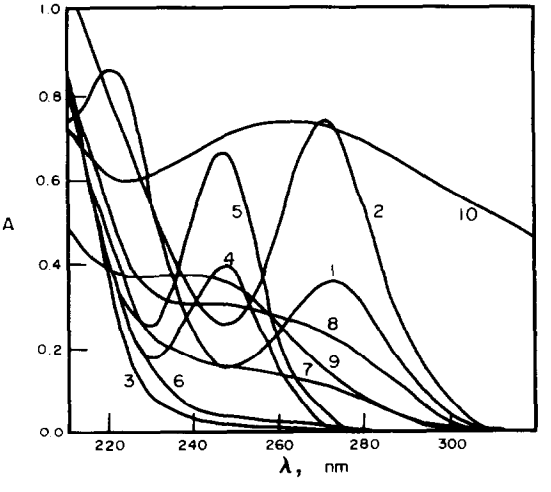


Fig. 2. Absorption spectra for complexes formed with 8.00×10^{-5} *M* metal ion and 4.00×10^{-4} *M* DTPA. Bi: 1–3.98 *M* $HClO_4$; 2–1.58 *M* $HClO_4$. Pb: 3–pH 0.40; 4–pH 1.20; 5–pH 2.00. Cu: 6–pH 0.00; 7–pH 0.70; 8–pH 1.20. Fe: 9–1.58 *M* $HClO_4$; 10–pH 2.30.

Table 1. Allowed concentrations of Fe(III), Cu(II) and Pb(II) in the determination of Bi(III) with some aminopolycarboxylic acids

Reagent	Bi, mg/25 ml	Fe, mg/25 ml	Cu, mg/25 ml	Pb, mg/25 ml	Ref.
EDTA	0.523	0.02	1	200	4
DCTA	0.523	0.02	5	900	4
HEDTA	0.523	0.2	8	1000	6
DTPA	0.418	2.0	10	1500	this work

Table 2. Determination of bismuth in lead samples

Sample	Bi, % Spectral method	This method
1	0.022	0.0221 ± 0.0004
2	0.011	0.0115 ± 0.0010
3	0.0054	0.0054 ± 0.0001

solution. Table 1 shows the tolerance limits for lead, iron and copper.

The anions perchlorate, sulphate (in the absence of lead) and chloride (<40 mg/25 ml) do not interfere. If the concentration of nitrate is greater than 30 mg/25 ml a positive error is obtained which can be avoided (for up to 200 mg/25 ml) if the comparison solution contains the same quantity of nitrate.

As the absorbance of DTPA at 270 nm is small its excess does not affect the results. Nevertheless a large excess is undesirable because it reduces the selectivity of the main reaction. The concentration of DTPA must not be greater than 4×10^{-4} *M* in the final solution.

The system obeys Beer's law for Bi(III) in the range 1–40 μg/ml.

A method for the determination of bismuth in pure lead and polymetallic ores with low iron contents (up to 5%) was developed.

Recommended procedure

Determination of bismuth in pure lead. Dissolve 5 g of sample with Bi content 0.001–0.05% in a 1:1 mixture of nitric and perchloric acids. Add 4–5 ml of conc. perchloric acid and evaporate nearly to dryness (repeat twice). Dissolve the residue in water and if a turbid solution is obtained filter through a thick filter into a 25-ml standard flask. Transfer a 10.00-ml portion into a 25-ml standard flask and neutralize it with 1*M* sodium hydroxide. Add 1.00 ml of 0.01*M* DTPA, 6.7 ml of 6.0*M* perchloric acid and dilute to the mark with distilled water. Measure the absorbance at 270 nm against a compensation solution, which is a sample prepared in the same way but without DTPA added to it.

The calibration curve is prepared from a mixture containing 2.00 g of lead per 25 ml and suitable amounts of standard bismuth perchlorate solution.

The method was tested on three lead samples containing traces of Fe, Cu, As and Sb. The average results (95% confidence limits), are given along with results from a spectral method in Table 2.

Determination of bismuth in polymetallic ores. Dissolve a suitable amount of ore in 10 ml of *aqua regia* and evaporate the mixture to 2 ml. If undissolved black particles are left add 5 ml of conc. nitric acid and warm to dissolve. Add 5 ml of conc. perchloric acid and evaporate nearly to dryness. Repeat the evaporation with perchloric acid twice more. Take up in distilled water by heating. Transfer the solution quantitatively into a 50-ml standard flask and dilute to volume. Filter the solution into a dry beaker through a dry slow-speed filter paper in a dry funnel. Transfer a 10.0-ml portion into a 25-ml standard flask and neutralize with 1*M* sodium hydroxide until a precipitate of $Fe(OH)_3$ appears. Add 1.00 ml of 0.01*M* DTAP, 6.7 ml of 6.0*M* perchloric acid and dilute to volume with distilled water. Measure the absorbance at 270 nm against a comparison solution prepared in the same way, but containing no DTPA.

For the calibration curve use a series of solutions containing 0.025–1.00 mg of Bi per 25 ml. Table 3 shows the results obtained for seven samples of polymetallic ores with low contents of iron and traces of antimony.

REFERENCES

1. P. W. West and H. Coll, *Anal. Chem.*, 1955, **27**, 1221.
2. R. N. Wilhite and A. L. Underwood, *ibid.*, 1955, **27**, 1334.
3. I. P. Alimarin, A. P. Golovina and I. M. Gibalo, *Vestn. Mosk. Univ. Khim.*, 1956, **2**, 135.
4. B. P. Karadakov and Khr. R. Ivanova, *Zh. Analit. Khim.*, 1973, **28**, 525.
5. N. Toru and K. Kunzi, *Nippon Kagaku Zasshi*, 1967, **88**, 1287.
6. B. P. Karadakov, P. P. Nenova and Khr. R. Ivanova, *Zh. Analit. Khim.*, 1976, **31**, 2058.
7. E. Bottari and G. Anderegg, *Helv. Chim. Acta*, 1967, **50**, 2349.
8. P. S. Edgaonkar, M. Atchayya and P. R. Subbaraman, *Indian J. Chem.*, 1975, **13**, 400.
9. D. St. Kantcheva, P. P. Nenova and B. P. Karadakov, *Compt. Rend. Acad. Bulg. Sci.*, 1977, **30**, 403.

Table 3. Determination of bismuth in polymetallic ores

Sample	Bismuth found, %	Confidence limits (95% probability)
1	0.051; 0.049; 0.052; 0.054; 0.054	0.052 ± 0.002
2	0.070; 0.074; 0.074; 0.074; 0.072	0.073 ± 0.002
3	0.090; 0.090; 0.090	0.090 ± 0.000
4	0.189; 0.192; 0.195; 0.187; 0.191	0.191 ± 0.003
5	0.188; 0.185; 0.190; 0.191; 0.189	0.189 ± 0.002
6	0.259; 0.265; 0.271; 0.262; 0.264	0.264 ± 0.005
7	0.403; 0.397; 0.397	0.399 ± 0.005

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MASKING OF MANGANESE IN RELATION TO STEPWISE COMPLEXOMETRIC DETERMINATION OF CALCIUM, MAGNESIUM AND MANGANESE

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(*Received* 19 *December* 1977. *Revised* 17 *April* 1978. *Accepted* 2 *June* 1978)

Summary—A critical study has been made of the masking of manganese with potassium cyanide in alkaline medium for complexometric titration of calcium and magnesium. It has been found that there is incomplete oxidation to manganese(III) unless the solution is aged for a sufficient period or air is bubbled through the solution at 35 ± 5° for 10 min. The manganese(III) complex can be reduced with ascorbic acid for titration with EDTA. Procedures are given for stepwise titration of magnesium, manganese and calcium in silicate materials. Mixed indicators are used, to improve the end-points.

Calcium, magnesium and manganese are often found present together in ores, slags and certain ceramic products such as enamels and amber glasses. Determination of calcium and magnesium in such materials is difficult owing to interference by manganese. Therefore, prior separation of manganese with hydrogen sulphide, solvent extraction or mercury cathode electrolysis is usually an essential step for gravimetric or titrimetric determination of calcium and magnesium. Manganese also interferes with the EDTA titration of calcium and magnesium by precipitating as manganese hydroxide, which absorbs metallochromic indicators. Thus masking or separation of manganese is again essential. The literature on the masking of manganese is confusing. The use of TEA (triethanolamine) was first proposed by Přibil[1,2] for masking up to 3 mg of manganese; with larger amounts the manganese(III)–TEA complex formed by aerial oxidation interferes by imparting a green colour to the solution and then slowly forming manganese hydroxide. The addition of reducing agents such as ascorbic acid, tartrate or hydroxylamine hydrochloride keeps the manganese in the bivalent state, which is co-titrated[3] with calcium and magnesium. Povondra and Přibil[4] used TEA and potassium cyanide in strongly alkaline medium in the absence of iron for complexing up to 80 mg of manganese, as $Mn(CN)_6^{3-}$. The sum of calcium and magnesium was then found by adding excess of EDTA and back-titrating. Yotsuyanagi *et al.*[5] also masked manganese with TEA and cyanide, but titrated calcium and magnesium directly. Manganese was then determined by a back-titration method after reduction to Mn(II) with ascorbic acid.

One of the main limitations of both methods[4,5] is that aluminium and iron interfere in the back-titration methods and must be separated first. We have found[6] that positive errors occur in the Yotsuyanagi method because of incomplete oxidation of Mn(II), unless the concentration of manganese is low (1.0 mg/250 ml). Asaoka[7] reported that in 0.2*M* sodium hydroxide/0.2*M* TEA solution as medium, manganese(III) ($10^{-3}M$) is slowly reduced to manganese(II) (within 10 hr) at high cyanide concentration (0.4*M*) but not at low (0.02*M*). We have now observed that at cyanide concentrations up to 0.1*M*, no significant reduction of Mn(III) to Mn(II) takes place in alkaline TEA medium during 6 hr, and so there is no effect on EDTA titration of calcium at pH 12.5. However, when the pH is lowered to 10 for titration of Ca + Mg, positive errors are obtained because of reduction of Mn(III) to Mn(II) unless it is kept oxidized either by aging or passage of air. Potassium cyanide in conjunction with hydrogen peroxide was used by Fog[8] for masking manganese in EDTA titration of magnesium. The use of hydrogen peroxide in alkaline medium was reported[9] to be objectionable because it oxidized EDTA in the presence of iron. Further it was found[6] that the peroxo–cyano-complex of manganese could not be demasked for subsequent titration of manganese with EDTA in presence of ascorbic acid. West[3] rightly described the masking of manganese as unsatisfactory. Přibil and Veselý[10] preferred separation of manganese with hydrogen peroxide in alkaline medium and titration of calcium and magnesium in the filtrate with EDTA or DCTA. Thus the literature reveals no completely satisfactory procedures for masking manganese at pH 10 for titration of Ca + Mg with EDTA.

The present communication reports the results of studies on quantitative masking of manganese for direct EDTA titration of calcium and magnesium and for demasking manganese from its complex for direct titration with EDTA without involving separation of aluminium and iron.

EXPERIMENTAL

Reagents

All reagents used were of analytical or general reagent grade.

Mixed indicator I.[11] Prepared by mixing 0.08 g of Naphthol Green, 0.05 g of *o*-cresolphthalein complexone and 20 g of ammonium chloride.

Calcein indicator. Calcein (0.2 g) mixed with potassium chloride (20 g).

Thymolphthalein, 0.1% in 30% TEA solution.

Mixed indicator II.[12] Eriochrome Black T (0.03 g), Titan Yellow (0.04 g) and Naphthol Green (0.01 g) dissolved in 25 ml of TEA.

Preparation of silicate sample solutions

A dried (105–110°) and weighed (0.5 g) sample is moistened with water in a platinum basin and treated with 10 ml of hydrofluoric acid and 1 ml of sulphuric acid

(18*N*). The mixture is heated on a sand-bath till fumes of sulphur trioxide are evolved. This treatment is repeated with a further 10 ml of hydrofluoric acid (after cooling) and the solution is evaporated to dryness. The residue is fused with 2–3 g of potassium hydrogen sulphate, cooled and dissolved in 5% hydrochloric acid (iron, titanium or zirconium, if more than 5 mg present, are removed by precipitating as hydroxides with 20% hexamine solution and then filtering). The solution is diluted to 250 ml in a standard flask.

Determination of (Ca + Mg)

A 25-ml or other suitable portion of the solution is diluted to about 100 ml with water, 20 ml of 30% TEA solution are added and the solution is thoroughly mixed. Then a mixture of 30 ml of buffer (pH 10) and 30 ml of 10% potassium cyanide solution is slowly added with swirling. The solution is diluted to 200 ml, air is bubbled through it at 30–40° for 10 min and then calcium and magnesium are titrated with EDTA, 0.2 g of mixed indicator I being used. The end-point is indicated by a sharp change of colour from pink to green.

Determination of Mn

After the titration of Ca and Mg, 2–3 g of ascorbic acid are added and dissolved. Manganese(II) is then titrated with EDTA, a few drops of mixed indicator II being used. The titration is done slowly up to the first change of colour from pink to blue. The solution is then warmed to about 40° and if a pink colour reappears is titrated to a permanent blue.

Determination of Ca

A 25-ml or other suitable portion of solution is diluted to 150 ml. Thymolphthalein solution (2 ml) is added followed by 10 ml of TEA added slowly with swirling. Then 1*M* potassium hydroxide is added dropwise till the solution turns blue or green. Then 5 ml of 10% potassium cyanide solution and 15 ml of 5*N* potassium hydroxide are added, followed by titration with EDTA in presence of 0.2 g of calcein indicator; the end-point is shown by a colour change to red with disappearance of the green fluorescence.

RESULTS AND DISCUSSION

It is well known that in alkaline medium the manganese(II) cyanide complex is titrated with EDTA along with alkaline earth elements whereas the manganese(III) cyanide complex, being very stable, is not. The conflict of opinion about masking of manganese at pH 10 with potassium cyanide alone or in conjunction with TEA is caused by the incomplete oxidation to the manganese(III) cyanide complex, as discussed in the introduction. The effect of

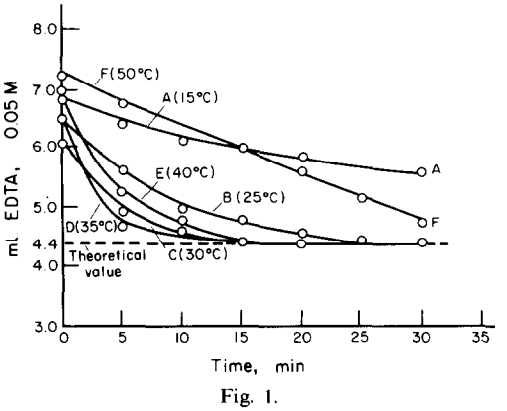


Fig. 1.

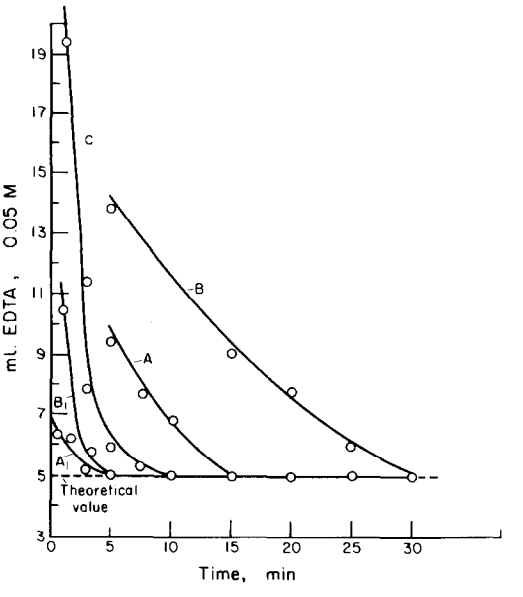


Fig. 2.

time and temperature on the oxidation was therefore critically studied. The results (Fig. 1) indicate that solutions aged for at least 15 min at 30–40° (curves C, D and E) give correct results for magnesium in presence of managanese (13.7 ng), indicating that the latter is quantitatively oxidized to form the manganese(III) cyanide complex. When the aging temperature is raised to 50° or above, erratic results (curve F) are obtained owing to hydrolysis to form a manganese hydroxide precipitate. When the temperature of aging is lowered much below 25° (curve A) the rate of oxidation is too slow to be analytically useful. Therefore, 30–40° is the optimum temperature range. The period of aging needed increases, however, with the concentration of manganese, *e.g.*, 15 min for up to 28 mg/200 ml (Fig. 2, curve A) and 30 min for up to 56 mg/200 ml (curve B). When the concentration is much above 56 mg/200, the Mn(II) cyanide complex slowly hydrolyses before it is all oxidized. To increase the rate of oxidation, and check the hydrolysis, air was bubbled through the solution at 35 ± 5° and it was observed that up to 110 mg of manganese could be quantitatively oxidized within 10 min (curve C), compared to 55 mg in 30 min (curve B) without air bubbling. The oxidation behaviour at pH 10 was found to be the same whether borate, ammonia or sodium hydroxide/TEA medium was used and irrespective of whether the pH was raised or lowered to pH 10.

The literature does not reveal whether TEA is essential for the oxidation. The experiments were therefore repeated without the addition of TEA and similar results were obtained, indicating that TEA is not essential. TEA is, however, found to be effective and useful for removal of the interference due to aluminium in EDTA titrations of alkaline earth elements and for keeping the manganese in solution at high pH (≥12).

During the oxidation of large amounts of manganese in ammonia–ammonium chloride medium, an interesting effect was the gradual formation of a pink complex which faded away before the oxidation was complete. The same phenomenon was not observed, however, when sodium hydroxide or borate buffer (pH 10) was used. This suggests formation of an intermediate mixed ligand ammine–cyanide complex. The oxidized complex can be reduced with ascorbic acid for EDTA titration.

These observations on the masking of manganese with cyanide have been utilized for working out the procedure described here for stepwise titration of calcium plus mag-

Table 1. Determination of calcium, magnesium and manganese in synthetic solutions containing 5 mg of iron

Ca taken, mg	Ca found, mg	Mg taken, mg	Mg found, mg	Mn taken, mg	Mn found, mg
40.08	40.27	10.49	10.39	26.92	26.75
20.04	20.04	20.98	20.85	26.92	26.90
10.02	10.00	10.49	10.59	26.92	26.78
2.00	2.01	5.25	5.28	26.92	26.89
10.02	10.00	5.25	5.33	13.46	13.50
2.00	2.05	1.05	0.93	5.38	5.45
40.08	40.09	10.49	10.35	5.38	5.38
10.02	9.93	1.05	1.07	2.69	2.65
2.00	2.11	5.25	5.37	2.69	2.60

nesium and then manganese with EDTA. Eriochrome Black T is oxidized by the manganese(III) cyanide complex, so cannot be used for the titration of Ca + Mg. *o*-Cresolphthalein complexone is not suitable for EDTA titration of Mn(II). It has been observed, in agreement with earlier workers,[12] that the use of calcein alone does not give a satisfactory end-point for calcium in the presence of a substantial amount of magnesium hydroxide percipitate. This is overcome by the addition of thymolphthalein, which improves the end-point and yields satisfactory results.

The procedures given do not require prior separation of aluminium, even when this is present in large amounts. However, more than a few mg of titanium or zirconium will precipitate as the hydroxide, which adsorbs the indicator, and iron (>5 mg) seriously affects the end-point. Therefore iron, titanium or zirconium, if present in more than 5-mg amounts, require at least semiquantitative separation. The results of determinations of Ca, Mg and Mn in synthetic solutions and in a few glass and enamel samples compare favourably with the certified values (Tables 1 and 2).

Table 2. Determination of CaO, MgO and MnO in glass and enamel samples

Sample	Found %	*Certified values %
Vitrate glass(I)		
CaO	1.95	2.10
MgO	1.60	1.53
MnO	4.80	4.69
Vitrate glass(II)		
CaO	7.90	7.83
MgO	5.09	5.21
MnO	10.31	10.29
Coloured glass		
CaO	7.22	7.15
MgO	0.30	0.32
MnO	3.60	3.51
Vitrate glass(III)		
CaO	15.55	15.64
MgO	1.16	1.18
MnO	14.37	14.25
Enamel		
CaO	8.99	9.01
MgO	3.78	3.75
MnO	4.00	4.15

* MnO by conventional bismuthate method, CaO and MgO by EDTA after separation of Mn by H_2S.

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REFERENCES

1. R. Přibil, *Collection Czech. Chem. Commun.*, 1954, **19**, 58.
2. *Idem, ibid.*, 1954, **19**, 465.
3. T. S. West, *Complexometry with EDTA and Related Reagents*, p. 106, BDH Poole.
4. P. Povondra and R. Přibil, *Collection Czech. Chem. Commun.*, 1961, **26**, 311.
5. T. Yotsuyanagi, T. Yamaguchi, K. Goto and M. Nagayama, *Bunseki Kagaku*, 1967, **16**, 1056.
6. B. C. Sinha and S. Dasgupta, unpublished work.
7. H. Asaoka, *Bunseki Kagaku*, 1963, **13**, 1144.
8. H. M. Fog, *Acta Chem. Scand.*, 1968, **22**, 791.
9. B. C. Sinha and S. K. Roy, *J. Inst. Chem. India*, 1974, **46**, 19.
10. R. Přibil and V. Veselý, *Chemist-Analyst*, 1966, **55**, 68.
11. R. M. Sales, *British Glass Industry Research Association, Technical Note* No. 6, 1957.
12. B. C. Sinha and S. K. Roy, *Analyst*, 1973, **98**, 289.
13. *Glass Technol.*, 1963, **4**, 109.

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ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF TUNGSTEN(VI) WITH AMMONIUM 1-PYRROLIDINECARBODITHIOATE

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Summary—A simple and rapid ultraviolet spectrophotometric method is proposed for the determination of trace amounts of tungsten(VI) with ammonium 1-pyrrolidinecarbodithioate (APDC). The method is based on measurement of the absorbance of the tungsten–APDC complex in fairly concentrated hydrochloric acid medium; no extraction is required. The complex is formed at an initial acidity of 6*M* hydrochloric acid and has an absorption maximum at 250 nm. The high absorption of the reagent blank at 250 nm disappears on decomposition of excess of reagent by heating. Beer's law is obeyed over the range 0.43–3.2 ppm of tungsten(VI). The molar absorptivity of the complex is 4.5×10^4 l.mole^{-1}.cm^{-1} at 250 nm. Tenfold amounts of aluminium, magnesium, calcium, cobalt, iron(II), lead, silver, sodium and titanium do not interfere in the determination of 50 μg of tungsten (VI).

Many methods have been proposed for the spectrophotometric determination of trace amounts of metal ions with ammonium 1-pyrrolidinecarbodithioate (APDC),[1–21] but only a few have been based on formation of APDC complexes which are soluble in strongly acidic medium.[22–24]

Many spectrophotometric determinations of trace amounts of tungsten have been reported, based on use of thiocyanate,[25–34] dithiol,[35–37] hydroquinone,[38] oxine,[39,40] pyrocatechol[41–43] and other reagents,[44–51] but APDC has not been exploited, although in a study of chromium(VI) with APDC,[24] it was found that tungsten(VI) formed a colourless and soluble APDC complex in 3*M* hydrochloric acid.

In this paper, this observation is made the basis for the determination of trace amounts of tungsten(VI).

EXPERIMENTAL

Reagents

Standard tungsten(VI) *solution, 1000 ppm.* Dissolve 1.749 g of sodium tungstate dihydrate in distilled water, dilute to 1 litre, and standardize gravimetrically. Prepare working solutions by appropriate dilution with distilled water.

APDC solution. Prepare a 0.5% aqueous solution before use.

Recommended procedure

Transfer a sample solution containing up to 80 μg of tungsten(VI) to a 100-ml beaker, add 10 ml of 12*M* hydrochloric acid and 2 ml of 0.5% APDC solution, and dilute to about 20 ml with distilled water. Heat the solution for 2 min in a boiling water-bath, keeping the temperature of the solution at about 70–90° for 1–1.5 min. Cool the solution to room temperature under the tap, transfer it to a 25-ml standard flask and dilute to the mark with distilled water. Measure the absorbance at 250 nm against a reagent blank solution.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the tungsten(VI)–APDC complex and the reagent blank in the wavelength range 220–320 nm are illustrated in Fig. 1. The maximum absorption of the complex is at 250 nm, where there is no absorption by the reagent blank, because the heating decomposes the excess of reagent.

It was found that less than 2 min of heating results in incomplete decomposition of excess of reagent and gives non-reproducible results, whereas more than 4.5 min of heating causes the absorbance of the complex at 250 nm to decrease, probably because of some dissociation or decomposition of the complex. Reproducible absorbance is obtained by heating for 2–4 min in a boiling water-bath.

Effect of initial acidity

No appreciable absorption in the ultraviolet was observed at an initial acidity of up to 3*M* hydrochloric acid, but increased with increasing acidity and became maximal at an initial acidity of 5.5–6.5*M* hydrochloric acid.

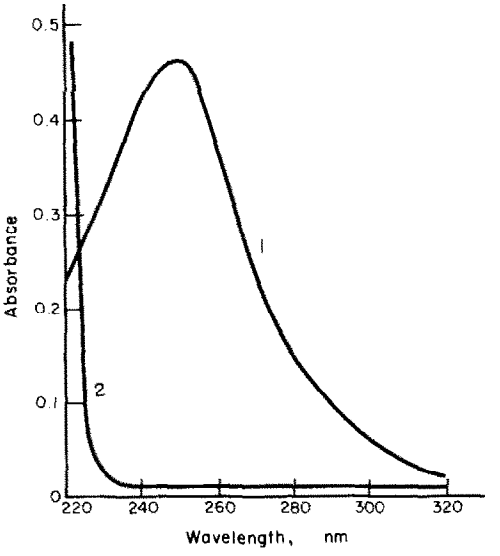


Fig. 1. Absorption spectra of W(VI)–APDC complex and reagent blank. 1: Complex (ref. reagent blank); 2: reagent blank (ref. 5.5*M* HCl); W(VI) 50 μg, APDC 2.44×10^{-3}*M*.

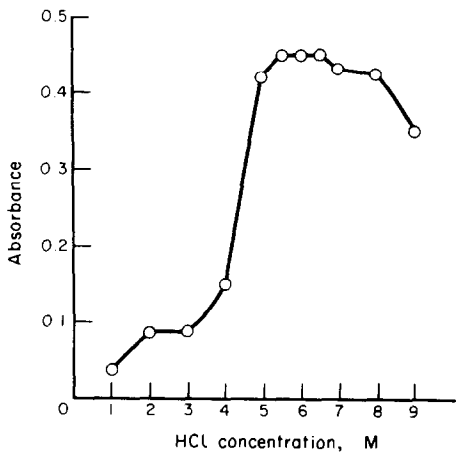


Fig. 2. Effect of initial acidity of hydrochloric acid solution on absorbance of complex. W(VI) 50 μg; wavelength 250 nm; reference reagent blank.

as shown in Fig. 2. Thus 6*M* hydrochloric acid is recommended as the optimum reaction medium.

Amount of reagent solution

As shown in Fig. 3, addition of more than 0.8 ml of 0.5% APDC solution is required to obtain maximal and reproducible absorbance for 50 μg of tungsten. Smaller amounts give incomplete complex formation. Hence 2 ml of 0.5% solution is recommended.

Selection of acid

The complexing behaviour of tungsten(VI) with APDC in hydrochloric, perchloric, nitric, sulphuric and phosphoric acids as reaction was studied.

Tungsten(VI) reacts with APDC in 3*M* hydrochloric and perchloric acids; in the latter medium there are absorption maxima at about 243 and 258 nm. No absorption was observed at wavelengths shorter than 360 nm at various concentrations of nitric, sulphuric and phosphoric acids. From the absorption spectra (Figs. 1 and 4), hydrochloric acid was chosen as the medium.

Calibration curve, sensitivity and precision

The calibration curve prepared by using the recommended procedure gave a straight line in the range 0.43–3.2 ppm of tungsten(VI). The molar absorptivity is 4.5×10^4 l.mole^{-1}.cm^{-1} at 250 nm.

The coefficient of variation is 0.4% for five determinations of 15 μg of tungsten(VI).

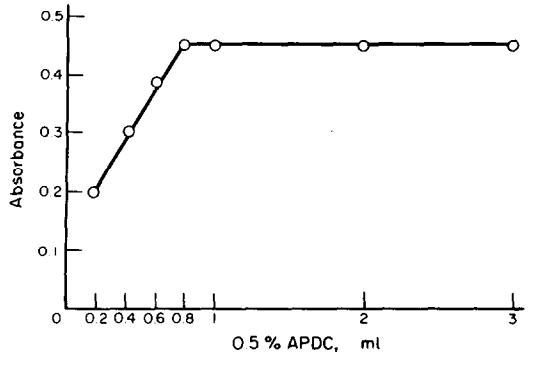


Fig. 3. Effect of amount of APDC solution added. W(VI) 50 μg; wavelength 250 nm; reference reagent blank

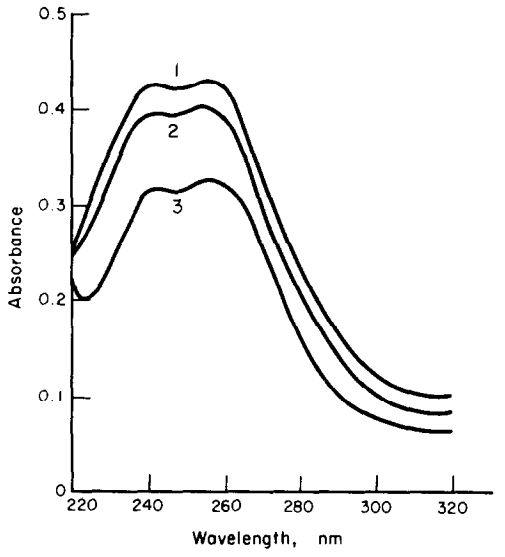


Fig. 4. Absorption spectra of W–APDC complex at various initial concentrations of perchloric acid, measured against reagent blank. 1: 6*M* $HClO_4$; 2:*M* $HClO_4$; 3: 5*M* $HClO_4$.

The absorbance of the complex remains constant for 1 hr, in 6*M* hydrochloric acid solution, after which it decreases gradually with standing time.

Effect of foreign metal ions

As shown in Table 1, 10-fold amounts of aluminium, calcium, magnesium, cobalt, iron(II), lead, silver, sodium and titanium do not interfere in the determination of 50 μg of tungsten(VI), but 10-fold amounts of copper, nickel, manganese(II), vanadium(V), tin(IV), molybdenum(VI), zinc and mercury(II), and 4-fold amounts of chromium(VI) and iron(III) interfere. These interferences could be removed by cation-exchange separation or solvent extraction. Proposed uses include determination of trace amounts of tungsten in high-purity zirconium or titanium oxide.

Table 1. The effect of diverse metal ions

Ion	Added as	Amount added μg	W(VI) found* μg	Error μg
Na(I)	$NaNO_3$	500	50.6	+ 0.6
Mg(II)	$MgSO_4$	500	50.2	+ 0.2
Al(III)	$AlCl_3$	500	49.1	− 0.1
Ca(II)	$CaCO_3$	500	50.0	± 0.0
Ti(IV)	$K_2TiO(C_2O_4)_2$	500	50.9	+ 0.9
V(V)	NH_4VO_3	500	30.6	− 19.4
Cr(VI)	K_2CrO_4	200	60.0	+ 10.0
Mn(II)	$MnSO_4$	500	45.7	− 4.3
Fe(II)	$FeSO_4$	500	49.4	− 0.6
Fe(III)	$Fe_2(SO_4)_3$	200	47.2	− 2.8
Co(II)	$Co(NO_3)_2$	500	50.8	+ 0.8
Ni(II)	$Ni(NO_3)_2$	500	ppte.	—
Cu(II)	$Cu(NO_3)_2$	500	ppte.	—
Zn(II)	$Zn(NO_3)_2$	500	44.6	− 5.4
Mo(VI)	Na_2MoO_4	500	ppte.	—
Mo(VI)	Na_2MoO_4	200	48.3	− 1.7
Ag(I)	$AgNO_3$	500	50.8	+ 0.8
Sn(IV)	$SnCl_4$	500	46.4	− 3.6
Hg(II)	$HgCl_2$	500	43.3	− 6.7
Pb(II)	$Pb(NO_3)_2$	500	50.6	+ 0.6

* W taken: 50 μg.

REFERENCES

1. H. Malissa and F. Schoffmann, *Mikrochim. Acta*, 1955, 187.
2. L. Rocks and H. Malissa, *Anal. Chim. Acta*, 1964, **30**, 106.
3. I. M. Gibalo, I. P. Alimarin and P. Davvadorzh, *Vestn. Mosk. Univ., Ser. II, Khim.*, 1965, **20**, 73.
4. C. E. Mulford, *At. Abs. Newsletter*, 1966, **5**, 88.
5. J. W. Husler, *ibid.*, 1970, **9**, 31.
6. M. B. Kalt and D. F. Boltz, *Anal. Chem.*, 1968, **40**,1068.
7. A. Traub and D. F. Boltz, *Mikrochim. Acta*, 1969, 749.
8. R. W. Looyenga and D. F. Boltz, *Anal. Lett.*, 1969, **2**, 491.
9. P. G. Brewer, D. W. Spencer and G. L. Smith, *ASTM Spec. Tech. Publ.*, 1969, No. 443, 70.
10. W. Likussar, G. Sparks and D. F. Boltz, *Anal. Chim. Acta*, 1970, **52**, 349.
11. W. Likussar, C. Sagan and D. F. Boltz, *Mikrochim. Acta*, 1970, 683.
12. K. Hayashi, Y. Sasaki, M. Nakanishi and S. Ito, *Bunseki Kagaku*, 1971, **19**, 1673.
13. K. Hayashi and K. Ito, *ibid.*, 1971, **20**, 1550.
14. H. K. Y. Lau, H. A. Droll and P. F. Lott, *Anal. Chim. Acta*, 1971, **56**, 7.
15. W. Likussar and D. F. Boltz, *Anal. Chem.*, 1971, **43**, 1273.
16. R. W. Looyenga and D. F. Boltz, *Mikrochim. Acta*, 1971, 507.
17. K. Hayashi, Y. Sasaki and K. Ito, *Bunseki Kagaku*, 1972, **21**, 1338.
18. R. W. Looyenga and D. F. Boltz, *Talanta*, 1972, **19**, 82.
19. H. Okusa, Y. Ueda, K. Ota and K. Kawano, *Bunseki Kagaku*, 1973, **22**, 84.
20. H. Sakurai, *ibid.*, 1975, **24**, 52.
21. T. Kamada and Y. Yamamoto, *Talanta*, 1977, **24**, 330.
22. W. Lukussar, G. H. Sparks and D. F. Boltz, *Anal. Chim. Acta*, 1970, **52**, 349.
23. A. S. Berger, W. Likussar and D. F. Boltz, *Microchem. J.*, 1971, **16**, 286.
24. Y. Yamamoto, T. Murata and S. Ueda, *Bunseki Kagaku*, 1976, **25**, 851.
25. W. Westwood and A. Mayer, *Analyst*, 1947, **72**, 464.
26. C. H. R. Gentry and L. G. Sherrington, *ibid.*, 1948, **73**, 57.
27. I. Geld and J. Carroll, *Anal. Chem.*, 1949, **21**, 1098.
28. H. Freund, M. L. Wright and R. K. Brookshier, *ibid.*, 1951, **23**, 781.
29. C. E. Crouthamel and C. E. Johnson, *ibid.*, 1954, **26**, 1284.
30. H. Nishida, *Bunseki Kagaku*, 1955, **4**, 523.
31. B. McDuffie, W. R. Bandi and L. M. Melnick, *Anal. Chem.*, 1959, **31**, 1311.
32. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd Ed., p. 886. Wiley, New York, 1959.
33. C. L. Luke, *Anal. Chem.*, 1964, **36**, 1327.
34. A. G. Fogg, D. R. Marriott and D. T. Burns, *Analyst*, 1970, **95**, 848.
35. C. C. Miller, *ibid.*, 1944, **69**, 109.
36. B. Bagshawe and R. J. Truman, *ibid.*, 1947, **72**, 189.
37. S. Kallmann, E. W. Hobart and H. K. Oberthin, *Talanta*, 1968, **15**, 892.
38. L. E. Bricker and C. R. Waterbury, *Anal. Chem.*, 1957, **29**, 1093.
39. K. Motojima and H. Hashitani, *Bunseki Kagaku*, 1960, **9**, 161.
40. A. R. Eberle, *Anal. Chem.*, 1963, **35**, 669.
41. M. Vrchlabsky and L. Sommer, *Talanta*, 1968, **15**, 887.
42. A. I. Busev and T. A. Sokolova, *J. Anal. Chem., USSR*, 1968, **23**, 1186.
43. L. I. Lebedeva, Z. G. Golubtsova and N. G. Yanklovich, *ibid.*, 1971, **26**, 1754.
44. G. J. Lennard, *Analyst*, 1949, **74**, 253.
45. M. Kiboku and C. Yoshimura, *Bunseki Kagaku*, 1958, **7**, 488.
46. N. Ishibashi and H. Kohara, *ibid.*, 1964, **13**, 239.
47. T. Shimizu, K. Kato, S. Oyama and K. Hosohara, *ibid.*, 1966, **15**, 125.
48. S. B. Savvin, E. G. Namvrina and R. S. Tramm, *J. Anal. Chem. USSR*, 1972, **27**, 87.
49. A. K. Chakrabarti and S. P. Bag, *Anal. Chim. Acta*, 1972, **59**, 225.
50. Y. Shijo and T. Takeuchi, *Bunseki Kagaku*, 1973, **22**,
51. I. Mori, *ibid.*, 1974, **23**, 291.

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N-HYDROXY-*N*,*N*'-DIPHENYLCINNAMAMIDINE (HDPCA) AS A NEW REAGENT FOR EXTRACTIVE SEPARATION AND PHOTOMETRIC DETERMINATION OF VANADIUM(V)

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(*Received* 7 *September* 1977. *Revised* 11 *May* 1978. *Accepted* 2 *June* 1978)

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The reagents and methods employed for the spectrophotometric determination of vanadium have been recently reviewed by Svehla and Tölg.[1]

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REFERENCES

1. H. Malissa and F. Schoffmann, *Mikrochim. Acta*, 1955, 187.
2. L. Rocks and H. Malissa, *Anal. Chim. Acta*, 1964, **30**, 106.
3. I. M. Gibalo, I. P. Alimarin and P. Davvadorzh, *Vestn. Mosk. Univ., Ser. II, Khim.*, 1965, **20**, 73.
4. C. E. Mulford, *At. Abs. Newsletter*, 1966, **5**, 88.
5. J. W. Husler, *ibid.*, 1970, **9**, 31.
6. M. B. Kalt and D. F. Boltz, *Anal. Chem.*, 1968, **40**,1068.
7. A. Traub and D. F. Boltz, *Mikrochim. Acta*, 1969, 749.
8. R. W. Looyenga and D. F. Boltz, *Anal. Lett.*, 1969, **2**, 491.
9. P. G. Brewer, D. W. Spencer and G. L. Smith, *ASTM Spec. Tech. Publ.*, 1969, No. 443, 70.
10. W. Likussar, G. Sparks and D. F. Boltz, *Anal. Chim. Acta*, 1970, **52**, 349.
11. W. Likussar, C. Sagan and D. F. Boltz, *Mikrochim. Acta*, 1970, 683.
12. K. Hayashi, Y. Sasaki, M. Nakanishi and S. Ito, *Bunseki Kagaku*, 1971, **19**, 1673.
13. K. Hayashi and K. Ito, *ibid.*, 1971, **20**, 1550.
14. H. K. Y. Lau, H. A. Droll and P. F. Lott, *Anal. Chim. Acta*, 1971, **56**, 7.
15. W. Likussar and D. F. Boltz, *Anal. Chem.*, 1971, **43**, 1273.
16. R. W. Looyenga and D. F. Boltz, *Mikrochim. Acta*, 1971, 507.
17. K. Hayashi, Y. Sasaki and K. Ito, *Bunseki Kagaku*, 1972, **21**, 1338.
18. R. W. Looyenga and D. F. Boltz, *Talanta*, 1972, **19**, 82.
19. H. Okusa, Y. Ueda, K. Ota and K. Kawano, *Bunseki Kagaku*, 1973, **22**, 84.
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21. T. Kamada and Y. Yamamoto, *Talanta*, 1977, **24**, 330.
22. W. Lukussar, G. H. Sparks and D. F. Boltz, *Anal. Chim. Acta*, 1970, **52**, 349.
23. A. S. Berger, W. Likussar and D. F. Boltz, *Microchem. J.*, 1971, **16**, 286.
24. Y. Yamamoto, T. Murata and S. Ueda, *Bunseki Kagaku*, 1976, **25**, 851.
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26. C. H. R. Gentry and L. G. Sherrington, *ibid.*, 1948, **73**, 57.
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51. I. Mori, *ibid.*, 1974, **23**, 291.

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N-Benzoylphenylhydroxylamine (BPHA) and its analogues[2–6] have enjoyed a vogue as reagents for vanadium, but have recently been criticised.[7–10]

In the light of this and in continuation of our studies on the chemistry of hydroxyamidines,[11-14] it was thought worthwhile to synthesize and investigate *N*-hydroxy-*N*,*N'*-diphenylcinnamamidine (HDPCA), **I**, which possesses a new type of functional grouping, –N=C–N(OH)–, in which a basic azomethine nitrogen atom provides the co-ordination site.

It can be prepared from common laboratory chemicals, and gives a water-insoluble blue-violet vanadium(V) complex in 1.0–9.5*M* acetic acid medium. This complex is quantitatively extractable into chloroform, and on this basis, a simple, rapid and highly selective spectrophotometric method for the determination of trace quantities of vanadium has been developed. Large amounts of almost all common ions, including iron, molybdenum, manganese, chromium and rare earths do not interfere. In concentrated acetic acid medium vanadium(V) is not reduced and hence the extraction is quantitative. Moreover, Ag, Pb, Hg and Tl form no precipitate in acetic acid medium and therefore their prior separation is not necessary. The presence of traces of alcohol, added as stabilizer in chloroform, affects neither the position of the absorption band nor the stability and absorbance of the complex. The sensitivity of the HDPCA method is comparable with that of the BPHA method. The method is reproducible and applicable to the determination of vanadium in alloy steels.

EXPERIMENTAL

Reagents

N-Hydroxy-N,N'-diphenylcinnamamidine. An ethereal solution of *N*-phenylcinnamimidoyl chloride, prepared by the action of thionyl chloride on cinnamanilide in toluene, following the method of Sonn and Muller[15] was added to an equimolar ethereal solution of *N*-phenylhydroxylamine over a period of 30 min. The temperature was maintained at 0–5 throughout. A light brown oil separated in the initial stages of the reaction. Shaking and scratching of the oil was continued for 2 hr and then the solvent was removed by distillation. Ammonia solution (5*M*, 40 ml) was added to the oil and triturated for 5 min. The resulting solid was washed with water and recrystallized from 60% ethanol to yield shining yellow crystals, m.p. 138–9°; yield 50%. Found: C, 80.5%; H, 6.0%; N, 8.5%: $C_{20}H_{18}N_2O$ requires C, 80.27%; H, 5.73%; N, 8.91%. The infrared spectrum recorded for the mull in nujol and hexaclorobutadiene) gave bands at 3120 cm^{-1} (strong intramolecular hydrogen bonding), 3050 cm^{-1} (aromatic C–H stretch.), 1595 cm^{-1} (C=N stretch), 1575 cm^{-1} (C=C aromatic) and 935 cm^{-1} (N–O). The ultraviolet spectrum (95% ethanol solution) gave maxima at; 213 nm (log ϵ, 4.322), 293 nm (log ϵ 4.260) and 357 nm (log ϵ, 4.076).

A 0.1% solution of the reagent in analytical reagent grade chloroform was used for extraction purposes.

Standard vanadium(V) stock solution. Prepared by dissolving 1.141 g of ammonium metavanadate in 1 litre of doubly distilled water and standardized titrimetrically.[16]

Recommended procedure

To 10 ml of solution containing up to 100 μg of vanadium(V), in a separatory funnel, add 10 ml of glacial acetic acid and dilute to 25 ml with distilled water. Add 6 ml of 0.1% reagent solution, shake vigorously for about 1 min and allow the phases to separate. Run the lower (organic) phase into a 50-ml beaker containing 2 g of anhydrous sodium sulphate. Wash the aqueous phase with two 5-ml portions of chloroform and add the washings to the beaker. After 30 sec decant the combined extracts into a 25-ml standard flask. Wash the sodium sulphate with chloroform, adding the washings to the main solution and dilute to volume. Measure the absorbance at 570 nm against a reagent blank. As the reagent has practically no absorbance at wavelengths $\geqslant$ 500 nm, chloroform can also be used as reference solution. Deduce the amount of vanadium in the sample solution from a calibration curve.

RESULTS AND DISCUSSION

The absorption spectra of the vanadium complex and the reagent are shown in Fig. 1. The complex shows maximum absorption at 570 nm, where the reagent has no significant absorption. The spectrum is unchanged if the acetic acid concentration used in the extraction lies between 1.0 and 9.5*M*. Inorganic acids such as sulphuric and hydrochloric are not suitable, as quantitative extraction of vanadium could not be accomplished even after shaking for 2 hr.

A number of organic solvents, including benzene, toluene, chloroform, *o*-dichlorobenzene, chlorobenzene and carbon tetrachloride, extract the complex quantitatively.

Table 1. Tolerance limits for diverse ions (V 4 ppm; acetic acid 7*M*)

Species added	Tolerance limit, *ppm*	Species added	Tolerance limit, *ppm*
F^-	1000	Fe^{3+}	1000
Cl^-	7000	Cr^{3+}	800
Br^-	3000	Tl^{3+}	1000
NO_3^-	5600	In^{3+}	840
SO_4^{2-}	5000	Ga^{3+}	800
PO_4^{3-}	1000	Cu^{2+}	1000
AsO_4^{3-}	500	Ni^{2+}	880
$B_4O_7^{2-}$	700	Co^{2+}	900
Thiourea	800	Mn^{2+}	1000
Triethanolamine	400	Pd^{2+}	60
Citrate	1000	Th^{4+}	1500
Tartrate	800	Ce(IV)	800
Ag^+	1400	Se(IV)	1000
Ca^{2+}, Ba^{2+} or Sr^{2+}	2400	Ti^{4+}	30
Be^{2+} or Mg^{2+}	1600	Zr^{4+}	60
Pb^{2+}	1500	Nb(V)	80
Zn^{2+}	1640	Ta(V)	60
Cd^{2+}	1600	La^{3+} or Gd^{3+}	2000
Hg^{2+}	1200	UO_2^{2+}	800
Sb^{3+}	1280	Mo(VI)	150
Bi^{3+}	800	Mn(VII)	120
Al^{3+}	1000		

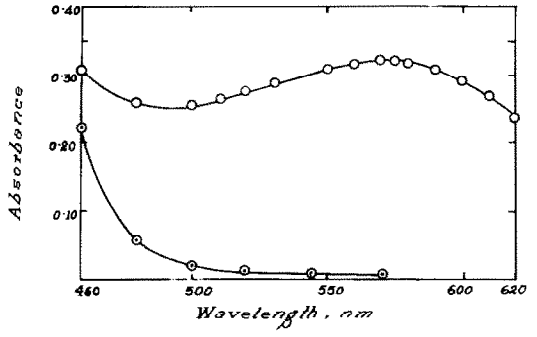


Fig. 1. Absorption spectra of vanadium(V) (4 ppm)–HDPCA complex (—○—○—○—○—) and HDPCA (0.003*M*; —⊙—⊙—⊙—) in chloroform.

Chloroform was preferred because of the solubility of the reagent and complex in it and the good sensitivity.

The colour development is instantaneous and the extraction complete within a minute. The extracted chelate is stable in chloroform for at least 5 days in the temperature range 20–40°. Job's plot and the mole ratio method[17] both indicate a 1:2 metal to ligand ratio. For maximal colour development the reagent:metal ratio must exceed 6:1. Hence, a 10:1 molar ratio is used for safety, up to a 30:1 molar ratio has no effect on the absorbance. The order of addition of reagents is not critical.

The system obeys Beer's law over the vanadium concentration range of 0.6–12.5 μg/ml. A Ringbom plot[18] indicates that the optimum concentration range is 3.0–12.0 ppm. The relative error per 1% absolute photometric error[19] is 2.7%. The molar absorptivity is 4.08×10^3 l.mole^{-1}.cm^{-1}.

Twenty independent determinations on solutions each containing 100 μg of vanadium gave a mean absorbance of 0.320 and a standard deviation of 0.002.

Influence of diverse ions

The tolerance limits for various ions are recorded in Table 1. Thiocyanate changes the colour of the complex to green and shifts λ_{max} to 600 nm with an increase in the absorbance, and thus seriously interferes. W(VI) inhibits colour development and all attempts to mask it with common masking agents fail. Mo(VI) reacts with the reagent throughout the acidity range to give a chloroform-extractable yellow complex. However, the colour of the extract has no significant absorption at 570 nm and thus does not interfere. Vanadium is completely masked by excess of EDTA.

Determination of vanadium in BCS steels

Three BCS steels were analysed accurately and precisely (Table 2).

Procedure for steel

Dissolve a steel sample, containing approximately 4 mg of vanadium, in 15–20 ml of *aqua regia*. Evaporate the solution nearly to dryness, on a hot-plate. Add 5 ml of concentrated hydrochloric acid and again evaporate to small volume. Cool, dilute to 30 ml, filter off silica, carbon and tungstic acid, washing with hot (1*M*) hydrochloric acid until free from iron. Concentrate the filtrate to 5 ml, dilute to 50 ml and transfer to a 250-ml standard flask. Wash the tungstic acid precipitate, which tends to retain appreciable amounts of vanadium,[20] with a few ml of hot 1*M* acetic acid, add the washings to the main solution and dilute to volume. Pipette 10 ml into a separatory funnel, add dilute potassium permanganate solution until a faint pink persists, adjust the acetic acid concentration to 7*M* and continue with the recommended procedure.

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REFERENCES

1. G. Svehla and G. Tölg, *Talanta*, 1976, **23**, 755.
2. S. C. Shome, *Analyst*, 1950, **75**, 27.
3. D. E. Ryan, *ibid*, 1960, **85**, 569.
4. U. Priyadarshini and S. G. Tandon, *Anal. Chem.*, 1961, **33**, 435.
5. A. K. Majumdar and G. Das, *Anal. Chim. Acta*, 1966, **36**, 454.
6. A. K. Majumdar, *N-Benzoylphenylhydroxylamine and its Analogues*, Pergamon, Oxford, 1972.
7. A. D. Shendrikar, *Talanta*, 1969, **16**, 51.
8. H. Goto and Y. Kakita, *Bunseki Kagaku*, 1961, **10**, 904; *Chem. Abstr.*, 1962, **56**, 12311 i.
9. O. A. Vita, W. A. Levier and E. Litteral, *Anal. Chim. Acta*, 1968, **42**, 87.
10. E. M. Donaldson, *Talanta*, 1970, **17**, 583.
11. K. Satyanarayana and R. K. Mishra, *Indian J. Chem.*, 1975, **13**, 295.
12. *Idem*, *J. Indian Chem. Soc.*, 1976, **53**, 63, 469, 928.
13. K. K. Deb and R. K. Mishra, *ibid.*, 1976, **53**, 178.
14. *Idem*, *Curr. Sci. (India)*, 1976, **45**, 134.
15. A. Sonn and E. Muller, *Ber.*, 1919, **52**, 1927.
16. G. Charlot and D. Bezier, *Quantitative Inorganic Analysis*, 3rd Ed., Wiley, New York, 1957.
17. A. E. Harvey Jr. and D. L. Manning, *J. Am. Chem. Soc.*, 1950, **72**, 4488.
18. A. Ringbom, *Z. Anal. Chem.*, 1939, **115**, 332.
19. G. H. Ayres, *Anal. Chem.*, 1949, **21**, 652.
20. S. G. Clarke, *Analyst*, 1927, **52**, 466.

Table 2. Determination of vanadium in steels

BCS* sample No.	Vanadium found, %	Vanadium certificate value, %	Relative error, %	Standard deviation, %
64a	1.56; 1.55; 1.56; 1.55; 1.55			
	Average value, 1.55	1.57	−1.1	±0.006
241/1	1.54; 1.55; 1.56; 1.54; 1.55			
	Average value, 1.55	1.57	−1.5	±0.008
252	0.452; 0.456; 0.460; 0.452; 0.455			
	Average value, 0.453	0.460	−1.5	±0.006

* Obtained from Bureau of Analysed Samples, Ltd. Newham Hall, Middlesbrough, Yorks, England.

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DETERMINATION OF MERCURY BY EXTRACTION AND ISOTOPE-DILUTION MASS SPECTROMETRY

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(*Received* 6 *December* 1977. *Revised* 29 *March* 1978 *Accepted* 29 *May* 1978)

Summary—The use of halides for determination of metals by stable-isotope mass spectrometry is suggested, and is illustrated by the use of mercury iodide for mercury determination.

For mass spectra of metals to be obtained by electron-impact mass spectrometry (EI–MS), the metals have first to be changed into compounds which have sufficient volatility in the ion-source.

For this purpose, many metal chelate compounds have been used, and applied for determination of metals by stable-isotope dilution mass spectrometry.[1,2] These chelates, however, give many fragment peaks, similarly to organic compounds in general.

We have reported mass spectra of some metal halides[3,4] which have sufficient volatility for EI–MS. The fragmentation paths of the metal halides are very simple, because they are composed of only a few ions. When the iodide is used, the metal can easily be identified from the mass spectrum at a glance, because the isotopic abundance of the metal is shown directly by the peak-ratio of the associated cluster, since iodine is monoisotopic.

In this study, mercury extracted as HgI_2 by an organic solvent is determined by stable-isotope dilution mass spectrometry.

EXPERIMENTAL

Reagents

Mercuric oxide enriched with ^{198}Hg was purchased from the Japan Isotope Center. Mercuric oxide (natural abundance) was used as the reference mercury compound. Other reagents were of guaranteed or pure-chemical grade.

Mass spectrometry conditions

A Hitachi RMS-4 mass spectrometer was used, with sample temperature 170°, electron current 80 μA and ionization voltage 80 eV.

Procedure

Extraction. A weighed amount of mercuric oxide (~0.5 mg) was put into a 50-ml separating funnel and mixed with 5 ml of 3*N* sulphuric acid and excess of potassium iodide. The mixture was shaken vigorously with 10 ml of methyl isobutyl ketone (MIBK), then stood for a few minutes to separate the phases. The upper (organic) layer was used for the mass spectrometry. An aliquot of 1 μl of the extract was placed in a glass capillary tube by microsyringe, and this tube was inserted directly into the ion-source.

A mixture of accurately weighed enriched HgO (~0.5 mg) and natural-abundance HgO (~0.5 mg) was treated and analysed in the same way. A suitable region of the spectrum was scanned repeatedly to increase the sensitivity and precision.

RESULTS AND DISCUSSION

In stable-isotope dilution mass spectrometry, the general equation for an element with n isotopes is

$$W = W_t \frac{(Q - R_{ij})}{(r_{ij} - Q)} \frac{\sum_i^n M_i r_{ij}}{\sum_i^n M_i R_{ij}} \quad (1)$$

where a quantity W of the normal element is mixed with a quantity W_t of the tracer element, and r_{ij} is the ratio of the abundances of isotopes i and j in the normal element, R_{ij} is the ratio in the tracer element, Q is the ratio in the mixture, and M_i is the atomic weight of isotope i. A single isotope is selected as j.

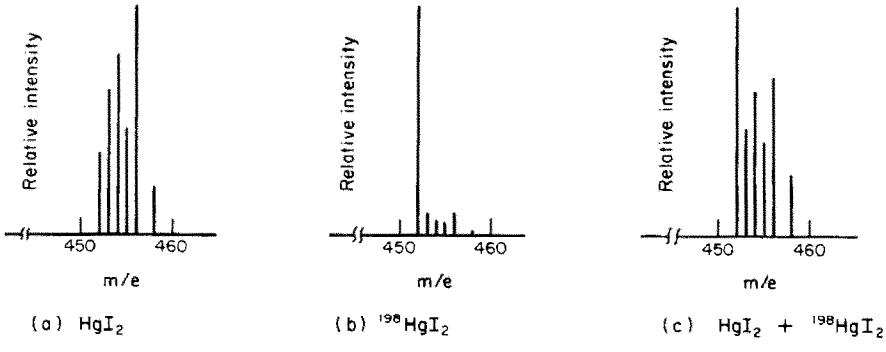


Fig. 1. Mass spectra of (a) HgI_2, (b) $^{198}HgI_2$ and (c) the mixture. (Molecular peak regions are shown).

Table 1. Relative abundances of Hg and enriched Hg obtained from the mass spectra in Fig. 1.

Mass number (M_i)	Relative abundance in natural Hg	Relative abundance in enriched Hg	Relative abundance in mixture
198 (M_1)	1.00	1.00	1.00
199 (M_2)	1.74	0.092	
200 (M_3)	2.07	0.069	
201 (M_4)	1.30	0.050	
202 (M_5)	2.80 ($=j$)	0.087 ($=j$)	0.70
204 (M_6)	0.59	0.021	

Figure 1 shows the mass spectra of MIBK extracts of HgI_2 and enriched HgI_2. From these, M_i, R_{ij} and r_{ij}, in equation (1) can be determined, and the results are summarized in Table 1. An accurately weighed amount of W_t is added as a spike to the unknown amount of sample (W); Q is estimated from the mass spectrum of the mixture. A mass spectrum of a mixture of enriched HgO (23 ng/μl) and the sample of HgO (54 ng/μl) is also recorded in Fig. 1, from which Q is calculated from the ratio of peak heights at M/e 198 and 202 (Table 2). From Table 1 and equation (1), the concentration of the HgO sample was calculated to be 56 ng/μl, in good agreement with that taken.

Stable-isotope dilution mass spectrometry with extraction is very useful for determining metals, even if the extraction is not complete, because the extraction ratio of the normal and labelled elements can be assumed to be the same.

We have reported earlier the mass spectra of metal halides extracted with organic solvents. These metals can also be determined by this method, if they are not monoisotopic and isotopically enriched specimens are available.

The iodide seems to be the best form for the determination of metals, because iodine is not only monoisotopic but also gives more intense peaks than the corresponding chloride or bromide.

REFERENCES

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2. S. Tuge, J. J. Leary and T. L. Isenhour, *ibid.*, 1974, **46**, 106.
3. K. Matsumoto, N. Kiba and T. Takeuchi, *Talanta*, 1975, **22**, 321.
4. *Idem*, *ibid.*, 1975, **22**, 695.

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DETERMINATION OF METALLIC IRON IN A MIXTURE OF LIME, CALCIUM SULPHIDE AND PYRRHOTITE*

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(*Received* 10 *March* 1978. *Accepted* 29 *May* 1978)

Summary—A method is described for the determination of metallic iron in a complex matrix consisting of calcium oxide, calcium sulphide, carbon and pyrrhotite. The procedure consists of leaching the sample with 5% ammonium chloride solution (10% sucrose solution in some cases) followed by treatment with mercury(II) chloride solution and titration with dichromate solution.

The pyrometallurgical treatment of metal sulphides involves oxidative roasting followed by a reduction process. The oxidative roasting of sulphides results in atmospheric pollution by the sulphur dioxide liberated. Thus there exists a need for other processes in which the sulphur is removed in a non-polluting form. Studies on the reduction of metallic sulphides such as pyrite and pyrrhotite with carbon in the presence of lime have been carried out in CANMET.[1] In order to follow the progress of this reduction process it is necessary to determine the amount of metallic iron formed in the reaction.

Metallic iron has been determined by reduction of copper(II)[2] or of mercury(II) chloride[3] in aqueous medium followed by a permanganate titration. Determination of metallic iron with copper sulphate is subject to errors due to the formation of soluble copper(I) salts.[4] The use of

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Metallic iron has been determined by reduction of copper(II)[2] or of mercury(II) chloride[3] in aqueous medium followed by a permanganate titration. Determination of metallic iron with copper sulphate is subject to errors due to the formation of soluble copper(I) salts.[4] The use of

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mercury as a catalyst in the copper sulphate method has been suggested by Habashy.[5] According to Weiss,[6] the use of larger quantities of mercury(II) chloride to dissolve metallic iron would favour the formation of calomel, but the latter tends to occlude some iron, giving low results. Morris[7] pointed out that recovery of iron is incomplete with samples coarser than 65-mesh. Methods are described in the literature for the determination of metallic iron in the presence of ferrous and ferric oxides, but there is hardly any information in the literature on the determination of metallic iron in complex matrix such as that composed of lime, calcium sulphide, pyrrhotite and carbon which is encountered in the pyrometallurgical treatment of metal sulphides. Thus a systematic investigation of the determination of metallic iron in the presence of this mixture was undertaken.

EXPERIMENTAL

Reagents

Fisher certified metallic iron (93.2%) was used without further purification.

Lime powder was obtained by heating reagent grade calcium carbonate at 800°.

Lamp black was used as the source of carbon.

All the other reagents such as mercuric chloride, potassium dichromate, calcium sulphide, sucrose, ammonium chloride and EDTA were of analytical reagent quality.

Tributyl phosphate and methyl isobutyl ketone, obtained from Fisher Co., were used without further purification.

Procedure

Transfer 0.25–1.0 g of the sample to a dry 250-ml flask. Add 150 ml of 5% ammonium chloride or 10% sucrose solution and stir at room temperature for about 2 hr, passing nitrogen through the solution for the entire period. Filter the solution through a 9-cm paper, transfer the residue to the paper and wash it with water. Reject the filtrate. Transfer the paper along with the residue into a 125-ml Erlenmeyer flask from which the air has been displaced by nitrogen. Add 3 g of solid mercury(II) chloride, stopper, and mix by shaking. Add 50 ml of boiling water, heat quickly to boiling and boil for 1 min. Immediately fill the flask almost to the top with boiling water and then stopper tightly with a rubber stopper. Place the flask in lukewarm water for 1–2 min, then transfer the flask to an ice-bath. Filter the cold solution with suction through a No. 42 filter paper into a 500-ml Erlenmeyer flask, washing with about 100 ml of cold water. Add 20 ml of acid mixture (500 ml of water + 200 ml of concentrated sulphuric acid and 300 ml of 35% phosphoric acid) and five drops of sodium diphenylaminesulphonate indicator solution and titrate with standard potassium dichromate solution.

RESULTS AND DISCUSSION

Since the matrix in which the metallic iron is to be determined is quite complex, initial experiments were carried out to determine the suitability of various leaching agents for removing the lime. Synthetic mixtures containing metallic iron, lime and calcium sulphide were prepared and leached with various reagents such as 5% EDTA solution, 20% di-(2-ethylhexyl)phosphoric acid in toluene, 0.1*M* thenoyltrifluoroacetone and 0.01*M* tributyl phosphate in methyl isobutyl ketone, 10% sucrose in water and 5% ammonium chloride in water. Metallic iron was then determined in the residue by the mercury(II) chloride treatment followed by titration with dichromate solution. The results obtained from these experiments are presented in Table 1.

It is clear that the 10% sucrose and 5% ammonium chloride solutions gave the best results. It was concluded that both sucrose and ammonium chloride are effective in leaching calcium compounds from the samples. It is to be noted that the error in the determination of metallic iron is small when ammonium chloride is used as the leaching agent.

Table 1. Effect of leaching agents on the determination of metallic iron

Leaching agent	Metallic iron, %
None	93.7*
EDTA	87.2
Di(2-ethylhexyl)phosphoric acid	82.7
TTA + TBP	13.4
Sucrose	91.6
NH_4Cl	94.0

* Certified value is 93.2%.

Table 2. Effect of various constituents on the determination of metallic iron

Constituent added	Metallic iron, %
None	93.7*
CaO	94.0
CaS	92.7
Pyrrhotite	94.2
Carbon	91.8

Certified value is 93.2%.

The effect of each of the individual components such as lime, pyrrhotite, carbon and calcium sulphide on the determination of metallic iron was examined, and the results are presented in Table 2. Synthetic mixtures of metallic iron and each component were prepared and leached with 5% ammonium chloride solution, and the residue in each case was then treated with mercury(II) chloride solution. The data in Table 2 show that calcium sulphide and carbon gave rise to lower results. The lower value in the case of carbon may be due to adsorption of metallic iron on to the carbon. The slightly higher value in the case of pyrrhotite may be due to the partial dissolution of pyrrhotite by mercury(II) chloride.

Metallic iron present in the samples obtained from the pyrometallurgical process was determined by leaching with ammonium chloride solution followed by mercury(II) chloride treatment and dichromate titration. The results thus obtained, along with the values calculated from the weight loss by thermogravimetric analysis of the starting mixture are presented in Table 3. Considering the complexity of the matrix in' which metallic iron was determined it is reasonable to state that the results obtained by the two methods are in fair agreement. It is appropriate to point out here that sucrose was effective as a leaching agent for the determination of metallic iron for some samples though in general ammonium chloride proved to be the better leaching reagent.

Table 3. Determination of metallic iron in samples

Sample	Metallic iron, % TGA, wt. loss	Analytical
1	8.9	8.7
2	6.7	7.1
3	14.6	14.3
4	10.3	10.7
5	18.5	16.9

Acknowledgements—The author thanks Mr. J. C. Ingles, formerly Head of the Chemical Analysis Section, for suggesting the problem and for the interest shown in the work.

REFERENCES

1. R. Kerby, Department of Energy, Mines and Resources, Extraction Metallurgy Division, Ottawa, Canada, *Rept., IR* 73-47, 1973.
2. J. P. Riott, *Ind. Eng. Chem., Anal. Ed.*, 1941, **13**, 546.
3. E. Merck, *Z. Anal. Chem.*, 1902, **41**, 710.
4. N. I. Stognii and A. G. Kirilenko, *Zavodsk. Lab.*, 1955, **21**, 254.
5. J. G. Habashy, *Anal. Chem.*, 1961, **33**, 586.
6. L. Weiss, *Z. Anal. Chem.*, 1934, **98**, 397.
7. J. P. Morris, *U.S. Bur. Mines Rept. Invest.*, No. 3824, 1945.

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STUDIES ON EXTRACTION OF BERYLLIUM FROM THIOCYANATE SOLUTIONS BY QUATERNARY AMMONIUM HALIDES

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Nuclear Chemistry Department, Atomic Energy Establishment, Cairo, Egypt

(*Received* 31 *December* 1977. *Revised* 2 *June* 1978. *Accepted* 16 *June* 1978)

Summary—A 0.4*M* tricaprylmethylammonium chloride solution in n-hexane was used for the quantitative extraction of beryllium from hydrochloric acid (pH 3) and 5*M* potassium thiocyanate. Beryllium was stripped from the organic phase with 1*M* sodium hydroxide, then determined volumetrically with bismuthyl perchlorate and Bromocresol Green indicator. Beryllium was extracted in presence of a large number of elements which are usually associated with it in beryl and in fission products of nuclear fuel.

The use of liquid ion-exchangers for the extraction of beryllium is receiving increased attention. Tri-n-octylamine and tri-iso-octylamine in various media[1,2] and also 1-(3-ethylpentyl)-4-ethyloctylamine sulphate,[3,4] have been used as long-chain amines for beryllium extraction. Tricaprylmethylammonium chloride in oxalic acid medium has also been used.[5] In the present investigation, beryllium was extracted quantitatively with tricaprylmethylammonium chloride from thiocyanate solution.

EXPERIMENTAL

Reagents

Tricaprylmethylammonium chloride, (Aliquat 336), a product of General Mills Inc., with a molecular weight of 422 and sp.gr. of 0.884, was used as received, without further purification. All diluents were of "pure" grade except the odourless kerosene which was the commercial grade (Sunrise) from Misr Petroleum Co. The ^{7}Be used as tracer was obtained from the Radiochemical Centre, Amersham. Other chemicals were of reagent grade.

Stock solution of beryllium was prepared by dissolving 1.52 g of analytical grade beryllium chloride tetrahydrate in 100 ml of distilled water. The solution was standardized titrimetrically.[6]

Recommended procedure

A 10-ml portion of solution containing 9 mg of beryllium in hydrochloric acid (pH 3)/5*M* potassium thiocyanate medium, is shaken mechanically for 20 min at room temperature (~25°) with an equal volume of 0.4*M* Aliquat 336 in n-hexane (containing 5% v/v octanol). After centrifugation, the two layers are separated. Beryllium is stripped from the loaded organic phase by shaking for 5 min with two successive equal volumes of 1*M* sodium hydroxide, then determined titrimetrically in the aqueous extract with bismuthyl perchlorate and Bromocresol Green indicator.

RESULTS AND DISCUSSION

Effect of initial thiocyanate concentration and pH

The extraction of beryllium from its aqueous 0.14*M* solutions with 0.23*M* Aliquat 336 in benzene was examined at different hydrochloric acid concentrations (pH 1, 2 and 3) and various thiocyanate concentrations (0.5–6*M*). The distribution ratio was calculated as the ratio of activity of the tracer in the organic phase to that in the aqueous phase, measured with a well-type NaI(Tl) γ-scintillation counter. The results showed that at 0.5, 1, 2, 3, 4, 5 and 6*M* potassium thiocyanate concentrations, the distribution ratios were 0.42, 0.62, 1.2, 1.5, 1.7, 1.8, and 1.5 at pH 1; 2.0, 3.0, 4.4, 5.0, 5.0, 5.1, and 4.8 at pH 2; 3.2, 4.2, 5.4, 6.0, 6.2, 7.4 and 7.1 at pH 3. The optimum conditions are thus pH about 3 and 5*M* potassium thiocyanate solution.

Effect of extractant concentration

The extraction of beryllium from its 0.1*M* solution in hydrochloric acid medium (pH 3 and 4*M* in potassium thiocyanate) with various Aliquat concentrations (0.05–0.6*M*) in benzene, was also examined. When the extractant concentrations were 0.05, 0.1, 0.2, 0.3, 0.4 and 0.6*M* the distribution ratios were 0.21, 1.0, 6.7, 16.2, 40.4 and 100.2 respectively. The distribution ratio is sharply increased with rise of extractant concentration, as expected, and extraction is incomplete with up to 0.2*M* Aliquat (87% recovery). For cleaner separation, a shorter disengagement time (1 min) and for economic reasons, an optimal Aliquat concentration of about 0.4*M* (98% recovery) are recommended.

Effect of diluent type

The extraction of beryllium from its 0.12*M* aqueous solutions in hydrochloric acid (pH 3) and 5*M* potassium thiocyanate with 0.4*M* Aliquat in various diluents was

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Table 1. Effect of diverse ions on recovery of 9 mg of Be

Tolerance limit, mg	Ion
950	Ca^{2+}, Ba^{2+}, Mg^{2+}, Hg^{+} SO_4^{2-}, PO_4^{3-}, $EDTA^{4-}$
450	Na^{+}, K^{+}, NH_4^{+}, Li^{+}, Hg^{2+}, BO_3^{3-}
45	tartrate, malonate, Cd^{2+}
22.5	Co^{2+}, Al^{3+}
nil	UO_2^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Th^{4+}

studied. The extractability decreased in the order: n hexane > cyclohexane > odourless kerosene > benzene > toluene > xylene, the distribution ratios being 58.8, 55.2, 48.4, 42.2, 38.8 and 32.4 respectively. Thus n-hexane is the best diluent to use.

Period of extraction

With optimum extraction conditions and n-hexane as diluent, the equilibration period was varied between 1 and 30 min. It was found that the optimum extraction duration was 20 min.

Effect of diverse ions

The effect of various ions on the extraction of beryllium in the suggested procedure was investigated. The tolerance limit was set at the amount of foreign ion required to cause ± 2% error in the beryllium recovery and results are shown in Table 1. It is possible to separate beryllium from a large number of elements. Beryllium occurs mainly in beryl and in fission products from nuclear fuel, and is usually associated with Mg^{2+}, Al^{3+}, Fe^{3+}, UO_2^{2+}, alkali and alkaline earth metal ions. UO_2^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Th^{4+} and Al^{3+} should be separated or masked before beryllium determination. The average beryllium recovery (from 8 experiments) was 99.5% and the standard deviation was ±0.6%.

REFERENCES

1. A. V. Novoselova, N. S. Tamm, T. I. Pochkaera and N. V. Likhanskaya, *Vestn. Mosk. Univ. Khim.*, 1973, **14**, 55.
2. H. J. De Bruin, D. Kairaitis and R. B. Temple, *Australian J. Chem.*, 1962, **15**, 457.
3. D. J. Crouse Jr. and F. G. Seeley, *U.S. Pat.* 3359064 (1967).
4. E. S. Etaix, *Commis. Energ. At. (Fr.) Rapp.*, CEA-R-3551, 1968.
5. G. V. Prasad and M. N. Sastri, *Indian J. Chem.*, 1974, **12**, 1318.
6. M. S. Das and V. T. Athavale, *Anal. Chim. Acta*, 1955, **12**, 6.

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A SIMPLE METHOD FOR IMPROVING CONTROL OF THE TIME CONSTANT IN RECORDING TRANSIENT SIGNALS IN ATOMIC-ABSORPTION SPECTROMETRY

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(*Received* 24 *May* 1978. *Accepted* 8 *June* 1978)

Summary—Significant improvements can be made in signal:noise ratios of transient signals arising in atomic-absorption spectroscopy by the use of resistor–capacitor damping. A suitable device is described and the effect it has on signals arising from instruments using analogue and digital forms of output is demonstrated.

Many of the methods used in atomic-absorption spectroscopy result in a transient absorbance, *e.g.*, flameless atomization,[1–3] hydride generation,[4] the mercury cold vapour method,[5] the tantalum boat,[6] the Delves cup[7] and the aspiration of discrete aliquots.[8] For such methods the time-constant devices available on current instruments have some limitations since they were designed when atomic-absorption analyses were predominantly done by flame excitation and continuous nebulization.

Two types of time-constant device are available to minimize high-frequency random noise without undue attenuation of the low-frequency signal (the analytical peak). In the first type, time constants based on a resistor–capacitor (RC) system can be used to provide damping of the instrument output without affecting the continuous nature of the signal. This type of damping will be referred to as "analogue" damping. In the other, the signal can be accumulated and averaged over a period of time. The resulting output is then a series of discrete readings with a frequency determined by the time period selected for averaging. This form of time-constant will be referred to as "digital" damping.

Both systems appear to give acceptable results for continuous absorbance readings, but in our experience commercial instruments do not permit sufficient variation for the effective monitoring of transient peaks. This paper describes a simple inexpensive device which enables the operator to select his own time constant with considerably more flexibility than is currently available. Such a device can readily be used on all atomic-absorption spectrometers.

Reasons for the failure of currently available systems

Digital signal-damping systems. In this form of damping the time for which the absorbance is monitored before averaging and display can be varied. It is claimed[7] that this

Table 1. Effect of diverse ions on recovery of 9 mg of Be

Tolerance limit, mg	Ion
950	Ca^{2+}, Ba^{2+}, Mg^{2+}, Hg^{+} SO_4^{2-}, PO_4^{3-}, $EDTA^{4-}$
450	Na^{+}, K^{+}, NH_4^{+}, Li^{+}, Hg^{2+}, BO_3^{3-}
45	tartrate, malonate, Cd^{2+}
22.5	Co^{2+}, Al^{3+}
nil	UO_2^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, Th^{4+}

studied. The extractability decreased in the order: n hexane > cyclohexane > odourless kerosene > benzene > toluene > xylene, the distribution ratios being 58.8, 55.2, 48.4, 42.2, 38.8 and 32.4 respectively. Thus n-hexane is the best diluent to use.

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REFERENCES

1. A. V. Novoselova, N. S. Tamm, T. I. Pochkaera and N. V. Likhanskaya, *Vestn. Mosk. Univ. Khim.*, 1973, **14**, 55.
2. H. J. De Bruin, D. Kairaitis and R. B. Temple, *Australian J. Chem.*, 1962, **15**, 457.
3. D. J. Crouse Jr. and F. G. Seeley, *U.S. Pat.* 3359064 (1967).
4. E. S. Etaix, *Commis. Energ. At. (Fr.) Rapp.*, CEA-R-3551, 1968.
5. G. V. Prasad and M. N. Sastri, *Indian J. Chem.*, 1974, **12**, 1318.
6. M. S. Das and V. T. Athavale, *Anal. Chim. Acta*, 1955, **12**, 6.

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Two types of time-constant device are available to minimize high-frequency random noise without undue attenuation of the low-frequency signal (the analytical peak). In the first type, time constants based on a resistor–capacitor (RC) system can be used to provide damping of the instrument output without affecting the continuous nature of the signal. This type of damping will be referred to as "analogue" damping. In the other, the signal can be accumulated and averaged over a period of time. The resulting output is then a series of discrete readings with a frequency determined by the time period selected for averaging. This form of time-constant will be referred to as "digital" damping.

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Reasons for the failure of currently available systems

Digital signal-damping systems. In this form of damping the time for which the absorbance is monitored before averaging and display can be varied. It is claimed[7] that this

system shows a better signal:noise ratio with respect to the time constant selected, than analogue damping does. Such a system will be exemplified by reference to chart traces obtained from an Instrumentation Laboratories IL 151 single-beam atomic-absorption spectrometer. Signals were recorded on a Servoscribe RE 541.20 chart recorder. The time constant of the spectrophotometer could be chosen from the values 0.0625, 0.25, 1, 4 and 16 sec.

The suitability of this system for monitoring transient peaks was determined by comparing the signals from the continuous aspiration of a 0.05-μg/ml aqueous manganese solution with those obtained from three 150-μl aliquots of the same solution; 20× scale expansion was used and the sample-uptake rate was 5 ml/min. The results obtained for digital time-constant settings of 0.0625, 0.25 and 1 sec are shown in Fig. 1A. It can be seen that the use of a time constant of 0.25 sec improved the signal:noise ratio relative to that obtained at 0.0625 sec, but whilst the use of a setting of 1 sec further reduced the noise level it produced smaller, irreproducible peaks for the transient signals. This was because the averaging interval was long in relationship to the duration of the transient peak. Thus, at present a poor compromise has to be made between precision and signal:noise ratio. An increase in the choice of time intervals available would produce an improvement but this is not easy for the analyst to achieve. It was felt that by combining the available digital time-constant options with some additional analogue settings a satisfactory choice would be available to the analyst.

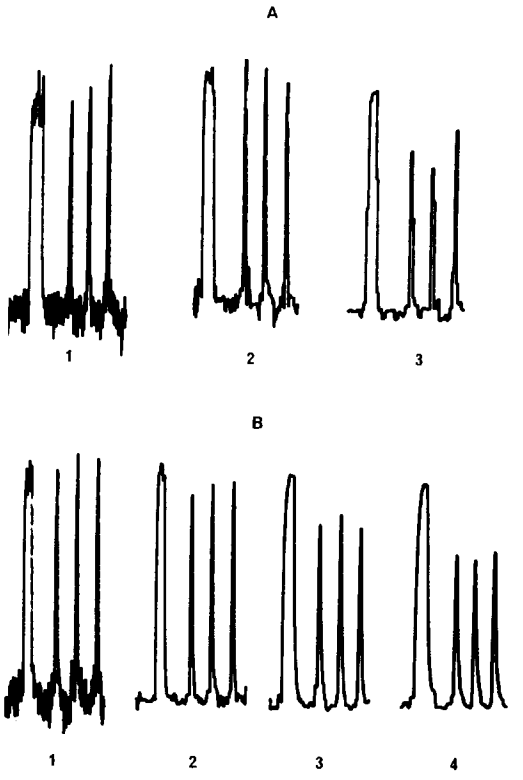


Fig. 1. Chart traces obtained for a 0.05 μg/ml solution of manganese, using an instrument designed with digital damping. Each set of peaks consists of a trace achieved by continuous aspiration, followed by the transient signals from three 150-μl aliquots of the same solution, A. Using the following digital time-constant settings available on the the IL 151: 1, 0.0625 sec; 2, 0.25 sec; 3, 1 sec. B. Using the minimum digital time-constant setting (0.0625 sec) in conjunction with the following external analogue time-constant values: 1, 0 sec; 2, 0.21 sec; 3, 0.45 sec; 4, 0.75 sec.

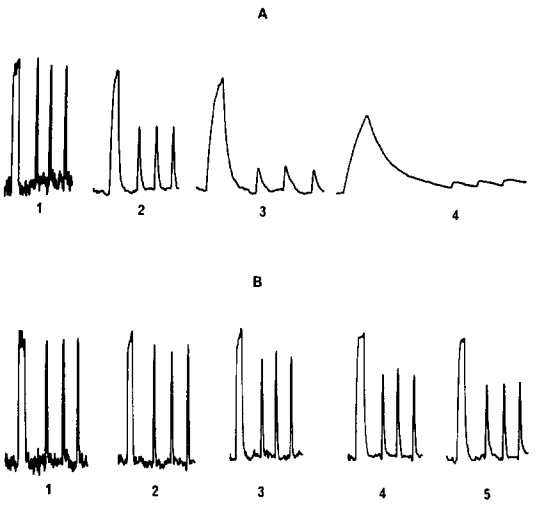


Fig. 2. Chart traces obtained for a 0.25 μg/ml solution of manganese, using an instrument designed with analogue damping. Each set of peaks consists of a trace achieved by continuous aspiration, followed by the transient signals from three 150-μl aliquots of the same solution. A. Using the four analogue time-constant settings available on the Perkin–Elmer 403 spectrophotometer: 1, 0.25 sec; 2, 1 sec; 3, 4 sec; 4, 16 sec. B. Using the smallest time-interval constant (0.25 sec) in conjunction with the following external analogue time-constant settings: 1, 0 sec; 2, 0.12 sec; 3, 0.25 sec; 4, 0.50 sec; 5, 0.67 sec.

Analogue damping systems. These are the most commonly encountered forms of time-constant device. An analogue damping system will be exemplified by reference to signals obtained from a Perkin–Elmer Model 403 double-beam atomic-absorption spectrophotometer. Signals were again recorded on a Servoscribe RE 541.20 chart recorder. The time constant on the spectrophotometer could be chosen from one of four settings, the time values being: 1—0.25 sec, 2—1 sec, 3—4 sec, 4—16 sec.

The suitability of this system for monitoring transient peaks was determined by comparing signals obtained from the continuous aspiration of a 0.25-μg/ml aqueous manganese solution with those obtained from three 150-μl aliquots of the same solution; 10× scale expansion was required and the solution-uptake rate was 10 ml/min. The results obtained for each of the time-constant settings are shown in Fig. 2A. Setting 2 shows a marked improvement in signal:noise ratio over setting 1 but the absorbance of the transient peaks is approximately half that obtained from continuous nebulization. Settings 3 and 4 show excessive damping and analytically unsuitable results. It appears that significant improvement might be possible if a wider selection of time constant values were available.

Additional equipment for use with either type of instrument

Variable resistor–capacitor damping (analogue damping) can be easily and cheaply achieved, and can offer a significant improvement in signal:noise ratio for transient peaks. Such damping is observed if a capacitor is placed across the input leads of the chart recorder and the instrument supply leads are connected in the normal way. The time constant obtained can be calculated from the expression:

Time constant (sec) = resistance (ohms) × capacitance (farads).

For the instruments used in these studies the output impedance (resistance) was 2.5 kΩ for the Perkin–Elmer 403 and 9.5 kΩ for the IL 151. With these values time constants were calculated for a number of capacitors: the results obtained are given in Table 1.

Table 1. Resistor-capacitor time constants for typical capacitors

Switch position	Capacitor, μF	Time constant, *sec* PE 403	IL 151
1	0	—	—
2	22	0.05	0.21
3	47	0.12	0.45
4	79	0.20	0.75
5	100	0.25	0.95
6	122	0.30	1.16
7	179	0.45	1.70
8	200	0.50	1.90
9	220	0.55	2.09
10	242	0.60	2.30
11	267	0.67	2.54

Note. The capacitors used in this work have a tolerance of from -10% to $+50\%$ on the rated value.

These capacitors were connected to a 12-position switch and wired in parallel with the spectrophotometer output terminals and recorder input.

RESULTS AND DISCUSSION

Figure 1B shows a series of results obtained by using the damping device with an IL 151 spectrophotometer. The use of this device in conjunction with an instrument equipped with digital damping allows the advantages of the original system to be obtained for continuous signals and the problems of truncation of transient peaks can be overcome whilst still achieving a satisfactory signal:noise ratio.

Figure 2B shows the results obtained with the proposed damping device in conjunction with the PE 403 spectrophotometer and demonstrates the range of results which can be obtained. Considerable improvements are observed in signal:noise ratio without the extensive suppression of signal which otherwise occurred with any but the lowest original instrument settings.

Conclusion

A simple inexpensive device has been described which allows the analyst considerably more freedom in his choice of signal damping, and such flexibility is not available on commercial instruments. By the use of such a device demonstrably better signal:noise ratios can be obtained for transient peaks than can otherwise be achieved at present.

REFERENCES

1. B. V. L'vov, *Spectrochim. Acta*, 1969, **24B**, 53.
2. H. Massmann, *ibid.*, 1968, **23B**, 215.
3. T. S. West and X. K. Williams, *Anal. Chim. Acta*, 1969, **45**, 27.
4. W. Holak, *Anal. Chem.* 1969, **41**, 1712.
5. G. Lindstedt, *Analyst*, 1970, **95**, 264.
6. H. L. Kahn, G. E. Peterson and J. E. Schallis, *At. Abs. Newsl.* 1968, **7**, 35.
7. H. T. Delves, *Analyst*, 1970, **95**, 431.
8. W. Slavin, *Atomic Absorption Spectroscopy*, p. 16. Interscience, New York, 1968.

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BENZOHYDROXAMIC ACID AS A REDUCTOMETRIC TITRANT DETERMINATION OF MANGANESE IN ORES AND ALLOYS

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Summary—Benzohydroxamic acid has been employed as a reductometric titrant for the determination of manganese in various ores and alloys. The determination is based on the fact that benzohydroxamic acid reduces Mn(VII) quantitatively to Mn(II) in 1.5*N* sulphuric acid.

Many titrimetric procedures for the determination of manganese have been developed, of which the most widely adopted is to oxidize Mn(II) to Mn(VII) with persulphate in sulphuric acid medium and titrate the Mn(VII) with As(III).[1,2] During our studies on the oxidation of benzohydroxamic acid with potassium permanganate, it was observed that benzohydroxamic acid is completely oxidized to benzoic acid and nitric acid in sulphuric acid medium and that 6 moles of the oxidant are consumed by 5 moles of the reductant. In this reaction the potassium permanganate is quantitatively reduced to Mn(II) in 1.5*N* sulphuric acid and it is possible to titrate permanganate with a standard benzohydroxamic acid solution. The reaction is instantaneous and stoichiometric. This titrimetric method has been successfully employed for the determination of manganese in some standard samples of pyrolusite, ferromanganese and steels, the results of which are presented in this communication.

RESULTS AND DISCUSSION

The reaction between permanganate ion and benzohydroxamic acid, $C_6H_5CONHOH$, in sulphuric acid medium is found to be instantaneous at room temperature. The effect of sulphuric acid concentration on the reaction was studied in the range 0.1–6*N* (Table 1). The reaction is complete in concentrations of sulphuric acid $\geq$ 1*N*. In all subsequent experiments the sulphuric acid concentration used was 1.5*N*.

Table 1. Effect of acidity

$[H_2SO_4]$, *N*	BHA, *ml*	Moles of $KMnO_4$ per mole of BHA
(A) BHA = $3.255 \times 10^{-3}M$; $KMnO_4$ = 0.01696*N* (10 ml); total volume = 20 ml		
0.11	11.65	0.894
0.22	10.50	0.992
0.30	9.70	1.074
0.40	9.50	1.098
0.51	9.40	1.110
0.59	9.35	1.116
0.70	8.75	1.188
0.81	8.65	1.206
0.89	8.65	1.206
1.00	8.65	1.206
(B) BHA = $3.612 \times 10^{-3}M$; $KMnO_4$ = 0.01386*N* (10 ml); total volume = 20 ml		
1.51	6.35	1.208
1.99	6.35	1.208
2.99	6.35	1.208
3.98	6.35	1.208
5.00*	6.35	1.208
5.99*	6.35	1.208

* Total volume = 50 ml.

Analysis of the products indicated that benzoic acid and nitric acid are the only products of oxidation of benzohydroxamic acid. The reaction can be represented as:

$$6MnO_4^- + 13H^+ + 5C_6H_5CONHOH \rightarrow 6Mn^{2+} + 5C_6H_5COOH + 5NO_3^- + 9H_2O$$

The results of some titrations (visual end-point detection) are recorded in Table 2. The end-point was also determined potentiometrically to check the accuracy of the results of the visual titrations. The results are given in Table 3.

Table 2. Determination of manganese in $KMnO_4$ (visual end-point; BHA = $3.408 \times 10^{-2}M$; $KMnO_4$ = 0.0513*N*; total volume = 100 ml)

$KMnO_4$, *ml*	BHA, *ml*	Mn taken, *mg*	Mn found, *mg*
5	1.25	2.82	2.81
30	7.50	16.9	16.9
60	15.10	33.8	33.9
70	17.55	39.5	39.4
85	21.20	47.9	47.6

Fe(III), Ni(II), Sn(IV), Cu(II), Co(II), Ti(IV), Nb(V), Ta(V) and V(V) and anions such as MoO_4^{2-} and WO_4^{2-} which are normally associated with manganese in alloy steels or ores were found not to interfere when present in up to 100:1 ratio to 5 mg of manganese.

Cr(VI), however, was observed to interfere to some extent. At lower levels of manganese, *i.e.*, 0.1 mg or less, Cr(VI) did not interfere even if present in 10-mg amount, but with increasing concentration of manganese the inter-

Table 3. Determination of manganese in $KMnO_4$ (BHA = $3.729 \times 10^{-2}M$; $KMnO_4$ = 0.0568*N*; total volume = 100 ml)

$KMnO_4$, *ml*	BHA, *ml*	
	Potentiometric end-point*	Visual end-point
25	6.36	6.35
50	12.70	12.70
75	19.12	19.10
100	25.32	25.35

* Values obtained from second derivative curves.

Table 4. Analysis of standard reference materials

Sample	Sample, *g*	Mn taken, *mg*	BHA, *M*	BHA, *ml*	Mn found, *mg*
5f Brass*	0.2969	0.356	1.47×10^{-3}	3.70	0.359
B.C.S.211/1	0.2626†	0.0336	5.16×10^{-4}	1.00	0.034
B.C.S.237/2	0.1193	0.537	1.47×10^{-3}	5.50	0.533
N.B.S., SRM 8J	0.3033	1.531	1.47×10^{-2}	1.58	1.53
B.C.S.238/2	0.1046	0.638	1.47×10^{-3}	6.60	0.640
B.C.S.219/2	0.1365	0.874	5.16×10^{-3}	2.55	0.867
60.B.Alloy Steel*	0.1093	0.700	5.16×10^{-3}	2.02	0.687
B.C.S.261	0.2603†	0.0687	5.16×10^{-4}	2.00	0.068
B.C.S.290	0.1022‡	2.647	5.16×10^{-3}	7.80	2.65
18.Pyrolusite*	0.2481†	2.541	1.47×10^{-2}	2.60	2.52
B.C.S.208/1	0.1383§	2.114	5.16×10^{-3}	6.25	2.13

* Analysed samples for students in Metallurgical Analysis issued by Bureau of Analysed samples Ltd., Newham Hall, Middlesbrough, Cleveland, U.K.
† Aliquots 1/25 of sample.
‡ Aliquots 1/5 of sample.
§ Aliquots 1/50 of sample.

ference also increased. For 1 mg of manganese the tolerance limit for chromium was found to be 6 mg, for 2.5 mg of Mn it was 12.5 mg and for 5 mg of Mn 15 mg. The Cr(VI) is presumed to interfere by oxidizing manganese (II) to manganese(III).

The reagent is stable for years in the solid state, if stored in an amber bottle in a cool place. Its aqueous solutions are stable for least a month.

The method has been successfully applied to some standard samples; the results are given in Table 4.

EXPERIMENTAL

Reagents

All reagents used were of analytical-reagent grade. Benzohydroxamic acid was prepared by Renfrow and Hauser's procedure.[3] All solutions were prepared in water twice distilled with alkaline permanganate.

Procedure for standard samples

An accurately weighed quantity of the sample (0.1–0.2 g) was dissolved in 20 ml of *aqua regia*. To the cooled solution 5 ml of concentrated sulphuric acid were added and the solution was heated till dense white fumes appeared. Solutions of alloys containing more than 5% Mn were diluted to standard volume after proper cooling at this stage, and aliquots were used. The sample (or its aliquot) was diluted to 100 ml and 10 ml of 1% silver nitrate solution and 0.5–1.0 g of potassium persulphate were added, followed by 5 ml of concentrated sulphuric acid, and the mixture was heated. When the oxidation was complete the mixture was gently boiled to decompose the excess of persulphate. The solution was cooled to room temperature and titrated with benzohydroxamic acid solution, standardized by using it to titrate a standard permanganate solution in 1.5*N* sulphuric acid medium. The end-point was signalled by the disappearance of the colour of the permanganate.

$$\text{ml of } 1M \text{ BHA} \equiv 65.9 \text{ mg of Mn}$$

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REFERENCES

1. E. C. Pigott, *Ferrous Analysis, Modern Practice and Theory*, p. 245, Chapman and Hall, London, 1953.
2. W. W. Scott and N. H. Furman, *Standard Methods of Chemical Analysis, Vol. II*, p. 1434. Technical Press, London, 1954.
3. W. B. Renfrow, Jr., and C. R. Hauser, *J. Am. Chem. Soc.*, 1937, **59**, 2308; in *Organic Synthesis, Vol. II* (ed. A. H. Blatt), p. 67. Wiley, New York, 1946.

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SPECTROPHOTOMETRIC DETERMINATION OF SOME PHENOTHIAZINE DERIVATIVES AND OPIPRAMOL WITH CHLORAMINE-T

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Summary—This paper describes a spectrophotometric method for the assay of phenothiazines (and also opipramol, which is similar but contains a C=C linkage instead of the S atom of the phenothiazines) as the pure drug or in tablets or solutions for injection. The colour is produced by heating a solution of the drug or drug preparation with a solution of chloramine-T. The coloured product can be extracted into chloroform before the colour measurement or the whole process carried out in ethanol solution, the colour of which is then measured.

Numerous methods are available for the determination of phenothiazine derivatives. The official methods depend on spectrophotometry or non-aqueous titration.[1] Two-phase titrations,[2–4] tetraphenylborate,[5–7] ammonium reineckate,[8] complexometric titrations[9–12] and oxidative titrations[13] have also been used. Chlorpromazine has been determined colorimetrically in acid medium with ferric chloride;[14] formation of the coloured complex did not involve an oxidation reaction. Phenothiazine derivatives have been titrated photometrically at 420 nm with ceric sulphate.[15]

Various oxidants have been used for colorimetric assay of phenothiazine derivatives: ferric chloride,[16] potassium bromate,[17] potassium iodate,[18] hydrogen peroxide[19] and *p*-benzoquinone.[20] The yellow nitration products of phenothiazine derivatives have also been determined colorimetrically after ether extraction.[21] Thioridazine in plasma has been evaluated fluorometrically after oxidation by potassium permanganate.[22]

Feigl and Hagenauer-Castro[23,24] give a method for the detection of phenothiazine with chloramine-T and *vice versa*.[23,24] In the present study, some phenothiazine derivatives and opipramol, either in pure form or in pharmaceutical preparations, are determined spectrophotometrically with chloramine-T.

EXPERIMENTAL

Reagent

Freshly prepared 20% aqueous chloramine-T solution.

Extraction method

Transfer 2 ml of an aqueous solution* of the drug to a test-tube (see concentration range in Table 1), add 1 ml of chloramine-T reagent and heat in a boiling water-bath for 10 min (5 min for triflupromazine or fluphenazine). Cool, add 15 ml of 1*M* sodium hydroxide and then extract with three portions of chloroform (15, 10, 10 ml). Transfer the extracts to a 50-ml standard flask and dilute to volume with chloroform. Dry the solution by passing it through a column of anhydrous sodium sulphate. Measure the absorbance at the appropriate wavelength against chloroform as blank.

*Water-insoluble drugs are dissolved in ethyl alcohol and diluted to known volume, 2 ml of the solution are transferred to a test-tube, the alcohol is evaporated, then 2 ml of water are added.

Homogeneous solution method

Transfer 4 ml of an alcohol solution of the drug to a test-tube (see concentration range in Table 2) followed by 1 ml of chloramine-T reagent, and heat in a boiling water-bath for 5 min. Cool, transfer to a 50-ml standard flask with ethanol (purified by refluxing with zinc dust and potassium hydroxide and then distilling) and dilute to volume with ethanol. Determine the absorbance at the appropriate wavelength against alcohol as blank.

Table 3. Recovery experiments for chlorpromazine hydrochloride (extraction method)

Taken, *mg*/100 *ml*	*A*	Found, *mg*/100 *ml*	Recovery, %	Mean %	Relative std. devn., %
3.2	0.311	3.16	98.9		
3.2	0.318	3.24	101.1		
4.0	0.382	3.90	97.5	99.7	±1.8
4.0	0.390	4.02	100.4		
8.0	0.783	8.05	100.7		
8.0	0.775	7.97	99.7		

The method is applicable to the determination of phenothiazine derivatives in pure form or in commercial pharmaceutical preparations. The results are good and comparable to those obtained with the official B.P. 1973 method (Tables 1 and 3). The proposed method, unlike the official ones, offers a fair degree of specificity.

Tablets

Weigh and powder 20 tablets. Transfer an accurately weighed quantity of the powder (see concentration range in Table 2 or 3) to a 100-ml standard flask, dissolve as completely as possible in 60 ml of purified ethanol (shaking for 15 min), dilute to volume and filter. The clear solution is assayed according to the procedures given.

Ampoules or vials

Dilute a suitable volume of the mixed contents of the ampoules (see concentration range in Table 2 or 3) to 100 ml with water or ethanol, and assay as described above.

RESULTS AND DISCUSSION

The phenothiazines studied exhibit different sensitivities in the two procedures, and the same drug might show a response with one procedure only (for opipramol and perphenazine

Table 1. Extraction method

Sample	Chloramine-T method						B.P. 1973	
	Taken, *mg*/100 *ml*	λ_{max} *nm*	*a*	*b*	*r*	Mean recovery ±S.D., %*	Taken, *mg*	Mean recovery ±S.D., %*
1—Chlorpromazine · HCl powder	1.6–9.6	555	0.0058	0.0964	0.9997	99.7 ± 1.8	50.0	98.1 ± 0.1
Neurazine tablets[M] (25 mg/tab.)	4.0					96.9 ± 0.9	0.5	97.3 ± 0.5
Neurazine ampoules[M] (50 mg/2 ml)	4.0					100.5 ± 3.1	0.5	104.2 ± 1.5
2—Opipramol · 2HCl powder	2.4–9.6	390	0.0122	0.0983	0.9998	100.4 ± 0.3	40.0	99.2 ± 0.6§
Insidon tablets[G] (50 mg/tab.)	8.0					101.5 ± 0.3	50.0	103.0 ± 0.6§
3—Promethazine · HCl powder	1.6–9.6	550	0.0038	0.0821	0.9996	101.5 ± 5.2	50.0	98.8 ± 0.2
Promantine ampoules[M] (25 mg/ml)	4.0					103.6 ± 2.3	0.5	104.1 ± 0.9
4—Perphenazine powder	4.8–19.2	555	0.0033	0.0433	0.9992	100.4 ± 2.1	50.0	98.8 ± 0.4
Trilafon tablets[Sc] (4 & 8 mg/tab.)	16.0					100.6 ± 0.2	0.5	102.2 ± 0.9
5—Fluphenazine · 2HCl powder	4.8–52.0	520	0.0040	0.0162	0.9998	99.9 ± 0.5	50.0	98.1 ± 0.4
Moditen tablets† (1 mg/tab.)	16.0					100.7 ± 3.7	6.0	98.8 ± 0.2
6—Thioridazine · HCl powder	2.4–24.0	520	0.0007	0.0347	0.9988	100.9 ± 1.4	—	—
Melleril tablets[SP] (10, 25 & 100 mg/tab.)	12.0					104.0 ± 1.0	—	—
7—Promazine · HCl powder	1.6–12.0	550	0.0044	0.0797	0.9997	100.1 ± 0.9	—	—
Sparine vials[W] (50 mg/ml)	8.0					102.9 ± 1.7	—	—
8—Trifluperazine · 2HCl powder	4.0–36.0	520	0.0219	0.0254	0.9982	101.0 ± 0.8	50.0	100.9 ± 0.4
Stelazine tablets[K] (5, 10 & 15 mg/tab.)	24.0					104.3 ± 0.8	8.0	105.1 + 0.9

*Average of 6 experiments.
†Laboratory-prepared tablets containing 10 mg of drug and tablet fillers composed of lactose, starch, talc and magnesium stearate (90:7:2.7:0.3 w/w).
§ = Not official but assayed by non-aqueous titration.
M = Misr, G = Geigy, Sc = Schering, SP = Swiss-pharma, W = Wyeth, K = Kahira.

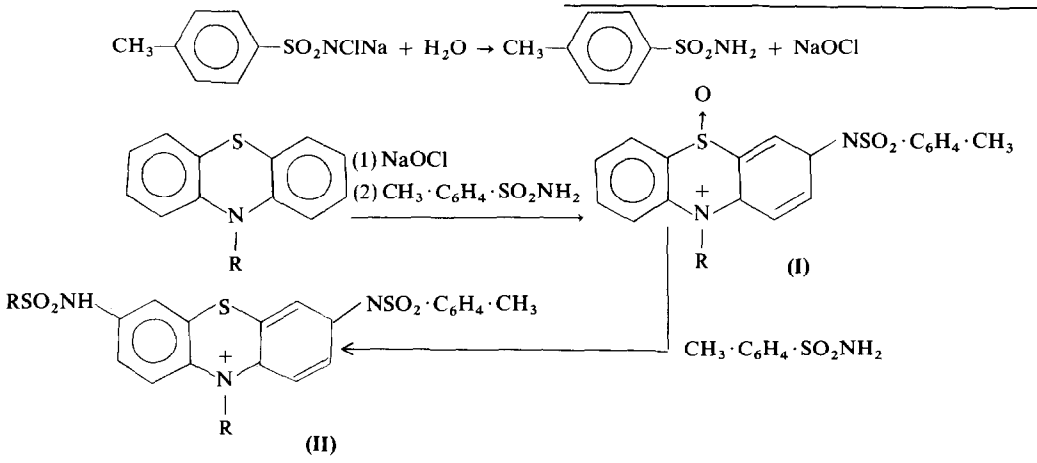
Table 2. Homogeneous solution method

	Chloramine-T method						B.P. 1973	
1—Chlorpromazine · HCl powder	4.0–24.0	565	0.0071	0.0033	0.9999	100.7 ± 0.9	50.0	98.1 ± 0.1
Neurazine tablets[M] (25 mg/tab.)	16.0					99.3 ± 0.4	0.5	97.3 ± 0.5
Neurazine ampoules[M] (50 mg/2 ml)	16.0					101.6 ± 1.8	0.5	104.2 ± 1.5
2—Acetophenazine maleate powder	4.8–19.2	550	0.0031	0.0444	0.9997	101.0 ± 1.0	50.0	98.2 ± 0.3
Acetophenazine maleate tablets†	8.0					100.6 ± 1.9	50.0	98.4 ± 0.2§
3—Promethazine · HCl powder	8.0–20.0	550	0.0045	0.0424	0.9991	101.2 ± 3.9	50.0	98.8 ± 0.2
Promantine ampoules[M] (25 mg/ml)	16.0					104.8 ± 1.2	0.5	104.2 ± 0.9
4—Fluphenazine · 2HCl powder	4.0–24.0	525	0.0081	0.0039	0.9997	100.5 ± 1.0	50.0	98.1 ± 0.4
Moditen tablets† (1 mg/tab.)	16.0					98.1 ± 0.7	6.0	98.8 ± 0.2
5—Promazine · HCl powder	4.0–16.0	550	0.0195	0.0529	0.9994	100.6 ± 0.3	—	—
Sparine vials[W] (50 mg/ml)	8.0					101.3 ± 1.1	—	—
6—Trifluperazine · 2HCl powder	4.0–32.0	520	0.0126	0.0280	0.9995	99.5 ± 2.3	50.0	101.0 ± 0.8
Stelazine tablets[K] (1, 5 & 15 mg/tab.)	16.0					102.5 ± 0.7	8.0	105.1 ± 0.9
7—Thiethylperazine powder	6.5–28.0	540	0.0016	0.0299	0.9994	102.5 ± 0.2	—	—
Torecan ampoules[SP] (6.5 mg/ml)	13.0					104.3 ± 2.5	—	—
8—Thioridazine · HCl powder	2.4–24.0	650	0.0091	0.0345	0.9996	101.0 ± 3.1	—	—
Melleril tablets[SP] (10, 25 & 100 mg/tab.)	12.0					101.2 ± 0.8	—	—

Footnotes as in Table 1.

only the extraction procedure works, and only the homogeneous solution method for acetophenazine). The reaction mixture should be about neutral.

The chemistry of the reaction is not clear, but it may involve oxidation of the drug by chloramine-T to give the sulphoxide, then the interaction of the latter with the sulphonamido group of the hydrolysed reagent to produce compound I or II [condensation is thought to take place in position 3 or 7, or both, of the phenothiazine nucleus]:



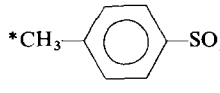
This suggestion, which is allied to that made by Feigl and Hagenauer-Castro,[23,24] is supported by the following facts.

(*a*) A neutral medium is found to be essential for the colour formation and the coloured product is extractable by organic solvents from alkaline medium. These results are completely different from those for oxidizing agents such as KIO_3, H_2O_2, $KBrO_3$, $KMnO_4$, $Ce(SO_4)_2$ or bleaching powder. With these oxidizing agents coloured products are formed only in acid medium, are not extractable with organic solvents from acid medium and are decomposed if the medium is made alkaline.

(*b*) Exhausted chloramine-T and tolbutamide* fail to produce any colour with the drugs examined, but if these drugs are first subjected to oxidation with chlorine water in neutral medium, addition of exhausted chloramine-T (or tolbutamide) produces the same colour as the active reagent.

Opipramol, though different from the phenothiazines, gives the same reaction but with totally different colour (λ_{max} 390 nm).

Beer's law is obeyed, as shown by the correlation coefficients (*r*) in Tables 2 and 3. A typical recovery experiment is shown in Table 1. The concentration was calculated from $A = a + bc$ where A is the absorbance measured in a 1-cm cell at λ_{max}, a the intercept at c = zero, b the slope of the calibration curve and c the concentration of the compound in mg per 100 ml.

* 

REFERENCES

1. *British Pharmacopoeia 1973.*
2. K. Kigasawa, H. Shimizu and M. Ibuki, *Yakugaku Zasshi*, 1972, **92**, 1009.
3. I. Simonyi and K. Zukovics-Sumeg, *Acta Pharm. Hung.*, 1975, **45**, 250.
4. S. Rolski and Z. Zakrzewski, *Farm. Pol.*, 1969, **25**, 621.
5. Gh. Morait, V. Turculet and Gh. Ciogolea, *Farmacia*, 1970, **18**, 267.
6. J. Debrecky, G. B. Gonzalez and E. Ortiz, *Rev. Asoc. Bioquim. Argent.*, 1969, **34**(184–5), 168.
7. S. Pinzati and S. V. Dalpiaz, *Boll. Chim. Farm.*, 1972, **111**, 512.
8. A. Olech, *Acta Pol. Pharm.*, 1972, **29**, 57.
9. M. Gajewska, *Chem. Anal. (Warsaw)*, 1973, **18**, 651.
10. H. Basinska and M. Tarasiewicz, *Acta Pol. Pharm.*, 1969, **26**, 343.
11. A. Olech, *ibid.*, 1973, **30**, 505.
12. B. Dembinski and K. Nowakowski, *Farm. Pol.*, 1974, **30**, 423.
13. G. Dusinsky, *Pharmazie*, 1958, **13**, 478.
14. F. Istvan, H. Floderer and H. Valeria, *Acta Pharm. Hung.*, 1957, **27**, 152.
15. P. S. Agarwal and I. M. Blake, *J. Pharm.*, 1969, **58**, 1011.
16. H. P. Reider, *Med. Exptl.*, 1960, **3**, 353.
17. H. Tarasiewiez, *Farm. Pol.*, 1970, **26**, 393.
18. M. Tarasiewiez and H. Tarasiewiez-Puzanowska, *Acta Pol. Pharm.*, 1970, **27**, 263.
19. H. Basinka, H. Tarasiewiez-Puzanowska and M. Tarasiewiez, *Chem. Anal. (Warsaw)*, 1970, **15**, 405.
20. J. Mounier and B. Viossant, *Ann. Pharm. Franc.*, 1968, **26**, 429.
21. A. H. Charles, *Clin. Chem.*, 1961, **7**, 130.
22. W. L. Pacha, *Experimenta*, 1969, **25**, 103.
23. F. Feigl and D. Haguenauer-Castro, *Anal. Chem.*, 1961, **33**, 1412.
24. *Idem, Chemist-Analyst*, 1962, **51**, 7.

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STUDIES ON EXTRACTION OF ZIRCONIUM BY QUATERNARY AMMONIUM HALIDES FROM HYDROCHLORIC ACID MEDIA AND ITS SEPARATION FROM HAFNIUM

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Summary—The distribution of Zr(IV) between hydrochloric acid media and Hyamine 1622 in the organic phase is described. The dependence of extraction on acidity, extractant concentration and type of diluent, was investigated. The possible extraction mechanism is discussed in the light of the results obtained. A method for the separation and determination of Zr(IV) in a mixture of Zr and Hf is outlined.

High molecular-weight amines have become of high interest in the analytical and hydrometallurgical aspects of nuclear materials refining.[1–3] In a previous work,[4] various types of amine were thoroughly investigated as extractants for Zr(IV). It has also been pointed out that the efficiency of quaternary ammonium halides is higher than that of the amines.[5–11] Although Hyamine 1622 has been used as a quaternary ammonium extractant for some metals,[12,13] no observations on Zr(IV) have been reported. The present investigation is a part of a programme of systematic studies on liquid–liquid extraction of some nuclear materials; it reports recently obtained data on extraction of Zr(IV) by Hyamine 1622 from hydrochloric acid solutions and the separation of the metal from Hf(IV).

EXPERIMENTAL

Reagents

Hyamine 1622 (Hn), $R_3R'NCl$, a pure crystalline quaternary ammonium halide of molecular weight 466.1 and bulk density 27.5 lb/ft^3, manufactured by Rohm and Haas Co., and used as received. All diluents were of reagent grade, except odourless kerosene which was the commercial grade "Sun rise" (Misr Petroleum Co.). $^{175+181}$Hf was provided by the Radiochemical Centre, Amersham, and used as tracer in the Hf–Zr separation experiments.

Extraction procedure

The organic phase was prepared by adding the calculated amount of Hn to the required diluent together with 3% v/v octanol (as modifier) to avoid emulsions. The aqueous phase was prepared by dissolving a high-grade hydrated zirconia in hydrochloric acid of appropriate concentration. The solution was standardized complexometrically by back-titration with iron, salicylic acid being used as indicator.[14] The concentration of Zr in the organic phase was determined after stripping with 1*M* nitric acid. The chloride concentration of the organic phase was determined by Volhard's method (with addition of nitrobenzene). All determinations were done in duplicate made and the averages are reported.

Equal volumes (10 ml) of the aqueous and pre-equilibrated organic phase were mixed together in separatory funnels, then shaken mechanically for 10 min at room temperature ($18 \pm 3°$) to ensure complete equilibration. Preliminary experiments showed that this time is sufficient for equilibrium to be reached and that the extraction is not influenced by temperature fluctuations within the range mentioned. The distribution ratio (D) was calculated as the ratio of the equilibrium concentrations of Zr in the organic and aqueous phases. The separation factor (selectivity, S), was computed from $S = D_{Zr}/D_{Hf}$.

RESULTS AND DISCUSSION

Effect of initial HCl concentration

The extraction of Zr from its 0.077*M* aqueous solution, with 0.1*M* Hn in benzene, was examined at different acidities (0.5–10.5*M*); results are shown in Fig. 1. Figure 2

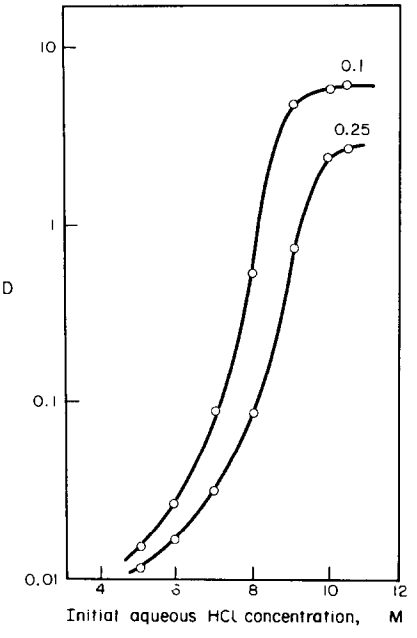


Fig. 1. Effect of initial hydrochloric acid concentration on the extraction of Zr(IV) by 0.1*M* and 0.05*M* Hyamine 1622 in benzene (numerals on curves are Hyamine 1622 concentrations, *M*).

shows the corresponding results for Hf. At lower acidities ($< 6M$) practically no extraction occurs, presumably because of formation of inextractable anionic complexes. Above 6*M* acidity, D increases pronouncedly because of the salting-out effect of the chloride ions and formation of an

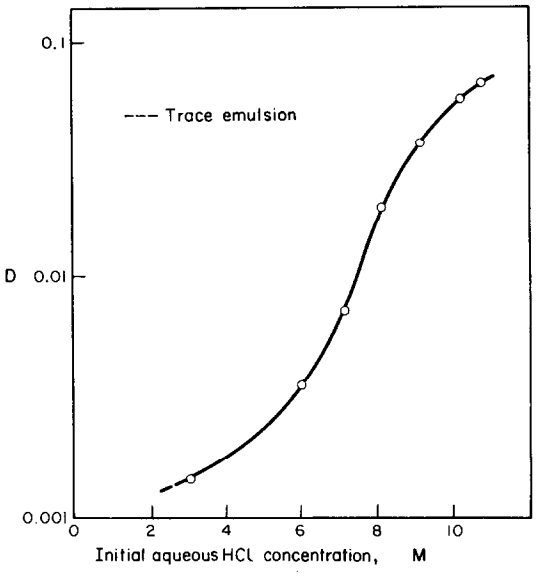


Fig. 2. Distribution ratio of Hf(IV) ($5\times10^{-4}M$) as a function of hydrochloric acid concentration: Hyamine 1622 concentration $0.1M$ in dichloroethane.

ion-association complex. Best results were attained at about $10M$ acidity.

When the hydrochloric acid in the aqueous phase is partly replaced with lithium chloride (Table 1), D for the HCl–LiCl mixture is found to be lower than that for the acid alone at the same chloride concentration, probably

Table 1. Extraction of Zr(IV) from $0.5M$ hydrochloric acid in presence of lithium chloride with $0.1M$ Hyamine 1622 in benzene

Total chloride concn., M	D	
	HCl	HCl + LiCl
4.5	0.01	0.004
6.2	0.03	0.02
8.0	0.55	0.48
9.0	5.0	4.2
10.0	6.2	5.8

because of hydrolysis and possible subsequent polymerization,[15] but follows the same general pattern, indicating that the controlling factor in the extraction is the chloride concentration.

Dependence on metal and extractant concentration

The variation of the Zr concentration in the organic phase was examined for $10M$ hydrochloric acid and $0.05M$ Hn in dichloroethane. A maximum loading of about $0.027M$ was obtained, indicating that two quaternary extractant molecules are associated with each metal ion extracted. This number was calculated from plots of $\log D$ *vs.* $\log[\mathrm{Hn}]$. The concentration of free Hn was assumed to be given by $(C_{tot}-2C_{Zr})$, where C_{tot} is the total Hn concentration and C_{Zr} is the Zr concentration in the organic phase. The aqueous phase was $0.06M$ Zr, and organic phases of various Hn concentrations (0.02–$0.5M$) were used. The plots indicated a linear increase in D with rise of Hn concentration up to about $0.1M$, after which D increased only slightly or remained nearly constant.

Although it has been reported that log–log plots of D *vs.* quaternary ammonium halide concentration do not generally give a reliable prediction for the stoichiometry of the extracted species,[16,17] in the present system more than one species is presumably extracted by Hn as extractant. Discrepancies encountered at higher Hn concentrations ($>0.1M$), may be due to non-ideality of the organic phase. At low Hn concentration ($\leqslant0.1M$), the plots give straight lines with slopes of approximately 2 (1.7 and 1.6 for 10 and $9M$ hydrochloric acid respectively), indicating a second-power dependence of D on Hn concentration. Since Zr^{4+} ions were considered to be the prevailing species in the acidic solutions rather than ZrO^{2+} ions,[15] the extraction mechanism is probably

$$ZrCl_{n(a)}^{(4-n)+} + (n-4)R_3R'NCl_{(o)} \rightleftharpoons (R_3R'N)_{(n-4)}ZrCl_{n(o)} + (n-4)Cl_{(a)}^{-}$$

where (o) and (a) denote the organic and aqueous phases respectively. It is thus assumed that under the conditions mentioned, Zr is extracted as the complex $(R_3R'N)_2ZrCl_6$. The formation of such a hexachloride complex was confirmed experimentally by saturation of an organic phase consisting of $0.1M$ Hn in dichloroethane, by shaking for 10 min with ten successive aqueous feeds of $0.05M$ Zr in $10M$ hydrochloric acid. The saturated organic phase was then analysed for Zr and chloride; a ratio of Hn : Zr : Cl^- of about 2:1:6 was obtained, justifying postulation of the hexachloride complex as the extracted species in this system.

Effect of diluent type

The degree of extraction of Zr ($0.06M$) from $9M$ hydrochloric acid with $0.1M$ Hn in various diluents is given in Table 2. The efficiency of the diluents used in the

Table 2. Extraction of Zr(IV) from $9M$ hydrochloric acid by $0.1M$ Hyamine 1622 in various diluents

Diluent	Dielectric constant at 20°	Donor properties*	D
Dichloroethane	10.5 (at 17°)	D	8.30
Benzene	2.283	I–D	5.20
Toluene	2.387	I–D	1.54
Xylene	2.420	I–D	1.00
Cyclohexane	2.052	I	0.287
n-Hexane	1.874	I	0.167
Kerosene	(2)	I	0.167

* D = donor, I = inert.

absence of the extractant was nearly negligible ($D<0.01$). It is obvious that no simple relationship holds between degree of extraction and physical parameters of the diluents used, although extraction with diluents of higher dielectric constant seems preferable. Extraction follows more or less the sequence: chlorinated paraffins > aromatics > cyclic paraffins > straight-chain hydrocarbons. This order of effectiveness is correlated with either the solvation power,[18] and/or the electron-donor properties of the diluents, giving higher efficiency for donors (halogenated hydrocarbons and aromatic compounds) and lower for inert diluents (cyclic and straight-chain hydrocarbons).[19] It should be stressed that no modifier was added in the diluent experiments, and that neither chloroform nor carbon tetrachloride could be used since Hn is insoluble in the former while the latter gives dense emulsions with it. The cheaper odourless kerosene and the efficient aromatic diluents are not recommended, because of the formation of a thin third layer at the interface. Dichloroethane, giving best results and cleaner separation, is recommended as the best diluent, though benzene is almost as good.

A log–log plot of D *vs.* Hn concentration in benzene (9M hydrochloric acid), also gave a straight line of slope nearly 2 (1.6) indicating a disolvate as the extracted species (at $\leqslant 0.1M$ Hn), as for dichloroethane. The extraction mechanism is presumably independent of the type of diluent used.

Separation and determination of Zr

The difficulty in Hf–Zr separation arises mainly from the close similarity in chemical behaviour of the two elements, but as Zr is generally associated with its chemical twin Hf which has a higher neutron-capture cross-section (Zr 0.18 and Hf 105 barns) efficient Hf removal is imperative if Zr is to be used in construction of thermal reactors.

In order to find the optimum conditions for Hf–Zr separation, the extraction was examined at different acidities (0.5–10.5M hydrochloric acid) of an aqueous phase consisting of 0.08M Zr and $6 \times 10^{-4}M$ Hf (i.e., with Hf/Zr ratio about 0.014, similar to that used in technology through zircon processing[4]), with an organic phase of 0.1M Hn in benzene. Zr (+Hf) was determined complexometrically[14] and Hf radiometrically as $^{175+181}$Hf; Zr was computed by difference. The optimum acidity is around 10M, the separation factor S being maximal (S is 0.07, 2.44, 106, 143 and 130 for 7, 8, 9, 10 and 10.5M hydrochloric acid). Even better values for S (with clean separation and lower disengagement time) were attained with 0.1M Hn in dichloroethane. From this study we suggest the following method for Hf–Zr separation, and for Zr determination.

An aliquot (0.07M in Zr and containing about 0.09 mg of Hf per ml, in 10M hydrochloric acid) is shaken mechanically for 10 min with an equal volume of pre-equilibrated 0.1M Hn in dichloroethane at room temperature (~20°). After centrifugation, the two layers are separated. The aqueous phase is extracted twice more with fresh organic phase. The organic phase is then scrubbed with one fifth of its volume of 3.5M hydrochloric acid and then Zr is stripped from the combined organic phases by shaking twice with equal volumes of 0.5–1M nitric acid. Zr in the back-extract is then determined complexometrically by back-titration with iron (salicylic acid as indicator).

It is worth mentioning that the stripped Zr is equivalent in purity to nuclear grade (with < 100 ppm Hf, as ascertained spectrographically). The recovery is 94.5%.

To confirm the validity of the method for determining Zr in Hf–Zr mixtures, Zr was determined in an aliquot of the stock feed by difference between the total Zr + Hf (measured complexometrically as mentioned above) and Hf measured spectrographically. The agreement is satisfactory (the mean error does not exceed 2%). The suggested method for the separation and determination of Zr is selective, simple and fairly rapid.

REFERENCES

1. E. L. Smith and E. J. Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.
2. C. F. Coleman, K. B. Brown and J. G. Moore, *Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1958, **28**, 278.
3. D. J. Crouse, K. B. Brown and F. G. Seeley, *Solvent Extraction Chemistry*, p. 327. Macmillan, London, 1966.
4. M. Y. Farah and I. S. El-Yamani, *Proc. 3rd U.N. Intern. Conf. Peaceful Uses Atomic Energy, New York*, 1965, **9**, 131.
5. E. A. Mason, *Prog. Rept.* TID-15450, 1962.
6. G. H. Morrison and H. Freiser, *Anal. Chem.*, 1962, **34**, 64R; 1964, **36**, 93R; H. Freiser, *Anal. Chem.*, 1966, **38**, 131R; 1968, **40**, 522R.
7. M. L. Good, S. L. Srivastava and F. F. Holland, Jr., *Anal. Chim. Acta*, 1964, **31**, 534.
8. T. Sato and H. Watanabe, *ibid.*, 1970, **49**, 463.
9. T. Sato, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3835.
10. T. Sato, S. Kotani and M. L. Good, *ibid.*, 1973, **35**, 2547.
11. T. Sato and H. Watanabe, *ibid.*, 1974, **36**, 451.
12. A. M. Wilson, L. Churchill, K. Kiluk and P. Hovsepian, *Anal. Chem.*, 1962, **34**, 203.
13. M. Gerrard, *Radiochim. Acta*, 1972, **17**, 153.
14. G. W. C. Milner and P. J. Phennah, *Analyst*, 1954, **79**, 475.
15. E. Matijevic, K. G. Mathai and M. Kerker, *J. Phys. Chem.*, 1962, **66**, 1799.
16. J. M. White, P. Kelly and N. C. Li, *J. Inorg. Nucl. Chem.*, 1961, **16**, 337.
17. M. L. Good and F. F. Hooland, Jr., *ibid.*, 1964, **26**, 321.
18. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, p. 757. Wiley, London, 1969.
19. J. Walkley, D. Glew and J. H. Hildebrand, *J. Chem. Phys.*, 1960, **33**, 621.

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DETERMINATION OF MEBENDAZOLE

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Summary—Direct and indirect non-aqueous titrimetric methods for the determination of mebendazole are presented. These methods are reproducible, with relative standard deviations of 0.3%. Mebendazole in tablets (100 mg per tablet) has also been determined spectrophotometrically with use of perchloric acid as solvent. The relative standard deviation was 1.4%. The methods are easy to automate for routine analysis.

Mebendazole[1] is an anthelmintic drug usually prescribed as tablets containing 100 mg per tablet. It is insoluble in water, alcohol, ether and chloroform, sparingly soluble in glacial acetic acid but soluble in formic acid and perchloric acid. The

A log–log plot of D *vs.* Hn concentration in benzene (9M hydrochloric acid), also gave a straight line of slope nearly 2 (1.6) indicating a disolvate as the extracted species (at $\leqslant 0.1M$ Hn), as for dichloroethane. The extraction mechanism is presumably independent of the type of diluent used.

Separation and determination of Zr

The difficulty in Hf–Zr separation arises mainly from the close similarity in chemical behaviour of the two elements, but as Zr is generally associated with its chemical twin Hf which has a higher neutron-capture cross-section (Zr 0.18 and Hf 105 barns) efficient Hf removal is imperative if Zr is to be used in construction of thermal reactors.

In order to find the optimum conditions for Hf–Zr separation, the extraction was examined at different acidities (0.5–10.5M hydrochloric acid) of an aqueous phase consisting of 0.08M Zr and $6 \times 10^{-4}M$ Hf (i.e., with Hf/Zr ratio about 0.014, similar to that used in technology through zircon processing[4]), with an organic phase of 0.1M Hn in benzene. Zr (+Hf) was determined complexometrically[14] and Hf radiometrically as $^{175+181}$Hf; Zr was computed by difference. The optimum acidity is around 10M, the separation factor S being maximal (S is 0.07, 2.44, 106, 143 and 130 for 7, 8, 9, 10 and 10.5M hydrochloric acid). Even better values for S (with clean separation and lower disengagement time) were attained with 0.1M Hn in dichloroethane. From this study we suggest the following method for Hf–Zr separation, and for Zr determination.

An aliquot (0.07M in Zr and containing about 0.09 mg of Hf per ml, in 10M hydrochloric acid) is shaken mechanically for 10 min with an equal volume of pre-equilibrated 0.1M Hn in dichloroethane at room temperature (~20°). After centrifugation, the two layers are separated. The aqueous phase is extracted twice more with fresh organic phase. The organic phase is then scrubbed with one fifth of its volume of 3.5M hydrochloric acid and then Zr is stripped from the combined organic phases by shaking twice with equal volumes of 0.5–1M nitric acid. Zr in the back-extract is then determined complexometrically by back-titration with iron (salicylic acid as indicator).

It is worth mentioning that the stripped Zr is equivalent in purity to nuclear grade (with < 100 ppm Hf, as ascertained spectrographically). The recovery is 94.5%.

To confirm the validity of the method for determining Zr in Hf–Zr mixtures, Zr was determined in an aliquot of the stock feed by difference between the total Zr + Hf (measured complexometrically as mentioned above) and Hf measured spectrographically. The agreement is satisfactory (the mean error does not exceed 2%). The suggested method for the separation and determination of Zr is selective, simple and fairly rapid.

REFERENCES

1. E. L. Smith and E. J. Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.
2. C. F. Coleman, K. B. Brown and J. G. Moore, *Proc. 2nd U.N. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1958, **28**, 278.
3. D. J. Crouse, K. B. Brown and F. G. Seeley, *Solvent Extraction Chemistry*, p. 327. Macmillan, London, 1966.
4. M. Y. Farah and I. S. El-Yamani, *Proc. 3rd U.N. Intern. Conf. Peaceful Uses Atomic Energy, New York*, 1965, **9**, 131.
5. E. A. Mason, *Prog. Rept.* TID-15450, 1962.
6. G. H. Morrison and H. Freiser, *Anal. Chem.*, 1962, **34**, 64R; 1964, **36**, 93R; H. Freiser, *Anal. Chem.*, 1966, **38**, 131R; 1968, **40**, 522R.
7. M. L. Good, S. L. Srivastava and F. F. Holland, Jr., *Anal. Chim. Acta*, 1964, **31**, 534.
8. T. Sato and H. Watanabe, *ibid.*, 1970, **49**, 463.
9. T. Sato, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3835.
10. T. Sato, S. Kotani and M. L. Good, *ibid.*, 1973, **35**, 2547.
11. T. Sato and H. Watanabe, *ibid.*, 1974, **36**, 451.
12. A. M. Wilson, L. Churchill, K. Kiluk and P. Hovsepian, *Anal. Chem.*, 1962, **34**, 203.
13. M. Gerrard, *Radiochim. Acta*, 1972, **17**, 153.
14. G. W. C. Milner and P. J. Phennah, *Analyst*, 1954, **79**, 475.
15. E. Matijevic, K. G. Mathai and M. Kerker, *J. Phys. Chem.*, 1962, **66**, 1799.
16. J. M. White, P. Kelly and N. C. Li, *J. Inorg. Nucl. Chem.*, 1961, **16**, 337.
17. M. L. Good and F. F. Hooland, Jr., *ibid.*, 1964, **26**, 321.
18. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, p. 757. Wiley, London, 1969.
19. J. Walkley, D. Glew and J. H. Hildebrand, *J. Chem. Phys.*, 1960, **33**, 621.

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DETERMINATION OF MEBENDAZOLE

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Summary—Direct and indirect non-aqueous titrimetric methods for the determination of mebendazole are presented. These methods are reproducible, with relative standard deviations of 0.3%. Mebendazole in tablets (100 mg per tablet) has also been determined spectrophotometrically with use of perchloric acid as solvent. The relative standard deviation was 1.4%. The methods are easy to automate for routine analysis.

Mebendazole[1] is an anthelmintic drug usually prescribed as tablets containing 100 mg per tablet. It is insoluble in water, alcohol, ether and chloroform, sparingly soluble in glacial acetic acid but soluble in formic acid and perchloric acid. The

present paper deals with the determination of mebendazole alone by direct and indirect titrimetric methods and in tablets by a spectrophotometric method.

EXPERIMENTAL

Reference solution

Weigh accurately about 50 mg of mebendazole into a 50-ml volumetric flask. Add 10 ml of 70% perchloric acid and shake to dissolve. Dilute to volume with distilled water. Pipette 1 ml into a 100-ml volumetric flask and dilute to volume with distilled water.

Assay of mebendazole

Direct titrimetric method. Weigh accurately about 200 mg of mebendazole into a dry conical flask and dissolve it in 2 ml of 99% formic acid. Add 60 ml of glacial acetic acid and titrate with 0.1*N* perchloric acid in glacial acetic acid, using Crystal Violet as indicator, to a persistent green colour. Perform a blank determination, and make any correction necessary. (1 ml of 0.1*N* perchloric acid is equivalent to 29.5 mg of $C_{16}H_{13}O_3N_3$).

Back-titration method. Weigh accurately about 200 mg of mebendazole into a dry conical flask. Add exactly 20 ml of 0.1*N* perchloric acid in glacial acetic acid. Titrate with 0.1*M* sodium acetate in glacial acetic acid, using Crystal Violet as indicator, to a bluish green colour.

Spectrophotometric determination in tablets

Weigh accurately a quantity of the powdered tablets equivalent to about 50 mg of mebendazole, into a 50-ml standard flask. Add 10 ml of 70% perchloric acid and shake for about 10 min. Dilute to volume with distilled water. Filter through a dry filter paper and reject the first portion of the filtrate. Pipette 1 ml into a 100-ml standard flask and dilute to volume with distilled water. Measure the absorbance in a 1-cm cell at 288 nm against a blank prepared by diluting 0.2 ml of 70% perchloric acid to 100 ml with distilled water. Calculate the concentration by taking 566 as the $E^{1\%}_{1\,cm}$ value at 288 nm or by using a suitable calibration curve.

RESULTS AND DISCUSSION

Seven samples of different weights ranging from 150 to 300 mg of mebendazole were assayed by the direct and back-titration methods. The mean recoveries were 100.2 and 100.3%; the relative standard deviations were 0.3%. Tablets containing 100 mg per tablet were prepared. Eight samples of different weights of the powdered tablets were assayed by the spectrophotometric method. The mean content found per tablet was 100.1 mg, standard deviation 1.4 mg.

Unlike thiabendazole,[2] mebendazole is sparingly soluble in glacial acetic acid. Nevertheless, the direct titrimetric method has been carried out in glacial acetic acid medium after dissolution of the sample in about 2 ml of 99% formic acid. The back-titration method was successful and the results obtained were as precise and accurate as those for the direct method. The correct colour for the indicator at the end-point was identified by conducting a potentiometric titration. However, the insoluble fillers make it difficult to discern the end-point in the non-aqueous titrations, which is why the spectrophotometric method is preferred for analysis of tablets.

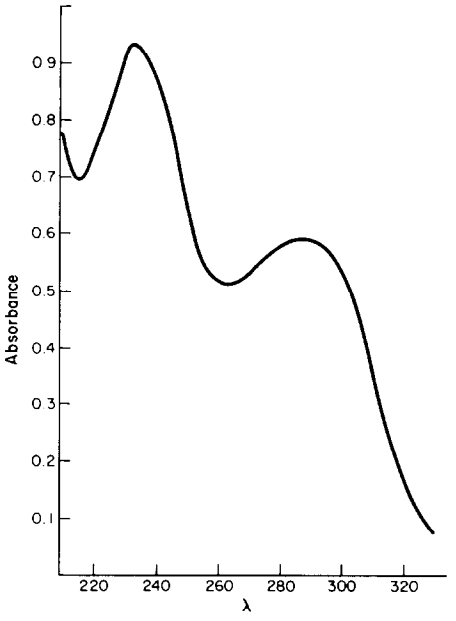


Fig. 1. Absorption curve of 0.0005% w/v mebendazole in aqueous 0.01*M* $HClO_4$.

Mebendazole in aqueous 0.01*M* perchloric acid exhibits two absorption maxima, at 234 and 288 nm (Fig. 1). The mean $E^{1\%}_{1\,cm}$ values at the two maxima were 886 and 566, respectively (four separate samples) and the relative standard deviations were both 0.2%. Beer's law was obeyed at these maxima over the range 0.2–1.4 mg per 100 ml.

Other solvents such as 0.01*M* hydrochloric acid and 0.1*M* sodium hydroxide (both in isopropyl alcohol) have been tried as solvents for extracting mebendazole from tablets, followed by spectrophotometric analysis, but variably low results were obtained. This has been attributed to incomplete dissolution of mebendazole in these two solvents. Perchloric acid (70%) was found the best solvent for the spectrophotometric determination of this drug in tablets. Lactose, starch, starch paste, magnesium powder and talc, used as tablet fillers, did not interfere in the spectrophotometry.

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REFERENCES

1. E. G. C. Clarke, *Isolation and Identification of Drugs*, Vol. 2, p. 1056. The Pharmaceutical Press, London, 1975.
2. *United States Pharmacopoeia, XIX*, p. 501.

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SPECTROPHOTOMETRIC DETERMINATION OF NICKEL AFTER SEPARATION BY ADSORPTION OF ITS α-FURILDIOXIME COMPLEX ON NAPHTHALENE

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Summary A new method is proposed for collecting traces of nickel from aqueous solution by precipitation as the α-furildioxime complex and adsorption of this onto microcrystalline naphthalene. The precipitate is collected, dried, and dissolved in chloroform, and the nickel is determined spectrophotometrically at 438 nm. The linear calibration range is 2–35 μg/10 ml. The molar absorptivity is 1.6×10^4 l. mole^{-1}. cm^{-1}. The main advantage is that the nickel is collected quantitatively after only a few seconds' shaking. The effect of varying pH, amount of reagent, naphthalene or buffer, shaking and standing time, and interferences have been investigated.

During the past several years we have developed a useful spectrophotometric method for the determination of trace metals by absorbance measurements after extraction of the metal complexes into molten naphthalene.[1–10] However, because of the time needed to separate and dry the naphthalene phase after extraction, this method takes longer than the conventional one using extraction directly into chloroform. In order to overcome this drawback, we have developed a new method based on adsorption of the metal complexes onto solid, crystalline naphthalene, and have successfully applied it to the determination of trace amounts of metals. With this method, many metal complexes can be easily and quantitatively collected on very small naphthalene crystals by vigorous shaking for several seconds at room temperature.

In the present study, the adsorption of the nickel α-furildioxime complex onto napthalene has been investigated.

EXPERIMENTAL

Reagents

Standard nickel solution, 5 ppm. Prepared by diluting 5 ml of 1000-ppm standard nickel solution to 1000 ml with water.

α-Furildioxime solution, 0.1% in ethanol.

Naphthalene solution, 20% in acetone.

Buffer solutions. Prepared from 1*M* acetic acid and 1*M* ammonium acetate for pH 3–6, and from 1*M* aqueous ammonia and 1*M* ammonium acetate for pH 8–11.

Naphthalene, acetone, chloroform and all other reagents were of analytical-reagent grade, and were used without further purification, but water was purified by passage through a demineralizer.

The naphthalene was dried with a Tabai Model K-2 drier (Tabai Mfg. Co. Ltd., Japan).

Procedure

Transfer about 40 ml of sample solution containing 2–35 μg of nickel to a 100-ml Erlenmeyer flask with a tightly fitting stopper, add 2.0 ml of ethanolic 0.1% α-furildioxime solution and adjust to pH 7–11 with 2.0 ml of buffer solution. Mix the solution well, let stand for 15 min, then add 3.0 ml of 20% solution of naphthalene in acetone and shake vigorously for 1 min. Filter off on a filter paper (e.g., No. 5C, Toyo Rosli Co.) placed flat on a filter plate in a funnel. Wash with water, and dry at 50–60°. Dissolve the solid in chloroform, dilute to 10 ml, and measure the absorbance in a 10-mm glass cell at 438 nm against a reagent blank prepared similarly. Calculate the amount of trace nickel from a calibration curve.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the absorption spectra of the reagent blank and of the nickel complex in naphthalene–chloroform solution resulting from taking 20 μg of nickel through the procedure. The nickel complex has one absorption maximum at 438 nm and a shoulder at 390 nm. At these wavelengths, there is practically no absorption due to the reagent blank, and 438 nm was therefore chosen as the most suitable wavelength.

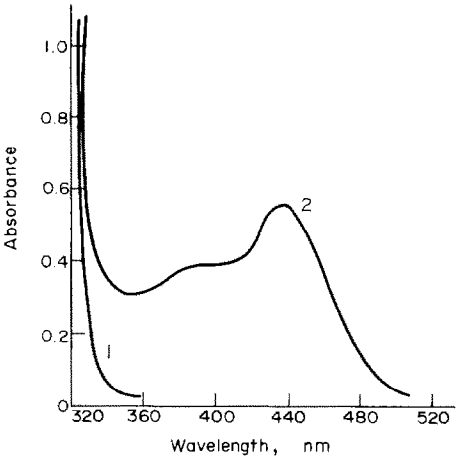


Fig. 1. Absorption spectra of α-furildioxime and nickel complex in naphthalene–chloroform solution. Ni 20 μg; 0.1% α-furildioxime 2.0 ml; buffer pH 9.8; shaking time 1 min; standing time 10 min; reference water. (1) Reagent blank; (2) Ni complex.

Effect of pH

The effect of pH on the recovery of the nickel complex is shown in Fig. 2. The pH measurements on the aqueous solution after adsorption were made at room temperature. The pH range 8.0–11.0 would seem to be suitable.

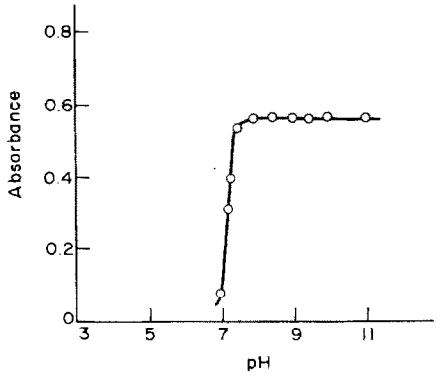


Fig. 2. Effect of pH on absorbance. Ni 20 μg; wavelength 438 nm; 0.1% α-furildioxime 2.0 ml; 20% naphthalene in acetone 3.0 ml; shaking time 1.0 min; standing time 10 min; reference reagent blank.

Effect of reagent concentration and of addition of buffer solution

Various amounts of the ethanolic 0.1% α-furildioxime solution were added to the solution containing 20 μg of nickel and 2.0 ml of the buffer solution (pH 10), and the procedure was otherwise followed as given above. Table 1 shows the

Table 1. Effect of reagent concentration

Reagent, *ml*	Absorbance
0.1	0.124
0.2	0.317
0.3	0.463
0.4	0.555
0.5	0.544
1.0	0.553
2.0	0.560
3.0	0.556
4.0	0.566
5.0	0.563

Ni: 20 μg; reagent: 0.1% α-furildioxime in ethanol.

variation in the measured absorbance with the reagent concentration. When volumes between 0.4 and 5.0 ml of reagent solution were used, the absorbance was effectively constant with an average of 0.557 and standard deviation of 0.007 for 7 values. Varying the volume of buffer solution from 0.5 to 5.0 ml at pH 10 did not affect the absorbance.

Effect of volume of aqueous phase

The volume of the aqueous phase was varied between 50 and 2000 ml while other factors were kept constant. The ten absorbance values for this series gave a mean of 0.557 with a standard deviation of 0.006. Though the volume of the aqueous phase clearly does not affect the accuracy, allowance must be made for large volumes by shaking for a longer time and using a larger volume of reagent solution. In this series of tests, 3 ml of reagent solution were taken, and the mixed solutions were shaken for 10 minutes.

Effect of naphthalene concentration

Varying volumes of 20% naphthalene solution in acetone were added to the solutions containing 20 μg of nickel and the procedure was followed. Six different volumes from 0.5 to 5.0 ml gave a mean absorbance of 0.559 with a standard deviation of 0.005, while a comparison in which no naphthalene was added gave an absorbance of 0.521.

Effect of shaking time and standing time

Three ml of 20% naphthalene solution in acetone were added to solutions containing the nickel complex, and the mixed solutions were shaken vigorously for times ranging from 2 sec to 3 min. The complex was recovered quantitatively on microcrystalline naphthalene by vigorous shaking for just a few seconds. The colour of the complex in naphthalene–chloroform solution was very stable even after standing for 3 hr. The absorbance did not change when the sample solution was kept at room temperature or even at elevated temperature (40–50°C).

Calibration curve

The optimum conditions described above were used and the absorbances for varying concentrations of nickel were measured at 438 nm. The absorbance showed a linear relationship to the concentration of nickel in the range 2–35 μg per 10 ml of chloroform. The molar absorptivity was 1.64×10^4 l.mole^{-1}.cm^{-1}.

Ten replicate determinations of the sample solution containing 20 μg of nickel gave a mean absorbance of 0.560 with standard deviation of 0.004 or relative standard deviation of 0.7%.

Effect of diverse ions

Possible interferences were looked for by taking 20 μg of nickel through the procedure in the presence of various amounts of alkali metal salts and metal ions. The following species did not interfere at the 500-mg level, Na_2SO_4, Na_2SO_3, NaCl, NaH_2PO_4, $2H_2O$, KBr, KNO_3, $CH_3COONa, 3H_2O$, sodium tartrate; and at the 200-μg level, Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Bi^{3+}, Hg^{2+}, Mg^{2+}, Ca^{2+}. Sodium oxalate, sodium citrate, NH_4Cl, KCN, Fe^{3+}, and Co^{2+} gave negative interferences while Na_2CO_3 and Cu^{2+} gave positive

Table 2. Effect of diverse interfering ions*

Ion or salt	Contents	Absorbance
none	– mg	0.560
NH_4Cl	100 mg	0.548
	300 mg	0.529
	500 mg	0.412
Na_2CO_3	100 mg	0.556
	300 mg	0.578
	500 mg	0.591
Sodium oxalate	100 mg	0.488
	500 mg	0.050
Sodium citrate	1 mg	0.561
	5 mg	0.553
	10 mg	0.521
	50 mg	0.293
	100 mg	0.070
	500 mg	0.002
KCN	20 mg	0.000
Fe(III)	30 μg	0.563
	60 μg	0.558
	100 μg	0.523
	200 μg	0.483
	300 μg	0.450
Cu(II)	50 μg	0.585
	100 μg	0.614
	200 μg	0.622
Co(II)	50 μg	0.554
	100 μg	0.533
	200 μg	0.235
	300 μg	0.085

* 20 μg of nickel.

interferences. Especially serious were the effects of small amounts of sodium citrate and potassium cyanide. Fe^{3+} and Cu^{2+} could be masked with 300 mg of sodium tartrate. The effects of interfering ions are summarized in Table 2.

Choice of solvent

Tests were made with various organic solvents to dissolve the mixture of the complex and the naphthalene. The complex is soluble in many organic solvents such as dimethylformamide, dioxan, benzene, chloroform, xylene, toluene, chlorobenzene, nitrobenzene, propylene carbonate, acetonitrile, dichloroethane, MIBK, isoamyl acetate, DMSO, but insoluble in *o*-dichlorobenzene. The spectrum of the complex dissolved in chloroform was the same as that for a dioxan or dimethylformamide solution, but the absorbance of the complex was higher in chloroform than in dioxan or dimethylformamide and the colour was more stable.

REFERENCES

1. T. Fujinaga, T. Kuwamoto, E. Nakayama and M. Satake, *Talanta*, 1969, **16**, 1225.
2. *Idem, Bunseki Kagaku*, 1969, **18**, 398.
3. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *ibid.*, 1969, **18**, 1113.
4. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 216.
5. *Idem, ibid.*, 1971, **20**, 1255.
6. *Idem, Bull. Chem. Soc. Japan*, 1973, **46**, 2090.
7. *Idem, Bull. Chem. Soc. Japan*, 1975, **48**, 899.
8. *Idem, Talanta*, 1972, **19**, 689.
9. T. Fujinaga, M. Satake and M. Shimizu, *Bunseki Kagaku*, 1976, **25**, 313.
10. M. Satake, *Anal. Chim. Acta*, 1977, **92**, 423.

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A NOTE ON THE CALCULATION OF ACID-BASE TITRATION CURVES AND THEIR EQUIVALENCE POINTS

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Summary—An equation has been developed for the calculation of the titration curve of any mixture of acids and bases, and an alternative way of defining an equivalence point, suitable for computer calculations, is presented.

Several general computer programs[1] are available for the calculation of the composition of a solution at equilibrium. There are, however, instances where programs dedicated to the solution of special types of equilibria can be used to advantage. The acid–base titration curve and quantities related thereto is an example.

The calculation of titration curves has recently been discussed by Sara and Still.[2] Since the computation of pH as a function of the volume of titrant (V) generally necessitates the solution of an equation of higher order unless approximations are introduced, they suggested that V should be calculated as a function of pH instead. While this procedure quickly yields the titration curve, it is less satisfactory for delineating those points for which the location on the curve is determined by V, the equivalence points for instance. Equations and algorithms for finding $pH = f(V)$ for special cases are frequent but the general case appears not to have been fully treated. This will now be attempted.

Let V_0 ml of the sample be titrated with V ml of titrant of concentration C (M). Suppose the sample to be composed of strong acid, H^+, of concentration C_H, and strong base, OH^-, of concentration C_{OH}, and a number, N, of conjugate acid–base systems. The fully protonated acid in each such system is denoted by $H_{m_i}A_i$ ($i = 1, 2, \ldots, N$) and any one member of the system by H_jA_i ($m_i \geqslant j \geqslant 0$). The average number of protons bound to A_i, calculated from the initial sample composition, will be denoted by n_i. Thus a mixture $0.1M$ in $H_2PO_4^-$ and $0.05M$ in HPO_4^{2-} will be represented by $C_{PO_4} = 0.15M$ and $n_{PO_4} = (2 \times 0.1 + 1 \times 0.05)/0.15 = 5/3$. This number should not be confused with the corresponding quantity at equilibrium, which is

$$j_i = \sum_{j=1}^{m_i} j[H_jA_i]/C_i.$$

The equations in Fig. 1A define the nominal concentrations of the individual components at any point on the titration curve (*i.e.*, the initial concentration multiplied by a dilution factor): $r = 1$ for a titration with strong acid and -1 for a titration with strong base. The equilibrium concentrations of the species are those given in Fig. 1B.

The mass balance for titratable protons[3,4] yields

$$V_0(C_H - C_{OH})/(V + V_0) + rVC/(V + V_0) + V_0 \sum_{i=1}^{N} n_i C_i/(V + V_0) = h - [OH] + \sum_{i=1}^{N} \sum_{j=0}^{m_i} j[H_jA_i] \quad (1)$$

Introducing the following relations and definitions into equation (1)

$$[V_0/(V + V_0)] \sum_{i=1}^{N} C_i = \sum_{i=1}^{N} \sum_{j=0}^{m_i} [H_jA_i] \quad (2)$$

$$\beta_{ij} = [H_jA_i]/h^j[A_i] \quad (3)$$

$$\beta_{i0} = 1 \quad (4)$$

$$[H_jA_i] = \beta_{ij}h^jV_0C_i/(V + V_0) \sum_{k=0}^{m_i} \beta_{ik}h^k \quad (5)$$

$$V_0C_i = CU_i \quad (6)$$

$$V_0(C_H - C_{OH}) = CU_H - CU_{OH} = CU \quad (7)$$

interferences. Especially serious were the effects of small amounts of sodium citrate and potassium cyanide. Fe^{3+} and Cu^{2+} could be masked with 300 mg of sodium tartrate. The effects of interfering ions are summarized in Table 2.

Choice of solvent

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REFERENCES

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6. *Idem, Bull. Chem. Soc. Japan*, 1973, **46**, 2090.
7. *Idem, Bull. Chem. Soc. Japan*, 1975, **48**, 899.
8. *Idem, Talanta*, 1972, **19**, 689.
9. T. Fujinaga, M. Satake and M. Shimizu, *Bunseki Kagaku*, 1976, **25**, 313.
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Summary—An equation has been developed for the calculation of the titration curve of any mixture of acids and bases, and an alternative way of defining an equivalence point, suitable for computer calculations, is presented.

Several general computer programs[1] are available for the calculation of the composition of a solution at equilibrium. There are, however, instances where programs dedicated to the solution of special types of equilibria can be used to advantage. The acid–base titration curve and quantities related thereto is an example.

The calculation of titration curves has recently been discussed by Sara and Still.[2] Since the computation of pH as a function of the volume of titrant (V) generally necessitates the solution of an equation of higher order unless approximations are introduced, they suggested that V should be calculated as a function of pH instead. While this procedure quickly yields the titration curve, it is less satisfactory for delineating those points for which the location on the curve is determined by V, the equivalence points for instance. Equations and algorithms for finding $pH = f(V)$ for special cases are frequent but the general case appears not to have been fully treated. This will now be attempted.

Let V_0 ml of the sample be titrated with V ml of titrant of concentration C (M). Suppose the sample to be composed of strong acid, H^+, of concentration C_H, and strong base, OH^-, of concentration C_{OH}, and a number, N, of conjugate acid–base systems. The fully protonated acid in each such system is denoted by $H_{m_i}A_i$ ($i = 1, 2, \ldots, N$) and any one member of the system by H_jA_i ($m_i \geqslant j \geqslant 0$). The average number of protons bound to A_i, calculated from the initial sample composition, will be denoted by n_i. Thus a mixture $0.1M$ in $H_2PO_4^-$ and $0.05M$ in HPO_4^{2-} will be represented by $C_{PO_4} = 0.15M$ and $n_{PO_4} = (2 \times 0.1 + 1 \times 0.05)/0.15 = 5/3$. This number should not be confused with the corresponding quantity at equilibrium, which is

$$j_i = \sum_{j=1}^{m_i} j[H_jA_i]/C_i.$$

The equations in Fig. 1A define the nominal concentrations of the individual components at any point on the titration curve (*i.e.*, the initial concentration multiplied by a dilution factor): $r = 1$ for a titration with strong acid and -1 for a titration with strong base. The equilibrium concentrations of the species are those given in Fig. 1B.

The mass balance for titratable protons[3,4] yields

$$V_0(C_H - C_{OH})/(V + V_0) + rVC/(V + V_0) + V_0 \sum_{i=1}^{N} n_i C_i/(V + V_0) = h - [OH] + \sum_{i=1}^{N} \sum_{j=0}^{m_i} j[H_jA_i] \quad (1)$$

Introducing the following relations and definitions into equation (1)

$$[V_0/(V + V_0)] \sum_{i=1}^{N} C_i = \sum_{i=1}^{N} \sum_{j=0}^{m_i} [H_jA_i] \quad (2)$$

$$\beta_{ij} = [H_jA_i]/h^j[A_i] \quad (3)$$

$$\beta_{i0} = 1 \quad (4)$$

$$[H_jA_i] = \beta_{ij}h^jV_0C_i/(V + V_0) \sum_{k=0}^{m_i} \beta_{ik}h^k \quad (5)$$

$$V_0C_i = CU_i \quad (6)$$

$$V_0(C_H - C_{OH}) = CU_H - CU_{OH} = CU \quad (7)$$

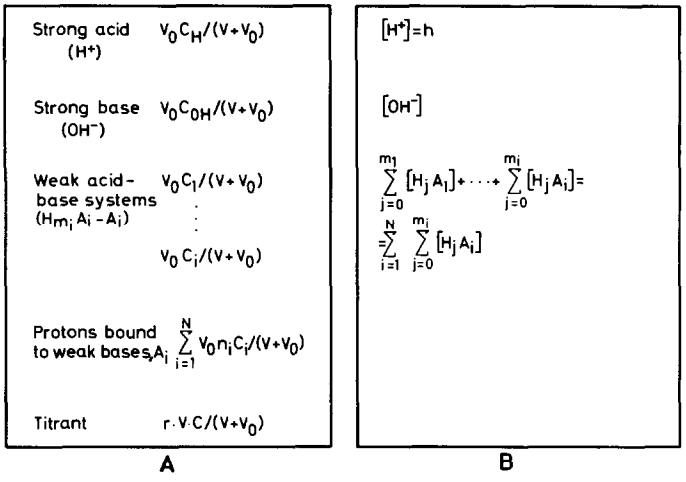


Fig. 1. Summary of the symbols used. (A) is the nominal composition calculated from the initial components and (B) the equilibrium composition at a point on the titration curve.

we obtain

$$U+rV+\sum_{i=1}^{N}\sum_{j=0}^{m_i}U_i(n_i-j)\beta_{ij}h^j\Big/\left(\sum_{k=0}^{m_i}\beta_{ik}h^k\right) = (V+V_0)(h-[\mathrm{OH}])/C \quad (8)$$

where U_H, U_{OH} and U_i are equivalence volumes, and $U = U_H - U_{OH}$ [(from equation (7)].

Relations for specific cases can quickly be derived from equation (8). Thus for a sample containing only monoprotic acids titrated with base we have $U = 0$, $r = -1$ and all $n_i = m_i = 1$ and obtain the familiar result

$$\left[\sum_{i=1}^{N}U_i/(1+K_ih)\right]-V=(V+V_0)(h-[\mathrm{OH}])K_iC=\beta_{i1}$$

is the protonation constant of A_i. It is, however, hardly worth while to make such simplifications explicitly, since the general expression can be efficiently solved by an algorithm which uses the method of interval halving along the pH-axis.[5] The right-hand side (R) of equation (8) is a continuously-increasing and the left-hand side (L) a continuously-decreasing function of pH. The sign of $(R-L)$ therefore suffices to determine the direction of the step in the algorithm. The program used by us and run on an HP9830A calculator comprises about 50 statements (in BASIC) including input and output.

An equivalence point can be characterized by an array of integers. The numerical value of the ith element, e_i, of this array states the formal number of protons on A_i. Suppose, for instance, that a mixture of acetic acid (1) and phosphoric acid (2) is titrated by base to the second equivalence point of H_3PO_4. This point can then be defined as having $e_1 = 0$ and $e_2 = 1$. The pH at the equivalence point is calculated from equation (8) by inserting

$$V = V_e = \left|U+\sum^{N}(n_i-e_i)U_i\right|.$$

The calculation of the conditions at the equivalence points can be made computer-controlled by adding a procedure which generates all conceivable arrays of e_i. The number of such arrays is

$$\prod^{N}(m_i+1).$$

Some of these arrays do not correspond to equivalence points in the normal sense, which are characterized by having $H_{e_i}A_i$ as the predominating species for each acid-base system. False equivalence points can be eliminated by this condition. As an example we may take the titration of a mixture of two monoprotic acids, acid (1) being the stronger. The arrays are $\{e_1, e_2\}$; $\{1,1\}$; $\{1,0\}$; $\{0,1\}$; $\{0,0\}$. Of these, $\{1,1\}$ corresponds to the neutralization of any strong acid present in the sample, $\{0,1\}$ to the titration of acid (1) and $\{0,0\}$ to the titration of both acids. $\{1,0\}$ is a false equivalence point because when an amount of base equivalent to acid (2) has been added, HA_1 does not predominate.

The procedures presented here can be supplemented by others which, for instance, plot the titration curve or its derivatives, calculate the titration errors from assumed uncertainties in the determination of the pH of the equivalent point, and so on. The analyst can then obtain from simulations most of the information needed for the design of a titration.

REFERENCES

1. D. J. Leggett, *Talanta*, 1977, **24**, 535.
2. R. Sara and E. Still, *J. Chem. Educ.*, 1977, **54**, 348.
3. I. M. Kolthoff, P. J. Elving and E. B. Sandell (eds.), *Treatise on Analytical Chemistry*, Pt. I, Vol. 1, p. 454. Interscience, New York, 1961.
4. D. Dyrssen, D. Jagner and F. Wengelin, *Computer Calculation of Ionic Equilibria and Titration Procedures*, p. 242. Almqvist & Wiksell, Stockholm, 1968.
5. W. S. Dorn and D. D. McCracken, *Numerical Methods with Fortran IV Case Studies*, Wiley, New York, 1972.

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ANNOTATIONS

A SIGNAL-COMPARISON PARAMETER FOR ZEEMAN BACKGROUND-CORRECTED SPECTROMETERS

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Summary—An ideal background-corrected spectrometer is suggested as a standard to which the sensitivity of any practical Zeeman-corrected spectrometer can be related. Appropriate equations describing the relation are derived.

At the present time there are no general parameters in use by which the experimentally observed signal magnitudes of different types of Zeeman-modulated (ZM) spectrometers can be compared. In view of the current variety of ZM spectrometer designs,[1–7] such a parameter would be of potential value as a measure of the efficiency with which the Zeeman effect is applied in any particular instrument to obtain a background-corrected signal: thus it would fulfil a function analogous to the 1% absorption sensitivity of conventional AAS. The purpose of the present communication is to suggest a basis for a suitable parameter of this nature.

An ideal background-correction technique should give an analyte signal with a magnitude, s_i, which is not affected by the background-correction process. The signal observed in practice, s_0, is often less than s_i. In the case of a ZM spectrometer this is usually due to a reduction in the atomic-absorption coefficient of the π-components combined with a finite absorption coefficient for the σ-components of the multiplet. A general comparative parameter, Z, applicable to any absorption instrument, can be defined by

$$Z = s_i/s_0 \qquad (1)$$

Thus Z is a measure of the ideality of the background-correction process. It can also be interpreted as the factor by which the 1% absorption sensitivity concentration for a single-beam instrument would have to be changed to maintain a constant signal upon application of the particular background-correction technique considered.[7]

Let $I_\parallel$ = source intensity polarized parallel to the magnetic axis
$I_\perp$ = source intensity polarized perpendicular to the magnetic axis
$s_\parallel$ and $s_\perp$ = electronic signals corresponding to $I_\parallel$ and $I_\perp$
$K_\parallel$ and $K_\perp$ = experimental atomic-absorption coefficients corresponding to $I_\parallel$ and $I_\perp$
${}^0K$ = experimental atomic-absorption coefficient of $I_\parallel$ or $I_\perp$ for the same instrument at zero field strength.
N = number of atoms in the absorption path.

Superscripts 0 and t will be used to denote intensities incident on and transmitted through the atomizer.

Then
$${}^tI_\parallel = {}^0I_\parallel \cdot e^{-K_\parallel N}$$
and
$${}^tI_\perp = {}^0I_\perp \cdot e^{-K_\perp N}$$
where
$${}^0I_\parallel = {}^0I_\perp = {}^0I$$

Most ZM spectrometers combine ${}^tI_\parallel$ and ${}^tI_\perp$ by one of the signal processing techniques in (*a*) or (*b*) below.

(*a*) The output signal s is taken as the difference between the absorbances with and without background correction:

$$s = \ln {}^tI_\parallel/{}^tI_\perp$$
$$= -(K_\parallel - K_\perp)N$$

but the maximum (*i.e.* ideal) value of $s = s_i$ occurs when $K_\parallel = {}^0K$ and $K_\perp = 0$ (*e.g.*) a normal Zeeman triplet at high field strength).

Then
$$Z = {}^0K/(K_\parallel - K_\perp) \qquad (2)$$

where $K_\parallel$ and $K_\perp$ should be measured directly on the $s_\parallel$ and $s_\perp$ channels of the spectrometer concerned, to allow for effects such as inefficient polarization separation of $I_\parallel$ and $I_\perp$.

(*b*) Output signal $= s = I_\perp - I$

This type of signal processing represents an approximation which is only valid at low N.[7]

Then
$$s = {}^0I(e^{-K_\perp N} - e^{-K_\parallel N}) \simeq {}^0IN(K_\parallel - K_\perp)$$
$$s_i = {}^0IN{}^0K$$
$$Z = {}^0K/(K_\parallel - K_\perp) \text{ as before.}$$

The consistency of equation (2) for other types of signal processing can be demonstrated similarly.

The derivation above applies to ZM instruments using the transverse Zeeman effect. For instruments using the longitudinal effect[2] the treatment is exactly analogous, and gives $Z = {}^0K/|K_{\sigma^+} - K_{\sigma^-}|$.

For instruments using a.c. magnetic modulation[4] equation (2) becomes

$$Z = {}^0K/(K_s - K_R) \qquad (3)$$

where K_s and K_R are the experimental atomic-absorption

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coefficients for the sample and reference signal channels of the spectrometer.

Equation (3) is of a general form and can be applied directly to other types of background-corrected instruments. Thus the Z parameter of equation (1) permits the signals of different ZM spectrometers to be compared both with each other and with non-ZM atomic-absorption instruments.

REFERENCES

1. T. Hadeishi and R. D. McLaughlin, *Science*, 1971, **174,** 404.
2. T. Hadeishi, *Appl. Phys. Lett.*, 1972, **21,** 438.
3. R. Stephens and D. E. Ryan, *Talanta*, 1975, **22,** 659.
4. Y. Uchida and S. Hattori, *Oyo Butsuri*, 1975, **44,** 852.
5. J. B. Dawson, E. Grassam, D. J. Ellis and M. J. Keir, *Analyst*, 1976, **101,** 315.
6. H. Koizumi and K. Yasuda, *Spectrochim. Acta*, 1976, **31B,** 523.
7. R. Stephens, *Talanta*, 1978, **25.**

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INFORMATION EFFICIENCY OF ANALYTICAL METHODS

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Summary—The concepts of information efficiency and profitability are discussed in relation to analysis.

Chemical analysis is defined as a process of obtaining relevant information on the chemical composition of matter. It is advantageous not only to obtain all the information necessary, but also to obtain it with the highest possible degree of efficiency. In order to assess the information properties of analytical results, the concept of information content was introduced[1,2] and in order to evaluate analytical methods, the ideas of time–information performance and specific price of information were formulated.[3] The last two are also suitable for optimization of analytical processes, but they are concerned solely with the accuracy (and its accordance with the preliminary assumption about the composition of the analysed sample) and the time or costs, respectively, required for carrying out the analysis. The complete evaluation of an analytical method as defined by Kaiser and Specker,[4] however, ought to comprise: (1) the accuracy expressed either by means of the standard or relative standard deviation, or as a signal-to-noise ratio; (2) the number of simultaneously determinable elements or compounds or the disturbing influence of other possible components of the analysed sample (*i.e.* specificity in one-component determination by a chemical method or selectivity in a simultaneous determination of more than one component by an instrumental method); (3) in local analysis, planar or spatial differentiating ability in determining the composition of different parts of a solid; (4) suitability for automatic control of production processes, particularly from the point of view of time-differentiating ability; (5) time needed to carry out the analysis; (6) costs of the analysis. To optimize an analytical method and/or to assess its suitability for solution of a particular analytical assignment, it will be convenient to include all parameters characterizing these properties [(1)–(6)] of an analytical method in a single relation.

A variable that would meet all these requirements can be called the *information efficiency* and defined as

$$E = \prod_{i=1}^{k} e_i \qquad (1)$$

where e_i is the efficiency coefficient and is assigned the values

$$e_i = \epsilon_i \text{ for } \epsilon_i \leq 1$$

$$e_i = 0 \text{ for } \epsilon_i > 1$$

ϵ_i being the degree of efficiency, defined[3] as the ratio of the value of the variable characterizing a property needed for solution of a given analytical assignment to the value of the same variable which the given analytical method provides. For example,

$$\epsilon_1 = I_p/I_A \qquad (2)$$

where I_p is the required information content and I_A is the information content actually provided by a given analytical method[2,3] and determined by the accuracy by means of the relation

$$I = \ln \frac{(x_{max} - x_{min})\sqrt{n}}{2s_x \cdot t_{xv}}. \qquad (3)$$

Because $\bar{x}/s_x$ is the signal-to-noise ratio (SN), where x_{max} and x_{min} give the range of n determinations with standard deviation s_x and t is Student's t-value for $x_{min} \ll x_{max}$, then at the fullest possible utilization of the whole measuring range of the apparatus, the relation (3) can be transformed into

$$I = 2.30 \log (k.\text{SN}) \qquad (4)$$

where, $k\ (= \sqrt{n}/2t_{xv})$ is constant for a given analytical process. The relation (2) may then be rewritten as

$$\epsilon_1 = \frac{\log [k_p.(\text{SN})_p]}{\log [k_A(\text{SN})_A]} \qquad (5)$$

where k_A and k_p are constants for a given problem and a given analytical method[1,5] and $(\text{SN})_p$ is the required and $(\text{SN})_A$ the real parameter of precision, which has the significance of the signal-to-noise ratio.[4] Similarly we can define $\epsilon_2 = n/N$, where n is the number of components to be determined and N is the number of components that can be determined simultaneously by a given analytical method. Obviously, in the case of $N > n$, each component included in n must also be included in N. Another degree of efficiency concerns local analysis and is defined as $\epsilon_3 = a/A$, where a is the required and A the real geometric resolution capability[7] of the equipment which is to be used for the analysis. The coefficient $\epsilon_4 = \theta$ where θ is the time for the solution of the problem needed and Θ the attainable time-resolution capability of the method. While the degree of efficiency ϵ_3 acquires significance only in local microanalysis, ϵ_4 is of use only in process analysis, *i.e.* in the case of systems changeable in time. In all other cases the value $e_i = 1$ is substituted in relation (1) for ϵ_3 or ϵ_4. Finally $\epsilon_5 = t_A/t_p$ may be defined, where t_A is the time needed to carry out the analysis and t_p the time within which the results should be available.[3] Other degrees of efficiency could be defined by simple analogy, provided other properties of an analytical method are definable by quantitative variables.

Table 1. Comparison of analytical methods for determination of manganese in low-alloy steels

Analytical method	Relative standard deviation (s_r), %	Number of determinable components, N	Time t_A, *min*	Relative costs, *currency units*	Amount of information $M(p, p_0)$, *bits*	Information efficiency E	Information profitability P, *bit/currency unit*
1. Titrimetry (persulphate–silver nitrate, after double ZnO separation)	2	1	60	16	4.00	(a) 0.018 (b) 0 (c) 0	0.0044 0 0
2. Potentiometric titration	2	1	30	8	4.00	(a) 0.088 (b) 0.42 (c) 0	0.0044 0.21 0
3. Photometry (permanganate)	3	1	30	8	3.41	(a) 0.010 (b) 0.49 (c) 0	0.0044 0.21 0
4. Atomic-absorption spectrophotometry	1	1	20	6	5.00	(a) 0.0047 (b) 0.22 (c) 0	0.0039 0.19 0
5. Optical emission spectroscopy	5	50	3	1	133.8	(a) 0.000026 (b) 0.0013 (c) 0	0.0035 0.17 0
6. Optical emission spectrography	10	50	30	12	83.8	(a) 0.0042 (b) 0.020 (c) 0	0.0029 0.14 0
7. Optical emission spectrometry	5	50	1	20	133.8	(a) 0.0000087 (b) 0.00042 (c) 0.0063	0.000058 0.0028 0.042

Optimally, the information efficiency can be $E = 1$, if the value of all the coefficients is $e_i = 1$. As a rule, however, at least one of them is smaller than unity and $E < 1$; from this it ensues that in most cases the utilization of analytical methods for practical purposes is suboptimal and the value of E characterizes the relative suitability of an analytical method for a given purpose. If any of the degrees of efficiency is $\epsilon_i > 1$, then $e_i = 0$ and thus also $E = 0$, which means that the analytical method is not applicable for solution of the given problem. In such a case the concept of information efficiency has no meaning.

Another variable highly useful in practice is the *information profitability*, defined as

$$P = E/\tau\, M(p, p_0) = E/C \qquad (6)$$

where $M(p, p_0) = \Sigma_i I(p, p_0)_i$ is the amount of information[5] obtained through simultaneous determination of N components, the information content of determination of the ith component, $I(p, p_0)_i$, being expressed by means of Kullback's divergence measure,[1,6] τ the cost of the analysis and C the specific price of the information, already defined[3,5] as $C = \tau/M(p, p_0)$. The information profitability is expressed in natural or binary units per currency unit. It indicates the amount of information obtainable for specific financial costs with simultaneous regard to the degree of efficiency with which the given analytical method is employed.

Application of a specific analytical method for a given analytical problem may be wholly profitable, even though it might be less efficient than other methods. This can be demonstrated in the case of manganese determination in low-alloy steels (0.05–6% Mn) if the result should be of such precision that the relative standard deviation $s_r = 10\%$ and the duration of the analysis should be shorter than (*a*) 1 day (1440 min), (*b*) 30 min or (*c*) 2 min. Table 1 shows the correlation of parameters and information efficiency according to relation (1) or information profitability according to relation (6), for seven possible analytical methods. For case (*a*) methods 1, 2 and 3 are evidently of greatest efficiency, greater by two orders and more than the spectroscopic methods. In spite of that, the profitability of methods 1–6 is nearly equivalent since the specific costs of analysis carried out by means of the spectroscopic methods 5 and 6 are lower than the specific costs of analysis performed by methods 1, 2 and 3. If the result of the analysis is to be available within the time $t_p = 60$ min, [*i.e.* case (*b*) or (*c*)], then application of method 1 is out of the question because for that method, $e_5 = 0$ and thus $E = 0$ and $P = 0$. If the result is required within the time $t_p = 2$ min, the only applicable method is method 7 (emission quantometry), but its profitability is rather low for the analysis can be carried out only at relatively high cost.

The variables of information efficiency and information profitability are of use in all those cases in which it is sought to assess suitability of application of a particular method in a particular analytical assignment and to compare it objectively with other possible methods. In addition, they allow selection of optimal analytical methods when, for example, a decision is to be taken about the equipment of an analytical control laboratory.

REFERENCES

1. K. Eckschlager, *Z. Anal. Chem.*, 1975, **277**, 1.
2. *Idem*, *Anal. Chem.*, in the press.
3. K. Danzer, *Z. Chem.*, 1975, **15**, 326.
4. H. Kaiser and H. Specker, *Z. Anal. Chem.*, 1956, **149**, 46.
5. K. Danzer, *Z. Chem.*, 1973, **13**, 69.
6. S. Kullback, *Information Theory and Statistics*, Wiley, New York, 1959.
7. K. Danzer, *Z. Chem.*, 1974, **14**, 73.

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ANALYTICAL ASPECTS OF LEAD SORPTION BY SOLIDS

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Summary—A critical account is given of the factors affecting preconcentration of traces of lead from solution by adsorption on various substrates. The recovery by various stripping techniques is also considered. Direct determination is recommended in preference to use of stripping methods.

It is now recognized that the soluble heavy metal ion content of environmental water samples can be influenced by parameters such as pH, the chemical form of the metal ion, and the sorptive power of associated suspended matter and sediments. Separation of the aqueous layer from solid phases during sampling or subsequent preparation steps removes a component of an equilibrium system, and the metal ions need to establish a new stable state. This can result in adsorption on container walls, hydrolysis, dissociation of complex species, *etc.*

If we consider the specific case of lead, it has been shown,[1] for example, that one third of the lead from a 400-μg/l. solution can be lost to a glass container in 5 minutes, and half can be adsorbed in an hour unless appropriate precautions are taken. Acidification of the solution (*e.g.*, to pH 2) is recommended for stabilizing water samples, while the addition of hydrogen peroxide[1] or EDTA[2] has been proposed for stabilizing standard solutions of μg/l. concentrations.

In recent years, our group has been interested in an associated aspect of this type of problem, namely, the effect of pH and complex formation on the uptake of heavy metal ions by clays[3,4] and cellulose,[5] and some comparison studies have been made with charcoal. The results obtained prompted an investigation of the potential of these solids as preconcentrating agents. The sorption studies also highlighted some sources of analytical error that are easily overlooked.

Preconcentration of lead ions on charcoal

Some interest has been shown in the "fixing" of the metal content of solutions on solids, partly because the process may be selective or stabilize the chemical form of metal ion, partly because separation of the phases in the field could eliminate transport of liquid samples, and partly because of the large preconcentration factors which can be achieved.

The ability of activated charcoal to scavenge traces of heavy metal ions, or their complexes, from solution has led a number of workers to adopt this material as a preconcentration medium (e.g. for Cu in sea-water,[6] several trace elements in solution,[7] anionic complexes of Hg, Cd, Zn,[8] *etc.*). A preliminary chelation or precipitation step prior to adsorption has been proposed for the isolation of the trace components (Ag, Bi, Cd, Co, Cu, Ni, Pb, Zn) present in a range of inorganic materials.[9–11] The metal content of the solid matrix has been evaluated by means of atomic-absorption spectroscopy (on nitric acid extracts[6,9–11] or a suspension in dilute acid[12]), emission spectroscopy,[7] neutron activation, X-ray fluorescence or spark-source mass-spectrometry.[13]

A re-examination of the efficiency of activated charcoal as a scavenger for Pb (made by using carbon-cup atomic-absorption spectroscopy to monitor filtrate levels) has confirmed its extractive power at levels as low as 2 μg/l. At the same time the study has highlighted some artifacts which could be of interest to those contemplating the use of this solid as a preconcentration medium.

The activated charcoal used in this study (85-mesh) was purified by washing successively with hot 0.1*M* EDTA, water, 0.1*M* nitric acid and water, and dried at 150° for 12 hr. The lead content of this material was about 4 μg/g. A more rigorous purification procedure has recently been outlined.[13]

Portions of the solid (0.50 g) were added to litre volumes of solution, shaken to mix well, and then allowed to stand. With lead nitrate solutions at pH ~ 4.5, the fraction of lead adsorbed increased with decreasing total lead loading (*e.g.*, ~96% with 2000 μg, ~99% with 100 μg). With low total loadings, uptake was not significantly reduced by reducing the pH to 2, or by adding a slight excess (~200%) of EDTA or NTA relative to lead.

While the charcoal proved to be an excellent collector, no satisfactory recovery procedure was found. Treatment of the isolated lead-bearing solid with hot acid (0.1*M* nitric acid) released only a fraction of the total uptake (*e.g.*, 25–35%). This result is consistent with the observation that lead is sorbed by charcoal in the presence of acid.

Bonding of the Pb–EDTA complex to charcoal is not as strong, and as a result extraction with hot 0.1*M* EDTA released a significant proportion of the total uptake (*e.g.*, from 60% (2000 μg) to 80% (100 μg of lead)). An acid wash, after the digestion of the charcoal filter pads with EDTA, improved the efficiency of the extraction process, but the per cent recovery still varied with total load, and the precision was so poor that chemical extraction could be discarded as a method of recovery.

Alternative approaches include matrix destruction or direct examination of the "metal-loaded solid".

Wet ashing was briefly investigated, but the results were not encouraging. Dry ashing at 600°, followed by leaching of the residue with a few ml of nitric acid gave nearly quantitative recoveries with very low loadings, but in general the recoveries varied with total load, temperature, time of ashing, *etc.* There were obvious losses attributable to volatilization of vapour, interaction with crucible surfaces *etc.*

The final option, namely direct examination of the isolated solid (by techniques such as neutron activation, XRF, emission spectroscopy or spark-source mass-spectroscopy[7,13]) must be recommended.

Collection on cellulose or membranes

Cellulose is capable of adsorbing lead ions from solution, the capacity depending on purity and solution pH. Filter papers[14] have been shown to have a capacity

of about 800 μg/g, and studies[13] with cellulose powder indicate that the capacity increases with pH (*e.g.*, from about 600 μg/g at pH 3.5 to 2000 μg/g at pH 5). At pH > 6 uptake from solution is nearly quantitaive owing to precipitation of hydrous oxide species, unless the lead is present as stable complex ions.

With lead ion concentrations of < 20 mg/l., uptake is controlled by an adsorption isotherm and total removal of metal ion from solution is not achieved. While cellulose is thus an unsuitable matrix for preconcentration, its sorptive powers can introduce errors during manipulative steps such as filtration through a paper disc.

The amount of metal ion sorbed by cellulose products initially varies with time, and as a result, less is retained during filtration than on prolonged contact, but the amount of lead withdrawn from solution can still be significant, (*e.g.*, > 50% of total content at < 10 mg/l. levels). The losses are not necessarily reduced to zero in the presence of acid, particularly if suspended matter has accumulated during the filtration process.

It has been proposed that the sorptive power can be enhanced by preparing papers saturated with dithizone or potassium dichromate, but in our studies we did not observe any marked increase in metal ion retention. An alternative is to use ion-exchange papers of different types. We found uptake to be slow and the degree of lead retention variable.

Cellulose cannot be totally disregarded as a "fixing" medium, since some useful applications are already known. For example, filter paper has been used to fix Pb in blood samples,[15] or to retain salts concentrated by the ring oven technique, and it has been investigated as a support for trace analysis standards.[16]

In preconcentration procedures based on precipitation, filtration is an important component step. The efficiency of this step may be improved by substituting membrane filters for paper but this does not necessarily ensure total recovery of metal ion. For example, when dilute lead solutions (mg/l. levels) were treated with an excess of precipitant ions such as S^{2-}, CrO_4^{2-}, CO_3^{2-} or $C_2O_4^{2-}$, significant amounts of lead was found in the filtrate. Inclusion of a host system (*e.g.*, La^{3+}/NH_3; Ba^{2+}/CrO_4^{2-}; Ca^{2+}/CO_3^{2-} or $C_2O_4^{2-}$) did not eliminate these residual levels. The addition of S^{2-} in the presence of Cu^{2+} yielded minimum soluble lead levels, but in this case the affinity of the sulphide precipitate for the vessel walls made quantitative recovery of the precipitate difficult.

Studies with organic precipitating reagents were not made since their effectiveness as components of solvent extraction procedures is well documented.

Sintered-glass filter supports

Some mass-balance studies were included in the studies of adsorption on filter paper. It was found that the amount of lead on the paper (determined by punched-disc, carbon-cup AAS) plus the content in the filtrate did not equal the original total lead loading. Pretreatment of the filter system with ammonia or sodium bicarbonate solution decreased the level in the filtrate, and enhanced both the amount on the paper level and the magnitude of the amount missing.

The additional adsorbent system present proved to be the sintered-glass disc used to support the filter. Passage of solutions (containing 1–4 μg of lead) directly through the support resulted in much of the lead being retained. There were distinct memory effects, with lead being released to more dilute solutions in amounts which varied with the concentration of lead in the sample previously filtered. Acid washes, after the filtration, released variable amounts of sorbed metal ion and did not eliminate the metal ion adsorption. The activity of the frit was increased by preliminary alkaline washes, and the amount of lead retained increased with time of contact, *i.e.*, with decrease in filtration rate.

The retention of lead by the support should have been predictable, since the affinity of lead for glass is well known[1] and it had been noted previously that a 30-ml soft glass tube adsorbed up to 35 μg of lead from 2-mg/l. lead solutions.

General comments

With the advent of analytical techniques capable of making determinations at the μg/l. level, the use of preconcentration procedures is regarded by many as an unnecessary complication. While this comment is justified for laboratory work, there still remains the problem of sample deterioration after collection.

The studies reported in this note imply that filtration of a natural sample prior to acidification can lead to significant losses of lead; acidification before filtration releases metal ion from suspended matter such as clays[1,2] or organic matter. These effects will be most pronounced at the μg/l. level. Fixation of the lead content on a solid matrix during sampling would not necessarily eliminate such problems. For example, the solid retrieved from unfiltered samples would contain both added matrix and suspended matter from the water.

Purified activated charcoal has the appropriate scavenging power for use as a preconcentration medium but for accurate recovery values the support needs to be examined directly; analyses of acid extracts appear to be subject to major errors and unsuitable for lead determinations.

Undesirable side-effects might be reduced by using other types of solid "extractants" and further studies in this field could readily be justified. Chelating resins have been widely used to collect the traces of metal ions present in waters, and superficially this approach appears to be nearly ideal, but even with this technique, uptake can be variable.[17] Other systems which have received some attention are sorption by chemically treated polyurethane foams or organic reagent suspensions. For some metal ions (including Pb) electrochemical deposition could prove to have distinct advantages. This approach is already widely used in anodic stripping voltammetry, and has been investigated as a preliminary stage for other techniques such as atomic-absorption spectroscopy.

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REFERENCES

1. H. J. Issaq and W. L. Zielinski, *Anal. Chem.*, 1974, **46**, 1329.
2. T. Fuyinaga, T. Kawamoto, M. Koyama and E. Kamano, *Nippon Kagaku Kaishi*, 1976, 1395; *Chem. Abstr.*, **87**, 106596.
3. H. Farrah and W. F. Pickering, *Aust. J. Chem.*, 1976, **30**, 1167, 1177, 1649; 1977, **30**, 1417.
4. *Idem, Water Air Soil Pollution*, 1977, **8**, 189; 1978, **9**, 23 and in the press.
5. *Idem., Aust. J. Chem.*, 1978, **31**, 150.
6. W. B. Kerfoot and R. F. Vaccaro, *Limnol. Oceanog.*, 1973, **18**, 689.
7. K. L. Lazebruk, M. I. Ovoutsku, A. N. Tomashevoskaya and I. A. Tarkovskaya, *Adsorbtsiya Adsorbenty*, 1974, **2**, 57; *Chem. Abstr.*, **81**, 114117.
8. H. Yoshida, K. Kamegawe and S. Arita, *Nippon Kagaku Kaishi*, 1977, 1231; *Chem. Abstr.* **87**, 141745.
9. E. Jackwerth, *Z. Anal. Chem.*, 1974, **271**, 120.
10. E. Jackwerth and H. Berndt, *Anal. Chim. Acta*, 1976, **74**, 299.

11. H. Berndt, E. Jackwerth and M. Kimura, *ibid.*, 1977, **93**, 45.
12. E. Jackwerth, J. Lokmer and G. Wittler, *Z. Anal. Chem.*, 1973, **266**, 1.
13. B. Vanderborght and R. Van Grieken, *Anal. Chim. Acta*, 1977, **89**, 399.
14. W. F. Pickering, *J. Chromatog.*, 1960, **4**, 481.
15. A. A. Cernik, *At. Abs. Newsletter*, 1973, **12**, 42.
16. D. E. Ryan and J. Holzbecher, *Anal. Chim. Acta*, in the press.
17. T. M. Florence and G. E. Batley, *Talanta*, 1975, **22**, 201.

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LETTER TO THE EDITOR

A FURTHER NOTE ON THE SAMPLING CONSTANT EQUATION

Sir:

A general sampling constant equation has been proposed:[1,2]

$$\underline{K}_s = \underline{R}^2\underline{w} = \frac{(\underline{B}\underline{d}_B - \underline{H}\underline{d}_H)^2\,(\underline{B} - \underline{K})(\underline{K} - \underline{H})\underline{u}^3}{\underline{d}_B(\underline{B} - \underline{K})(\underline{B} - \underline{H}) + \underline{d}_H(\underline{K} - \underline{H})(\underline{B} - \underline{H})} \cdot \frac{10^{-8}}{\underline{K}^2} \qquad (1)$$

in which $\underline{K}_s$ is the sampling constant for an element X in a mixture to be sampled (i.e., the weight in grams which must be taken to ensure a sampling uncertainty of no more than 1% with 68% confidence), $\underline{R}$ is the relative sampling uncertainty (in % of the amount present) when a $\underline{w}$-gram sample is taken, $\underline{K}$ is the overall X-content of the mixture, $\underline{B}$ and $\underline{H}$ are the X-contents of the minerals in a two-component mixture of uniform linear grain size $\underline{u}$ (μm) which has the same sampling characteristics as the real mixture to be examined, and $\underline{d}_B$ and $\underline{d}_H$ are the densities, in g/cm^3, of the two minerals.

The sampling constant $\underline{K}_s$ may be found experimentally by identifying $\underline{R}$ with the coefficient of variation in a series of assays using $\underline{w}$-gram samples, or estimated from (1) if $\underline{B}$, $\underline{H}$, $\underline{K}$, $\underline{d}_B$, $\underline{d}_H$ and $\underline{u}$ can be found.

Given an estimate of $\underline{K}_s$, the relative sampling uncertainty to be expected when a sample of $\underline{w}$ grams is taken can be calculated from

$$\underline{R} = \sqrt{\underline{K}_s/\underline{w}} \qquad (2)$$

or, if a series of assays is available, the analytical uncertainty may be estimated: if $\underline{C}$ is the observed coefficient of variation,

$$\underline{R}_{\text{analytical}} = \sqrt{\underline{C}^2 - \underline{K}_s/\underline{w}} \qquad (3)$$

This device is valuable during the testing of determinative methods using standard reference materials for which sampling constants are reported in certificates of analysis.[3]

The most useful approximation of (1) is

$$\underline{K}_s \sim 10^{-8}(\underline{B} - \underline{H})(\underline{K} - \underline{H})\underline{u}^3\underline{d}_B/\underline{K}^2 \qquad (4)$$

which applies when the constituent of interest resides in a minor mineral, as in ores of heavy metals. In (4), $\underline{d}_B$ is the density of this minor mineral and $\underline{B}$ is its X-content; $\underline{u}$ is often well estimated from the screen through which the material has been passed, and $\underline{H}$ is the X-content of the gangue. The overall content, $\underline{K}$, must of course be expressed in the same units as $\underline{B}$ and $\underline{H}$. This approximation has been used[4] in a scheme for evaluating exploration data carrying large sampling errors.

Several correspondents have pointed out that when the two minerals in a mixture have $\underline{B}\underline{d}_B = \underline{H}\underline{d}_H$, the sampling constant calculated from (1) is zero, and this appears to be incorrect. For example, a mixture of a mineral with 20% beryllium and density 2 g/cm^3 with a gold alloy of density 20 g/cm^3 and 2% beryllium gives $\underline{B}\underline{d}_B = \underline{H}\underline{d}_H$, and hence $\underline{K}_s$ equal to zero.

The difficulty lies in the Bernoulli (binomial) relationships

$$R_H = \frac{100}{\sqrt{n}}\sqrt{\frac{q}{p}} \quad \text{and} \quad R_B = \frac{100}{\sqrt{n}}\sqrt{\frac{p}{q}} \qquad (5)$$

where R_H and R_B are the relative errors incurred in sampling the constituents with X-contents H and B respectively, p and q are their volume proportions in the mixture, and n is the number of equant grains in a sample of w grams. These relationships are used in deriving (1) as though n is a constant, which it is not, for equal-sized grains, unless $d_B = d_H$. However, when $Bd_B = Hd_H$, each equant grain of either species contains the same weight of the element of interest (beryllium in the example given above), and substitution of a grain of one species with a grain of the other does not change the X-content of the sample, though it does alter the sample weight.

Equation (1) thus applies exactly only to samples of constant volume, not to samples of constant weight. Only in extreme cases will the number of equant grains in a sample of w grams, and consequently its volume, vary appreciably from one sample to another. In such cases, the approximation (4), which has been shown by other means[5] to apply when p is large and q is small, is applicable.

These considerations point up the fact, noted by Wilson[6] and others, that the statistics of sampling depend on volume proportions, though we are actually interested in weight proportions. The claim previously made,[2] that (1) is free from approximations, is therefore not strictly correct; the approximation implicit in (5) is incorporated in (1).

It may be noted that most real mixtures contain more than two minerals and particles of a wide range of grain sizes: estimates of the parameters B, H, d_B, d_H and u must always be rather artificial. Development of (1) and (4) depends on the proposition[7]

> "The sampling characteristics of most mixtures in which a single element X is of interest may be duplicated in a hypothetical mixture of uniform grain size which contains only two minerals, each of different X-content."

The adjective "equant" has been used[8] to describe the grains in such a mixture: an equant grain is a grain in the hypothetical mixture which has the same sampling characteristics as the real mixture to be examined. An equant grain need not have the same density, mesh size or composition as a real grain. Nevertheless, in most cases, useful estimates of the physical characteristics of the hypothetical mixture can be made from corresponding characteristics of the real mixture.

The assistance of several correspondents and colleagues in preparing this letter is very much appreciated.

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REFERENCES

1. C.O. Ingamells and P. Switzer, Talanta, 1973, 20, 547.
2. C.O. Ingamells, Talanta, 1976, 23, 263.
3. J.C. Engels and C.O. Ingamells, Geostandards Newsl., 1977, 1, 51.
4. C.O. Ingamells, F.F. Pitard, J.J. Fox, P.K. Samland and M.J. Bright, Proceedings, IUPAC International Symposium on Analytical Chemistry in the Exploration, Mining and Processing of Materials, Johannesburg, 1976, Abstract No. 68.
5. C.O. Ingamells, Talanta, 1974, 21, 141.
6. A.D. Wilson, Analyst, 1964, 89, 18.
7. C.O. Ingamells, Geochim. Cosmochim. Acta, 1970, 38, 1225.
8. J.C. Engels and C.O. Ingamells, ibid., 1970, 34, 1007.

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TALANTA REVIEW*

THE APPLICATION OF GAS CHROMATOGRAPHY TO FOOD ANALYSIS

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Summary—Gas chromatography is widely used in food analysis, especially for trace analysis, determination of volatiles, and identification of sources of adulteration and undesired flavours. The literature on the applications is reviewed.

Gas chromatography (GC) has been applied to food analysis for almost 30 years. Part of the book "Gas Chromatography In Food Analysis" by G. J. Dickes and P. V. Nicholas (Butterworths, London, 1976) reviewed the applications up to 1974 and this review updates the book and appraises the current situation.

There are many areas of food analysis where it is desirable to detect or determine a number of compounds in a given organic class, and the various chromatographic techniques have invariably constituted the main weaponry in the analyst's armoury. Despite the advent and impact of high-performance liquid chromatography (HPLC) in recent years, GC continues to provide a steady flow of analytical methods. The emphasis in research and application of GC to food analysis has changed according to the problems current at the time. In the 1950s, when the basic technique was still being developed, applications were restricted to the classes of organic compounds used in that development, *e.g.*, amino-acids, fatty acids, hydrocarbons and alcohols. When new detector systems were developed in the late 1950s and early 1960s, with increased specificity and sensitivity designed chiefly to help the pesticide-residue analyst, fashion turned to the detection and determination of food additives and contaminants.

A re-examination of the determination of quality-control parameters came with the development of newer volatile derivatives for GC, *e.g.*, trimethylsilyl derivatives of sugars, and with the formation of derivatives having much lower detection limits than the parent compound, *e.g.*, the *N*-trifluoroacetyl derivatives of amino-acids.

The art has naturally advanced considerably since the early 1950s. Quality control analysis is routine and so is the determination of established additives and contaminants. However, as new additives are formulated and legalized or banned, and as the presence of new contaminants is discovered, GC is an automatically considered method of analysis. Currently, there is renewed interest in the determination of mycotoxins, drug residues and compounds leachable from food-packaging materials.

This review is divided into four parts; the first deals with the influence of food analysis on GC technique; the second covers the determination of those compounds naturally present in foods and used to give an assessment of quality; the third deals with the determination of food additives and contaminants; the fourth is a short conclusion which includes value judgements.

INFLUENCE OF FOOD ANALYSIS ON GC TECHNIQUE

The greatest impact that food analysis has had on improving GC technique has been in detector technology and derivative exploitation. Pesticide-residue analysis was the impetus for the development of such detectors as electron capture (EC), alkali metal flame ionization (AFID), flame-photometric (FPD), and microcoulometric (MCD). The many methylation and trimethylsilylation (TMS) derivative methods have been formulated or improved as a result of demands by the food analyst, as have sampling techniques, such as headspace and preconcentration procedures, *e.g.*, solid trapping. The difficult task of trapping and detecting food volatiles has led to the development of cryogenic temperature-programming and some refinements in capillary column technology.

Injection and sample concentration

Because of the complex matrix of many foods, it is only drinks *e.g.*, alcoholic beverages, that can normally be directly injected into the chromatograph. Not surprisingly, this type of sample is suitable for automatic injection, and Stockwell and Sawyer[1] introduced such a system, with an internal standard added before the injection. This system was a modification of

* For reprints of this review, see Publisher's announcement near the end of this issue.

the one designed by Boer.[2] The system was applied to automatic sampling of tinctures and essences for determination of dutiable spirit.[3]

The direct GC analysis of headspace vapours over food products eliminates the risk of artefact formation in concentration procedures, and is the easiest and most convenient way to study volatile flavour and aroma components. The container can be fitted with a rubber stopper or septum which is penetrated with a syringe needle for sampling.[4–6]

Gases may be sampled with gas-sampling loops or large-volume gas-tight syringes, and specially toughened syringe needles are available for direct insertion into the headspace of food cans and other containers, without opening them. Such a procedure was used by Novák *et al.*[7] for taking representative liquid or gaseous samples from moderately pressurized containers, *e.g.*, canned beverages. The headspace technique was used by Sinclair *et al.*[8] for the determination of dimethyl sulphide in beer. The sample was chilled to 0° and mixed with sodium chloride, and n-butanol was added as internal standard. The mixture was left at 30° for 1.5 hr before the headspace was sampled.

Fore *et al.*[9] and Dupuy *et al.*[10] used the headspace technique for the determination of residual propan-2-ol and acetone in oilseed meals and flours. Headspace above wine was analysed for volatiles by Bertuccioli and Montedoro,[11] who used a 2-litre syringe as container and so could sample the vapour directly; the sample was passed through a Porapak Q trap to remove ethanol and water, which would otherwise swamp the other volatiles.

For the detection of trace components some advantage may be obtained by using the cryogenic injection technique of Rushneck[12] in combination with large headspace samples.[13] In this procedure, successive injections are made into the GC and the sample is condensed at low temperatures in the initial portion of the column. After temperature-programmed GC the trace components are thus accumulated in amounts sufficient for detection.

A novel technique was used by Senanayake *et al.*[14] for analysis of the root, stem, bark and leaves of *cinnamon zeylanicum* for terpenes. Between 15 and 60 mg of thin strips of plant material were placed in a stainless-steel gauze basket fitted inside the injection port, and the unit was heated at 180° for 5 min, with the GC column kept cool; the volatiles were then swept on to the column. β-Caryophyllene was detected in greater amount by this technique than by others which required sample treatment.

Brown *et al.*[15] also used a liner as a pre-column for the study of volatiles from peanuts. Such pre-columns in the form of packed injection-port liners have been used extensively in the GC determination of volatiles where it was necessary to remove the non-volatile material. A large sample was diffused into a packed liner, which was inserted in the heated injection port so that the volatiles could be swept directly on to the column. Injection-port liners packed with sand were used initially but glass wool appears to be favoured.[16] Dupuy *et al.*[17] trapped the volatile components of salad oils and shortenings in a glass liner containing glass wool. The liner was subsequently placed in the inlet system of the GC and the volatiles released at 120°. Besides the natural components there would be any residues of solvents, *e.g.*, aliphatic hydrocarbons. Hexane residues, when present in vegetable oils, can be released by this method.[18] Bonney *et al.*[19] used a system of concentric liners, *i.e.* an inner one of glass surrounded by one of stainless steel, when examining hop extracts for methyl esters of fatty acids. Non-volatile material trapped in the liners could be periodically removed.

The limitation of headspace analysis can be the requirement of exceedingly large volumes of headspace vapour for detection of trace amounts of many components. The minor components may be so diluted with carrier gas that they escape detection. Low-temperature GC pre-columns are often used to concentrate headspace vapours.[20,21] Such a method for concentration was chosen by Morgan and Day[22] in the analysis of flavour volatiles. A screw-capped vial containing sufficient anhydrous sodium sulphate to saturate the aqueous sample was left overnight in an oven at 105°. The sample was then added, a drilled cap containing a silicone rubber liner was fitted and the vial was attached to the apparatus. The vial was heated to the desired entrainment temperature and agitated intermittently. Carrier gas was passed through the apparatus into the GC column where the volatiles were condensed in the initial portion of the column, which had been cooled in solid carbon dioxide. At the end of the entrainment period the column was disconnected from the apparatus and coupled to the GC injection port. The oven was heated to the analysis temperature and GC carried out in the usual manner.

The other important technique for concentration of volatiles is adsorption on an activated solid, such as charcoal.[23,24] Hartman *et al.*[25] isolated and concentrated volatiles from vegetable oil by bubbling helium through the sample, heated to 350°. The volatile components were collected in activated charcoal over a period of 2 hr and then extracted with carbon disulphide containing an internal standard. A 400-fold concentration of the volatiles was achieved with this procedure, which gave good reproducibility.

The development of porous polymers as trapping materials in GC (because of their adsorption and retention properties) has led to a greater use of the solid trapping technique. Murray[26] concentrated headspace volatiles from wines and spirits on various adsorbents, including Chromosorb 102, 105 and 106 and also Tenax GC (2,6-diphenyl-*p*-phenylene oxide). Novotny *et al.*[27] used Tenax GC to concentrate the volatiles of dried sage leaves.

Alumina and acid-washed Celite 545 were both used as adsorbents by Clark and Cronin[28] for trapping flavour volatiles. The open-tubular glass column

containing the adsorbent was disintegrated in a small volume of water to release the volatiles for GC analysis. A combination of solid and liquid trapping was used by Jennings *et al.*[29] to isolate beer volatiles. The headspace sample was trapped on a small Porapak column which was subsequently back-flushed at 100° with carrier gas, the volatiles being condensed in a cold trap. This double preconcentration was necessary to remove ethanol, which otherwise interfered with the separation of the minor components.

Controlled rate of injection through a pressure-lock system was used by Grob and Grob[29] to prevent decomposition of mustard oil from radishes.

Column materials and temperature programming

Food analysis had little impact on the early development of columns, which was mainly done by the petroleum industry. The analysis of polar compounds, however, which is the main concern of the food analyst, has required some further exploration.

In a study of column efficiency for determination of polychlorinated biphenyls (PCBs) and fatty acid methyl esters, Onuska and Comba[30] modified open tubular glass columns by etching the internal surface with hydrofluoric acid to increase the surface area. The resulting "whiskered" column walls produced an excellent surface for coating. Similar columns were used by Schieke and Pretorius[31] for separation of essential oil components.

It is well known that certain metal columns can cause breakdown of some compounds during GC. Glass columns are generally accepted as non-reactive and Ackman and Sipos[32] have gone a stage further than most workers and incorporated glass linings in the metal connectors in their chromatographs. This refinement aided the separation of the methyl esters of heptadecanoic, heptadecenoic and eicosanoic acids in a lard–corn oil mixture.

Benzotriazole (1% in acetone) has been used to deactivate the stainless-steel transfer lines between column and detector,[32a] to prevent decomposition of thiols present in mixtures of food volatiles.

In a study to obtain an open tubular column coating of maximum separating capacity for the determination of the fatty acid composition of various fatty vegetable oil glycerides, Flanzy *et al.*[33] used Carbowax 20M modified by terephthalic acid to give a layer thickness of 0.1 μm. This gave an efficiency of greater than 70,000 theoretical plates. In the separation of beer volatiles Witheycombe and Lindsay[34] used a 0.03-in. bore open tubular column to increase the capacity of the column coating, compared to the conventional 0.01-in. column. The wider column can carry a loading of 1 mg per peak compared to 5 μg per peak with the narrower one.

The current interest in the erucic acid content of fats and oils has prompted better separation of its methyl ester from the others and Ackman and Eaton[33a] used open tubular columns coated with Silar-5CP to achieve this.

Poly(methyl methacrylate) and a series of polyesters prepared from butanediol and dibasic acids and from alkanediol adipates have been used by Vernon[33b] to separate methyl esters of fatty acids of vegetable oils. These polymers showed a wide range of polarity and high temperature stability, although some, *e.g.*, poly(methyl methacrylate), were inefficient.

In a study of separation of the methyl esters of the fatty acids of rapeseed oil glycerides on a wall-coated open tubular column, Mayzaud and Ackman[35] found that the response with helium or hydrogen as carrier gas was twice that with either nitrogen or argon.

Many ways have been used to overcome adsorption of compounds on the support during GC. Cochrane,[36] in the separation of free fatty acids, incorporated formic acid in the helium carrier gas. It was assumed that formic acid was preferentially adsorbed on the support; there was also the advantage that if any excess was eluted from the column it would not be detected by the FID.

The thermostable cyanopropylphenylsilicone stationary phase, SP-2300, has been used to separate methyl esters of the fatty acids of rapeseed and peanut oils.[35a] The advantage of this stationary phase lies in the relatively short retention times of those compounds containing more than 20 carbon atoms and this results in a speedier analysis.

In an appraisal of polyhydric alcohols as stationary phases for separation of beer volatiles, Verachtert *et al.*[37] found that 10% erythritol was the best of the seven phases tested, overcoming the swamping effect of ethanol and giving good separation of the flavour volatiles.

The separation of 18 alkylamines on various stationary phases modified by trisodium phosphate was studied by Golovnya and Zhuravleva.[38] They used equations relating the retention indices to number of carbon atoms and to boiling points, for evaluation of food aroma components.

The advantages of temperature programming (TP) in GC are well known. The main influence of food analysis in this connection is in cryogenic TP. It is often necessary to use low temperatures in the separation of flavour constituents, and if it is necessary to include the less volatile constituents in the analysis then TP is used, starting at temperatures as low as −80°.[39] The range of cryogenic temperature-programmed GC was widened by Merritt *et al.*[40] to include temperatures starting at −196°, liquid nitrogen being used to cool the column chamber. These workers showed the necessity for employing very low starting temperatures for complete resolution of mixtures containing many volatile components, *e.g.*, those from irradiated samples of beef. Iverson and Sheppard[41] have shown the advantages of normal TP in their separation of the butyl esters of butter fatty acids and also of the methyl esters of the fatty acids of coconut oil glycerides.

An alternative to TP is pressure programming; this has the advantages of instant re-set following a parti-

cular analysis and of less chance of column bleed. Scott[42] used pressure programming to advantage in the analysis of lemongrass oil. Both types of programming can be used together in the analysis of complex essences to obtain increased resolution in a shorter time.[43]

Detectors

The biggest influence of food analysis on detector development is in determination of pesticide residues. The EC detector was initially developed to detect and determine organochlorine (OC) pesticide residues and the previously low sensitivity in organophosphorus (PO) pesticide residue analysis gave the impetus for the development of the AFID, FPD and MCD.

Alkali metal flame ionization detector. In addition to its normal use in OP pesticide residue analysis, the AFID has been used by Lakota and Aue[44] in the determination of OC pesticide residues. Using a potassium chloride pellet and varying the geometry of the electrodes, Verga and Poy[45] obtained good selectivity between nitrogen and phosphorus in the determination of carbamates, triazines and OP pesticides. Gough and Sugden[46] used a rubidium chloride annulus in order to increase stability of the detector, when examining various foods for nitrosamines. They obtained a sensitivity ten times better than that of the orthodox flame ionization detector, and although the sensitivity diminished with age, it could be restored by cleaning. Kawabata[47] found that using glass connections from the column to the detector improved sensitivity in the determination of nitrosamines in fish products.

Flame photometric detector. The FPD developed by Brody and Chaney[48] has extremely high selectivity for both phosphorus and sulphur, together with adequate sensitivity. This makes it particularly suitable for analyses in which the sample solution contains large amounts of co-extracted material. Thus, the application of this detector to the determination of OP pesticide residues in foods has the advantage that there is no need for extensive clean-up before the GC. As well as for pesticide residue analysis, this detector can be used for the determination of sulphur-containing volatiles. One of the problems with the detector is that the flame is often quenched by the solvent vapour and has to be re-ignited. Hasinski,[49] in determining OP pesticide residues in foods, altered the geometry of the detector so that less than 50 μl of solvent did not quench the flame.

Emission spectrometric detector (microwave plasma detector). This detector was applied to the determination of pesticide residues in foods by Bache and Lisk,[50–53] for both phosphorus and iodine compounds. Because of the high selectivity, full clean-up of food extracts was not always necessary. The same workers applied this detector to the determination of organic mercury compounds in fish.[35]

Electrolytic conductivity detector (Coulson conductivity detector). In the determination of nitrogen-containing pesticide residues, *e.g.*, carbamates, Patchett[55] made several refinements in the basic detector and lowered the limit of detection for nitrogen to 0.1 ng from 1 ng. These refinements were incorporated in the detector used by Cochrane and Wilson[56] for the determination of residues of triazines, substituted ureas and carbamates.

A procedure for the determination of nitrosamines in foods and beverages was suggested by Rhoades and Johnson.[57] The detector was converted for determination of amines by using argon as the carrier gas and substituting an empty quartz tube for the catalyst reactor tube. This unit was operated at 400–600° since in this temperature range ammonia is obtained as a degradation product of many amines and nitrosamines, whereas other organic nitrogen-containing compounds produce virtually none.

In the determination of atrazine residues in potatoes, Lawrence and Moore[58] used a water jacket round the detector, and other refinements, to improve the sensitivity by a factor of five.

The Hall micro-electrolytic conductivity detector has been used in the pyrolytic mode by von Rappard *et al.*[59] for the determination of five nitrosamines.

Microcoulometric detector. Although the main use of this detector was originally in the analysis of organohalogen and organosulphur compounds, it was modified by Burchfield *et al.*[60–62] to determine phosphorus in pesticide residue analysis. In this system, the detector was operated in the reductive mode with molecular hydrogen at 950°, phosphine being formed from OP compounds, and hydrogen sulphide and hydrogen chloride from organosulphur and OC compounds, respectively. All these products could be titrated in the silver-ion cell, and to avoid co-titration when determining phosphorus an alumina column was inserted after the furnace to remove hydrogen sulphide and hydrogen chloride. If silica gel was used in place of alumina, hydrogen chloride was removed and left the phosphine plus hydrogen sulphide to be detected. The MCD is specific and is very useful in residue analysis, particularly where clean-up is difficult.

Electron capture detector. The great interest in OC pesticide residue analysis, which probably reached its peak in the 1960s led to a demand for a detector that was specific and sensitive, and the ECD was devised. Modifications to the detector have been made, OC pesticides or PCBs being used as the analytical models. For example, Brechbuehler *et al.*[63] have produced a micro ECD, reducing the internal volume to approximately 140 μl for use with high-resolution capillary columns.

In a comparison of the efficiency of the ECD with the electrolytic conductivity detector, Lawrence and Ryan[64] used the heptafluorobutanoyl derivative of stilboestrol from beef liver and also carbofuran residues from turnips. They found that the ECD was the more sensitive, but the electrolytic conductivity detector was more selective.

Chemiluminescent detector. Gough *et al.*,[65] in the screening of foods for the presence of volatile nitrosamines, used a chemiluminescent detector which measured the infrared emission resulting from the interaction of NO and ozone. The NO was produced from the nitrosamines by oxidation in a catalytic chamber and then cooled before detection.

The human nose as detector. Much has been written about the sniffing of effluent vapours from GC columns but there has been little attempt to rationalize the technique, which could be put to better use than at present for identification of aroma constituents in foods. Tucknott and Williams[66] have pointed to several disadvantages, which include the distortion of the odour owing to the elevated temperature of the carrier gas, the speed at which one component often follows another, the fact that some components are more concentrated in the effluent than in the original food matrix and also that only one person at a time can conveniently sniff the effluent. To overcome these problems, these workers used 10- or 20-ml disposable syringes for effluent collection, with subsequent dispensing of 1-ml portions to individual aroma panellists.

Derivative formation

Because of the sensitivity and resolving power of GC, the conversion of involatile species into volatile derivatives, though time-consuming, has been found worthwhile. In food analysis, alkylation techniques for fats, and silylation for sugars, are the most important developments.

Alkylation. The formation of alkyl derivatives has probably been the most frequently applied of these procedures, and food has frequently been the medium for experimentation with alkylation techniques. Methylation is most commonly used, followed by propylation and butylation.

Scoggins and Fitzgerald[67] used dimethyl sulphate for the methylation of chlorophenoxyacetic acid herbicides and found it to be quicker and more quantitative than acid-catalysed methylation. A simple procedure for the quantitative methylation of fatty acids from the glycerides in fats and oils was described by Luddy *et al.*[68] It was based on alkali-catalysed reaction of the oil with potassium methoxide in anhydrous methanol. If the free fatty acid content was high, the procedure was modified to include treatment with the acidic catalyst boron trifluoride in methanol after initial reaction with the potassium methoxide catalyst. A similar procedure was used for methylating the fatty acids of the glycerides of peanut oil[69] and of milk fat.[70] Triglycerides of soyabean, safflower and linseed oils were methylated, in a microreactor, by Davison and Dutton.[71] A 3-μl portion of 2.7*M* sodium methoxide in methanol was injected into the microreactor, followed by 2–3 μl of vegetable oil sample. Trans-esterification occurred. This method permits the analysis of microsamples.

Bitner *et al.*[72] methylated fatty acids with tetramethylammonium hydroxide in a microreactor. Churchill *et al.*[72a] used trimethylanilinium hydroxide similarly for methylation of residues of malathion and parathion methyl; the detection limit for these insecticides was 0.4 ng. Sheppard and Iverson[73] have reviewed the various methods of esterification of the fatty acids of glycerides and conclude that careful control of conditions is necessary if artefact formation is to be avoided. They find that artefacts can occur if the temperature of the alkali concentration is too high.

Hydroxyl groups can be converted into methyl ethers by reaction with methyl iodide and silver oxide in dimethylformamide (DMF), a reaction used in the determination of sugars.[74] Fedeli *et al.*[75] prepared the methyl ethers of sterols from the unsaponifiable fraction of olive and sunflower seed oils with dimethyl phosphite in the presence of toluene-4-sulphonic acid.

A chromatographic reaction method for the methylation of OP pesticides was used by Moye.[76] It entailed trans-esterification achieved by injecting the compounds (in methanolic solution) into the chromatograph injection port (at 225°) which contained glass microbeads pretreated with 2*M* sodium hydroxide. Moye[77] had previously used a similar method for the determination of carbamate pesticide residues. In a similar method, Dale *et al.*[78] injected trimethylanilium hydroxide solutions of residues of the insecticide and nematocide, chlorphoxim, obtained from cat-fish, into the chromatograph injection port at 280°. This gave a 70% yield of methyl ester.

Johnson and Wong[79] used a stainless-steel trap containing 10% silver oxide on 60/80 Celite as a reaction chamber for the methylation of the fatty acids of mutton fat. Methyl iodide was injected as methylating agent and the trap was heated at 100° for 2 min to complete the reaction. Diazomethane in a pre-column of alkaline Celite was used by Schwartz and Bright[80] to methylate the fatty acids of milk fat.

Methanolic (3-trifluoromethylphenyl)trimethylammonium hydroxide (0.2*M*) has recently been used as a methylating agent for the trans-esterification of the fatty acids from the glycerides of corn, olive and peanut oils.[80a] The method is rapid and can be carried out at room temperature.

Staruszkiewicz *et al.*[81,82] used boron trifluoride and propanol to form the propyl ester of β-hydroxybutyric acid in the determination of this indicator of putrefaction in eggs. The procedure was a modification of the one used by Salwin and Bond[83] for determination of lactic and succinic acids in eggs. The short-chain fatty acids in butter oil and cheese were determined by Iyer *et al.*[84] by butylation with butanol and sulphuric acid, although it was considered that boron trifluoride would have been a better catalyst.

Halogen-esters. After the realization that the EC detector could be used for other electron-capturing compounds as well as OC pesticides, a conscious effort was made to exploit derivatives containing a large proportion of halogen.

Islam and Darbre[85,86] used the trifluoroacetyl derivatives of the methyl esters of fatty acids in an analysis of protein hydrolysates, these derivatives being formed by reaction with trifluoroacetic anhydride. Trifluoroacetylated mono-, di-, tri- and tetrasaccharides were prepared with *N*-methylhexafluorodiacetamide by Sullivan and Schewe.[87] This reagent, first suggest by Donike,[88] was found to be very satisfactory, and in temperature-programmed GC could separate 13 components from a sugar syrup in 15 min.

Heptafluorobutanoyl esters have been favoured in the determination of steroids at the picogram level. In a study of the sterol contents of virgin and solvent-extracted olive oils, Tateo[89] used the esterification of the sterols with heptafluorobutyric anhydride to produce derivatives of β-sitosterol and stigmasterol, which could be completely resolved and measured by GC. The same reagent was used by Lawrence[90] in the residue analysis of carbamate insecticides, *e.g.*, propoxur and methiocarb.

Silylation. The importance of silylation in GC, *i.e.*, substitution of the active hydrogen in the OH, SH and NH functions by the trimethylsilyl (TMS) group, has increased since its introduction for the preparation of volatile derivatives. The increase in popularity of TMS derivatives is partly due to development of easier methods of preparation. Most of the development work involved pure organic species, and Zuercher and Hadorn[91] compared seven silylation methods, using a mixture of common sugars as the test medium. Sugars may also be reacted with hydroxylammonium chloride to form oximes before silylation. Zuercher *et al.*[92] used this procedure in the separation and estimation of sugars in honey, orange concentrate, grapejuice, and chocolate for diabetics. The silylating agent was heptafluoro-*N*-methyl-*N*-trimethylsilylbutyramide and trimethylchlorosilane.

In a chromatographic reaction method for the separation of cheese volatiles, McGugan and Howsam[93] used a pre-column held at between $-140°$ and $-150°$ and containing 10% OV-101 on 80/100 Chromosorb W-HP. The silylating reagent, *N*-methyl-*N*-trimethylsilylfluoroacetamide was introduced into the pre-column, which was then heated to 180° during 5 min, the ensuing derivatives being swept on to the GC column for separation.

2,4-Dinitrophenylhydrazones. Volatile carbonyl compounds are often important flavour components of foods, accounting for many off-flavours and also pleasant ones. Since the concentration of these volatiles is generally low, they are frequently difficult to detect. Fifteen carbonyls known to be flavour constituents were determined as their 2,4-dinitrophenylhydrazones by Kallio *et al.*[94] It was shown that the ECD gave greater sensitivity and selectivity than the FID.

Oxidation and hydrogenation. Oxidation is not a popular method of derivative formation in GC analysis. However, the oxidation of nitrosamines to nitramines was used to advantage by Althorpe *et al.*[95] They found that nitramines, detected by EC, gave a response about 200 times greater than that for nitrosamines detected by FID. A similar procedure was used by Sen[96] in the determination of dimethylnitrosamine isolated from nitrite-treated fish.

Several different procedures and types of apparatus were described by Beroza and Sarmiento[97] for direct hydrogenation of many organic compounds; some were particularly useful in the quantitative hydrogenation of fatty acid esters of glycerides of vegetable oils. The hydrogenator, which used 1% palladium on 60/80 Gas Chrom P, with hydrogen as carrier gas, was situated in the GC oven and, consequently, operated at the same temperature as the column. Another apparatus used the injection port as reactor so that the temperature could be different from that of the column. Results showed that the hydrogenation procedures were sufficiently powerful to saturate multiple bonds in straight-chain, ring and substituted compounds. If the pre-column was provided with a bypass,[98] so that part of the sample escaped hydrogenation, the original and hydrogenated portions appeared on the same chromatogram. Consequently, the change in retention caused by hydrogenation could be directly observed.

GC IN FOOD QUALITY CONTROL

Most types of food have been analysed by GC. Dairy products, fats and oils, meat, fish, eggs, fruit, vegetables, essential oils, beverages, sugars and cereals are examples of foods for which quality control can be based, in part, on GC. Before the advent of GC, it was not always possible to separate and determine, within a matrix such as food, mixtures of aliphatic acids, amino-acids, sugars, alcohols, esters, ketones, *etc.*, even though these classes of compounds are often present in relatively high concentration. It was also virtually impossible to detect the low concentrations of flavour and other volatile components on which the quality of a large number of foods depends.

Milk, cream and yogurt

Milk is essentially an emulsion of fatty acid glycerides, water, proteins and sugars, and it is logical that milk quality is assessed by the determination of these constituents. The fatty acid constitution of the fatty acid glycerides can be assayed by GC of the free acids or their alkylated derivatives after hydrolysis, or GC of the original glycerides. Although the determination of the fatty acids has been used,[99,100] their relative non-volatility compared with the alkyl esters often causes difficulty and the determination of the methyl or butyl esters is preferred. The three basic methods of methylation are acid-catalysed methanolysis, methanol–boron trifluoride reaction, and methanol–sodium methoxide reaction under sealed conditions. These methods have been critically assessed by de Man,[101] who concluded that losses of lower fatty acids occurred with the first two methods. The third method not only produced satisfactory recoveries of

butyric, caproic, caprylic and capric acids, but also gave better recoveries of linoleic and linolenic acids.

Smith[102] separated the methyl esters of the C_4–C_{18} fatty acids of milk fat, using a small injection volume for one chromatogram but a larger injection for another chromatogram in order to detect the minor constituents, *e.g.*, the C_{13}, C_{15} and C_{17} acids. Glass *et al.*[103] used a trans-esterification technique before GC of the methyl esters of the fatty acids in order to determine the fat content of milk. The technique has particular value when the available sample is small, *e.g.*, <60 mg of milk. The fat is extracted into a mixture of methanol, dimethyl carbonate and benzene, and methyl tridecanoate is added as internal standard. The areas under the peaks are related directly to the area given by the internal standard. Several other workers[70,104–106] have separated the methyl esters of the fatty acids of milk fat. Hadorn and Zuercher[107] use the butyric acid concentration to calculate milk fat content. The milk fat content of milk chocolate was estimated by Iverson.[108] He methylated the fatty acids after saponification and used the lauric acid concentration as a measure of the milk fat content, cocoa butter containing only 0.013% of this acid.

GC of butyl esters of fatty acids was used by Gander *et al.*,[109] and led to exploration of a superior method of preparing butyl esters.[110] The esters were prepared in a few minutes by heating the fat with di-n-butyl carbonate and sodium butoxide and temperature programming was used so that a single chromatogram covered the whole range of fatty acids in milk fat, in contrast to the two chromatograms often required for the separation of all the methyl esters.

Lysine has been determined in heat-treated milk powder after acid hydrolysis of the protein.[110a] The lysine was converted into homoarginine which was chromatographed as the trifluoroacetyl derivative of the butyl ester.

The main interest in the flavour of milk and cream is associated with volatiles which give off-flavours to these products. Patton[111] found δ-deca and δ-dodecalactones in processed milk but not in raw milk, and Arnold *et al.*[112] attributed the stale flavour of stored sterilized milk to lactones, ketones and aldehydes. Mabbitt and McKinnon[113] examined the volatiles produced in milk during storage, using a cold trapping technique and GC, and found that the 2-butanone content increased as souring progressed. An off-flavour of heated milk, termed "cooked", was correlated with hydrogen sulphide production by Thomas *et al.*,[114] using a headspace sampling technique; as little as 10 μg/ml could be detected.

Goitrin, an antithyroid compound, may be found in milk from cattle fed on a diet containing rapeseed meal and can be determined by means of its hexafluorobutyryl derivative and EC detection.[114a]

2-Hydroxy-4-(methylthio)butyric acid residues in milk can be determined after extraction and formation of the trimethylsilyl derivative; FP detection is used (sulphur mode).[114b]

Wong and Patton[115] determined the normal flavour volatiles of cream, and listed methyl sulphide, acetone, 2-butanone and ethanol as important constituents. Hempenius and Liska[116] steam-distilled acetic acid from sour cream before GC determination, and a rapid method for the determination of lactic acid and lactates, as the butyl ester, in whey was used by Gray[117] as an improvement on existing colorimetric methods.

The sugar content of milk has received scant study by GC methods. Lactose was determined by Jaynes and Asan,[118] who used the trimethylsilyl (TMS) derivatives of the α- and β-anomers and the same derivatives were used by Reineccius *et al.*[119] in the separation and determination of glucose, galactose and lactose from whole and skimmed milk. A similar method was used by Mouillet *et al.*[120] in a study of the fate of these sugars, particularly lactose, in the manufacture and storage of yogurt. More recently, the Lane and Eynon method for lactose determination in milk was compared with a GC method utilizing the TMS derivative of the oxime, good agreement being obtained.[120a]

Interest has been shown in the vitamin D content of milk and non-fat dried milk. Janecke and Brendel[121] separated the unsaponifiable matter from the milk and, following clean-up, determined the vitamin as its TMS derivative. Panalaks[122] isolated vitamins D_2 and D_3 from non-fat dried milk and subjected them to GC after modification with antimony trichloride. Vitamin D_2 in full-cream dried milk was determined as its TMS derivative by Bell and Christie[123] after saponification and clean-up. GC has also been used to determine the vitamin C content of infant milk products.[124]

Some concern has been expressed about the possibility of iodine and its compounds finding their way into milk, either through the feeding of cattle with iodine-containing mineral supplements, or by contamination with iodophor disinfectants. In this connection, Grys[125] has produced a GC method suitable for the determination of iodine after its conversion into iodoacetone. A similar method was used by Gabrio *et al.*[126]

Butter

The main interest in butter analysis is whether or not it has been adulterated with vegetable oils or hydrogenated oils and, if so, to what degree. Many analysts have used GC to enumerate and determine the fatty acids present in butter fat and there have been two basic approaches in using the results to discover adulteration.

The first is due to Wolff,[127] who separated the methyl esters of butter-fat fatty acids and introduced the concept of fatty acid ratios as a means of assessing quality. He found that butter contained approximately 3% lauric acid (C_{12}), but palm kernel oil and

coconut oil contained 47–49%. Either this criterion or that of the ratio of lauric to capric acids (C_{12}/C_{10}) was found to give a very good indication of butter purity, the ratio being 1.07–1.13 for 8 French butters compared to 1.64 for butter containing 3% palm kernel oil and 1.96 for butter containing 5% of that oil. Many workers followed Wolff's lead and looked at other fatty acid ratios as indicators of adulteration and it is reported that in genuine butter the ratio $C_4/(C_6 + C_8)$ acids does not exceed 1.8,[128] and that the ratio of unsaturated to saturated C_{18}-acids is close to 3.[129] Methylation techniques improved during the 1960s and the 1968 figures of Luddy *et al.*[68] for pure butter oil were C_{12}/C_{10} acids = 1.18; $C_4/(C_6 + C_8)$ acids = 1.45; C_{14}/C_{12} acids = 4.00 and unsaturated/saturated C_{18}-acids = 2.39.

The second approach was to take the concentration of butyric acid (averaged over many samples) as the standard for 100% butter purity, because margarine and the oils used in its manufacture contain very little butyric acid. In the standard wet chemical method of Reichert *et al.*[130] for assessing butter quality, the fatty acids are divided into three categories, *viz.*, water-soluble volatile, water-insoluble volatile, and water-soluble volatile forming water-soluble silver salts. GC is able to define the acids within each category and leads to a more exact interpretation of quality. Karleskind *et al.*[131] saponified the glycerides and distilled the acidified extract according to the Reichert–Meissl method. The methyl esters were made and GC was applied, with methyl valerate as internal standard. These authors showed that French butter fat contained between 3.2 and 4.0% butyric acid, whereas lard, tallow, palm oil and palm kernel oil contained 0.02, 0.04, 0.01 and 0.03% butyric acid respectively. These results showed that the amount of butyric acid in these oils is equivalent to approximately 1% of that in butter.

Kirschner values, which are directly related to the water-soluble volatile acids which form soluble silver salts, are essentially a measure of butyric acid concentration in butter; Withington,[132] who trans-esterified butter fat with alkaline ethanol, found that the average content of ethyl butyrate from 19 pure butters of various countries of origin was 4.79%. This value was used as the standard for calculation of butter content, particularly where butter was present in other foods at a concentration of 10% or less. Hadorn and Zuercher[133] used a similar method with trans-methylated butter fat.

A semimicro method of determining butter fat in fat mixtures was devised by Phillips and Sanders.[134] They found it simpler to measure free butyric acid after saponification and acidification, obtaining an average figure of 3.6% of the acid for pure butter fat, which is in excellent agreement with Withington's 4.79% for ethyl butyrate. The method was used in the determination of butter fat in such foods as milk chocolate coatings, cream soups, butter confectionery and meat or fish pastes containing butter.

The fact that butter contains no sitosterol, which constitutes the main sterol fraction of vegetable oils, is another means of detecting the presence of margarine in butter. In 1962, Eisner *et al.*[135] extracted sterols from the unsaponifiable matter of margarine–butter mixtures and separated β-, γ- and δ-sitosterol from cholesterol. Using the β-sitosterol peak as a quantitative indicator for margarine, it was possible to detect as little as 0.2% margarine in butter.

Digitonin precipitation followed by acetylation of the sterols was used by Cannon,[136] who separated the acetates of cholesterol and sitosterol and claimed that 2% margarine in butter could be detected. TMS derivatives of the sterols were used by Cerutti *et al.*,[137] who claimed 1% of margarine in butter could be detected. The BSI method for the detection of foreign fats in dairy products[138] is based on sterol analysis; β-sitosterol is used as the indicator, 0.5% being detectable.

The flavour constituents of butter, as found by GC analysis, include δ-lactones,[139–141] aldehydes[142] and indole and skatole.[143] Most work has been carried out on δ-lactone determination and van der Ven[139] concluded that fresh butter contains γ- and δ-keto acids, and that these may be precursors of the corresponding lactones.

Cheese

Most GC investigations of cheese have concerned flavour and aroma and particularly the volatiles responsible for the subtle differences between varieties of cheese. Any interest in fatty-acid analysis of cheese fat is invariably a result of the effect on flavour.

Iyer *et al.*[84] studied the fatty-acid composition of the glycerides of Provolone cheese fat by using GC to separate the butyl esters, and concluded that the short-chain volatile fatty acids were important contributors to flavour. The determination of free acetic, propionic and butyric acids in cheese was subsequently facilitated by using Chromosorb 101 in the gas–solid chromatography (GSC) method of Keen and Walker.[144] Fatty acids can have a deleterious effect on flavour quality and lead to rancidity. It was found by de Man[145] that Cheddar cheese monoglycerides contained short-chain fatty acids and that when the cheese became rancid there was a higher proportion of these monoglycerides present, particularly monobutyrin.

In an examination of cheese for neutral volatile constituents, Liebich *et al.*[146] used the entrainment method, placing the sample in a liner attached to the injector. The liner was held at 190° for 10 min to allow the volatiles to be swept on to the column by the carrier gas, leaving the oil behind. These authors examined the Cheddar, Blue, Roquefort, Romano, Swiss and Limburger varieties and found that methyl ketones were an important flavour group.

As early as 1958, dimethyl sulphide was found in Cheddar cheese[147] and was considered to be an important good flavour factor. GC, coupled with mass

spectrometry (MS), was used by Langler, *et al.*[148] to separate the major volatiles of Swiss cheese. They also found that dimethyl sulphide was an important flavour component, often being present in concentrations above its flavour threshold.

In a series of ripening experiments, Scarpellino and Kosikowski[149] found that the acetic acid and ethanol content increased during the ripening of Cheddar cheese, whereas there was a decrease in the concentration of the trace constituent, acetyl methyl carbinol. Butyric acid, 2-butanol and 2-butanone appeared as ripening proceeded.

Tyramine is an indirectly acting sympathomimetic amine that releases noradrenaline from adrenergic neurones, and it is found in foods such as cheese, red wine and pickled herrings. Kaplan *et al.*[150] determined the tyramine in South African cheeses by GC of its TFA derivative and found that its concentration ranged from 5 ppm for a cream cheese to 775 ppm for a mature Cheddar. Phenethylamine, which is also known as a "migraine precipitant", has been detected in cheese by means of its TFA derivative.[151] Foods containing such sympathomimetic amines must not be consumed by patients taking monoamine oxidase inhibitors as antidepressant drugs.

Animal fats

Lard is probably the most important animal fat, if the interest in its quality is a yardstick. It has been the subject of adulteration by beef and mutton fats, horse fat and many hardened vegetable and fish oils. The GC examination of the fatty acids of lard glycerides has been a popular medium for the testing of preseparation and methylation methods,[68, 152, 153] and also for the assessment of adulteration by tallow or horse fat.[154,155]

Pascussi and Paolini[156] successfully applied the fatty acid ratio to classify pure lard and found that the $C_{14:0+16:0+18.0}/C_{18:2}$ acid ratio lay between 4 and 5, and considered that a value greater than 5.5 indicated adulteration. Similarly, the $C_{18:3}/C_{18:1}$ acid ratio lay between 100 and 200 and values greater than 200 could indicate adulteration. Castledine and Davies[157] used a trans-esterification technique to obtain methyl esters of the fatty acids of a number of animal fats. They calculated the $C_{16:0}/C_{14:0}$, $C_{18:1}/C_{18:0}$, $C_{18:1}/C_{14:0}$ and $C_{18:1}/C_{16:0}$ acid ratios for these fats. The $C_{16:0}/C_{14:0}$ and $C_{18:1}/C_{14:0}$ acid ratios are normally greater than 6 for pure lard, whereas beef and lamb tallow give ratios of less than 4. In addition, lard has a greater total C_{18} unsaturated acid concentration than does beef or mutton tallow.

A different approach to determining adulteration of lard was used by Grieco,[158] who specifically looked for branched-chain and minor-constituent fatty acids, which were found to be present in small concentration in beef tallow but absent in lard. Bastijns,[159] in a similar study, found that the concentration of C_{14} and C_{16} branched-chain acids was 5–10 times as high in beef fat as in lard. He also discovered that the total of C_{15} acids present in lard was less than 0.03%, but 0.2–1.0% in beef fat.

In a comprehensive survey of animal fats, Hubbard and Pocklington[160] substantiated the findings of most other workers. In their survey they also included the fatty acid composition of the fats from chicken, turkey, game birds and rabbit.

There is some interest in the adulteration of goose fat with lard, the fatty acid ratios being successfully employed for detection and sometimes simiquantitative estimation.[161–163]

It is virtually impossible to differentiate beef and lamb fats by chemical methods and the chromatograms of the fatty acid methyl esters are very similar, although it is generally acknowledged that beef fat has the superior organoleptic quality. Hoffmann and Meijboom[164] deduced that the major volatiles of both fats were 4-heptenal and 2,6-nonadienal. It can be assumed that the fine differences between beef and lamb or mutton fats must lie in the minor volatile concentrations.

Horse fat has been used to adulterate beef fat. Suitably chosen fatty acid ratios can give strong indications of such adulteration.[157,165]

Vegetable oils and fats

Vegetable oils are used mainly in margarine manufacture, as cooking oils and as salad dressings. The suspicions surrounding the possible harmful health effects of cholesterol, which is present in animal fats, has indirectly created a greater market for vegetable oils, particularly those for the cooking of food. Oils such as corn, cotton seed, soyabean, peanut and sunflower are used for frying, and palm kernel, coconut, soyabean, sunflower and rape seed are used in margarine manufacture. Margarine is also made from hydrogenated vegetable and fish oils.

Much attention has been paid to the purity and fine quality of various vegetable oils and to the presence of vegetable oils in animal fats. In the latter case, while GC of the fatty acids of the various glycerides can establish the presence of vegetable oils in animal fat, a superior method is to look for phytosterol in a GC sterol analysis because its presence indicates the indisputable presence of vegetable oil.

In contrast to the extensive literature on the analysis of the fatty acid and unsaponifiable fraction, the determination of flavour constituents of vegetable oils has received little attention. General methods have been published for the determination in vegetable oils of lactones at the 1 ppm level[166] and of various carbonyl volatiles by means of their 2,4-dinitrophenylhydrazones.[167]

The neutral volatiles of mayonnaise have been separated after trapping of the acidic volatiles on a pre-column of glass wool coated with sodium bicarbonate.[168] Aliphatic alcohols and aldehydes were predominant among the 21 volatiles identified.

Before hardened vegetable and fish oils were

exploited, margarine was produced largely from mixtures of coconut and palm kernel oils. The lauric acid concentration in the glycerides of both these oils is approximately half that of the total fatty acids. Glyceride and fatty-acid analyses of both coconut and palm kernel oils have been the subject of study by many workers.[169–172]

Some vegetable oil monoglycerides, which result from the enzymatic splitting of some of the triglycerides, are important because they can influence the rheological properties of emulsified oils, *e.g.*, margarine. Halvarson and Ovist,[173] in a GC method for the determination of monoglycerides, found that coconut and palm kernel oils contained the abnormally high level of 0.5% monoglycerides, which made them eminently suitable for margarine manufacture.

There has been recent interest in the GC determination of *trans* unsaturated fatty acids in margarine, primarily to check the existing infrared method. Ottenstein *et al.*[174] used OV-275 as stationary phase to achieve the separation of the methyl esters of *trans* and *cis* isomers of oleic, linoleic and elaidic acids. The same stationary phase and also Silar IOC and SP-2340, two other cyanosilicone phases, which are highly polar and thermally stable, were used by Conacher *et al.*[175,175a] in a similar analysis of margarine. Geometric isomers of unsaturated fatty acids have also been separated after trans-esterification with sodium methoxide.[175b]

Analysis of the unsaponifiable matter of coconut and palm kernel oils has yielded useful information about their triterpene alcohol and sterol content.[176–178] Fedeli *et al.*[178] investigated the unsaponifiable matter of all the common vegetable oils. They found that coconut oil contains β-amyrin, whereas palm kernel oil does not, and this could be used as a distinguishing feature, if required. The volatile flavour constituents of coconut oil have been isolated by Allen,[179] who considered that, among the methyl ketones and lactones identified, δ-octalactone was largely responsible for the typical coconut flavour and aroma.

Whereas palm kernel oil is made from the nut part of the fruit, palm oil is made from the outer flesh. Some study has been made of its glyceride fatty-acid composition,[169,171,172] palmitic acid being the major constituent, and also of its unsaponifiable matter.[176–178]

Cocoa butter and illipe butter contain stearic acid as the major fatty acid constituent of their glycerides. Cocoa butter is used in chocolate manufacture and, on occasion, has been adulterated with coconut and palm kernel oils. The glyceride fatty acid composition of pure cocoa butter has been deduced[180–182] and Iverson[183] showed that the difference in lauric acid content of the cocoa butter and these added oils could be exploited analytically. Coconut and palm kernel oils contain approximately 50% lauric acid whereas cocoa butter contains only approximately 0.01%. Since it is possible by GC to detect 0.25% of lauric acid, it should be possible to detect addition of 0.5% of either of the two oils to cocoa butter. The sterol content of the unsaponifiable matter of cocoa butter has been determined by Fincke[184] and the triterpene alcohols have also been separated.[178]

Those oils which have a predominance of glyceride oleic acid include olive, peanut, almond kernel, peach kernel and hazel nut. Olive oil is the major ingredient of the majority of salad oils and finds particularly good commercial outlets in Mediterranean countries. Because of its commercial importance, it is prone to blending with inferior quality olive oils or adulteration by other cheaper vegetable oils. A large amount of work has been done on evaluating the glyceride fatty-acid composition of olive oil, that of Youngs and Subbaram[180] and Hivon *et al.*[185] being particularly noteworthy.

When it is suspected that low-quality olive oil has been used to supplement the top-grade product, an analysis may reveal the presence of elaidic acid, which is produced by the isomerization of oleic acid, this being encouraged by the heat treatment used to extract low-quality oil; Averill[186] employed GC to separate methyl oleate and methyl elaidate and detect and adulteration. The adulteration of olive oil with seed oils was investigated by Galanos *et al.*[187] Argentation–silica gel thin-layer chromatography (TLC) of the poly-unsaturated glycerides was followed by GC of the methyl esters of the fatty acids containing four or more double bonds. In pure olive oils, this fraction contained 35–37% linoleic acid, whereas the same fraction of most seed oils contained 65–70%.

The sterol and triterpene alcohol analysis of the unsaponifiable matter has been evaluated by Karleskind *et al.*[176] and by Fedeli *et al.*[178]

The importance of the quality of olive oil is illustrated by the 1972 world production of 1.4×10^6 tonnes. For quality assessment, the aroma constituents were determined by Flath *etal.*,[188] who listed 77 components, identified by GC–MS.

Gonzalez-Quijano *et al.*[189] used a headspace technique to trap the volatiles of 13 different varieties of Spanish olive oil for statistical evaluation of organoleptic tests with components identified by GC.

Peanut oil is extensively used as a cooking and frying oil and its glyceride fatty-acid composition has been evaluated.[181] Tests for the presence of peanut oil in other oils, *e.g.*, sesame oil, usually depend on the presence of arachidic and lignoceric acids in peanut oil and their virtual absence in seed oils, the determination of these acids being conveniently carried out by GC. Fedeli *et al.*[178] have determined the triterpene alcohol composition of peanut oil and Murata[190] has analysed the triglycerides.

The free fatty acid content, expressed as oleic acid, was determined by Phillips and Singleton by GC of the methyl esters, with SP-2340 as the stationary phase.[190a]

Peanuts have been used to adulterate sesame seeds, and Letan *et al.*[191] used methylation of the glycerides

and a urea-complexation method before GC in order to concentrate the methyl behenate. Under standard conditions peanut oil was found to contain between 2.3 and 4.3% behenic acid, and sesame oil a maximum of 0.3%. This difference was used to detect the presence of peanuts in tehina and halva, which are sesame-seed products. Sesame oil is used as a frying oil and also as an ingredient of some margarines and its glyceride fatty-acid composition has shown that it contains mainly linoleic and oleic acids, in approximately equal proportions.[171,172]

Cotton seed oil is produced relatively cheaply and is economically important as a margarine ingredient. The glyceride fatty-acid analysis shows that its predominant acid is linoleic.[171,185,192] Schneider *et al.*[193] specifically looked for cyclopropenoid acids and found that 0.5% of the total fatty acid content was malvalic and sterculic acids. Cotton seed oil has been adulterated with such oils as soyabean, rapeseed and rice-bran, and Imai *et al.*[194] used both fatty acid and sterol analyses to detect this adulteration. They found that the presence of erucic acid pointed to rapeseed oil adulteration, and this could be confirmed by identification of brassicosterol. Soyabean and rice-bran oils were detected by means of the presence of linolenic acid and stigmasterol.

Soyabean oil is extensively used in margarine production. Because of this the quality of soyabean oil has received considerable analytical appraisal. The glyceride fatty acids have been determined by several workers,[171,172,185,192,195] and the intact glycerides have been separated by Youngs and Subbaram.[180] In the identification of triterpene alcohols, Fedeli *et al.*[178] found cycloartenol, α- and β-amyrin and cycloaudenol. Soyabean oil is unusual in containing cycloaudenol and not containing 24-methylene cycloartanol and this could be exploited in specifications for the oil. One of the major problems in the storage of soyabean oil is its tendency to autoxidation, which leads to an off-flavour frequently described as "beany". This oxidation is known as reversion and has led to investigation of the compounds which are responsible for the off-flavour. Hoffmann[196] separated the neutral volatiles of the oil into six fractions by GC, and described them in terms of odour. The fraction called "green beans" was further examined by GC and by infrared spectroscopy and was found to contain 3-*cis*-hexenal, which was considered to be the major contributor to the off-flavour. On the other hand, Chang *et al.*[197] attributed the reversion flavour to 2-pentylfuran, which was present in soyabean oil to the extent of 1–10 ppm. Some oil chemists[198,199] have shown that formation of pentane is a good indicator of the presence and extent of decomposition; it presumably arises by autoxidation of methyl linoleate. Even hydrogenated soyabean oil can develop an off-flavour on storage, and Yasuda *et al.*[200] have attributed this mainly to 2-*trans*-6-*trans*-octadienal.

The glyceride and sterol composition of many other oils has been examined by GC, among the more important being corn, sunflower, safflower, linseed, rapeseed and mustard seed oils. The last two are characterized by their high concentration of erucic acid. Separation of the methyl esters of the higher unsaturated fatty acids can be difficult but has been achieved in a rapid automated method for rapeseed oil analysis by Heisz.[201] MS detection of natural erucic acid (as the methyl ester) of rapeseed oil and the ^{14}C-labelled methyl ester added as internal standard has been used to determine erucic acid in the oil.[201a] Rapeseed oil is also characterized by its relatively high concentration of brassicosterol (approximately 8–10% of the unsaponifiable fraction).[176,177]

Fish oils

Fish oils contain relatively high concentrations of unsaturated fatty acids and are hydrogenated before use in margarine manufacture. Many fish oils contain polyenoic acids with up to six double bonds and Lambertsen *et al.*[202] have exploited the different numbers of double bonds of the fatty acids by using TLC before GC. They found that the major acids were $C_{18:4}$, $C_{20:5}$, $C_{22:5}$ and $C_{22:6}$. Many fish oils were also found to contain branched and unbranched C_{17} acids, which are uncommon in vegetable oils. There is such a broad range of fatty acids in fish oils that two chromatograms may be needed to include them all. However, Ackman[203] showed that one chromatogram sufficed with EGSP-Z as stationary phase.

Litchfield *et al.*[204] found that fish oils contain up to 5% of odd carbon-number fatty acids, although mullet is exceptional in containing approximately 10%; vegetable oils contain minimal odd carbon-number fatty acids. Most GC work has centred on herring oil with some attention paid to the oils of capelin, salmon, mullet, tuna, menhaden, pilchard, shrimp and sardine. Gershbein and Singh[205] found that a quarter of the unsaponifiable fraction of herring oil consisted of hydrocarbons, predominantly pristane and squalene. GC has been applied to fish liver oils, mainly for vitamin assay, *e.g.*, the determination of vitamin D in cod liver oil.[206]

Meat

Early studies of meat flavour concerned the considerable contribution from meat fat. Hornstein *et al.*[207] followed the production of free fatty acids in stored cured and cooked meat, using GC of the methyl esters, and related the total acid content to deterioration in quality. Hornstein *et al.*[208] suggested that the volatiles of the lean portions of beef and whale meat were identical, except that the latter contained trimethylamine, and Hornstein and Crowe,[209] in a review on general meat flavour, opined that the volatiles of lean meat of beef, pork and lamb had similar compositions and that the true flavour differences lay in the fatty tissues.

Many procedures have been used for the isolation of meat volatiles before their separation and determination by GC. These include solvent extraction,

cold trapping, trapping in chemical reagents and headspace sampling. El-Gharbawi and Dugan[210] used steam distillation to isolate carbonyls and sulphur-compounds from freeze-dried beef; acetaldehyde, propanal, pentanal, hexanal, acetone, methyl mercaptan and methyl disulphide were positively identified, which indicates the types of volatiles frequently discovered in meat.

Liebich *et al.*[211] used GC coupled with MS to identify roast-beef volatiles in lean and fatty portions. They used vacuum distillation for isolation, followed by solvent extraction, and ultimately identified alkanals, alk-2-enals, alk-2,4-dienals, 3-hydroxy-2-butanone and γ-butyrolactone.

Roedel[211] tried several methods of isolating and concentrating volatiles from raw and roasted beef and concluded that the most efficient was adsorption on glass beads (or Gas Chrom Q) cooled in liquid nitrogen. In the determination, the GC eluate was split so that 90% was sniffed in order to assess the matching of aroma with individual peaks. In the examination of roast beef, he found that the components did not possess the typical aroma and assumed that the flavour and aroma came from a combination of the volatiles.

In comparison with cooked meat, raw meat has little flavour. However, a hot water extract of meat yields a product which has the flavour character of the cooked meat itself and this fact has been exploited commercially in the production of meat extracts. Bender and Ballance[212] used a 2,4-dinitrophenylhydrazine solution to trap carbonyls from a beef extract before application of GC.

Irradiation can be used to preserve meat but there have been problems associated with the production of an off-flavour by this treatment. Wick *et al.*[213] considered that the major contributor to the unpleasant odour and flavour was 3-(methylthio)propionaldehyde. As already mentioned, Merritt *et al.*[40] used a cryogenic temperature-programmed procedure to separate and identify volatiles of irradiated beef.

The components of lamb flavour have not received as much attention as those of beef, but Jacobson and Koehler[214] isolated roast lamb volatiles by cold trapping and GC and used other techniques for identification. The "sweaty" flavour of mutton has been the subject of study by Johnson *et al.*,[215] who considered that 4-methyloctanoic acid was responsible.

The main interest in pork volatiles has been the problem of boar taint. The substance responsible, which has been described as "urine-like" and "sweaty", 5α-androst-16-en-3-one, has been extracted and identified by GC.[216,217]

Volatiles from cured and uncured ham were compared by Cross and Ziegler,[218] who found that carbonyls and sulphur-compounds were predominant in both types. They used either a trapping pre-column of 1% DC-500 on glass microbeads or a series of chemical traps to separate the various classes before GC. In a study of bacon volatiles with a Likens–Nickerson apparatus, Mottram and Puckey[218a] found that the artefacts, 2-methyl-3-nitrobutan-2-ol and its nitrate, were formed from solvent impurities and the oxides of nitrogen produced by nitrite using in the curing process.

The large increase in consumption of chicken has led to interest in its storage and retention of flavour quality, particularly after deep-freezing. Pippen and Nonaka[219] identified n-hexanal and 2,4-decadienal as flavour components worth preserving, and Minor *et al.*,[220] in an examination of the volatiles of cooked breast and leg portions, emphasised the importance of sulphides, disulphides and mercaptans. Nonaka *et al.*[221] obtained cooked-chicken volatiles by isopentane extraction of an aqueous distillate. From 227 peaks, they identified 62 compounds by GC–MS. Hobson-Frohock[222] used a pre-column of molecular sieve 5A to remove aromatic hydrocarbons and branched cyclic compounds before GC of the remaining chicken volatiles. The sieve material was extracted with hexadecane for subsequent analysis of n-alkanes. Chicken carcass has been analysed by GC for n-alkanes in the range C_{12}–C_{33}.[223]

The sulphur- and nitrogen-compounds in meat volatiles were determined with a multi-detector system by Hřivnáč *et al.*[224] The capillary column effluent was split into two streams, and each was split again by metal capillaries; detectors used were FID and FPD, both in different modes, and "sniffing".

In some countries, there is a restriction on the concentration of sorbitol in cooked sausage products, and it has been determined after aqueous extraction and formation of trimethylsilyl derivatives.[224a]

Fish

Other than fish oil analysis, the main application of GC methods to fish is in the study of flavour volatiles. Most fish is transported long distances for sale, and even in iced-storage conditions some bacterial degradation can occur, leading to off-flavours. The commonest volatiles formed as fish ages are amines, particularly dimethylamine and trimethylamine. Examples studied in this context are cod[225–227] and caviar.[288] Mendelsohn *et al.*[20] used different extraction procedures for isolating volatiles from haddock, and found that vacuum distillation gave the greatest yield.

In a study of the carbonyl volatiles of salted salmon and caviar, Golovnya and Uraletz[229] used the system of isothermal retention indices. They used isothermal chromatography at 50° and then at 25° intervals up to 200° and recorded the retention indices at each temperature, the information being used to confirm the identities of the volatiles.

The headspace volatiles of canned tuna have been collected and examined for ethanol content as a means of measuring its spoilage.[230] As spoilage progressed, the size of the ethanol peak increased. Staruszkiewicz found that the spoilage of shrimp can be judged by the formation of indole.[231] He detected

no indole in fresh shrimp and between 0.14 and 1.15 ppm in decomposed samples. The method was later improved by use of a mixture of three internal standards.[231a]

The organoleptic appeal of certain shellfish has been found to be due, in part, to sulphur compounds, *e.g.*, in oysters,[232] and to carbonyl compounds, *e.g.*, in clams.[233]

Fish protein concentrate has become a commercial product and is used in animal feeding stuffs. The degree of "fishiness" is attributed to amines and these have been separated and determined.[234,235]

Eggs

The U.S. Food and Drug Administration has taken particular interest in the quality of eggs in shell. When microbial or enzymic action proceeds in food, aliphatic hydroxy-acids are frequently produced together with other relatively simple organic compounds. Bethea and Wong[236] examined the volatile acid fraction of various quality-graded eggs and detected butyric, isovaleric and valeric acids. By GC of the propyl esters of the aliphatic acids, Salwin and Bond[83] found that fresh eggs contained approximately 4 mg of lactic acid per 100 g of egg and no succinic acid. After the sample had been kept at room temperature for 16 hr the lactic acid content rose to 30.3 mg per 100 g of egg and there was 16.7 mg of succinic acid per 100 g of egg. Further work with this method confirmed these findings.[237, 238] Staruszkiewicz *et al.*[81] found that 3-hydroxybutyric acid could also be used as an indicator of egg decomposition and a collaborative study was conducted to establish that "passable" eggs should not contain more than 0.3 mg of this acid per 100 g of egg.[82]

The benzyl esters of those acids indicative of protein decomposition have been used in GC analysis of eggs.[238a] BCl_3–benzyl alcohol was used in a one-step reaction and has been applied in the determination of formic, acetic, propionic, butyric and isobutyric acids.

The cholesterol content of egg has been used to estimate the egg content of cakes and hamburgers.[239] GC of trimethylsilyl derivatives of sterols present in the unsaponifiable matter showed that whole dried egg had a range of 1.64–1.81% of cholesterol. Provided there was very little or no cholesterol in the other constituents of the confectionery, the dried egg content could be calculated. The egg content of noodles has been estimated by Armandola,[240] on the basis of the fatty acid composition, particularly the oleic/linoleic acid ratio.

Fruits and their products

The analytical interest in fruits is concerned with a variety of organic components which can be divided into macro- and micro-constituents. Classical methods have been used to determine macro-constituents, *e.g.*, sugars and fixed acids. GC methods, although facilitating separation of these constituents, have found their greatest application in the detection and determination of flavour volatiles, which make up the bulk of the micro-constituents.

The major fruit products are extracted oils, which are either purified and added to suitable foods or are diluted with alcohol for use as essences, which are used for the same purpose. GC analysis has had a great impact in the elucidation of the quality of these essential oils, particularly in the detection of terpenes and their oxygenated derivatives.

Fixed fruit acids have been the subject of study by Harvey *et al.*[241] and Fernandez-Flores *et al.*[242] Harvey *et al.* quantitatively separated the methyl esters of malic, citric and oxalic acids extracted from lemon, lime, tomato, grape and prune. Fernandez-Flores *et al.* made ethanolic extracts of fruits, precipitated the acids as their lead salts and converted these into their trimethylsilyl (TMS) derivatives. Concentrations of glycollic, succinic, fumaric, malic, tartaric, citric, syringic and quinic acids in 26 varieties of fruit were determined, and in some instances, the chromatographic "fingerprint" was typical of a fruit or its sub-variety. Among the fruits analysed were apple, pear, grape, peach, plum, prune, cherry, strawberry, blueberry, orange, lemon, grapefruit, melon and banana.

Fernandez-Flores *et al.*[243] have determined of amino-acids in 22 varieties of fruit, including those just listed. They cleaned up the fruit extracts on an ion-exchange resin and used the TFA–n-butyl derivatives for the GC. As little as 0.5 mg of amino-acid per 100 g of fruit could be detected. Kline *et al.*[244] have also analysed these fruits for sugars (*e.g.*, fructose, glucose, sucrose and sorbitol) by GC of the TMS derivatives. The examination of a fruit for fixed acids, amino-acids and sugars by GC yields three sets of data which, taken together, can help in identification of sub-varieties of fruits, and analysis of fruit mixtures.

Fruit pectin was pyrolysed by Zamorani *et al.*[245] in an attempt to obtain compounds suitable for GC. The pectin was deposited from solution on to a platinum spiral and dried until approximately 1 mg of solid had been accumulated. Unfortunately conditions of drying and pyrolysis are rather critical.

The flavour patterns of fruit are very complex, and some workers have concentrated on specific organic classes while others have attempted to elucidate the complete flavour structure. Flavanol glycosides and aglycones have been detected as their TMS derivatives[246] and this analysis has been applied to apple, pear and strawberry. Much work has been carried out in identifying the flavour volatiles of apple and pear, and the work of Gasco *et al.*[247] is particularly important because of the different methods used for concentration and clean-up. In a comparison of methods for measuring apple fruit-volatiles, Knee and Hatfield[248] concluded that passing air over pieces of apple under headspace-trapping conditions gave the most accurate profile of the flavour volatiles.

In an early application of GC in fruit analysis, Meigh[249] studied the evolution of ethylene from

stored apples. Ethylene can be used to stimulate the ripening of fruits and is emitted naturally from apples.

More study has been made of the volatiles of wine than those of grapes but Mattick *et al.*[250] determined the important flavour constituent, methyl anthranilate, in grape juice. The importance of lactones as flavour constituents in fruit was illustrated by Jennings and Sevenants[251] in their analysis of peach. Molina *et al.*[252] made a similar analysis of apricot. 4-(4-Hydroxyphenyl)butan-2-one has been determined specifically in raspberry by Braun and Hieke[253] who suggested that this method could be used to determine the raspberry content of essences and other raspberry products.

The importance of aldehydes as flavour volatiles was illustrated by Forss *et al.*[254] in their analysis of cucumber. They found that the important flavour constituent was nona-2,6-dienal which has the typical flavour of cucumber. Hex-2-enal, non-2-enal and n-hexanal were other aldehydes found. More recently, several alcohols have been discovered in trace amounts, as well as aldehydes.[255]

An example of GC being used to find an unpleasant fruit flavour, is the deduction by Brown[256] that the bitter flavour of unripe avocado was due to C_{17} oxygenated aliphatic compounds.

The main analytical interest in capsicum is capsaicin, which is the pungent principle. Mueller-Stock *et al.*[257] made a study of capsaicin and the related compounds dihydrocapsaicin, nordihydrocapsaicin and *N*-(4-hydroxy-3-methoxybenzyl)nonanamide. The TMS derivatives of these capsicum constituents were separated by Todd *et al.*[258] and the pungencies of the individual compounds were also assessed organoleptically. A GC method utilizing the TMS derivative of capsaicin was found to be more accurate than a spectrophotometric method, for determinations at the 0.5% level in capsicum oleoresins.[258a]

Of all the essential oils prepared from fruits, citrus oils have been most often examined. A popular preseparation before GC is into the terpene hydrocarbon and oxygenated terpene fractions. Ikeda *et al.*[259] examined the hydrocarbon fractions of the oils of lemon, lime, orange and grapefruit. They found that *d*-limonene was the major terpene of lemon, lime and orange oils and confirmed that, generally, monoterpenes form the greatest portion of the total terpene fraction. In oxygenated terpene fraction analysis, Stanley *et al.*[260] separated the aldeydes of lemon, orange and grapefruit oils after clean-up utilizing the formation of aldehyde–Girard T compounds. They found that geranial and neral were the major aldehydes of lemon oil. These aldehydes can be reduced with sodium borohydride to give the corresponding alcohols, which can be determined.[261]

Hunter and Moshonas[262,263] analysed lemon, lime, orange, grapefruit and tangerine oils for alcohols, using glycerol or propylene glycol as the separational solvent, the extract being cleaned up on alumina and subjected to GC–MS analysis.

The problem of deducing quality from the complex array of peaks due to all types of volatiles has been helped by computerization, a good example being the analysis of orange essential oil.[264]

Ikeda *et al.*[265] have also studied the monoterpene composition of several non-citrus essential oils, including bergamot, caraway, nutmeg, cardamom and black pepper.

The analysis of hop oil is particularly important to the brewing industry. Brewing chemists have paid much attention to the quality of hop oil which depends, usually, on the presence of certain compounds in the oxygenated fraction. Roberts[266] found that the important hop-oil constituents were myrcene, farnesene, β-caryophyllene and humulene. He also maintained that esters and ketones were important flavour contributors.[267] More than 120 volatiles have been identified in stored hops by GC–MS.[267a]

Vegetables and their products

Although vegetables have been studied less than fruits, aroma and flavour are important parameters in their quality control and GC has been used to estimate major volatiles and detect off-flavours in stored materials.

One of the first recorded headspace-sampling methods was used by Buttery and Teranishi[268] to measure the compounds responsible for off-flavours in stored potato and carrot. The potato off-flavour described as "baked" was examined by Pareles and Chang,[269] who found that methylpyrazines were the agents responsible.

Various aldehydes and ketones have been found in stored potato crisps by Dornseifer and Powers.[270] Changes occurred in the balance between these flavour volatiles and were related to the state of autoxidation of the oil present in the crisps.

Ayers *et al.*[271] attributed an off-odour of carrots, described as "violets" to β-ionone 5,6-epoxide. The carbonyl volatiles associated with carrot aroma have been determined as their 2,4-dinitrophenylhydrazones.[271a]

It is known that plants of the *solanum* genus contain glycoalkaloids which are potentially toxic, *e.g.*, α-solanine and α-chaconine. The TMS derivatives of these compounds were separated by GC in the analysis of potato tubers, sprouts and leaves.[272]

Geosmin, (*trans*-1,10-dimethyl-*trans*-9-decalol), considered to be one of the characteristic aroma constituents of beetroot, has recently been determined by GC.[272a] The volatiles of cooked artichokes have been removed by steam distillation and analysed by capillary column GC–MS.[272b] The major components found were the terpenes, selinene and caryophyllene.

GC in the analysis of onion, garlic and chive has centred on sulphur-containing volatiles. Brodnitz and Pollock[273] identified nine such compounds in onion oil, mainly di-1-propyl disulphide and other sulphides. Because the EC detector is more sensitive than the FID in its response to di- and trisulphides, a

dual channel system, splitting the GC effluent between both detectors, was used in an examination of garlic oil by Oaks *et al.*[274]

Sulphur-containing volatiles are important flavour constituents of the *cruciferae* genus. Thioglucosides have been determined in cabbage;[275] the interest in them arises from the possibility of their metabolism to simple toxicants, such as thiocyanates. Alkyl isothiocyanates have also been determined in cruciferous vegetables.[275a]

The flavour and aroma volatiles of peas[276] and mushrooms[277] have also been examined.

Some plants or their leaves or roots are pressed to yield essential oils which are employed as flavouring agents. A number of these oils have been extensively analysed by GC.

The peppermint group, which includes rue, pennyroyal and spearmint oils as well as the parent oil, has received considerable attention. Menthol, menthone, menthofuran and eucalyptol have been separated and determined in Yakima Valley peppermint oil by Cieplinski and Averill[278] and by using discriminant analysis, Hartmann and Hawkes[279] successfully identified the geographical origins of 45 different oils. A similar analysis correctly assigned almost all spearmint oils to their sources.[280]

A standard method for the determination of limonene and 1,8-cineole has recently been published.[280a]

A collaborative study of a method put forward for the determination of 1,8-ceneole in various oils, including sage oil, showed that the latter contained between 10.8 and 12.1% of the compound. A similar collaborative study produced a recommended method for the determination of eugenol in bay oil.

Ginger oil has been analysed for flavour volatiles[283] and Clark *et al.*[284] specifically looked for paradols in the oil, considering that the pungency characteristics of these compounds might make them attractive alternatives to capsaicin additives.

A comparison of the distribution of the volatiles of oil of cinnamon from leaf, stem and root was made by Senanayake *et al.*[284a] Altogether 72 compounds were identified and most of them were present in all three oils, but in different proportions.

Coffee, tea and cocoa

Since coffee is of great commercial importance, it is not surprising that a great deal of research has been conducted into the flavour and aroma of different varieties of roasted and unroasted coffees. GC has supplemented the work of the flavour panellist, and with the combination of GC–MS and computerization, most of the compounds responsible for the unique aroma of coffee have been deduced.

Rhoades,[285] in an early paper, described the extraction and separation of 19 volatiles from commercial coffees and found that the ratio of diacetyl to acetylpropionyl increased almost linearly with increase in the roasting temperature.

Quantitative analysis, using a GC–computer system with measurement of peak heights and ratios of volatiles, was used by Biggers *et al.*[286] to differentiate between *Coffea Arabica* and *Coffea robusta*. In one chromatogram there were 404 peaks or inflections, 32 of which were used for discriminant analysis. Sulphur-containing volatiles of the two varieties were separated by temperature-programmed GC and detected with the FPD in the sulphur mode.[286a] There were significant quantitative differences in the amounts of some of the volatiles and these were used to estimate the presence of as little as 1% *Coffea robusta* in *Coffea Arabica*. Volatile phenols,[286b] dihydroxyphenols and furyl derivatives,[286c] and hydrocarbons[286d] have been extracted from and determined in various varieties of coffees.

Tassan and Russell[287] collected the headspace vapours over a coffee brew and entrained the volatiles on a Porapak Q column before GC, then compared the flavour profiles with organoleptic evaluations.

Although caffeine is normally determined by classical methods, the use of a nitrogen-sensitive detector facilitates its estimation in coffee.[288]

Apart from the examination of tea for general flavour volatiles, *e.g.*, the investigation of black tea constituents,[289] GC has been used to determine flavanols in green tea. Pierce *et al.*[290] extracted powdered tea and prepared the TMS derivatives of the flavanols. The derivatives of catechin, epicatechin, epigallocatechin and gallate esters were separated and determined.

Several workers have studied the flavour and aroma composition of roasted and unroasted cocoa beans, not only because of their use as the basis for a beverage but also because the nib portion of the bean is an essential ingredient of chocolate couverture.

Bailey *et al.*[291] examined several cocoa varieties and found that they contained the same volatiles but in differing ratios. They found that aldehydes were very important flavour contributors and their ratios were related to the roasting temperature. A headspace-sampling technique was used for cocoa volatiles by van Praag *et al.*,[292] who confirmed the presence of 56 compounds by GC–MS. A similar sampling technique has recently been used with temperature programmed GC with a stationary phase of Cekachrom (styrene–divinyl benzene copolymer).[292a]

In the last few years the importance of the contribution of pyrazines to flavour and aroma in heat-treated foods has been recognized, and roasted cocoa beans have been analysed accordingly,[293] trimethyl- and tetramethyl-pyrazines being considered the important flavour contributors.

Fogden and Urry[294] differentiated two distinct types of cola drink by GC determination of the caffeine content; one type contained less than 2 mg/l. and the second contained between 70 and 200 mg/l. A similar method was used by Erndt *et al.*[294a]

Beer, wort and cider

The main original criterion for beer was its alcoholic content, but this is now supplemented by consideration of flavour quality. The well-established wet-chemical methods of measuring the ethanol content has given way, in part, to GC methods, which are usually more specific. GC methods have also been used in determining the sugar and amino-acid contents of wort, since these classes of compounds are precursors of some of the flavour volatiles of the beer.

In the determination of ethanol in beer, Trachman[295] used a Porapak Q column in a GSC method and found good agreement with distillation and gravity measurement, but the GC method was faster. Although the presence of methanol in beer is not such a problem as it is in distilled alcoholic beverages, GC gives satisfactory results with samples containing between 0.01 and 0.35% methanol.[296]

Before the advent of GC, it was almost impossible to separate and determine all the sugars present in beer and wort. Clapperton and Holliday,[297] using TMS derivatives, found that the dominant sugar in wort was maltose (2.7–4.8%) with smaller concentrations of fructose, glucose, sucrose and maltotriose. Jamieson[298] converted the sugars of wort or beer into their oximes, before silylation, and this simplified interpretation of the GC results because each reducing sugar gave only one peak instead of one for each anomer present.

Feil and Marinelli[299] determined the glycerol content of lager by direct injection onto the stationary phase Par 1, which is a macroreticular resin. Eleven lagers gave an average value of 1.6 mg/l.

Analysis of the amino-acids in wort can yield valuable information regarding the proteolytic changes as fermentation proceeds and beer is produced. Kurosky and Bars[300] determined the amino-acid contents of beer and wort by using the TFA methyl esters after clean-up on an ion-exchange resin, and in a similar method, Otter and Taylor[301] used the TFA n-butyl esters.

The volatile components in wort and beer, particularly the fusel oils, esters, diketones and sulphur-compounds, have been the subject of considerable investigation, especially by GC. The short-chain fatty acids, *viz.*, C_6–C_{10}, have been determined in wort and beer[302] as have the long-chain fatty acids which can be contributors to the so-called "cardboard" off-flavour.[303] Fusel oil and 2-phenylethanol are important flavour contributors in beer and Morgan[304] has compared the concentrations of these volatiles in stout, pale ale, brown ale and lager. Beers have also been analysed for esters and higher alcohols, with isolation by distillation into a cold trap, a method preferred to headspace analysis.[304a] Engan[305] considered 2-phenylethanol to be the most important aromatic alcohol of beer and found concentrations of between 5.6 and 27 ppm in Norwegian products.

The importance of flavour to the brewing chemist is illustrated by the large amount of analytical literature on the subject, including GC methods in particular. Among the most important papers are some on the determination of diketones,[306–306b] sulphur-containing compounds,[307–308a] phenolic compounds,[309] cetechin[310] and non-2-enal.[311]

An apparatus and procedure for the analysis of a whole range of beer volatiles has been recently described by Williams and Strauss.[312] In this method, headspace sampling precedes flushing onto a trap of Chromosorb 105 and subsequent desorption and GC analysis.

The influence of the flavour constituents of hops on the final beers was studied by Tressl *et al.*[312a] and that of roasted barley by Harding *et al.*[312b]

Kieser *et al.*[313] determined the 2-phenylethanol content of various ciders and Pollard *et al.*[314] determined their fusel oil contents. Subsequently, a whole range of cider flavour constituents was separated and identified by using a concentration technique on Porapak Q and GC–MS.[314a]

Wine and must

The methods used for the determination of ethanol and methanol in beer and wort can be applied to wine or must.

Fixed acids in wine were determined by Brunelle *et al.*,[315] as the TMS derivatives after removal of sugars. Of various fruit wines examined, only grape wine contained tartaric acid.

The fusel oil content of wines of various origins has been determined by Webb and Kepner.[316] They experimented with GC parameters to increase the efficiency of separation of the fusel oil components and found that the major component was always 3-methyl-1-butanol.

The quality of wine depends largely on its flavour and aroma and much work has been carried out on the analysis of the volatile fraction. One of the fundamental problems in analysis of volatiles is their extraction without loss or artefact formation. Hardy and Ramshaw[317] suggested trichlorofluoromethane as extraction solvent since it does not extract water, ethanol or higher alcohols. They used GC–MS to confirm the identities of 41 volatiles in a Riesling wine.

The anthocyanins of red wines have been determined by Drawert and Leupold[318] by use of the TMS derivatives.

Some countries incorporate a tax on carbonated wines and Ashmead *et al.*[319] used GSC on a charcoal column to determine carbon dioxide in wines.

Addeo *et al.*[319a] determined cyanide residues in wine down to the 1-μg/l. level after formation of cyanogen bromide, which was subjected to GSC with EC detection.

Ethylidine glycols are thought to be partly responsible for the characteristic aroma introduced into sherry by the flor process, and these compounds have been estimated together with other volatiles in Australian sherries.[319b]

Brandy

Brandy, being the distilled and matured product of wine, contains the most volatile constituents of wine in addition to newly-formed volatiles. It is to identify these, therefore, that GC is mostly used in brandy analysis.

Methanol is concentrated and formed in the distillation process, and a U.K. Research Committee has recommended three GC methods for the determination of methanol in brandy and other spirits.[320] The methanol content of brandy was shown by Dyer[321] to be between 0.018 and 0.067%.

In addition to exercising control over the methanol content of spirits, the producer should be aware of their fusel oil contents, since these can also reach harmful levels, although the range and balance of low concentrations are essential for the flavour and aroma of the products. Martin *et al.*[322] examined brandy, whisky and rum for fusel oil content and in a similar study Singer and Stiles[323] found that the sum of the concentrations of the C_3–C_5 alcohols could be taken as the total fusel oil content of brandy.

The concept of using the ratios of the fusel oil components as a measure of brandy quality was introduced by Singer;[324,325] he used various ratios of the concentrations of propanol, 2-methyl-1-propanol, 2-butanol, 2-methy-1-butanol and 3-methyl-1-butanol; in a similar approach, brandies imported into Australia have been analysed for the presence of fermented fruit juice other than grape.[326]

A partially successful attempt has been made recently to characterize brands of spirits, including brandy, by using fusel oil analysis.[327]

Esters play an important part in the flavour and aroma of spirits and Guymon and Crowell[328] have related the characteristic brandy flavours to ethyl octanoate, decanoate and dodecanoate. Ethyl acetate and higher alcohols have recently been determined in brandies.[328a]

Whisky and bourbon

The quality of whisky and bourbon, which are grain-based distilled beverages, depends on their flavour and aroma compounds and the same analytical approach can be used as that for fusel oil determination in brandy.[322–325] Hall[329] considered that whiskies could be classified according to the ratio of isopentanol to isobutanol and successfully showed that a whisky labelled as a Scotch blend was in fact a bourbon.

There has been some interest in the analysis of whisky for sugars and glycerol during maturation in newly charred white-oak casks; GC of the TMS derivatives has shown that the glycerol content increased from 0.8 to 2.4 g/l. in a 100° proof whisky.[330]

The differences between malt and grain whiskies are important organoleptically and, therefore, commercially. Duncan and Philp[331] used three different sets of GC conditions to evaluate alcohols, phenols, esters and carbonyls in both types of whisky, in an attempt to produce a method to deduce the proportion of both types in blends. Malt whisky is found to contain a number of alcohols, carbonyl compounds and higher alkanoic acid esters that do not occur in grain whisky; there is a particularly high concentration of 3-methyl-1-butanol (0.16%).

Martin *et al.*[332] specifically looked for ethyl esters of fatty acids and isoamyl acetate in whiskies and rums, in an attempt to relate their concentrations to flavour and aroma character.

More recently, successful attempts have been made to distinguish high-grade and ordinary whiskies by applying statistical and pattern-recognition techniques to the chromatograms of the volatiles.[332a]

Gin

Some of the flavour constituents of gin have been identified by GC–MS by Clutton and Evans.[332b] The terpenes, aldehydes and alcohols detected were consistent with the composition of the essential oils used in gin production, *e.g.*, juniper berry, coriander, cinnamon and cassia.

Rum

Rum, being the distilled product of sugar cane juice or molasses, has a distinctive flavour and aroma. Its fusel oil content has been measured, and often compared with that of brandy or whisky, but a great deal of research has been applied to the satisfactory separation and detection of rum esters. Stevens and Martin[333] considered that the quality of rum was proportional to the concentration of ethyl esters of fatty acids of even carbon number between 8 and 16.

Vinegar

Vinegar, being a fermentation product, is characterized by its volatile constituents as well as its fixed acetic acid. GC has been applied to the determination of volatiles and, in particular, diacetyl and 3-hydroxybutan-2-one.[334] In a general analysis of volatiles, Kahn *et al.*[335] determined alcohols, esters and acids in spirit and cider vinegars.

Sugar and its products

Many sections of the food industry require sugar or sugar syrups as a raw material. The determination of single sugars in foods is relatively straightforward but sugar mixtures often present major analytical problems. The development of TMS derivatives of sugars[336] has resulted in GC often being the method of choice for sugar determination.

There are many methods in the literature for the preparation and separation of the TMS derivatives of sugars, *e.g.*, that of Brobst and Lott[337] for a glucose syrup to be used in the brewing industry. However, most reducing sugars give more than one peak because of the different anomers present. Reduction of the sugars with sodium borohydride to the corresponding alditols, before formation of the TMS deriva-

tives, removes anomerization,[338] but formation of the oximes before alkylation is more convenient.[298] With an open tubular column the TMS derivative of sucrose has been separated in only a minute.[339] A 40 m × 0.5 mm column coated with OV-17 was used. Other sugar derivatives have been used in GC methods, *e.g.*, methyl glycosides,[340] hexa-acetates[341] and TFA derivatives,[342] but TMS derivatives remain the most popular.

Pyrolysis has been little used in the application of GC to food analysis, but the high-frequency pyrolysis of carbohydrates, including glucose, fructose and sucrose, with a Curie-point pyrolyser, was used by Baltes and Schmahl.[342a] The volatile products were subjected to temperature-programmed GC and detected by MS.

Aconitic acid is the predominant organic acid in sugar cane and sorghum cane syrups, and its concentration is important since high levels can cause clarification problems. Johnson and Fernandez-Flores[343] have devised a GC method for aconitic acid as its TMS derivative.

Some interest has been shown by the sugar industry in use of the lactic acid concentration of sugar beet juice and molasses as a direct indicator of microbiological action. Oldfield *et al.*[344] converted lactic acid into acetaldehyde for its GC determination.

Sugars caramelized by heating are used for colouring and flavouring. Sugisawa[345] has identified glucose caramel volatiles and found that acids, aldehydes, alcohols, ketones and furans are the main flavour constituents.

Caramel is produced commercially by the reaction between sugars and ammonia, and there has been some concern that small quantities of substituted imidazoles are formed in the process. A recent GC method for the determination of 4-methylimidazole, the main imidazole contaminant, involves solvent extraction from alkaline solution and results in a detection limit of 0.2 ppm in the caramel.[346]

The U.S. Department of Agriculture has produced a number of GC methods for the detection and determination of volatiles in maple syrup. Among the more important volatiles found are vanillin, syringaldehyde and dihydroconiferyl alcohol. Filipic and Underwood[347] have been responsible for a great deal of the studies.

The main GC analytical interest in honey is the separation and identification of the volatiles. In isolating 120 components from a honey, Cremer and Riedmann[348] considered that the alcohols, ketones, aldehydes and esters found resulted not only from the flowers, but also from the fermentation process.

Cereals and their products

GC has been applied in analysis of the fatty acids that constitute the glycerides of the lipid portion of flour, which can produce up to 4% of the total fat in bread. As early as 1958 Coppock *et al.*[349] examined wheat flour oil; they considered that some of the fatty acids found had an influence on bread aroma and flavour.

Fisher and Broughton[350] have fractionated wheat flour lipids. Linoleic acid (~63%) is the dominant acid in all fractions, followed by palmitic (17–22%) and oleic (9–14%) acid. In an analysis of whole wheat, bran, germ and endosperm for free lipids, Burkwall and Glass[351] also found that linoleic was the major glyceride fatty acid.

Franciosi and Giovannini[352,353] determined the egg content of pastas by analysis of the glyceride fatty acids. Even a small addition of egg significantly reduced the linoleic to oleic acid ratio of the pasta, and other fatty acid ratios were also significantly changed. These workers also indicated differences in fatty acid ratios in hard and mixed wheat pastas.

Various aldehydes and ketones were sought in the volatiles of bread by Hunter and Walden.[354] They used semicarbazide to form derivatives of the carbonyls, regenerating the latter with phosphoric acid for GC determination. Recently, 19 carbonyls and 34 amines have been identified in wheat flour.[355] The volatiles of maize and rice[355a] and of wild rice[355b] have recently been studied by GC methods.

The amino-acid contents of maize and soyabean meal have been determined by GC of the butyl esters of their TFA derivatives, following acid hydrolysis of the proteins.[356] Glutamic acid was the predominant amino-acid found in both products.

GC APPLIED TO ANALYSIS OF ADDITIVES AND CONTAMINANTS

The widespread use of food additives has necessitated the development of organic microanalytical methods, in which GC has played a prominent part. Most countries allow food preservation and the addition to food of antioxidants, emulsifiers, stabilizers, flavourings and artificial sweeteners. Fashion is ever changing and the food manufacturing and legal enforcement analysts have to keep a check on levels of these additives.

Pesticide residue analysis in foods has given great impetus to the use and development of GC techniques in food laboratories. Other contaminants which are determined by GC techniques are PCBs, methylmercury, nitrosamines, solvent residues, food packaging materials, mycotoxins and drug residues.

Preservatives

With the notable exception of sulphur dioxide, most food preservatives can be determined satisfactorily by GC, which has superseded conventional colorimetric methods which, in general, are less sensitive and less specific. GC has been used in the determination of benzoic acid and its hydroxy and halogenated derivatives, dehydroacetic acid, acetic acid derivatives, propionic acid, sorbic acid, salicylic acid, diethyl pyrocarbonate, diphenyl, *o*-phenyl-

phenol, ethylene oxide, nitrous oxide, thiabendazole and imazalil.

Benzoic acid and 4-hydroxybenzoate esters are extensively used as preservatives. Similar methylation methods for the separation and determination of these preservatives were developed by Vogel and Deshusses[357] and by Groebel,[358] the former also separating 2-chlorobenzoic acid, 4-chlorobenzoic acid, dehydroacetic acid, sorbic acid and salicylic acid. Groebel used his method in the analysis of margarine, mayonnaise and meat and fish pastes.

A scheme for the GC determination of 22 preservatives and antioxidants in beer was developed by Silbereisen and Wagner,[359] using methyl derivatives on a capillary column.

Benzoic acid, sorbic acid and the methyl, ethyl and propyl esters of 4-hydroxybenzoic acid have been successfully separated and determined in marmalade, margarine, mustard, mayonnaise, canned fish, beer and wine, by means of the TMS derivatives.[360] Benzoic and sorbic acids have also been determined in fruit juices, syrups and soda-water.[360a]

As little as 5 ng of benzoic acid can be detected in margarine by the simple method of Graveland[361] which merely entails suspending the sample in solvent and analysing the supernatant liquid after centrifugation. A similar method has been used to determine propionic acid and sorbic acid in rye bread.

Fogden *et al.*[362] detected and determined benzoic acid, 4-hydroxybenzoates and sorbic acid in a variety of foods by a GSC method using tris(hydroxymethyl)-methylamine as an additive at the drying stage before the GC, which minimized evaporation losses of the preservatives. A rapid method for the determination of benzoic acid in soft drinks and sugar syrups has recently been published.[362a]

Propionic and sorbic acids were extracted together from bread by steam distillation before solvent extraction and GC determination of the free acids, by Walker *et al.*[363] Nose *et al.*[364] preferred to form the phenacyl ester of propionic acid in their determination of this preservative, using 4-chlorophenacyl bromide as reagent.

Sorbic acid has been determined in prunes down to the 1 mg/kg level by GC–MS of the n-butyl ester.[364a]

Diethyl pyrocarbonate is used as an additive in wine, beer and non-alcoholic beverages to prevent undesirable fermentations. Wunderlich[365] used a method based on the hydrolysis of this preservative to yield ethanol which further reacted with the diethyl pyrocarbonate to give diethyl carbonate which was subsequently determined.

The carcinogen ethyl carbamate can be formed from diethyl pyrocarbonate and ammonia, when the latter is present in a beverage with the preservative. Joe *et al.*[366] used a GC method to determine ethyl carbamate in wine and found between 1 and 20 μg/l.

Biphenyl is normally incorporated in the wrapping papers of oranges and other citrus fruits, to prevent mould growth. *o*-Phenylphenol or its sodium salt is used as a dipping solution for a similar purpose. The usual method of isolation of these preservatives is by steam distillation and solvent extraction of the distillate, followed by GC determination.[367,368] Sweep co-distillation has been used as an isolation technique before the determination of these preservatives, but lemon-peel essential oil ingredients have to be removed with alumina,[368a] whereas the combined steam distillation and solvent extraction procedure incorporated in the Likens–Nickerson apparatus produces a relatively clean extract.[368b] Tanaka *et al.*[368c] used steam distillation isolation and improved the specificity of their method by chromatographing the pentafluorobenzyl derivative of *o*-phenylphenol and using EC detection. Lord *et al.*,[368d] in evaluating methods for the determination of these preservatives in citrus peel, preferred their own GC technique to those specified in certain EEC Recommended Methods.

Biphenyl-impregnated pads used for the packaging of citrus fruits in transportation have been extracted and analysed for the preservative by GC and the results compared with those obtained by HPLC.[369]

Thiabendazole is used in a similar way to biphenyl and *o*-phenylphenol and Mestres *et al.*[370] used a GC method with an FPD used in the sulphur mode for determining down to 0.1 μg of thiabendazole. The methyl derivative[371] and the pentafluorobenzoyl derivative[372] have also been used for GC.

Imazalil has similar properties to thiabendazole and Greenberg and Resnick[373] determined this compound after its solvent extraction and were able to measure down to 0.5 ppm.

In experiments to discover the reaction products of nitrite preservation of meat products, nitrous oxide was evolved thermally and determined by GC on a Porapak Q column.[374] More recently, nitrite and nitrate have been determined in meat products by nitrating added benzene and determining the resulting nitrobenzene,[375] or by nitrating added 2,4-xylenol and determining the resulting 6-nitro-2,4-xylenol.[375a]

Formaldehyde has been used to preserve certain concentrated liquid flavourings, *e.g.*, apple and smoke, and may be determined at the 10 mg/kg level by GC of its 2,4-dinitrophenylhydrazone.[375b]

Antioxidants

GC has been used in the detection and determination of most of the manufactured antioxidants used in food. These include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), gallate esters, nordihydroguaiaretic acid (NDGA), dilauryl 3,3′-thiodipropionate (DLTDP), 3,3′-thiodipropionic acid (TDPA), 4-hydroxymethyl-2,6-tert-butylphenol (Ionox 100), 2,4,5-trihydroxybutyrophenone (THBP), tert-butylhydroquinone (TBHQ), ethoxyquin, ethyl protocatechuate and guaiac resin.

GC methods have largely replaced colorimetric ones for BHA, BHT and gallate esters. Hartman and Rose,[376] in their determination of BHA and BHT in

vegetable oils, used two different stationary phases to confirm their results. BHA is eluted before BHT on a DC-200 column; the elution is reversed on a Carbowax 20M column.

A vacuum-sublimation clean-up procedure was the feature of a method for the determination of BHA, BHT, propyl gallate, NDGE, DLTDP, TDPA, Ionox 100 and THBP in lard by McCaulley *et al.*[377] These antioxidants were clearly separated on a GE-XE-60 stationary phase.

TMS derivatives of BHA, BHT, propyl gallate, TBHQ and NDGA were used by Stoddard[378] for their determination in vegetable oils. A two-solvent extraction system was used before the GC. If Florisil clean-up was used, BHT could be determined without forming its derivative. Some of the extraction procedures have been improved.[378a]

Heptafluorobutanoyl derivatives of BHA, propyl gallate and TBHQ were separated on an OV-3 stationary phase by Page and Kennedy.[379] EC detection increased the sensitivity of the method. Unfortunately, the BHT derivative is not formed in this method.

Antioxidants are also added to certain vitamin preparations and BHA plus BHT have been determined in vitamin A concentrates.[380]

BHA may be well separated from BHT by use of its TFA derivative.[381]

Ethoxyquin is used as an antioxidant on apples in storage. Winell[382] used the heptafluorobutanoyl derivative of ethoxyquin for GC after extraction of the antioxidant with hexane. With EC detection, down to 0.02 ng of ethoxyquin could be detected.

Citric acid has been used as an antioxidant synergist and can be determined in fats and oils by means of its butyl ester.[383]

Emulsifiers and stabilizers

GC has been used in the determination of emulsifiers and stabilizers which are natural to food, *e.g.*, glycerides, polyglycerides and polysaccharides, and those which have been specifically made to fulfil certain needs, *e.g.*, sorbitan esters and their polyoxyethylene derivatives, brominated vegetable oils, sucrose diacetate hexaisobutyrate and triethyl citrate.

The main problem arising from glyceride and polyglyceride determinations is their separation into groups before GC. The popular technique is column chromatography on silica gel, a good example being given by Sahasrabudhe and Legari[384] who completed the analysis by using the TMS derivatives of mono- and diglycerides. TMS derivatives are most popular in the determination of polyglycerides and Sahasrabudhe[385] applied preparative TLC for their separation before formation of the TMS derivatives of the eight fractions.

An early attempt to determine sorbitan monostearate depended on the presence in the emulsifier of a small concentration of 1,4-3,6-dianhydrosorbitol. This anhydride was determined in cake mixes by Wetterau *et al.*[386] and the sorbitan monostearate concentration was calculated. The TMS derivative of the anhydride has also been used as an indicator of sorbitan ester concentrations in various foods.[387]

Another approach, introduced by Lundquist and Meloan, was the hydrolysis of the sorbitan esters and GC separation of the resulting polyols.[388]

In some countries, brominated vegetable oils (bromine addition products of vegetable oils such as sesame, olive, corn and cotton seed) are used as dispersing agents for the flavouring oils employed in the soft drinks industry.

The GC methods put forward for the separation and determination of brominated vegetable oils have depended on extraction, hydrolysis, methylation and GC determination. In this way, chromatograms are produced which show compounds such as methyl tetrabromostearate, methyl dibromostearate and other methyl esters of fatty acids. By using standard brominated vegetable oils for comparison, Conacher *et al.*[389] were able to deduce which oil had been used in such samples as citrus soft drinks.

Brominated vegetable oils are prohibited in foods in some countries and sucrose diacetate hexaisobutyrate has been used in their place. The most satisfactory method for the determination of this dispersant is through the decyl acetate and decyl isobutyrate formed from it after extraction and treatment with decanol in sulphuric acid.[390]

Triethyl citrate and triacetin are additives used in egg whites to facilitate emulsion and so reduce the time required to produce whipped egg. Kogan and Strezleck[391] ether-extracted these emulsifiers from egg whites in acid medium and determined them on an SE-30 stationary phase.

Polysaccharide gums, such as guar, carob-bean, agar, carrageenan, karaya, methyl cellulose, tragacanth, pectin, acacia and alginate have been detected and, in some cases, determined in foods either by extraction, methylation followed by hydrolysis,[391] or by formation of the TMS derivatives,[392] or through the aldonitrile acetates of the monosaccharides isolated from hydrolysis products.[393,394]

Artificial sweeteners

The addition of artificial sweeteners to food, although long used for reasons of economy because sugar is relatively expensive, has become significant for the reason that they reduce the calorific value when they replace sugar, and weight-conscious populations may benefit. However, the increasing suspicions that not all artificial sweeteners are toxicologically safe have lent weight to their detection and determination in food.

The artificial sweeteners, cyclamates, saccharin, dulcin, sorbitol and the methyl ester of L-aspartyl-L-phenylalanine have been determined by GC methods, which are usually the most sensitive or selective.

The GC determination of cyclamates in soft drinks was pioneered by Rees,[395] using the reaction between cyclamate and nitrous acid to yield cyclohexene

which he measured on an Apiezon L stationary phase. Richardson and Luton,[396] in a modification of this method, used it to determine down to 0.2% sodium cyclamate in soft drinks.

Cyclohexene has also been measured in headspace samples, following the same reaction, and the method has been applied to the analysis of fruit juices, soft drinks, wines and preserves.[397]

The TFA derivative[398] and the heptafluorobutanoyl derivative of cyclamate[399] have also been utilized in its determination.

Cyclohexylamine is the basis of the synthesis of cyclamate and trace amounts are often carried through into the final product and it has been found in various citrus and cola beverages which contained cyclamate. The GC methods depend on either determining the free amine[400] or forming the 2,4-dinitrophenyl derivative, which has strong electron-capturing properties.[401]

Cyclamate often occurs in soft drinks with saccharin, which has been used as an artificial sweetener for over 50 years. Conacher and O'Brien[402] methylated both sweeteners after their solvent extraction and the methyl derivatives were separated on an SE-30 stationary phase.

Koenig[403] separated the methyl esters of cyclamate and saccharin and also free dulcin, which is a sweetener used some time ago but now in only a few countries.

The TMS derivative of saccharin was utilized by Gerstl and Ranfft[404] for its determination in foods, a mixed stationary phase of OV-7 and OV-22 being used.

Toluene-2-sulphonamide is an important trace impurity in saccharin and could be present in detectable amounts in foods to which saccharin has been added. The TMS derivative of this impurity has been used for its GC determination,[405] although the free sulphonamide may also be used.[405a,405b]

A relatively new dipeptide sweetener, the methyl ester of L-aspartyl-L-phenylalanine, has been determined with its degradation products, by GC separation of the TMS derivatives.[406]

When large amounts of sweetener are needed in a dietetic or diabetic food, saccharin and cyclamate are unsuitable because they impart a bitter aftertaste on the palate when used in high concentration. Sorbitol has therefore been used extensively in these special foods and GC determination of the hexa-acetate is common.[407,408] Fernandez-Flores and Blomquist[409] have employed the TMS derivative, finding it particularly useful in the determination of sorbitol in dietetic candies and cakes.

Flavourings

GC has been greatly used in studies of the natural flavourings of many foods, such flavourings being made up of large numbers of components. The analysis of synthetic flavourings can be less difficult since the number of inherent components is ususlly smaller. A great deal of GC analytical work is devoted to the detection and determination of certain flavouring components which could be present and are either known to be toxic or are suspected to be so, *e.g.*, benzaldehyde, coumarin, safrole and its derivatives, methyl salicylate, β-asarone, pulegone and thujone. GC methods have also been used for the determination of ammonium glycyrrhizinate, monosodium glutamate, maltol, ethylmaltol and vanilla.

Benzaldehyde is a major flavour ingredient of cherry and almond flavourings. Brunelle and Martin[410] determined the free aldehyde isolated by steam distillation. They found that natural cherry flavourings contained approximately 0.2% benzaldehyde and that imitations contained up to 2.3%.

Bucci *et al.*[411] have reviewed the public health problems involved in the use of certain flavourings in food and produced a quantitative method for coumarin, detecting as little as 0.2 μg. May wine, a light grape wine flavoured with woodruff herbs, has also been examined for coumarin.[412]

The recommended method of the International Organisation of the Flavour Industry[412a] for the determination of coumarin in foods involves solvent extraction and direct GC.

Liddle and de Smedt[413] used solvent extraction, followed by GC–MS analysis, to look for coumarin, safrole, β-asarone and thujone as flavour agents in vermouth.

Safrole, isosafrole, dihydrosafrole, dihydroanethole and methyl salicylate have been determined in non-alcoholic beverages by Larry,[414] by GC after their isolation by steam distillation and solvent extraction. The International Organisation of the Flavour Industry has recently published similar methods for the determination of safrole and isosafrole in foods and beverages[415] and of α- and β-thujone.[416]

β-Asarone is a component of oil of calamus and this oil has been used as part of the flavouring of vermouth. A steam distillation, solvent extraction and GC method was put forward by Larry[417] for 5–100 ppm levels of β-asarone in vermouth. The recommended method of the International Organisation of the Flavour Industry[417a] for the determination of β-asarone in alcoholic drinks and sugar confectionery involves solvent extraction and direct GC.

β-Asarone, and α- and β-thujone have been determined in aperitifs, including vermouth, by distillation followed by solvent extraction and GC.[418] The limit of detection was 0.01 ppm.

A steam distillation, solvent extraction and GC procedure has recently been recommended as a standard method for the determination of pulegone by the International Organisation of the Flavour Industry in the analysis of confectionery, ice cream, beverages and essential oils.[419]

Ammonium glycyrrizinate can be used as a flavour potentiator in chocolate- and caramel-flavoured beverages. Larry *et al.*[420] have put forward a method for its determination as the TMS derivative, formed after hydrolysis of the sample.

Monosodium glutamate is used primarily as a flavour potentiator in "meaty" food products. Analytical methods usually depend on measurement of glutamic acid and Gal and Schilling[421] have developed a method for its determination as the TFA derivative of the butyl ester. They applied their method to the analysis of soups and seasonings for monosodium glutamate concentrations of between 2 and 17%.

Pesticides

The technology of GC has benefited from analysis for pesticide residues in foods and crops. It is difficult to imagine what would have happened to pesticide residue analysis without the technique, and it was in the late 1950s that GC was given perhaps its biggest advertisement as a microanalytical technique, by the multiresidue analysis of OC insecticides. In this context, the development of the EC detector was all-important,[422] followed by the development of the MC detector.[423] No subject has done more to stimulate detector technology than pesticide residue analysis and by the time analysts became interested in organophosphorus (OP) residues, most of the methods were ready-made, having been developed for organochlorine (OC) residues, except for a specific and sensitive detector; this was to follow in the shape of the AFID.[424]

Because of the persistence and, therefore, accumulation of OC pesticides and their possible hazards to health, many of them have been replaced by alternatives, *e.g.*, carbamates and, therefore, GC has been applied increasingly to these and other organonitrogen (ON) pesticides.

Thousands of papers have been published concerning the application of GC to pesticide residue analysis and it is only possible in this review to include some of the more important contributions.

Organohalogen pesticides. The concern shown internationally about the persistence of OC insecticide residues and their ecological effects has led to numerous surveys of such residues in virtually all types of food. Once the detector systems had been established, the largest variations in published methods were in the extraction and clean-up of the residues.

The initial extraction is mainly done with acetone, hexane or petrol, acetonitrile, dimethylformamide, dimethylsulphoxide and propylene carbonate. Clean-up of samples is usually done by solvent partition followed by column chromatography on Florisil, alumina or activated carbon.

In 1960, Goodwin *et al.*[425] applied GC to the detection of aldrin, dieldrin, *pp'*-DDT and γ-BHC at the 0.05-ppm level in crop extracts, a method later improved upon by a change from argon ionization detection to EC.[426]

Acetone extraction, followed by addition of sodium sulphate solution and extraction of OC compounds into petrol, was used by Hamence *et al.*[427] in the examination of food samples. For clean-up they used further partition into acetonitrile, addition of sodium sulphate solution to the acetonitrile extract and re-extraction into petrol.

The direct extraction of food samples with acetonitrile, thus omitting acetone, is the main difference in the American procedure, *e.g.*, in the official AOAC method. The method is used for the analysis of residues of both OC and OP pesticides. The sample, blended with acetonitrile, is extracted with petrol after the addition of water, and the petrol extract is cleaned up on Florisil, mixtures of petrol and diethyl ether being used for elution. The stationary phase used is 10% DC-200 and detection is by EC for OC compounds. This official method was based on the original work of Burke and Giuffrida.[429]

Although little work had been carried out until the 1970s on combining GC with MS detection in residue analysis, the fact that PCBs can be co-extracted with OC pesticides created interest. Bellman and Barry used GC–MS to examine foods for both species.[430]

Luckas *et al.*,[430a] in a method involving the determination of DDT and TDE by means of reaction with MgO to produce alkenes for GC, were able to separate these OC insecticides from PCBs, which did not react.

A useful identification method for use before GC of OC pesticide residues depends on the partition of the compounds between two immiscible solvents, such as hexane and acetonitrile. Beroza and Bowman[431] used this technique by determining the characteristic degree of extraction (%) of individual OC pesticides when equal volumes of the two phases were used, and applied the values for analysis of crop residues; the co-extractives did not affect the degree of extraction.

In 1965, Storherr and Watts[432] introduced the clean-up method termed sweep co-distillation as part of the determination of both OC and OP pesticides. These workers noticed that crop extractives not removed by hitherto standard clean-up procedures were deposited on the glass-wool packing at the injection end of the GC column. Taking advantage of this, they produced a heated pre-column of glass wool, complete with injection port and carrier gas inlet. Large volumes of pesticide extracts were introduced into the heated tube and the pesticides were swept from it by nitrogen into a cooling coil, before GC. The portion of glass wool containing the co-extractives was periodically replaced. The technique has been found particularly useful in the analysis of fatty foods and many variations on the original technique have been used, *e.g.*, a silanized glass bead pre-column in place of the glass wool.[433]

In an effort to simplify the clean-up procedure, Telling *et al.*[434] have recently used acetone–hexane as extractant and a single alumina column for clean-up, with hexane as eluent.

Fumigants are used extensively for the control of insects and moulds in stored foods such as grain or flour, and many of these are simple halogen-contain-

ing aliphatic compounds which are amenable to GC separation and determination.

Bielorai and Alumot[435] used a GC method for determining the fumigants chloroform, carbon tetrachloride, trichloroethylene and carbon disulphide in cereal grain, with a steam-distillation step incorporating toluene as co-distilling solvent.

Ragelis *et al.*[436] extracted wheat flour and ground pepper by percolating diethyl ether through a column of the sample, in a method to determine chlorohydrins resulting from fumigation of stored food with ethylene and propylene oxides. The compounds 2-chloroethanol and 1-chloro-2-propanol were directly determined in the percolate from the wheat flour, and after clean-up on Florisil, in the percolate from the ground pepper.

Ethylene dibromide, methyl bromide and also 2-chloroethanol from ethylene oxide were determined in flour and grain by Heuser and Skidmore.[437] The samples was extracted with aqueous acetone, and after settling the supernatant liquid was examined by GC.

The most widely applied halogen-containing fungicides are the chlorinated benzenes. Di Muccio *et al.*[438] successfully separated the α-, β-, γ-, and δ-isomers of BHC and hexachlorobenzene, the feature of the GC being the mixed stationary phase comprising 3% OV-61, 7.5% QF-1 and 3% XE-60, (2:2:1 v/v), which is necessary to separate these compounds, which have short retention times on most phases.

Residues of the well-known organochlorine herbicides, 2,4-D, 2,4,5-T, MCPA and MCPB have been successfully determined by GC after methylation[439] or silylation.[440]

Organophosphorus pesticides. The OP pesticides are almost exclusively insecticides and acaricides. Much of the experience gained in the extraction and clean-up of OC pesticide residues has been applied to OP pesticide residues, which has saved time in method formulation. Solvents used for extraction include chloroform, dichloromethane, ethyl acetate, methanol, benzene, hexane and propylene carbonate, whereas the column chromatographic materials used in the clean-up procedures are the same as those used in OC pesticide residue analysis.

Detectors sensitive to phosphorus have been used to advantage, *viz.* the AFID, FPD and the plasma detector; the MCD has been used in the determination of sulphur-containing OP compounds.

The sweep co-distillation clean-up technique used for OC pesticide residues has also been used for OP pesticide residues[432] and, with initial ethyl acetate extraction of food samples, this technique has been incorporated into the Official Methods of Analysis of the AOAC.[428]

Bowman *et al.* analysed 39 foods for multiresidues of pesticides containing phosphorus and/or sulphur.[441] Four extraction procedures were used, depending on the nature of the food. OV-101 and OV-210 were the stationary phases used and detection was by FPD in both the phosphorus- and sulphur-sensing modes.

The choice of clean-up procedure and detector in the GC of OP pesticide residues has overshadowed other factors in the analysis. Many stationary phases are suitable for single OP compounds, but the choice of a phase to separate and determine large numbers of OP compounds is limited. Bowman and Beroza[442,443] tabulated the retention data of 138 pesticides on OV-101, OV-17, OV-210 and OV-225 as stationary phases and 146 pesticides on Dexsil 300.

Various methods were recently examined in a collaborative study for the analysis of residues of common OP pesticides, including malathion, dichlorvos, dimethoate, omethoate, parathion and azinphos methyl,[444] and certain procedures were recommended; guidance on the preparation of GC columns was also given.

Residues of thioether OP pesticides, *e.g.*, carbophenothion and demeton, have been determined in fruits and vegetables after oxidation by permanganate to the corresponding *S,S*-dioxides.[444a]

MS was used as detector in a recent GC method for the determination of 23 OP pesticides liable to be present in fruits and vegetables.[445] Ten pesticides were determined at the 40-ppM (parts per milliard) level, by fragment measurement with single- and multiple-ion detection.

Organonitrogen pesticides. Organonitrogen (ON) pesticides include carbamates, substituted ureas, thiocarbamates, triazines, substituted phthalimides and cyano- and nitro-phenols.

The detection and determination of sub-ppm levels of multiresidues of ON pesticides has lagged behind those of OC and OP pesticide analysis. Discouragement of the use of DDT and other OC pesticides has enhanced the use of carbamates, especially carbaryl.

Martin's detector,[446] which incorporates a furnace in which the nitrogen released from the compound is reduced to ammonia and titrated coulometrically, is an example of detection methods developed for ON compounds.

Coulson[447] used his electrolytic conductivity detector after reductive pyrolysis of ON compounds with a nickel-wire catalyst. A method incorporating this type of detector system has recently been evaluated for 15 ON pesticides, including carbamates and triazines.[448]

Examples of use of derivatives for the estimation of carbamate pesticide residues include 2,4-dinitroaniline derivatives[449] and on-column trans-esterification.[77]

For its GC determination, carbaryl has been converted into its *N*-methylthio derivative, with methylsulphenyl chloride.[449a]

Thiocarbamates are largely used as fungicides, and in 1971 Onley and Yip[450] applied a GC method to the determination of ethylene thiourea residues. Ethylene thiourea is a degradation product of thiocarbamate and although its determination gives neither a specific nor quantitative estimation of the former presence of thiocarbamates, it is a very good indicator of

it. Many procedures are based on the same general idea. The pentafluorobenzoyl derivative of ethylene thiourea was used by Newsome[450a] for its GC determination in vegetables, down to 20 μg/kg.

The triazines used are almost all herbicides. As early as 1962, 6 triazines were separated and determined,[451] and later 9 triazines from crops were extracted, cleaned up and determined by Delley *et al.*[452]

The important substituted phthalimides, namely captan, captafol and folpet, are foliar fungicides. Baker and Flaherty[453] extracted and cleaned up residues of these fungicides from samples of fruit and, after chemical separation techniques, determined all three compounds by GC.

Pyrethrins. Pyrethrin compounds are used extensively as insecticides and of several GC methods that by Bevenue *et al.*[454] is recommended.

Paraquat and diquat. Paraquat may be determined in residues on crops by acid-extraction, hydrogenation and clean-up by column chromatography on alumina, before GC separation and determination with an AFID.[455] Diquat in potatoes may be determined by extraction, reduction with $NaBH_4$ to yield a diamine derivative, and GC with a nitrogen-selective detector.[455a]

Phosphine. This is used as an insecticidal fumigant in wheat. Direct headspace sampling has been used,[455b] and so has gas sampling after the wheat has been extracted with dilute sulphuric acid.[455c]

Polychlorinated biphenyls. PCBs show plasticizing and dielectric properties and have been used in the manufacture of paints, rubbers, resins, lubricants and dielectric fluids of capacitors and transformers. Like OC pesticides, they are fat-soluble and persistent, and have found their way into animals and animal products which may be used for human consumption, *viz.* fish, eggs and game birds. Because PCBs are structurally similar to OC pesticides, much of the analytical literature concerning PCBs deals with their separation from OC pesticides, before GC determination, usually with EC detection.

In 1967, Holmes *et al.*[456] pointed out that analysts had long been aware that some bird and fish samples produced additional peaks in standard OC pesticide residue analysis and that some of these, at least, were probably due to co-extracted PCBs. Jensen[457] had earlier emphasised the presence of PCBs in conjunction with OC pesticide residues.

Risebrough *et al.*[458] found that the chromatograms resulting from the examination of bird and fish samples exhibited mutual interference by DDT-type insecticides and PCBs. It was possible to hydrolyse DDT and its metabolites with ethanolic potassium hydroxide and record the removal of the signals due to these compounds.

Another method of dealing with the interference is to irradiate the GC effluent with ultraviolet light to degrade the PCBs and then to re-chromatograph the degradation products.[459]

PCBs can also be degraded by reaction with a palladium catalyst. Asai *et al.*[460] applied this technique to 8 PCB mixtures and to members of the DDT family. The degradation, which can produce hydrogenation, dehydrogenation and hydrogenolysis, results in biphenyl and cyclohexylbenzene from PCBs, and different products from the DDT family.

There is some concern regarding the presence of toxic polychlorinated dibenzodioxins in PCBs and these compounds have been separated and determined by GC–MS from samples of Yusho oil.[461]

Methylmercury. Mercury compounds have found their way into waterways as a result of the depositing of mercury-containing industrial effluents, and through the leaching of organomercurial fungicides from soil. Fish and other aquatic life can accumulate mercury residues, most of which is converted into methylmercury, and this has a relatively high mammalian toxicity.

Much of the earlier GC work on methylmercury in such foods as fish, meat and eggs, was due to Westoo.[462,463] These methods were based on benzene extraction of the acidified sample and clean-up of the extract, and finally chromatography of methylmercuric chloride. A step was later introduced to split methylmercury from certain natural sulphur compounds with which it can be complexed.

An atomic-absorption spectrometric detector was used by Gonzales and Ross[464] in GC studies on alkylmercury-containing effluents and fish. The methylmercuric halide was separated on the column and determined by flame or flameless atomic-absorption. The microwave-powered plasma detector has been used specifically for the determination of methylmercury in fish samples.[54]

Inorganic mercury compounds have been converted into methylmercuric halides for subsequent GC determination by using such reagents as 4,4-dimethyl-4-silapentane-1-sulphonate[465] and tetramethyltin.[466]

N-*Nitrosamines.* *N*-Nitrosamines may be formed by reaction between secondary amines and nitrous acid. It is well established that some of the nitrosamines, particularly nitrosodimethylamine, have hepatotoxic and carcinogenic properties, and there has been some concern about the finding of trace amounts of nitrosamines in such foods as fish, meat, bacon and cheese. Many analytical techniques have been employed for their detection and determination but there is general agreement among analysts that the only foolproof technique is GC coupled to MS. Hence some results published before 1970 should be treated with caution since MS was not in general use for that purpose before that date.

Gough[466a] has reviewed the determination, by GC-MS, of those *N*-nitroso compounds which may occur in such foods as bacon, fish and cheese.

Gough and Webb,[467,468] described a membrane separator which is capable of transferring nanogram quantities of nitrosamines from the GC column to the

mass spectrometer, a detection limit corresponding to 1 μg of nitrosamine per kg of food being obtained. This GC–MS method was used successfully by Crosby *et al.*[469] in the confirmatory determination of steam-volatile nitrosamines in bacon, fish, meat and cheese samples, which was a development of an earlier method.[470]

Telling *et al.*[471] determined five volatile nitrosamines in meat products, *e.g.*, pork luncheon meat, using a GC–MS method which was subsequently made more sensitive[472] by monitoring ions other than NO^+ (which was first used). Fish was examined for nitrosamines by Fazio *et al.*,[473] nitrosodimethylamine (4–26 μg/kg) being found in sable, salmon and shad. A sample of ham was found to contain 5 μg of nitrosodimethylamine per kg by the same method.[474] Recent results for nitrosamines in meat products include nitrosopyrrolidone in fried bacon samples, in the range 5–75 μg/kg,[474a] and its 3-hydroxy derivative in fried bacon and sausage, in the range 1–10 μg/kg[474b] and also in fried bacon and its "fried-out" fat, in the range 0.3–3.9 μg/kg.[474c]

Nitrosamines in foods have also been determined as their heptafluorobutanoyl derivatives by EC detection[475] and also after oxidation to the corresponding nitramines.[476]

Pokrovskii *et al.*[476a,476b] converted nitrosamines into their dansylamides, by means of secondary amines, and chromatographed these derivatives, using MS detection.

Methylguanidine is considered to be a precursor of nitrosamines in fresh beef and certain varieties of fish, and a GC method for its determination has recently been published.[477]

Solvents. Solvents such as ethanol and 2-propanol are used for incorporation into foods of such additives as flavourings, essential oils, colourings and antioxidants. Solvents such as hexane and acetone are used in the food industry to remove fats and oils, and aliphatic chlorinated hydrocarbons are also used to remove caffeine from coffee. As a result of these practices, there is a possibility that trace solvent residues may remain in the foods and GC is ideally suited to their detection and determination.

Aliphatic hydrocarbons and acetone. In an attempt to determine a number of solvent residues liable to be encountered in oils and spice oleoresins, Dean *et al.*[478] used a solid sampling device to avoid a clean-up procedure. The sample was introduced into a glass capillary which was sealed and enclosed in the sampler, which was then connected to the GC column and brought to equilibrium temperature; the glass capillary was broken by a plunger and the volatile solvents were swept into the column by the carrier gas. The method can be used for different classes of solvents by using different stationary phases and examples of the determination of hexane and trichloroethylene in vegetable oils were given.

Hexane is the most common residue found in edible oils or their associated meals or flours. Soyabean and cottonseed meals and flours were examined for hexane and acetone residues by Fore and Dupuy,[479] by solvent extraction followed by GSC. The same workers have used a headspace-sampling technique,[480] which was subsequently modified by using a glass injection port liner in place of a serum bottle as the sample container.[481] Further improvement in headspace sampling has recently been claimed.[482]

Hop extract, used as a brewing additive, can contain residual hexane, and Litchman *et al.*[483] used headspace sampling and GSC, achieving a detection limit below 25 ppm.

Hirayama and Imai,[484] in the determination of hexane in edible oils, pyrolysed samples in a platinum boat inserted into the pyrolyser, in order to free the solvent from the oil.

Besides hexane residues in oil samples, 2-methylpentane, 3-methylpentane and methyl cyclopentane have also been determined.[485]

Headspace sampling has been used for the determination of acetone in oilseed meals and flours.[10]

Chlorinated hydrocarbons. Roberts[486] conducted a collaborative study on the GSC determination of dichloromethane, ethylene dichloride and trichloroethylene in oleoresins of paprika, ginger and capsicum after their extraction with ethanol. By using vacuum distillation extraction technique with toluene as carrier, Page and Kennedy[487] have improved this analysis.

Dichloromethane is a popular solvent for decaffeinating coffee and Gal and Schilling[488] used steam-distillation and GSC for its determination. Page and Charbonneau[489] improved the extraction technique by using their co-distillation method in the determination of dichloromethane and trichloroethylene residues in instant and roasted coffees.

Methanol and 2-propanol. Methanol is sometimes used in the production of hop extract additives for the brewing industry, and Litchman and Upton[490] devised a GC method based on the reaction of methanol with nitrite and measurement of the product after headspace collection.

2-Propanol has been used to detoxify mould damage in oilseed meals and flours, and a headspace technique has been used for its collection before GSC determination.[9] 2-Propanol has also been used for dewaxing apple peel, and a headspace technique has been used to collect it.[491]

Food packaging materials

There has been increasing interest in the migration of food packaging materials and their additives into foods, particularly those foods containing oil or fat, which are good solvents for these materials. The earlier GC analytical literature was almost exclusively German and concerned the migration of phthalate plasticizers. The more recent literature is concerned with the migration of vinyl chloride monomer from

poly(vinyl chloride) containers into beverages and vinegar.

Phthalate esters. Phthalate esters are used as plasticizers in a variety of food packagings and solvation by fatty or alcoholic foods or beverages can lead to the uptake of these esters.

In 1963, Wandel and Tengler[492] investigated the possible transfer of diethyl phthalate from plastic wrappings into fat-containing foods, using solvent extraction and a GC method with a detection limit of 2 ppm. The same workers[493] also devised a method for the determination of bis-(2-ethylhexyl) phthalate and tributyl *O*-acetyl citrate by means of corresponding alcohols, produced by hydrolysis. A similar method was used by Pfab[494] in migration studies of dibutyl phthalate and dicyclohexyl phthalate from lacquered foil into cheese and lard.

Because of the wide use of phthalate plasticizers, there has been concern that oceans and other waterways may become contaminated and that fish may accumulate these esters. Accordingly, dibutyl phthalate and bis-(2-ethylhexyl) phthalate have been sought in fish.[495]

Vinyl chloride. Vinyl chloride monomer can be present at the ppm level in poly(vinyl chloride) used for food packaging. Because it is alcohol- and fat-soluble, alcoholic beverages and fatty foods packaged in poly(vinyl chloride) are prone to dissolve any monomer present in the container.

Williams and Miles[496] determined vinyl chloride in alcoholic beverages, vinegar and peanut oil by headspace collection followed by GSC. The presence of vinyl chloride can be confirmed by conversion into 1,2-dibromo-1-chloroethane and detection by EC.[497] A solvent extraction method was used for vinyl chloride by Ernest and van Leirop,[498] who used an electrolytic conductivity micro detector, the vinyl chloride having been converted into hydrogen chloride. The method could detect 4 ng of vinyl chloride. A headspace collection of vinyl chloride followed by GC–MS determination has been successfully used in recovery studies on olive oil.[499] The method is also claimed to be suitable for the analysis of wine, soft drinks and margarine. A detection limit of 1 ppm has recently been obtained in a headspace–GC method for vinyl chloride in corn oil.[500]

Styrene. Polystyrene used for food packaging often contains small amounts of styrene momomer, which is fat-soluble. Roseli and Marek[501] recently determined styrene monomer in yogurt, cream and curds by a GC method after solvent extraction.

Acrylonitrile. Polymers containing acrylonitrile are used extensively in the manufacture of containers for carbonated beverages and other foods, such as luncheon meat, margarine and vegetable oils. Since the small fraction of unreacted monomer in the polymer can migrate into the food, GC methods have recently been used to detect it, either by direct injection[501a] or by headspace sampling for carbonated beverages after decarbonation.[501b] By the latter method, traces (less than 5 μg/kg) of acrylonitrile were found in some samples of beers and soft drinks.

Mycotoxins

GC has been applied to the determination of the following mycotoxins resulting from mouldy or damaged foods.

Patulin. Patulin is a carcinogenic, mutagenic metabolite produced by certain strains of penicillin. Since storage rot in apples is caused by a similar penicillin to that known to produce patulin, there is a possibility that the mycotoxin could be transmitted to the juice, cider or cider vinegar. The presence of patulin in apple juice has been tested for by means of the trichloroacetate derivative,[502] and in cider vinegar by means of its acetate.[503] Rosen and Pareles[504] determined patulin as its TMS derivative and this method was applied to the analysis of cereals and rice.[505]

Penicillic acid. Penicillic acid is a mycotoxin which has been proved to be a carcinogen in rats. It is formed from certain species of *penicillium* and *aspergillus*. The TMS derivative can be used in its GC determination in cereals,[505] rice,[505] and maize, dried beans and apple juice:[506]

Sterigmatocystin. Sterigmatocystin is a secondary metabolite produced by several *aspergillus* species and has exhibited hepatotoxic effects. This toxin has been extracted from and determined in grain, with a detection limit of 20 ng.[507]

Trichothecenes. Mouldy grain can yield trichothecenes, which are fungal metabolites found in grain. Ikediobi *et al.*[508] used solvent extraction and GC of the TMS derivatives of those trichothecenes which contain free hydroxyl groups. A similar method was used for trichothecenes in maize and freeze-dried potato powder.[508a]

Ipomeamarone. Ipomeamarone is a hepatotoxin produced by fungal attack of sweet potato. Boyd and Wilson[509] extracted the mycotoxin from samples of sweet potato by homogenizing with 5% methanol in chloroform, and determined the concentration by GC. A similar method was used by Wood and Huang.[510]

Diethylstilboestrol. This is a synthetic oestrogen used as an animal feed additive to increase the feeding efficiency in cattle and lambs. This hormone has carcinogenic properties and residues have been found in tissues of animals treated with it, with concentration in the liver and kidneys. Coffin and Pilon[511] described a GC method for the determination of diethylstilboestrol in beef, lamb and chicken tissues, which involved solvent extraction, clean-up and chromatography of the TFA derivative. Other derivatives used in similar methods include the TMS derivative[512] and the dichloroacetate.[513] Ryan and Pilon,[514] in an analysis of beef liver, made the TFA derivative and, after hydrolysis to yield the free sterol, prepared the heptafluorobutanoyl derivative. With EC detection, the sensitivity was better by a factor of 4 than that for the TFA derivative.

The synthetic steroid melengestrol has also been determined in beef tissues by GC.[515]

Chlorophenols

Chlorophenols are used as wood preservatives, and shavings of the treated timber have been used as litter in broiler poultry houses. Pentachlorophenol and 2,3,4,6-tetrachlorophenol can permeate the chickens and the flesh has been analysed for these compounds, as the 2,4-dinitrophenyl ether derivatives, by GC.[516] Milk has been tested for pentachlorophenol residues by chromatographing either the acetate[516a] or the methyl derivative[516b] after solvent extraction. Broiler chickens have also been found to accumulate 6-chloro-*o*-cresol from cresylic acid disinfectant, and the tainted flesh has been analysed by GC–MS.[517] Griffiths and Land[518] determined the same cresol in biscuits contaminated with a similar disinfectant.

CONCLUSIONS

GC has been of inestimable value in the detection and determination of the organic constituents of food, those organic compounds deliberately added to food and those accidentally contaminating it. But what influence has food analysis had on GC and where do future technology and applications lie?

The three areas of GC technology where food analysis has had greatest impact are sampling, derivative formation and detection.

In sampling, foods which require qualitative and quantitative assessment of volatiles have lent themselves to experimentation which has aided the chromatographer in other applied fields; headspace sampling, preconcentration techniques on solid adsorbents and post-column removal of relatively large concentrations of interfering compounds before separation of minor ones, are examples.

The fatty-acid composition of the glycerides which make up edible fats and oils has frequently been the driving force behind the development of alkylation techniques, particularly methylation. In halogeno-esterification, sterols extracted from foods have been the media for development of methods in which EC detection has enhanced sensitivity.

The silylation of sugars was a major breakthrough in the analysis of sugar mixtures and most sugar-containing foods have been used as bases for enhancing the knowledge of silylation techniques.

Detector technology owes a great deal to the impetus afforded by the necessity to determine groups of pesticide residues in crops and foods, *e.g.*, the use of the EC detector, AFID, FPD and MCD, in the analysis of OC, OP and ON pesticide residues. It is probably in the advancement of detector technology that food contaminant analysis has had greatest impact.

As analytical requirements become more detailed, the demand will be for greater sensitivity and selectivity. This is particularly relevant in the analysis of food volatiles where quality assurance and trades description requirements combine to demand determination of hundreds of minor constituents. In this area, the greater availability of MS, the application of pattern-recognition techniques and the increasing use of microprocessors will mean more detailed examination of a variety of foods and additives, *e.g.*, beverages, essential oils and food flavours.

The uncertainties and vagaries of biological detectors, *e.g.*, moths and the human nose, have resulted in little use of these. Yet food analysis could clearly benefit from use of sniffing of separated components concurrently with MS and the other conventional detection methods.

The microprocessor revolution could also mean a greater use of pyrolysis techniques in GC applications in food analysis, where one drawback has been the difficulties in separating and relating pyrolysis products to the foreign compounds sought within an array of compounds derived from the food matrices.

Although large areas of food quality-control methods suitable for GC application have been exploited, there remains scope in pattern-recognition analyses, particularly for flavour constituents and other volatiles of butter, cheese, animal fats, meat flavours, fruits, vegetables and essential oils.

Fine differences in the ratios of glyceride fatty acids of edible oils continue to be the subject of considerable research as does the balance of volatiles in both alcoholic and non-alcoholic beverages to assess quality and origin.

As new additives are put forward for use, analytical methods are required and GC is often applicable. Changes occur from time to time in permitted lists of preservatives, antioxidants, emulsifiers, stabilizers, artificial sweeteners and flavouring agents and trends in concentrations are usually downward, requiring more sensitive methods.

Similarly, as new contaminants are encountered, the food analyst usually has to add to his repertoire of GC methods. Technology in food packaging is changing and very sensitive methods are required for the determination of compounds associated with migration of contaminants from packaging materials into foods; low levels of monomers are contained in polymeric packaging materials and have been known to migrate into foods.

The large increase in the use of drugs and other pharmaceuticals in animal husbandry has alerted analysts to seek residues of these substances in such foods as milk and meat. New pharmaceuticals are frequently being introduced in veterinary practice and relevant analytical methods are subsequently required.

In conclusion, there is no evidence to suggest any reduction in the activities of the food analyst with GC applications. New compounds requiring analysis will be incorporated into existing systems, which will continue to undergo advantageous changes in data-processing, resulting in increased sensitivity and selectivity.

REFERENCES

1. P. B. Stockwell and R. Sawyer, *Anal. Chem.*, 1970, **42**, 1136.
2. *Idem, Lab. Pract.*, 1970, **19**, 279.
3. H. Boer, *J. Sci. Instrum.*, 1964, **41**, 365.
4. R. Bassette, S. Ozeris and C. H. Whitnah, *Anal. Chem.*, 1962, **34**, 1540.
5. P. E. Nelson and J. E. Hoff, *Food Technol.*, 1968, **22**, No. 11, 61.
6. P. L. Davis, *J. Chromat. Sci.*, 1970, **8**, 423.
7. J. Novák, J. Gelbičová-Růžičková and S. Wičar, *J. Chromatog.*, 1971, **60**, 127.
8. A. Sinclair, R. D. Hall, D. T. Burns and W. P. Hayes, *J. Sci. Food Agric.*, 1970, **21**, 468.
9. S. P. Fore, E. T. Rayner and H. P. Dupuy, *J. Am. Oil Chem. Soc.*, 1971, **48**, 140.
10. H. P. Dupuy, E. T. Rayner and S. P. Fore, *ibid.*, 1971, **48**, 155.
11. M. Bertuccioli and G. Montedoro, *J. Sci. Food Agric.*, 1974, **25**, 675.
12. D. R. Rushneck, *J. Gas Chromatog.*, 1965, **3**, 318.
13. J. T. Heins, H. Maarse, M. C. ten Noever de Brauw and C. Weurman, *ibid.*, 1966, **4**, 395.
14. U. M. Senanayake, R. A. Edwards and T. H. Lee, *J. Chromatog.*, 1976, **116**, 468.
15. D. F. Brown, F. G. Dollear and H. P. Dupuy, *J. Am. Oil Chem. Soc.*, 1972, **49**, 81.
16. H. P. Dupuy, S. P. Fore and L. A. Goldblatt, *ibid.*, 1971, **48**, 876.
17. *Idem, ibid.*, 1973, **50**, 342.
18. H. P. Dupuy, S. P. Fore and E. T. Rayner, *ibid.*, 1975, **52**, 118.
19. B. Bonney, F. Norman and A. M. Humphrey, *Chem. Ind. (London)*, 1973, 749.
20. J. M. Mendelsohn, M. A. Steinberg and C. J. Merritt, *J. Food Sci.*, 1966, **31**, 389.
21. D. E. Heinz, M. R. Sevenants and W. G. Jennings, *ibid.*, 1966, **31**, 63.
22. M. E. Morgan and E. A. Day, *J. Dairy Sci.*, 1965, **48**, 1382.
23. J. H. Dhont and C. Weurman, *Analyst*, 1960, **85**, 419.
24. W. G. Jennings and H. E. Nursten, *Anal. Chem.*, 1967, **39**, 521.
25. K. T. Hartman, L. C. Rose and R. L. Vandaveer, *J. Am. Oil Chem. Soc.*, 1971, **48**, 178.
26. K. E. Murray, *J. Chromatog.*, 1977, **135**, 49.
27. M. Novotny, M. L. Lee and K. D. Bartle, *Chromatographia*, 1974, **7**, 333.
28. R. G. Clark and D. A. Cronin, *J. Sci. Food Agric.*, 1975, **26**, 1009.
29. W. G. Jennings, R. H. Wohleb and M. J. Lewis, *Tech. Q. Master Brewers Ass. Am.*, 1974, **11**, 104.

29a. K. Grob and K. Grob, *J. Chromatog.*, 1978, **151**, 131.

30. F. I. Onuska and M. E. Comba, *ibid.*, 1976, **126**, 133.
31. J. D. Schieke and V. Pretorius, *ibid.*, 1977, **132**, 231.
32. R. G. Ackman and J. C. Sipos, *J. Chromatog. Sci.*, 1976, **14**, 568.

32a. J. W. Gramshaw and A. Hussain, *J. Chromatog.*, 1978, **157**, 267.

33. J. Flanzy, M. Boudon, C. Leger and J. Pihet, *J. Chromatog. Sci.*, 1976, **14**, 17.

33a. R. G. Ackman and C. A. Eaton, *Fette, Seifen Anstrichmitt.*, 1978, **80**, 21.

33b. F. Vernon, *J. Chromatog.*, 1978, **148**, 397.

34. D. W. Witheycombe and R. C. Lindsay, *Tech. Q. Master Brewers Ass. Am.*, 1973, **10**, 130.
35. P. Mayzaud and R. G. Ackman, *Chromatographia*, 1976, **9**, 321.

35a. A. Shibaharu, H. Yoshida and G. Kajimoto, *Yukagaku*, 1978, **27**, 233.

36. G. C. Cochrane, *J. Chromatog. Sci.*, 1975, **13**, 440.
37. H. Verachtert, D. Van Oevelen and J. Bevers, *J. Chromatog.*, 1976, **117**, 295.
38. R. V. Golovnya and I. L. Zhuravleva, *Zh. Analit. Khim.*, 1974, **29**, 1406.
39. C. Merritt and J. T. Walsh, *Anal. Chem.*, 1963, **35**, 110.
40. C. Merritt, J. T. Walsh, D. A. Forss, P. Angelini and S. M. Swift, *ibid.*, 1964, **36**, 1502.
41. J. L. Iverson and A. J. Sheppard, *J. Chromatog. Sci.*, 1975, **13**, 505.
42. R. P. W. Scott, *Gas Chromatography 1964*, A. Goldup, ed., p. 25. Institute of Petroleum, London, 1965.
43. W. D. Macleod, *J. Agric. Food Chem.*, 1968, **16**, 884.
44. S. Lakota and W. A. Aue, *J. Chromatog.*, 1969, **44**, 472.
45. G. R. Verga and F. Poy, *ibid.*, 1976, **116**, 17.
46. T. A. Gough and K. Sugden, *ibid.*, 1973, **86**, 65.
47. T. Kawabata, *I.A.R.C. Scient. Publ.*, 1975, **9**, 154; *Anal. Abstr.*, 1976, 30, 4F5.
48. S. S. Brody and J. E. Chaney, *J. Gas Chromatog.*, 1966, **4**, 42.
49. S. Hasinski, *Chem. Analit. (Warsaw)*, 1975, **20**, 1135.
50. C. A. Bache and D. J. Lisk, *Anal. Chem.*, 1965, **37**, 1477.
51. *Idem, ibid.*, 1966, **38**, 783.
52. *Idem, ibid.*, 1966, **38**, 1757.
53. *Idem, ibid.*, 1967, **39**, 786.
54. *Idem, ibid.*, 1971, **43**, 950.
55. G. G. Patchett, *J. Chromatog. Sci.*, 1970, **8**, 155.
56. W. P. Cochrane and B. P. Wilson, *J. Chromatog.*, 1971, **63**, 364.
57. J. W. Rhoades and D. E. Johnson, *J. Chromatog. Sci.*, 1970, **8**, 616.
58. J. F. Lawrence and A. H. Moore, *Anal. Chem.*, 1974, **46**, 755.
59. E. von Rappard, G. Eisenbrand and R. Preussmann, *J. Chromatog.*, 1976, **124**, 247.
60. H. P. Burchfield, D. E. Johnson, J. W. Rhoades and R. J. Wheeler, *J. Gas Chromatog.*, 1965, **3**, 28.
61. H. P. Burchfield, J. W. Rhoades and R. J. Wheeler, *J. Agric. Food Chem.*, 1965, **13**, 511.
62. H. P. Burchfield and R. J. Wheeler, *J. Assoc. Off. Anal. Chem.*, 1966, **49**, 651.
63. B. Brechbuehler, L. Gay and H. Jaeger, *Chromatographia*, 1977, **10**, 478.
64. J. F. Lawrence and J. J. Ryan, *J. Chromatog.*, 1977, **130**, 97.
65. T. A. Gough, K. S. Webb and R. F. Eaton, *ibid.*, 1977, **137**, 293.
66. O. G. Tucknott and A. A. Williams, *Chem. Ind. (London)*, 1974, 784.
67. J. E. Scoggins and C. H. Fitzgerald, *J. Agric. Food Chem.*, 1969, **17**, 156.
68. F. E. Luddy, R. A. Barford, S. F. Herb and P. Magidman, *J. Am. Oil Chem. Soc.*, 1968, **45**, 549.
69. P. C. Barnes and C. E. Holaday, *J. Chromatog. Sci.*, 1972, **10**, 181.
70. S. W. Christopherson and R. L. Glass, *J. Dairy Sci.*, 1969, **52**, 1289.
71. V. L. Davison and H. J. Dutton, *J. Lipid Res.*, 1967, **8**, 147.
72. E. D. Bitner, A. C. Lauser and H. J. Dutton, *J. Am. Oil Chem. Soc.*, 1971, **48**, 633.

72a. F. C. Churchill, D. N. Ku and J. W. Miles, *J. Agric. Food Chem.*, 1978, **26**, 1108.

73. A. J. Sheppard and J. L. Iverson, *J. Chromatog. Sci.*, 1975, **13**, 448.
74. H. W. Kircher, *Anal. Chem.*, 1960, **32**, 1103.
75. E. Fedeli, N. Cortesi and C. Mariani, *Riv. Ital. Sostanze Grasse*, 1976, **53**, 130.
76. H. A. Moye, *J. Agric. Food Chem.*, 1973, **21**, 621.
77. *Idem, ibid.*, 1971, **19**, 452.
78. W. E. Dale, J. W. Miles and F. C. Churchill, *J. Assoc. Off. Anal. Chem.*, 1976, **59**, 1008.

79. C. B. Johnson and E. Wong, *J. Chromatog.*, 1975, **109**, 403.
80. D. P. Schwartz and R. S. Bright, *Anal. Biochem.*, 1974, **61**, 271.
80a. D. K. McCreary, W. C. Kossa, S. Ramachandran and R. R. Kurtz, *J. Chromatog. Sci.*, 1978, **16**, 329.
81. W. F. Staruszkiewicz, J. F. Bond and H. Salwin, *J. Chromatog.*, 1970, **51**, 423.
82. W. F. Staruszkiewicz and M. K. Starling, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 773.
83. H. Salwin and J. F. Bond, *ibid.*, 1969, **52**, 41.
84. M. Iyer, T. Richardson, C. H. Amundson and A. Boudreau, *J. Dairy Sci.*, 1967, **50**, 285.
85. A. Islam and A. Darbre, *J. Chromatog.*, 1969, **43**, 11.
86. A. Darbre and A. Islam, *Biochem. J.*, 1968, **106**, 923.
87. J. E. Sullivan and L. R. Schewe, *J. Chromatog. Sci.*, 1977, **15**, 196.
88. M. Donike, *J. Chromatog.*, 1973, **78**, 273.
89. F. Tateo, *Riv. Ital. Sostanze Grasse*, 1973, **50**, 453.
90. J. F. Lawrence, *J. Chromatog.*, 1976, **123**, 287.
91. K. Zuercher and H. Hadorn, *Dt. Lebensmittel Rdsch.*, 1974, **70**, 425.
92. K. Zuercher, H. Hadorn and C. Strack, *Mitt. Geb. Lebensmitt. Hyg.*, 1975, **66**, 92.
93. W. A. McGugan and S. G. Howsam, *J. Chromatog.*, 1973, **82**, 370.
94. H. Kallio, R. R. Linko and J. Kaitaranta, *ibid.*, 1972, **65**, 355.
95. J. Althorpe, D. A. Goddard, D. J. Sissons and G. M. Telling, *ibid.*, 1970, **53**, 371.
96. N. P. Sen, *ibid.*, 1970, **51**, 301.
97. M. Beroza and R. Sarmiento, *Anal. Chem.*, 1966, **38**, 1042.
98. J. Franc and V. Kolouśková, *J. Chromatog.*, 1965, **17**, 221.
99. C. L. Hankinson, W. J. Harper and E. Mikolajcik, *J. Dairy Sci.*, 1958, **41**, 1502.
100. V. Palo, J. Hrivnák and F. Goerner, *Nahrung*, 1968, **12**, 225.
101. J. M. de Man, *Lab. Pract.*, 1967, **16**, 150.
102. L. M. Smith, *J. Dairy Sci.*, 1961, **44**, 607.
103. R. L. Glass, L. W. Lohse and R. Jenness, *ibid.*, 1968, **51**, 1847.
104. D. D. Bills, L. L. Khatri and E. A. Day, *ibid.*, 1963, **46**, 1342.
105. W. Leeman and O. F. Stahel, *Beckmann Rep.*, 1970, **1**, 11.
106. J. Hrivnák, V. Palo and J. Krupčik, *Milchwissenschaft*, 1973, **28**, 699.
107. H. Hadorn and K. Zuercher, *Dt. Lebensmittel Rdsch.*, 1970, **66**, 77.
108. J. L. Iverson, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 934.
109. G. W. Gander, R. G. Jensen and J. Sampugna, *J. Dairy Sci.*, 1962, **45**, 323.
110. J. Sampugna, R. E. Pitas and R. G. Jensen, *ibid.*, 1966, **49**, 1462.
110a. M. B. Nair, A. Laser, A. Burvall and N. G. Asp, *Food. Chem.*, 1978, **3**, 283.
111. S. Patton, *J. Dairy Sci.*, 1961, **44**, 207.
112. R. G. Arnold, L. M. Libbey and E. A. Day, *J. Food Sci.*, 1966, **31**, 566.
113. L. A. Mabbitt and G. McKinnon, *J. Dairy Res.*, 1963, **30**, 359.
114. E. L. Thomas, G. A. Reineccius, G. J. De Waard and M. S. Slunkard, *J. Dairy Sci.*, 1976, **59**, 1865.
114a. H. A. McLeod, G. Benns, D. Lewis and J. F. Lawrence, *J. Chromatog.*, 1978, **157**, 285.
114b. H. L. Pease, J. L. Prince and E. F. Johnston, *J. Agric. Food Chem.*, 1978, **26**, 331.
115. N. P. Wong and S. Patton, *J. Dairy Sci.*, 1962, **45**, 724.
116. W. L. Hempenius and B. J. Liska, *ibid.*, 1968, **51**, 221.
117. I. K. Gray, *N.Z.J. Dairy Sci. Technol.*, 1976, **11**, 54.
118. H. O. Jaynes and T. Asan, *J. Milk Food Technol.*, 1973, **36**, 333.
119. G. A. Reineccius, T. E. Kavanagh and P. G. Keeney, *J. Dairy Sci.*, 1970, **53**, 1018.
120. L. Mouillet, F. M. Luquet, J. F. Boudier and A. Degros, *Ann. Falsif. Exp. Chim.*, 1977, **70**, 145.
120a. S. Adachi and A. Yamaji, *J. Dairy Res.*, 1978, **45**, 127.
121. H. Janecke and R. Brendel, *Naturwissenschaften*, 1971, **58**, 54.
122. T. Panalaks, *Analyst*, 1970, **95**, 862.
123. J. G. Bell and A. A. Christie, *ibid.*, 1974, **99**, 385.
124. J. E. Schlack, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 1346.
125. S. Grys, *J. Chromatog.*, 1974, **100**, 43.
126. T. Gabrio, H. Konrad and G. Penner, *Nahrung*, 1977, **21**, K43.
127. J.-P. Wolff, *Ann. Falsif. Exp. Chim.*, 1960, **53**, 318.
128. F. De Francesco and D. Avancini, *Boll. Lab. Chim. Prov.*, 1961, **12**, 422.
129. S. Valussi and G. Cofleri, *ibid.*, 1962, **13**, 3.
130. *Analyst*, 1936, **61**, 404.
131. A. Karleskind, G. Valmalle and J.-P. Wolff, *J. Assoc. Off. Anal. Chem.*, 1970, **53**, 1082.
132. D. F. Withington, *Analyst*, 1967, **92**, 705.
133. H. Hadorn and K. Zuercher, *Mitt. Geb. Lebensmitt. Hyg.*, 1971, **62**, 123.
134. A. R. Phillips and B. J. Sanders, *J. Assoc. Publ. Anal.*, 1968, **6**, 89.
135. J. Eisner, N. P. Wong, D. Firestone and J. Bond, *J. Assoc. Off. Anal. Chem.*, 1962, **45**, 337.
136. J. H. Cannon, *ibid.*, 1964, **47**, 577.
137. G. Cerutti, G. Volonterio and P. Resmini, *Riv. Ital. Sostanze Grasse*, 1969, **46**, 356.
138. *BSI Methods for detection of foreign fats in dairy products*, BS 5475: Part 2: 1977.
139. B. van der Ven, *Rec. Trav. Chim.*, 1964, **83**, 976.
140. J. Boldingh, P. Haverkamp, A. P. de J. Begeman and R. J. Taylor, *Rev. Franc. Corps Gras*, 1966, **13**, 235.
141. W. Stark, G. Urbach and J. S. Hamilton, *J. Dairy Res.*, 1976, **43**, 469.
142. O. W. Parks, M. Keeney and D. P. Schwartz, *J. Dairy Sci.*, 1961, **44**, 1940.
143. W. Stark, G. Urbach and J. S. Hamilton, *J. Dairy Res.*, 1976, **43**, 479.
144. A. R. Keen and N. J. Walker, *ibid.*, 1974, **41**, 397.
145. J. M. de Man, *J. Dairy Sci.*, 1966, **49**, 343.
146. H. M. Liebich, D. R. Douglas, E. Bayer and A. Zlatkis, *J. Chromatog. Sci.*, 1970, **8**, 351.
147. S. Patton, N. P. Wong and D. A. Forss, *J. Dairy Sci.*, 1958, **41**, 857.
148. J. E. Langler, L. M. Libbey and E. A. Day, *J. Agric. Food Chem.*, 1967, **15**, 386.
149. R. Scarpellino and F. V. Kosikowski, *J. Dairy Sci.*, 1962, **45**, 343.
150. E. R. Kaplan, N. Sapeika and I. M. Moodie, *Analyst*, 1974, **99**, 565.
151. J. P. Chaytor, B. Crathorne and M. J. Saxby, *J. Sci. Food Agric.*, 1975, **26**, 593.
152. P. Magidman, S. F. Herb, F. E. Luddy and R. W. Riemenschneider, *J. Am. Oil Chem. Soc.*, 1963, **40**, 86.
153. S. F. Herb, P. Magidman, R. A. Barford and R. W. Riemenschneider, *ibid.*, 1963, **40**, 83.
154. B. Doro and S. Remoli, *Riv. Ital. Sostanze Grasse*, 1965, **42**, 138.
155. B. Doro, *ibid.*, 1967, **44**, 349.
156. E. Pascussi and F. Paolini, *ibid.*, 1964, **41**, 315.
157. S. A. Castledine and D. R. A. Davies, *J. Assoc. Publ. Anal.*, 1968, **6**, 39.
158. D. Grieco, *Riv. Ital. Sostanze Grasse*, 1964, **41**, 261.
159. L. J. Bastijns, *Chem. Ind. (London)*, 1968, 721.
160. A. W. Hubbard and W. D. Pocklington, *J. Sci. Food Agric.*, 1968, **19**, 571.

161. F. Pupin and R. Vuillaume, *Ann. Falsif. Exp. Chim.*, 1968, **61**, 13.
162. L. Brixius and H. Treiber, *Fette Seifen Anstrichmitt.*, 1974, **76**, 83.
163. M. Warmbier, *ibid.*, 1974, **76**, 86.
164. G. Hoffmann and P. W. Meijboom, *J. Am. Oil Chem. Soc.*, 1968, **45**, 468.
165. H. J. Langner, *Fette Seifen Anstrichmitt.*, 1969, **71**, 893.
166. E. Martin and C. Berner, *Mitt. Geb. Lebensmitt. Hyg.*, 1972, **63**, 122.
167. D. C. Johnson and E. G. Hammond, *J. Am. Oil Chem. Soc.*, 1971, **48**, 653.
168. S. P. Fore, M. G. Legendre and G. S. Fisher, *ibid.*, 1978, **55**, 482.
169. K. Sato, M. Matsui and N. Ikekawa, *Bunseki Kagaku*, 1966, **15**, 954.
170. G. R. Jamieson and E. H. Reid, *J. Chromatog.*, 1965, **17**, 230.
171. H. Hadorn and K. Zuercher, *Mitt. Geb. Lebensmitt. Hyg.*, 1967, **58**, 351.
172. D. Grieco and G. Piepoli, *Riv. Ital. Sostanze Grasse*, 1964, **41**, 283.
173. H. Halvarson and O. Ovist, *J. Am. Oil Chem. Soc.*, 1974, **51**, 162.
174. D. M. Ottenstein, L. A. Wittings, G. Walker, V. Mahadevan and N. Pelick, *ibid.*, 1977, **54**, 207.
175. H. B. S. Conacher, J. R. Iyengar and J. L. Beare-Rogers, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 899.
175a. H. B. S. Conacher and J. R. Iyengar, *ibid.*, 1978, **61**, 702.
175b. A. Blumenthal, M. Cerny and E. Taube, *Mitt. Geb. Lebensmitt. Hyg.*, 1978, **69**, 116.
176. A. Karleskind, F. Audiau and J.-P. Wolff, *Rev. Franc. Corps Gras*, 1966, **13**, 168.
177. J. W. Copius-Peereboom, *J. Gas Chromatog.*, 1965, **3**, 325.
178. E. Fedeli, A. Lanzani, P. Capella and G. Jacini, *J. Am. Oil Chem. Soc.*, 1966, **43**, 254.
179. R. R. Allen, *Chem. Ind. (Lond)*, 1965, 1560.
180. C. G. Youngs and M. R. Subbaram, *J. Am. Oil Chem. Soc.*, 1964, **41**, 218.
181. M. R. Subbaram and C. G. Youngs, *ibid.*, 1964, **41**, 445.
182. Z. E. Shoeb, *Grasas Aceit.*, 1969, **20**, 4.
183. J. L. Iverson, *J. Assoc. Off. Anal. Chem.*, 1972, **55**, 1319.
184. A. Fincke, *Fette Seifen Anstrichmitt.*, 1971, **73**, 534.
185. K. J. Hivon, S. N. Hagan and E. B. Wile, *J. Am. Oil Chem. Soc.*, 1964, **41**, 362.
186. W. Averill, *Instrument News*, 1967, **17**, 13.
187. D. S. Galanos, V. M. Kapoulas and E. C. Voudouris, *J. Am. Oil Chem. Soc.*, 1968, **45**, 825.
188. R. A. Flath, R. R. Forrey and D. G. Guadagni, *J. Agric. Food Chem.*, 1973, **21**, 948.
189. R. Gutierrez Gonzalez-Quijano, J. M. Olias Jimenez, F. Gutierrez Rosales, J. Cabrera Martin and A. del Barrio Perez-Cerezal, *Grasas Aceit.*, 1975, **26**, 21.
190. T. Murata, *Anal. Chem.*, 1977, **49**, 2209.
190a. R. J. Phillips and B. Singleton, *J. Am. Oil. Chem. Soc.*, 1978, **55**, 255.
191. A. Letan, B. Turzynski and A. Raveh, *J. Assoc. Off. Agric. Chem.*, 1965, **48**, 897.
192. R. T. O'Connor and S. F. Herb, *J. Am. Oil Chem. Soc.*, 1970, **47**, 186.
193. E. L. Schneider, P. L. Sook and D. T. Hopkins, *ibid.*, 1968, **45**, 585.
194. C. Imai, H. Watanabe, N. Haga and T. Ii, *ibid.*, 1974, **51**, 326.
195. J. L. Iverson, *J. Assoc. Off. Agric. Chem.*, 1965, **48**, 902.
196. G. Hoffmann, *J. Am. Oil Chem. Soc.*, 1961, **38**, 1.
197. S. S. Chang, T. H. Smouse, R. G. Krishnamurthy, B. D. Mookherjee and R. B. Reddy, *Chem. Ind. (London)*, 1966, 1926.
198. R. G. Scholz and L. R. Ptak, *J. Am. Oil Chem. Soc.*, 1966, **43**, 596.
199. G. Bigalli, *ibid.*, 1977, **54**, 229.
200. K. Yasuda, R. J. Peterson and S. S. Chang, *ibid.*, 1975, **52**, 307.
201. O. Heisz, *GIT Fachz. Lab.*, 1977, **21**, 22.
201a. J. Blomstrand, L. Svensson and B. Herslof, *Lipids*, 1978, **13**, 283.
202. G. Lambertsen, H. Myklestad and O. R. Braekkan, *J. Food Sci.*, 1966, **31**, 48.
203. R. G. Ackman, *J. Gas Chromatog.*, 1966, **4**, 256.
204. C. Litchfield, R. D. Harlow and R. Reiser, *Lipids*, 1967, **2**, 363.
205. L. L. Gershbein and E. J. Singh, *J. Am. Oil Chem. Soc.*, 1969, **46**, 554.
206. M. Hommes and L. P. van der Mijll Dekker, *Intern. J. Vitam. Nutr. Res.*, 1973, **43**, 271.
207. I. Hornstein, J. A. Alford, L. E. Elliott and P. F. Crowe, *Anal. Chem.*, 1960, **32**, 540.
208. I. Hornstein, P. F. Crowe and W. L. Sulzbacher, *Nature*, 1963, **199**, 1252.
209. I. Hornstein and P. F. Crowe, *J. Gas Chromatog.*, 1964, **2**, 128.
210. M. I. El-Gharbawi and L. R. Dugan, *J. Food Sci.*, 1965, **30**, 814.
211. H. M. Liebich, D. R. Douglas, A. Zlatkis, F. Muegglar-Chavan and A. Douzel, *J. Agric. Food Chem.*, 1972, **20**, 96.
211a. W. Roedel, *Nahrung*, 1978, **22**, 721, 729.
212. A. E. Bender and P. E. Ballance, *J. Sci. Food Agric.*, 1961, **12**, 683.
213. E. L. Wick, T. Yamanishi, L. C. Wertheimer, J. E. Hoff, B. E. Proctor and S. A. Goldblith, *J. Agric. Food Chem.*, 1961, **9**, 289.
214. M. Jacobson and H. H. Koehler, *ibid.*, 1963, **11**, 336.
215. C. B. Johnson, E. Wong, E. J. Birch and R. W. Purchas, *Lipids*, 1977, **12**, 340.
216. G. Kaufmann and K. Schubert, *Nahrung*, 1975, **19**, K5.
217. R. H. Thompson and A. M. Pearson, *J. Agric. Food Chem.*, 1977, **25**, 1241.
218. C. K. Cross and P. Ziegler, *J. Food Sci.*, 1965, **30**, 610.
218a. D. S. Mottram and D. J. Puckey, *Chem. Ind. (London)*, 1978, 385.
219. E. L. Pippen and M. Nonaka, *J. Food Sci.*, 1963, **28**, 334.
220. L. J. Minor, A. M. Pearson, L. E. Dawson and B. S. Schweigert, *ibid.*, 1965, **30**, 686.
221. M. Nonaka, D. R. Black and E. L. Pippen, *J. Agric. Food Chem.*, 1967, **15**, 713.
222. A. Hobson-Frohock, *J. Sci. Food Agric.*, 1970, **21**, 152.
223. G. F. Bories and J. E. Tulliez, *ibid.*, 1977, **28**, 996.
224. M. Hřivnáč, W. Frischknecht and L. Čechová, *Anal. Chem.*, 1976, **48**, 937.
224a. F. A. Moseley, J. S. Salinsky and R. W. Woods, *J. Assoc. Off. Anal. Chem.*, 1978, **61**, 164.
225. N. P. Wong, J. N. Damico and H. Salwin, *ibid.*, 1967, **50**, 8.
226. L. S. Gasco, G. A. Valverde and R. P. Barrera, *Inform. Quim. Anal.*, 1971, **25**, 193.
227. J. N. Keay and R. Hardy, *J. Sci. Food Agric.*, 1972, **23**, 9.
228. R. V. Golovnya, G. A. Mironov and I. L. Zhuravleva, *Zh. Analit. Khim.*, 1967, **22**, 956.
229. R. V. Golovnya and V. P. Uraletz, *J. Chromatog.*, 1971, **61**, 65.
230. P. A. Lerke and R. W. Huck, *J. Food Sci.*, 1977, **42**, 755.
231. W. F. Staruszkiewicz, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 813.

231a. W. F. Staruszkiewicz and J. F. Bond, *ibid.*, 1978, **61**, 136.
232. A. P. Ronald and W. A. B. Thomson, *J. Fish Res. Bd. Can.*, 1964, **21**, 1481.
233. D. F. Gadbois, J. M. Mendelsohn and L. J. Ronsivalli, *J. Food Sci.*, 1967, **32**, 511.
234. E. L. Wick, E. Underriner and E. Paneras, *J. Food Sci.*, 1967, **32**, 365.
235. R. A. Scanlan, M. Leonard, H. Petropakis and A. F. Anglemier, *J. Agric. Food Chem.*, 1973, **21**, 451.
236. S. Bethea and N. P. Wong, *J. Assoc. Off. Anal. Chem.*, 1968, **51**, 1216.
237. W. F. Staruszkiewicz, *ibid.*, 1969, **52**, 471.
238. S. Bethea, *ibid.*, 1970, **53**, 468.
238a. W. F. Staruszkiewicz, E. Fernandez-Flores and J. F. Bond, *ibid.*, 1978, **61**, 973.
239. R. G. Johansen and S. S. Voris, *Cereal Chem.*, 1971, **48**, 576.
240. P. Armandola, *Tec. Molitoria*, 1963, **14**, 94.
241. W. R. Harvey, R. W. Hale and R. M. Ikeda, *Tobacco Sci.*, 1970, **14**, 141.
242. E. Fernandez-Flores, D. A. Kline and A. R. Johnson, *J. Assoc. Off. Anal. Chem.*, 1970, **53**, 17.
243. E. Fernandez-Flores, D. A. Kline, A. R. Johnson and B. L. Leber, *ibid.*, 1970, **53**, 1203.
244. D. A. Kline, E. Fernandez-Flores and A. R. Johnson, *ibid.*, 1970, **53**, 1198.
245. A. Zamorani, G. Roda and G. Lanzarini, *Ind. Agrar.*, 1971, **9**, 35.
246. M. B. Duggan, *J. Assoc. Off. Anal. Chem.*, 1969, **52**, 1038.
247. L. S. Gasco, R. P. Barrera and F. C. de la Cruz, *J. Chromatog. Sci.*, 1969, **7**, 228.
248. M. Knee and S. G. S. Hatfield, *J. Food Technol.*, 1976, **11**, 485.
249. D. F. Meigh, *J. Sci. Food Agric.*, 1960, **11**, 381.
250. L. R. Mattick, W. B. Robinson, L. D. Weirs and D. L. Barry, *J. Agric. Food Chem.*, 1963, **11**, 334.
251. W. G. Jennings and M. R. Sevenants, *J. Food Sci.*, 1964, **29**, 796.
252. P. Molina, A. Soler and J. Cambronero, *An. Bromatol.*, 1974, **26**, 51.
253. G. Braun and E. Hieke, *Dt. Lebensmitt. Rdsch.*, 1977, **73**, 273.
254. D. A. Forss, E. A. Dunstone, E. H. Ramshaw and W. Stark, *J. Food Sci.*, 1962, **27**, 90.
255. T. R. Kemp, D. E. Knavel and L. P. Stolz, *J. Agric. Food Chem.*, 1974, **22**, 717.
256. B. I. Brown, *J. Chromatog.*, 1973, **86**, 239.
257. A. Mueller-Stock, R. K. Joshi and J. Buechi, *ibid.*, 1971, **63**, 281.
258. P. H. Todd, M. G. Bensinger and T. Biftu, *J. Food Sci.*, 1977, **42**, 660.
258a. J. Caencina, J. L. Gimenez, J. Cano and G. Guzman, *An. Bromatol.*, 1977, **29**, 377.
259. R. M. Ikeda, W. L. Stanley, L. A. Rolle and S. H. Vannier, *J. Food Sci.*, 1962, **27**, 593.
260. W. L. Stanley, R. M. Ikeda, S. H. Vannier and L. A. Rolle, *ibid.*, 1961, **26**, 43.
261. A. R. Jones, M. E. Neale and J. Ridlington, *J. Chromatog.*, 1977, **130**, 368.
262. G. L. K. Hunter and M. G. Moshonas, *J. Food Sci.*, 1966, **31**, 167.
263. *Idem, Anal. Chem.*, 1965, **37**, 378.
264. G. B. Gostecnic and A. Zlatkis, *J. Chromatog.*, 1975, **106**, 73.
265. R. M. Ikeda, W. L. Stanley, S. H. Vannier and E. M. Spitler, *J. Food Sci.*, 1962, **27**, 455.
266. J. B. Roberts, *Nature*, 1962, **193**, 1071.
267. *Idem, J. Inst. Brew.*, 1962, **68**, 197.
267a. R. Tressl and L. Friese, *Z. Lebensmitt. Forsch.*, 1978, **166**, 350.
268. R. G. Buttery and R. Teranishi, *Anal. Chem.*, 1961, **33**, 1439.
269. S. R. Pareles and S. S. Chang, *J. Agric. Food Chem.*, 1974, **22**, 339.
270. T. P. Dornseifer and J. J. Powers, *Food Technol.*, 1963, **17**, 1330.
271. J. E. Ayers, M. J. Fishwick, D. G. Land and T. Swain, *Nature*, 1964, **203**, 81.
271a. R. R. Linko, H. Kallio and K. Rainio, *J. Chromatog.*, 1978, **155**, 191.
272. C. Roosen-Runge and E. Schneider, *Z. Lebensmitt. Forsch.*, 1977, **164**, 96.
272a. L. D. Tyler, T. E. Acree, R. R. Nelson and R. M. Butts, *J. Agric. Food Chem.*, 1978, **26**, 774.
272b. R. G. Buttery, D. G. Guadagni and L. C. Ling, *ibid.*, 1978, **26**, 791.
273. M. H. Brodnitz and C. L. Pollock, *Food Technol.*, 1970, **24**, 78.
274. D. M. Oaks, H. Hartmann and K. P. Dimick, *Anal. Chem.*, 1964, **36**, 1560.
275. M. E. Daxenbichler and C. H. Van Etten, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 950.
275a. W. J. Mullin, *J. Chromatog.*, 1978, **155**, 198.
276. B. Bengtsson and I. Bosund, *Food Technol.*, 1964, **18**, 773.
277. A. F. Thomas, *J. Agric. Food Chem.*, 1973, **21**, 451.
278. E. W. Cieplinski and W. Averill, *Gas Chromatography Applications*, No. GC-AP-002, Perkin-Elmer Corp., 1962.
279. N. Hartmann and S. J. Hawkes, *J. Chromatog. Sci.*, 1970, **8**, 610.
280. A. M. C. Davies, *J. Chromatog.*, 1975, **115**, 293.
280a. Analytical Methods Committee, *Analyst*, 1978, **103**, 375.
281. Society for Analytical Chemistry, Essential Oils Sub-Committee, *ibid.*, 1973, **98**, 616.
282. *Idem, ibid.*, 1975, **100**, 593.
283. M. C. Nigam, I. C. Nigam, L. Levi and K. L. Handa, *Can. J. Chem.*, 1964, **42**, 2610.
284. J. Clark, R. Dewan, H. D. Locksley and R. Maynard, *J. Chromatog.*, 1977, **134**, 315.
284a. U. M. Senanayake, T. H. Lee and R. B. H. Wills, *J. Agric. Food Chem.*, 1978, **26**, 822.
285. J. W. Rhoades, *ibid.*, 1960, **8**, 136.
286. R. E. Biggers, J. J. Hilton and M. A. Gianturco, *J. Chromatog. Sci.*, 1969, **7**, 453.
286a. D. Nurok, J. W. Anderson and A. Zlatkis, *Chromatographia*, 1978, **11**, 188.
286b. R. Tressl, K. G. Gruenewald, H. Koeppler and R. Silwar, *Z. Lebensmitt. Forsch.*, 1978, **167**, 108.
286c. R. Tressl, D. Bahri, H. Koeppler and A. Jensen, *ibid.*, 1978, **167**, 111.
286d. W. Rahn and W. A. Koenig, *J. High Resolut. Chromatog. Chromatog. Commun.*, 1978, **1**, 69.
287. C. G. Tassan and G. F. Russell, *J. Food Sci.*, 1974, **39**, 64.
288. O. G. Vitzthum, M. Barthels and H. Kwasny, *Z. Lebensmitt. Forsch.*, 1974, **154**, 135.
289. W. Renold, R. Naef-Mueller, U. Keller, B. Willhalm and G. Ohloff, *Helv. Chim. Acta*, 1974, **57**, 1301.
290. A. R. Pierce, H. N. Graham, S. Glassner, H. Madlin and J. G. Gonzalez, *Anal. Chem.*, 1969, **41**, 298.
291. S. D. Bailey, D. G. Mitchell, M. L. Bazinet and C. Weurman, *J. Food Sci.*, 1962, **27**, 165.
292. M. van Praag, H. S. Stein and M. S. Tibbetts, *J. Agric. Food Chem.*, 1968, **16**, 1005.
292a. K. Valdeig, *Nahrung*, 1978, **22**, 745.
293. G. A. Reineccius, P. G. Keeney and W. Weissberger, *J. Agric. Food Chem.*, 1972, **20**, 202.
294. E. Fogden and S. Urry, *J. Assoc. Publ. Anal.*, 1973, **11**, 104.
294a. A. Erndt, K. Gosik, A. Krajewska and T. Scibor, *Chem. Analit. (Warsaw)*, 1978, **23**, 811.

295. H. Trachman, *Communs. Wallerstein Labs.*, 1969, **32**, 111.
296. R. H. Dyer, *J. Assoc. Off. Anal. Chem.*, 1972, **55**, 564.
297. J. F. Clapperton and A. G. Holliday, *J. Inst. Brew.*, 1968, **74**, 164.
298. A. M. Jamieson, *J. Am. Soc. Brew. Chem.*, 1976, **34**, 44.
299. M. F. Feil and L. Marinelli, *Proc. Am. Soc. Brew. Chem.*, 1969, 29.
300. A. Kurosky and A. Bars, *J. Inst. Brew.*, 1968, **74**, 200.
301. G. E. Otter and L. Taylor, *ibid.*, 1976, **82**, 264.
302. G. T. Taylor and B. H. Kirsop, *ibid.*, 1977, **83**, 97.
303. P. Sandra and M. Verzele, *ibid.*, 1975, **81**, 302.
304. K. Morgan, *ibid.*, 1965, **71**, 166.
304a. B. Gisler and V. Makinen, *Brauwissenschaft.*, 1978, **31**, 177.
305. S. Engan, *Brygmesteren*, 1969, **26**. 23.
306. A. D. Haukeli and S. Lie, *J. Inst. Brew.*, 1971, **77**, 538.
306a. C. Barcelo, M. Gassiot and M. Ferrer, *J. Chromatog.*, 1978, **147**, 463.
306b. J. D. R. Mawer and P. A. Martin, *J. Inst. Brew.*, 1978, **84**, 244.
307. H. Hashimoto and Y. Kuroiwa, *Proc. Am. Soc. Brew. Chem.*, 1966, 121.
308. G. A. F. Harrison and C. M. Coyne, *J. Chromatog.*, 1969, **41**, 453.
308a. T. Takahashi, S. Nakajima, I. Konishi, H. Miedaner and L. Narziss, *Brauwissenschaft*, 1978, **31**, 1.
309. F. Drawert, G. Leupold and V. Lessing, *ibid.*, 1977, **30**, 13.
310. J. D. McGuinness, D. R. J. Laws, R. Eastmond and R. J. Gardner, *J. Inst. Brew.*, 1975, **81**, 237.
311. A. M. Jamieson and G. Van Gheluwe, *J. Am. Soc. Brew. Chem.*, 1977, **35**, 73.
312. P. J. Williams and C. R. Strauss, *J. Inst. Brew.*, 1977, **83**, 213.
312a. R. Tressl, L. Friese, F. Fendesack and H. Koeppler, *J. Agric. Food Chem.*, 1978, **26**, 1422, 1426.
312b. R. J. Harding, J. J. Wren and H. E. Nursten, *J. Inst. Brew.*, 1978, **84**, 41.
313. M. E. Kieser, A. Pollard, P. M. Stevens and O. G. Tucknott, *Nature*, 1964, **204**, 887.
314. A. Pollard, M. E. Kieser, P. M. Stevens and O. G. Tucknott, *J. Sci. Food Agric.*, 1965, **16**, 384.
314a. A. A. Williams, H. V. May and O. G. Tucknott, *J. Inst. Brew.*, 1978, **84**, 97.
315. R. L. Brunelle, R. L. Schoeneman and G. E. Martin, *J. Assoc. Off. Anal. Chem.*, 1967, **50**, 329.
316. A. D. Webb and R. E. Kepner, *Am. J. Enol. Viticult.*, 1961, **12**, 51.
317. P. J. Hardy and E. H. Ramshaw, *J. Sci. Food Agric.*, 1970, **21**, 39.
318. F. Drawert and G. Leupold, *Z. Lebensmitt. Forsch.*, 1976, **162**, 401.
319. H. L. Ashmead, G. E. Martin and J. A. Schmit, *J. Assoc. Off. Agric. Chem.*, 1964, **47**, 730.
319a. F. Addeo, G. Nota and L. Chianese, *Am. J. Enol. Vitic.*, 1978, **29**, 7.
319b. P. J. Williams and C. R. Strauss, *J. Inst. Brew.*, 1978, **84**, 144.
320. Research Committee on the Analysis of Potable Spirits, *J. Assoc. Publ. Anal.*, 1972, **10**, 49.
321. R. H. Dyer, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 785.
322. G. E. Martin, G. Caggiano and H. Schlesinger, *ibid.*, 1963, **46**, 294.
323. D. D. Singer and J. W. Stiles, *Analyst*, 1965, **90**, 290.
324. D. D. Singer, *ibid.*, 1966, **91**, 127.
325. *Idem*, *ibid.*, 1966, **91**, 790.
326. R. Hogben and M. Mular, *J. Sci. Food Agric.*, 1976, **27**, 1108.
327. J. H. Barnett and J. R. Einsmann, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 297.
328. J. F. Guymon and E. A. Crowell, *Am. J. Enol. Viticult.*, 1969, **20**, 76.
328a. P. Beaud and A. Ramuz, *Mitt. Geb. Lebensmitt. Hyg.*, 1978, **69**, 423.
329. P. S. Hall, *J. Assoc. Publ. Anal.*, 1976, **14**, 41.
330. R. A. Black and A. A. Andreasen, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 111.
331. R. E. B. Duncan and J. M. Philp, *J. Sci. Food Agric.*, 1966, **17**, 208.
332. G. E. Martin, R. H. Dyer and P. C. Buscemi, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 610.
332a. B. E. H. Saxberg, D. L. Duewer, J. L. Booker and B. R. Kowalski, *Anal. Chim. Acta*, 1978, **103**, 201.
332b. D. W. Clutton and M. B. Evans, *J. Chromatog.*, 1978, **167**, 409.
333. R. K. Stevens and G. E. Martin, *J. Assoc. Off. Agric. Chem.*, 1965, **48**, 802.
334. A. Cesari, A. M. Cusmano and L. Boniforti, *Boll. Lab. Chim. Prov.*, 1964, **15**, 444.
335. J. H. Kahn, G. B. Nickol and H. A. Conner, *J. Agric. Food Chem.*, 1966, **14**, 460.
336. C. C. Sweeley, R. Bentley, M. Makita and W. W. Wells, *J. Am. Chem. Soc.*, 1963, **85**, 2497.
337. K. M. Brobst and C. E. Lott, *Proc. Am. Soc. Brew. Chem.*, 1966, 71.
338. T. Cayle, F. Viebrock and J. Schiaffino, *Cereal Chem.*, 1968, **45**, 154.
339. D. Nurok and T. J. Reardon, *Carbohydr. Res.*, 1977, **56**, 165.
340. H. W. Kircher, *Tappi*, 1962, **45**, 143.
341. J. A. Hause, J. A. Hubicki and G. G. Hazen, *Anal. Chem.*, 1962, **34**, 1567.
342. M. A. Luke, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 937.
342a. W. Baltes and H.-J. Schmahl, *Z. Lebensmitt. Forsch.*, 1978, **167**, 69.
343. A. R. Johnson and E. Fernandez-Flores, *J. Assoc. Off. Anal. Chem.*, 1969, **52**, 559.
344. J. F. T. Oldfield, R. Parslow and M. Shore, *Intern. Sugar J.*, 1970, **72**, 35.
345. H. Sugisawa, *J. Food Sci*, 1966, **31**, 381.
346. R. A. Wilks, M. W. Johnson and A. J. Shingler, *J. Agric. Food Chem.*, 1977, **25**, 605.
347. V. J. Filipic and J. C. Underwood *J. Food Sci.*, 1964, **29**, 464.
348. E. Cremer and M. Riedmann, *Z. Anal. Chem.*, 1965, **212**, 31.
349. J. B. M. Coppock, N. Fisher and M. L. Ritchie, *J. Sci. Food Agric.*, 1958, **9**, 498.
350. N. Fisher and M. E. Broughton, *Chem. Ind. (London)*, 1960, 869.
351. M. P. Burkwall and R. L. Glass, *Cereal Chem.*, 1965, **42**, 236.
352. A. Franciosi and G. Giovannini, *Boll. Lab. Chim. Prov.*, 1964, **15**, 131.
353. A. Franciosi and G. Giovannini, *ibid.*, 1964, **15**, 336.
354. I. R. Hunter and M. K. Walden, *J. Gas Chromatog.*, 1966, **4**, 246.
355. R. V. Golovnya, N. G. Enikeeva, I. L. Zhuravleva and A. S. Zyuzko, *Nahrung*, 1974, **18**, 143.
355a. M. G. Legendre, H. P. Dupuy, R. L. Ory and W. O. McIlraith, *J. Agric. Food Chem.*, 1978, **26**, 1035.
355b. D. A. Withycombe, R. C. Lindsay and D. A. Stuiber, *ibid.*, 1978, **26**, 816.
356. R. W. Zumwalt, K. Kuo and C. W. Gehrke, *J. Chromatog.*, 1971, **55**, 267.
357. J. Vogel and J. Deshusses, *Mitt. Geb. Lebensmitt. Hyg.*, 1965, **56**, 35.
358. W. Groebel, *Dt. Lebensmitt. Rdsch.*, 1965, **61**, 209.
359. K. Silbereisen and B. Wagner, *Monatsschr. Brau.*, 1970, **23**, 57.
360. J. A. W. Gossele, *J. Chromatog.*, 1971, **63**, 429.
360a. A. Bertrand and C. Sarre, *Ann. Falsif. Exp. Chem.*, 1978, **71**, 35.
361. A. Graveland, *J. Assoc. Off. Anal. Chem.*, 1972, **55**, 1024.

362. E. Fogden, M. Fryer and S. Urry, *J. Assoc. Publ. Anal.*, 1974, **12**, 93.
362a. M. E. Neale and J. Ridlington, *ibid.*, 1978, **16**, 135.
363. G. H. Walker, M. S. Green and C. E. Fenn, *ibid.*, 1964, **2**, 2.
364. N. Nose, Y. Hoshino, T. Suzuki, Y. Kikuchi and A. Watanabe, *J. Food Hyg. Soc. Japan*, 1976, **17**, 290.
364a. A. E. Stafford and D. R. Black, *J. Agric. Food Chem.*, 1978, **26**, 1442.
365. H. Wunderlich, *J. Assoc. Off. Anal. Chem.*, 1972, **55**, 557.
366. F. Joe, D. A. Kline, E. M. Miletta, J. A. G. Roach, E. L. Roseboro and T. Fazio, *ibid.*, 1977, **60**, 509.
367. R. Thomas, *Analyst*, 1960, **85**, 551.
368. G. Westoo and A. Andersson, *ibid.*, 1975, **100**, 173.
368a. L. Bertling, J. Delventhal and I. Tietz, *Dt. Lebensmitt. Rdsch.*, 1978, **74**, 41.
368b. H. Pyysalo, A. Kiviranta and S. Lahtinen, *J. Chromatog.*, 1978, **168**, 512.
368c. A. Tanaka, N. Nose, T. Suzuki, A. Hirose and A. Watanabe, *Analyst*, 1978, **103**, 851.
368d. E. Lord, N. G. Bunton and N. T. Crosby, *J. Assoc. Publ. Anal.*, 1978, **16**, 25.
369. P. L. Davis and K. A. Munroe, *J. Agric. Food Chem.*, 1977, **25**, 426.
370. R. Mestres, M. Campo and J. Tourte, *Ann. Falsif. Exp. Chim.*, 1970, **63**, 160.
371. A. Tanaka and Y. Fujimoto, *J. Chromatog.*, 1976, **117**, 149.
372. N. Nose, S. Kobayashi, A. Tanaka, A. Hirose and A. Watanabe, *ibid.*, 1977, **130**, 410.
373. R. Greenberg and C. Resnick, *Pestic. Sci.*, 1977, **8**, 59.
374. K. Moehler and H. Ebert, *Z. Lebensmitt. Forsch.*, 1971, **147**, 251.
375. W. S. Wu and P. W. Saschenbrecker, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 1137.
375a. M. Toyoda, H. Suzuki, Y. Ito and M. Iwaida, *ibid.*, 1978, **61**, 508.
375b. E. Merat, *J. Chromatog.*, 1978, **153**, 530.
376. K. T. Hartman and L. C. Rose, *J. Am. Oil Chem. Soc.*, 1970, **47**, 7.
377. D. F. McCaulley, T. Fazio, J. W. Howard, F. M. Di Ciurco and J. Ives, *J. Assoc. Off. Anal. Chem.*, 1967, **50**, 243.
378. E. E. Stoddard, *ibid.*, 1972, **55**, 1081.
378a. D. A. Kline, F. L. Joe and T. Fazio, *ibid.*, 1978, **61**, 513.
379. D. B. Page and B. P. C. Kennedy, *ibid.*, 1976, **59**, 1208.
380. P. S. Menon and V. S. Kulkarni, *Indian J. Technol.*, 1967, **5**, 168.
381. S. Dilli and K. Robards, *J. Chromatog.*, 1977, **133**, 363.
382. B. Winell, *Analyst*, 1976, **101**, 883.
383. K. Miyakoshi and M. Komoda, *J. Am. Oil Chem. Soc.*, 1977, **53**, 331.
384. M. R. Sahasrabudhe and J. J. Legari, *ibid.*, 1967, **44**, 379.
385. M. R. Sahasrabudhe, *ibid.*, 1967, **44**, 376.
386. F. P. Wetterau, V. L. Olsanski and C. F. Smullin, *ibid.*, 1964, **41**, 791.
387. J. M. Murphy and L. H. Grisley, *ibid.*, 1969, **46**, 384.
388. G. Lundquist and C. E. Meloan, *Anal. Chem.*, 1971, **43**, 1122.
389. H. B. S. Conacher, J. C. Meranger and J. Leroux, *J. Assoc. Off. Anal. Chem.*, 1970, **53**, 571.
390. H. B. S. Conacher, R. K. Chadha and J. R. Iyengar, *ibid.*, 1973, **56**, 1264.
391. L. Kogan and S. Strezleck, *Cereal Chem.*, 1966, **43**, 470.
391a. E. Mergenthaler and H. Scherz, *Z. Lebensmitt. Forsch.*, 1978, **166**, 225.
392. W. Schmolck and E. Mergenthaler, *ibid.*, 1973, **152**, 263.
393. E. Mergenthaler and H. Scherz, *ibid.*, 1976, **162**, 25.
394. *Idem*, *ibid.*, 1976, **162**, 159.
395. D. I. Rees, *Analyst*, 1965, **90**, 568.
396. M. L. Richardson and P. E. Luton, *ibid.*, 1966, **91**, 520.
397. W. Groebel and A. Wessels, *Dt. Lebensmitt. Rdsch.*, 1972, **68**, 393.
398. K. Nagasawa, T. Shinozuka and A. Ogamo, *Eisei Kagaku*, 1974, **20**, 337.
399. K. Nagasawa, A. Ogamo and T. Shinozuka, *J. Chromatog.*, 1975, **111**, 51.
400. J. W. Howard, T. Fazio, B. A. Klimeck and R. H. White, *J. Assoc. Off. Anal. Chem.*, 1969, **52**, 492.
401. R. E. Weston and B. B. Wheals, *Analyst*, 1970, **95**, 680.
402. H. B. S. Conacher and R. C. O'Brien, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 1135.
403. H. Koenig, *Z. Anal. Chem.*, 1971, **255**, 123.
404. R. Gerstl and K. Ranfft, *ibid.*, 1972, **258**, 110.
405. H. Jacin, *Dt. Lebensmitt. Rdsch.*, 1975, **71**, 428.
405a. R. A. Janiak, H. H. Damon and T. C. Mohr, *J. Agric. Food Chem.*, 1978, **26**, 710.
405b. J. L. Kacpvzak, *J. Assoc. Off. Anal. Chem.*, 1978, **61**, 1528.
406. I. Furda, P. D. Malizia, M. G. Kolor and P. J. Vernieri, *J. Agric. Food Chem.*, 1975, **23**, 340.
407. H. G. Jones, D. M. Smith and M. Sahasrabudhe, *J. Assoc. Off. Anal. Chem.*, 1966, **49**, 1183.
408. H. K. Hundley, *ibid.*, 1973, **56**, 66.
409. E. Fernández-Flores and V. H. Blomquist, *ibid.*, 1973, **56**, 1267.
410. R. L. Brunelle and G. E. Martin, *ibid.*, 1963, **46**, 950.
411. F. Bucci, L. Boniforti and A. Cesari, *Boll. Lab. Chim. Prov.*, 1965, **16**, 195.
412. R. H. Dyer, G. E. Martin and B. B. Butts, *J. Assoc. Off. Anal. Chem.*, 1975, **58**, 140.
412a. *Intern. Flavours Food Addit.*, 1978, **9**, 224.
413. P. A. P. Liddle and P. de Smedt, *Ann. Falsif. Exp. Chim.*, 1976, **69**, 857.
414. D. Larry, *J. Assoc. Off. Anal. Chem.*, 1969, **52**, 481.
415. *Intern. Flavours Food Addit.*, 1977, **8**, 27.
416. *Ibid.*, 1977, **8**, 28.
417. D. Larry, *J. Assoc. Off. Anal. Chem.*, 1973, **56**, 1281.
417a. *Intern. Flavours Food Addit.*, 1978, **9**, 228.
418. E. Merat, E. Martin and J. Vogel, *Mitt. Geb. Lebensmitt. Hyg.*, 1976, **67**, 521.
419. *Intern. Flavours Food Addit.*, 1977, **8**, 161.
420. D. Larry, M. J. Fuller and P. G. Harrill, *J. Assoc. Off. Anal. Chem.*, 1970, **53**, 698.
421. S. Gal and P. Schilling, *Z. Lebensmitt. Forsch.*, 1972, **148**, 18.
422. J. E. Lovelock and S. R. Lipsky, *J. Am. Chem. Soc.*, 1960, **82**, 431.
423. D. M. Coulson, L. A. Cavanagh, J. E. de Vries and B. Walther, *J. Agric. Food Chem.*, 1960, **8**, 399.
424. L. Giuffrida, *J. Assoc. Off. Agric. Chem.*, 1964, **47**, 293.
425. E. S. Goodwin, R. Goulden, A. Richardson and J. G. Reynolds, *Chem. Ind. (London)*, 1960, 1220.
426. E. S. Goodwin, R. Goulden and J. G. Reynolds, *Analyst*, 1961, **86**, 697.
427. J. H. Hamence, P. S. Hall and D. J. Caverly, *ibid.*, 1965, **90**, 649.
428. *Official Methods of Analysis of the Association of Official Analytical Chemists*, 11th Ed., p. 475. AOAC, Washington, 1970.
429. J. Burke and L. Giuffrida, *J. Assoc. Off. Anal. Chem.*, 1964, **47**, 326.
430. S. W. Bellman and T. L. Barry, *ibid.*, 1971, **54**, 499.
430a. B. Luckas, H. Pscheidl and D. Haberland, *J. Chromatog.*, 1978, **147**, 41.

431. M. Beroza and M. C. Bowman, *Anal. Chem.*, 1965, **37**, 291.
432. R. W. Storherr and R. R. Watts, *J. Assoc. Off. Agric. Chem.*, 1965, **48**, 1154.
433. L. Gay and M. Cerny, *Mitt. Geb. Lebensmitt. Hyg.*, 1975, **66**, 225.
434. G. M. Telling, D. J. Sissons and H. W. Brinkman, *J. Chromatog.*, 1977, **137**, 405.
435. R. Bielorai and E. Alumot, *J. Agric. Food Chem.*, 1966, **14**, 622.
436. E. P. Ragelis, B. S. Fisher and B. A. Klimeck, *J. Assoc. Off. Anal. Chem.*, 1966, **49**, 963.
437. S. G. Heuser and K. A. Scudamore, *Chem. Ind. (London)*, 1967, 1557.
438. A. Di Muccio, L. Boniforti and R. Monacelli, *J. Chromatog.*, 1972, **71**, 340.
439. G. Yip, *J. Assoc. Off. Agric. Chem.*, 1962, **45**, 367.
440. T. P. Garbrecht, *ibid.*, 1970, **53**, 70.
441. M. C. Bowman, M. Beroza and K. R. Hill, *ibid.*, 1971, **54**, 346.
442. M. C. Bowman and M. Beroza, *ibid.*, 1970, **53**, 499.
443. *Idem*, *ibid.*, 1971, **54**, 1086.
444. *Analyst*, 1977, **102**, 858.
444a. J. Hild and H.-P. Thier, *Z. Lebensmitt. Forsch.*, 1978, **166**, 9.
445. H. J. Stan, *ibid.*, 1977, **164**, 153.
446. R. L. Martin, *Anal. Chem.*, 1966, **38**, 1209.
447. D. M. Coulson, *J. Gas Chromatog.*, 1965, **3**, 134.
448. J. F. Lawrence and H. A. McLeod, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 979.
449. E. R. Holden, W. M. Jones and M. Beroza, *J. Agric. Food Chem.*, 1969, **17**, 56.
449a. S. B. Mathur, Y. Iwata and F. A. Gunther, *ibid.*, 1978, **26**, 768.
450. J. H. Onley and G. Yip, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 1366.
450a. W. H. Newsome, *J. Agric. Food Chem.*, 1978, **26**, 1325.
451. E. D. Chilwell and D. Hughes, *J. Sci. Food Agric.*, 1962, **8**, 425.
452. R. Delley, K. Friedrich, B. Karlhuber, G. Szekely and K. Stammbach, *Z. Anal. Chem.*, 1967, **228**, 23.
453. P. B. Baker and B. Flaherty, *Analyst*, 1972, **97**, 713.
454. A. Bevenue, Y. Kawano and F. De Lano, *J. Chromatog.*, 1970, **50**, 49.
455. S. U. Khan, *Bull. Environ. Contam. Toxicol.*, 1975, **14**, 745.
455a. R. R. King, *J. Agric. Food Chem.*, 1978, **26**, 1460.
455b. C. A. Brockwell, *ibid.*, 1978, **26**, 962.
455c. T. W. Nowicki, *J. Assoc. Off. Anal. Chem.*, 1978, **61**, 829.
456. D. C. Holmes, J. H. Simmons and J. O'G. Tatton, *Nature*, 1967, **216**, 227.
457. S. Jensen, *New Scientist*, 1966, **32**, 612.
458. R. W. Risebrough, P. Reiche and H. S. Olcott, *Bull. Environ. Contam. Toxicol.*, 1969, **4**, 192.
459. E. J. Hannan, D. D. Bills and J. L. Herring, *J. Agric. Food Chem.*, 1973, **21**, 87.
460. R. I. Asai, F. A. Gunther, W. E. Westlake and Y. Iwata, *ibid.*, 1971, **19**, 396.
461. J. Nagayama, M. Kuratsune and Y. Masuda, *Bull. Environ. Contam. Toxicol.*, 1976, **15**, 9.
462. G. Westoo, *Acta Chem. Scand.*, 1966, **20**, 2131.
463. *Idem*, *ibid.*, 1967, **21**, 1790.
464. J. G. Gonzales and R. T. Ross, *Anal. Lett.*, 1972, **5**, 683.
465. P. Jones and G. Nickless, *J. Chromatog.*, 1974, **89**, 201.
466. C. J. Cappon and J. C. Smith, *Anal. Chem.*, 1977, **49**, 365.
466a. T. A. Gough, *Analyst*, 1978, **103**, 785.
467. T. A. Gough and K. S. Webb, *J. Chromatog.*, 1972, **64**, 201.
468. *Idem*, *ibid.*, 1973, **79**, 57.
469. N. T. Crosby, J. K. Foreman, J. F. Palframan and R. Sawyer, *Nature*, 1972, **238**, 342.
470. J. K. Foreman, J. F. Palframan and E. A. Walker, *ibid.*, 1970, **225**, 554.
471. G. M. Telling, T. A. Bryce and J. Althorpe, *J. Agric. Food Chem.*, 1971, **19**, 937.
472. T. A. Bryce and G. M. Telling, *ibid.*, 1972, **20**, 910.
473. T. Fazio, J. N. Damico, J. W. Howard, R. H. White and J. O. Watts, *ibid.*, 1971, **19**, 250.
474. T. Fazio, R. H. White and J. W. Howard, *J. Assoc. Off. Anal. Chem.*, 1971, **54**, 1157.
474a. D. C. Havery, T. Fazio and J. W. Howard, *ibid.*, 1978, **61**, 1374.
474b. C. Janzowski, G. Eisenbrand and R. Preussmann, *J. Chromatog.*, 1978, **150**, 216.
474c. J. S. Lee, L. M. Libbey, R. A. Scanlan and D. D. Bills, *Bull. Environ. Contam. Toxicol.*, 1978, **19**, 511.
475. T. G. Alliston, G. B. Cox and R. S. Kirk, *Analyst*, 1972, **97**, 915.
476. G. M. Telling, *J. Chromatog.*, 1972, **73**, 79.
476a. A. A. Pokrovskii, Y. L. Kostyukovskii, D. B. Melamed and F. A. Medvedev, *Zh. Analit. Khim.*, 1978, **33**, 970.
476b. A. A. Pokrovskii, F. A. Medvedev, D. B. Melamed and Y. L. Kostyukovskii, *ibid.*, 1978, **33**, 1396.
477. T. Kawabata, H. Ohshima, T. Ishibashi, M. Matsui and T. Kitsuwa, *J. Chromatog.*, 1977, **140**, 47.
478. A. C. Dean, E. Bradford, A. W. Hubbard, W. D. Pocklington and J. Thomson, *ibid.*, 1969, **44**, 465.
479. S. P. Fore and H. P. Dupuy, *J. Am. Oil Chem. Soc.*, 1970, **47**, 17.
480. H. P. Dupuy and S. P. Fore, *ibid.*, 1970, **47**, 231.
481. S. P. Fore and H. P. Dupuy, *ibid.*, 1972, **49**, 129.
482. P. J. Wan, M. Chittwood, C. M. Cater and K. F. Mattil, *ibid.*, 1977, **54**, 542.
483. M. A. Litchman, L. A. Turano and R. P. Upton, *ibid.*, 1972, **55**, 1226.
484. S. Hirayama and C. Imai, *J. Am. Oil Chem. Soc.*, 1977, **54**, 190.
485. J. O. Watts and W. Holswade, *J. Assoc. Off. Anal. Chem.*, 1967, **50**, 717.
486. L. A. Roberts, *ibid.*, 1968, **51**, 825.
487. B. D. Page and B. P. C. Kennedy, *ibid.*, 1975, **58**, 1062.
488. S. Gal and P. Schilling, *Z. Lebensmitt. Forsch.*, 1971, **145**, 30.
489. B. D. Page and C. F. Charbonneau, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 710.
490. M. A. Litchman and R. P. Upton, *Anal. Chem.*, 1972, **44**, 1495.
491. M. J. Calhoun and E. S. Dellamonica, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 1342.
492. M. Wandel and H. Tengler, *Dt. Lebensmitt. Rdsch.*, 1963, **59**, 326.
493. *Idem*, *ibid.*, 1964, **60**, 335.
494. W. Pfab, *ibid.*, 1967, **63**, 72.
495. C. S. Giam, H. S. Chan and G. S. Neff, *Anal. Chem.*, 1975, **47**, 2225.
496. D. T. Williams and W. F. Miles, *J. Assoc. Off. Anal. Chem.*, 1975, **58**, 272.
497. D. T. Williams, *ibid.*, 1976, **59**, 32.
498. G. F. Ernst and J. B. H. van Lierop, *J. Chromatog.*, 1975, **109**, 439.
499. J. B. H. van Lierop and W. Stek, *ibid.*, 1976, **128**, 183.
500. G. W. Diachenko, C. V. Breder, M. E. Brown and J. Dennison, *J. Assoc. Off. Anal. Chem.*, 1977, **60**, 570.
501. M. Roseli and B. Marek, *Mitt. Geb. Lebensmitt. Hyg.*, 1977, **68**, 440.
501a. M. E. Brown, C. V. Breder and T. P. McNeal, *J. Assoc. Off. Anal. Chem.*, 1978, **61**, 1383.
501b. G. B. M. Gawell, *Analyst*, 1979, **104**, 106.

502. A. E. Pohland, K. Sanders and C. W. Thorpe, *J. Assoc. Off. Anal. Chem.*, 1970, **53**, 692.
503. J. W. Ralls and R. M. Lane, *J. Food Sci.*, 1977, **42**, 1117.
504. J. D. Rosen and S. R. Pareles, *J. Agric. Food Chem.*, 1974, **22**, 1024.
505. Y. Fujimoto, T. Suzuki and Y. Hoshino, *J. Chromatog.*, 1975, **105**, 99.
506. C. W. Thorpe and R. L. Johnson, *J. Assoc. Off. Anal. Chem.*, 1974, **57**, 861.
507. A. S. Salhab, G. F. Russell, J. R. Coughlin and D. P. H. Hsieh, *ibid.*, 1976, **59**, 1037.
508. C. O. Ikediobi, I. C. Hsu, J. R. Bamburg and F. M. Strong, *Anal. Biochem.*, 1971, **43**, 327.
508a. R. Siegfried and H. K. Frank, *Z. Lebensmitt. Forsch.*, 1978, **166**, 363.
509. M. R. Boyd and B. J. Wilson, *J. Agric. Food Chem.*, 1971, **19**, 547.
510. G. Wood and A. Huang, *ibid.*, 1975, **23**, 239.
511. D. E. Coffin and J-C. Pilon, *J. Assoc. Off. Anal. Chem.*, 1973, **56**, 352.
512. H. O. Guenther, *Fleischwirtschaft*, 1972, **52**, 625.
513. E. W. Day, L. E. Vanatta and R. F. Sieck, *J. Assoc. Off. Anal. Chem.*, 1975, **58**, 520.
514. J. J. Ryan and J-C. Pilon, *ibid.*, 1976, **59**, 817.
515. J. J. Ryan and J. A. Dupont, *J. Agric. Food Chem.*, 1975, **23**, 917.
516. D. S. Farrington and J. W. Munday, *Analyst*, 1976, **101**, 639.
516a. D. R. Erney, *J. Assoc. Off. Anal. Chem.*, 1978, **61**, 214.
516b. L. L. Lamparski, N. H. Mahle and L. A. Shadoff, *J. Agric. Food Chem.*, 1978, **26**, 1113.
517. R. L. S. Patterson, *Chem. Ind. (London)*, 1972, 609.
518. N. M. Griffiths and D. G. Land, *ibid.*, 1973, 904.

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EFFECT OF HYDROGEN-ION CONCENTRATION ON THE EXTRACTION OF COBALT, NICKEL, CADMIUM AND LEAD WITH APDC/MIBK: TIME STABILITY OF THE EXTRACTS

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Summary—The extraction of cobalt, nickel, cadmium and lead ions by means of APDC/MIBK has been studied at various acidities of the aqueous phase (pH 0.2–6). Lead and nickel are extracted equally well over this pH-range, while cobalt and cadmium require pH > 1. The time stability of the extracted complexes in MIBK increases in the order cadmium < lead < nickel < cobalt. The decomposition of the complexing agent or the metal complexes is rapid in the two-phase system MIBK/water.

Several investigators have used the diethyldithiocarbamate (DDC) or the tetramethylenedithiocarbamate ion (commonly called pyrrolidinedithiocarbamate, PDC) as chelating agents in the determination of various heavy metals in trace amounts. The complexed metal ions are extracted into an organic solvent and determined by atomic-absorption spectrophotometry *etc.*

The extraction of the metal complex into the organic phase depends upon the hydrogen-ion concentration of the aqueous phase. With other experimental parameters kept constant, the amount of the metal ion extracted will decrease steeply if the pH is less than some critical value. Thus, pH-control is necessary for complexation and extraction. Many analytical procedures require precise (±0.1 unit) adjustment of pH, usually in the range 2–4. However, some studies indicate that the pH-range for quantitative extraction with PDC is fairly wide for lead, (the pH interval is given as 0.1–6,[1] or 0.25–8,[2]) and cobalt (pH 1–10,[3]), but more restricted for cadmium (pH 1–4,[3]). The pH interval suitable for nickel has been given as 2–4[1] and 3.5–8.[4] Extraction *vs.* pH data are presented here for these four metal ions, supplementing the earlier data.

The chelating agents mentioned above are unstable in acidic aqueous solution. The decomposition proceeds through the dithiocarbamic acid, according to the scheme:[5]

$$R_2NCS_2^- + 2H^+ \rightleftharpoons R_2NCS_2H + H^+ \rightleftharpoons R_2NH_2^+ + CS_2 \quad (1)$$

The decomposition is favoured when the pH of the solution is less than the pK_a value of the $R_2NH_2^+$ ion. The half-life for decomposition, $t_{1/2}$, will be independent of pH when the pH is much less than the pK_a value of the dithiocarbamic acid ($pK_a \sim 4$ for HDDC, $pK_a \sim 3$ for HPDC).[5] The half-life is reported to be of the order of seconds for HDDC[2,6] and 25–32 min for HPDC[2,6] under acidic conditions.

PDC is often preferred to DDC when extractions are performed in acidic solution. Contradictory reports have appeared concerning the usefulness of DDC for extractions in the pH-range 2–4.[7,8]

From a practical point of view, the decomposition of pure dithiocarbamic acid in aqueous solution is not so important as the time stability of the various metal complexes after extraction into an organic solvent, e.g., methyl isobutyl ketone (MIBK). Several reports[2–4,9–14] have commented on the limited time stability of PDC-complexes in MIBK, but a more precise comparison of the various values reported is difficult, owing to differences in experimental conditions. It is clear, however, that the time stability is different for different metal ions. The manganese–PDC extract in MIBK seems to be unstable,[12] but the cobalt complex has good stability.[4] The lead and nickel extracts are said to be stable for 5 and 3 hr, respectively,[4] and the nickel extract for more than 15–20 hr.[14] The cadmium complex is said to be stable for more than 72 hr,[11] but very easily decomposed during the extraction step.[13]

Some difficulties encountered in our laboratory seemed to be caused by decomposition of the MIBK extracts and we have, therefore, investigated the stability of the ligand in water/MIBK mixtures. We have also studied the variation in time stability of cobalt, nickel, cadmium and lead tetramethylenedithiocarbamate complexes in methyl isobutyl ketone with the pH of the aqueous phase and the contact area between the MIBK and aqueous phases.

EXPERIMENTAL

Apparatus

A Perkin–Elmer 403 atomic-absorption spectrophotometer with a 10-cm single slot burner was used and was operated as recommended by the manufacturer.

Procedures

To 100 ml of demineralized water were added a suitable amount of the metal ion (0.1 μmole of Cd, 1 μmole of Ni or Pb, 2 μmole of Co), 5 ml of 20% ascorbic acid solution and 5 ml of 1% ammonium PDC solution. Ascorbic acid was added to imitate the conditions of analysis of some samples at this laboratory (it is used to diminish the interference from iron). After adjustment of pH, by addition of hydrochloric acid or ammonia solution, the solution was transferred to a 200-ml standard flask and extracted with 20.0 ml of MIBK by vigorous shaking for 1 min. The organic phase was raised into the neck of the flask by addition of an aqueous solution with the same pH value as the aqueous phase.

The time stability of the extracts was studied under various conditions. In some experiments, the MIBK phases were separated from the extracted aqueous phase, transferred to test-tubes and stored, without water present, or with 5 ml of demineralized water. In other experiments, the MIBK was kept in contact with the extracted aqueous phase. The aqueous phase was stirred with a magnetic stirrer either very gently (*ca.* 120 r.p.m.) or more vigorously.

The stability of the cadmium complexes in MIBK solution in contact with the extracted aqueous phase was studied at different acidities with the aqueous phase either unstirred or stirred very slowly.

The absorbances of "aged" samples were compared with those of freshly prepared standards. The experiments were duplicated and average values are given in the tables. The absorbances are accurate to ±3%.

The rate of decomposition of pyrrolidinedithiocarbamic acid, HPDC, was measured by taking samples at various time intervals and analysing for PDC by addition of copper chloride solution in excess and spectrophotometric determination of the copper complex, extracted into chloroform.[15] The temperature was 21 ± 2°. The pH values are the readings given on a pH-meter set calibrated with a commercial buffer solution of nominal pH-value as near as possible to that of the sample solution (buffers of pH = 1, 2, 3, 4, 5 or 6 were used).

RESULTS AND DISCUSSION

Figure 1 shows the results of the extraction of the various metals at different pH-values. They confirm the earlier observations on the extraction of lead and cobalt. The poor extraction of cadmium found by Kinrade and Van Loon[3] in the pH range 4–6 was not found here. The wide extraction range for nickel found here has not previously been reported. An "optimum" value for the extraction of any of these metal ions does not exist, in the sense that there is not a particular pH-value that gives better extraction than other values slightly different from it. Thus, there is no need for precise pH control anywhere in the range 1–6.

Table 1 shows half-life values ($t_{1/2}$) for PDC in water, MIBK and some two-phase systems. The $t_{1/2}$ values found here for PDC in water are somewhat lower than those reported by Aspila *et al.*,[6] but are in fair agreement with those of Everson and Parker.[2] The rate of decomposition of PDC extracted into MIBK is low. However, the rate of decomposition of PDC in the two-phase system water/MIBK is very much greater than in either single-phase system. The $t_{1/2}$ value was found to depend on the contact area between water and MIBK. In keeping with this, shaking of the mixture greatly promotes the decomposition. As $t_{1/2}$ is not affected very much if the water contains 10% of acetone (v/v), the MIBK dissolved in the water (about 2%) should not affect the rate of decomposition. This rapid decomposition is also observed when instead of MIBK the corresponding alcohol, 4-methylpentan-2-ol, is used. Chloroform does not increase the rate of decomposition. The $t_{1/2}$ for the water/MIBK system did not change when the experiment was performed in the dark and with oxygen absent. It is suggested that the decomposition of PDC proceeds rapidly at the phase boundary between water and MIBK or similar organic compounds with polar groups.

Tables 2–4 show that the time stability of the metal ion PDC complexes in MIBK depends on the metal ion and on the treatment of the extract.

In the light of the results discussed here, the time instability of the extracted metal complexes may be described as follows. Kinetically labile complexes will

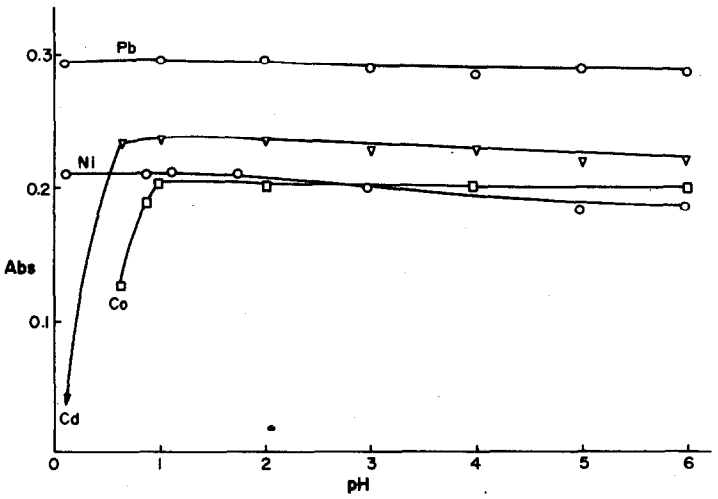


Fig. 1. Effect of pH on the amount (expressed in terms of absorbance) of Co, Ni, Cd and Pb extracted with APDC/MIBK.

Table 1. Half-life for PDC at 21 ± 2°

Conditions	$t_{1/2}$
In 0.8*M* HCl	18 ± 5 min
In acetate buffer, pH = 5.0	25 ± 3 hr
In acetate buffer, pH = 4.3	6.0 ± 0.5 hr
In acetate buffer, pH = 4.5, 10% v/v acetone added	6.0 ± 0.5 hr
In MIBK, extracted from 0.8*M* HCl	18 ± 3 hr
In MIBK, extracted from acetate buffer, pH = 5.0	22 ± 3 hr
Two phases:	
MIBK/0.8*M* HCl, intermittent shaking*	4 ± 1 min
MIBK/acetate buffer, pH = 5.0, continuous shaking	2.5 ± 0.5 min
MIBK/acetate buffer, pH = 5.0, intermittent shaking	12 ± 3 min
MIBK/acetate buffer, pH = 4.3, in dark, stirred by bubbling nitrogen gas	2.5 ± 1 min
$CHCl_3$/acetate buffer, pH = 4.3, intermittent shaking	6.2 ± 0.5 hr
MIAA†/acetate buffer, pH = 4.3, intermittent shaking	5 ± 1 min

* The flask was inverted once every minute.
† 4-Methylpentan-2-ol.

Table 2. Time stability of Cd/PDC extracts in MIBK at various pH-values of the aqueous phase

pH		Absorbance × 1000 1 hr	4 hr	7 hr	24 hr	30 hr	48 hr	80 hr
1.0	Unstirred	160	157	157	145	130	22	0
	Stirred	160	155	157	4	0		
2.0	Unstirred	158	157	158	146	149	145	50
	Stirred	159	157	159	142	68	0	
3.0	Unstirred	156	157	156	146	145	144	147
	Stirred	156	158	158	152	152	126	68

decompose when the concentration of free ligand has decreased below the level necessary for the formation of the extractable (*i.e.*, neutral) complex (the decomposition products of the ligand may also react with the metal ions to form precipitates). If the MIBK extract is separated from the aqueous phase, the rate of decomposition of the ligand will be low and the extracts will be stable for a long time (Table 4). When the MIBK phase is not separated from the aqueous phase, the decomposition will be faster and will depend on the treatment of the extracts. The decomposition is accelerated when there is a large contact

Table 3. Time stability of Co, Ni, Cd, Pb/PDC solutions in MIBK; extraction at pH = 1

		Absorbance × 1000 45 min	3 hr	7 hr	24 hr	48 hr	105 hr
MIBK-phase over pure water	Co	104	116	113	113	113	114
	Ni	99	100	102	107	—	112
	Cd	111	110	108	113	111	112
	Pb	101	101	107	111	—	123
MIBK-phase over aqueous phase at pH = 1: slow stirring	Co	103	116	114	112	116	115
	Ni	96	98	104	98	—	81
	Cd	112	109	110	0		
	Pb	102	102	111	40	—	0
MIBK-phase over aqueous phase with pH = 1: rapid stirring	Co	103	117	120	120	118	116
	Ni	95	100	103	98	—	68
	Cd	110	107	0			
	Pb	104	103	112	0		

Table 4. Time stability of Ni, Cd, Pb/PDC solutions in MIBK; extraction at pH = 1.0; MIBK-solution separated from the aqueous phase

Element	Absorbance × 1000			
	3 hr	22 days	30 days	70 days
Ni	258	266	229	209
Cd	197	198	195	191
Pb	188	190	194	184

area between the two phases (produced by the geometry of the system or by shaking), and when the acidity of the aqueous phase is increased.

The rate of decomposition decreases in the order Cd > Pb > Ni > Co. The cobalt complex is oxidized by air to $Co(PDC)_3$. One report[16] claims that this complex is not inert, which is at variance with other reports on related systems.[5,17] Experiments on the exchange between Ni^{2+} and bis(di-n-propyldithiocarbamate)nickel(II) in acetone have shown that the rate of exchange is very low.[18] We are not aware of any data for lead and cadmium, but their PDC complexes are probably labile. The order of decomposition found here is the same as that found by Usatenko and Tulyupa for the corresponding DDC complexes.[19] Our results may explain why Tweeten and Knoeck had difficulties with DDC/isoamyl alcohol extractions, as they used very long times for the separation of the phases.[7] The decrease in extraction of cadmium with increase in shaking time[13] also conforms with the findings discussed here. It should, however, be emphasized that factors other than ligand decompositions, such as adsorption,[10] are important for the stability of the extracts.

In this laboratory the following practice has been found satisfactory. Extractions are carried out in standard flasks. After shaking, the MIBK phase is raised into the neck of the flask by addition of water. All of the MIBK should be in the neck of the flask. The added water will then form a "buffer" between the organic layer and the extracted aqueous sample, where the pH is around 1. Care is taken to avoid shaking or stirring the flasks. Even the cadmium complex will then be stable for at least 2 days.

REFERENCES

1. C. E. Mulford, *At. Absorpt. Newsl.*, 1966, **5**, 88.
2. R. J. Everson and H. E. Parker, *Anal. Chem.*, 1974, **46**, 1966.
3. J. D. Kinrade and J. C. Van Loon, *ibid.*, 1974, **46**, 1894.
4. R. R. Brooks, B. J. Presley and I. R. Kaplan, *Talanta*, 1967, **14**, 809.
5. A. Hulanicki, *ibid.*, 1967, **14**, 1371.
6. K. I. Aspila, V. S. Sastri and C. L. Chakrabarti, *ibid.*, 1969, **16**, 1099.
7. T. N. Tweeten and J. W. Knoeck, *Anal. Chem.*, 1976, **48**, 64.
8. P. Hannaker and T. C. Hughes, *ibid.*, 1977, **49**, 1485.
9. S. R. Koirtyohann and J. W. Wen, *ibid.*, 1973, **45**, 1986.
10. A. D. Shendrikar, V. Dharmarajan, H. Walker-Merrick and P. W. West, *Anal. Chim. Acta*, 1976, **84**, 409.
11. M. J. Dudas, *At. Absorpt. Newsl.*, 1974, **13**, 109.
12. R. F. Roberts, *Anal. Chem.*, 1977, **49**, 1862.
13. A. Dornemann, H. Kleist and W. Görgens, *Z. Anal. Chem.*, 1977, **284**, 97.
14. E. A. Jenne and J. W. Ball, *At. Absorpt. Newsl.*, 1972, **11**, 90.
15. R. W. Looyenga and D. F. Boltz, *Talanta*, 1972, **19**, 82.
16. E. Papp-Molnar, H. Vasarhelyi-Nagy and K. Burger, *Acta Chim. Acad. Sci. Hung.*, 1970, **64**, 317.
17. W. Regenass, S. Fallab and H. Erlenmeyer, *Helv. Chim. Acta*, 1955, **38**, 1448.
18. J. E. Johnson and N. F. Hall, *J. Am. Chem. Soc.*, 1948, **70**, 2344.
19. Yu. I. Usatenko and F. M. Tulyupa, *Zavodsk. Lab.*, 1960, **26**, 783.

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HYDROXIDE COMPLEXES OF LANTHANIDES—II†

SAMARIUM(III) IN PERCHLORATE MEDIUM

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Summary—From the precipitation borderline in the pM′–pH diagram, determined experimentally under CO_2-free conditions, the stability constants of the mononuclear and polynuclear species of samarium hydroxide have been established. The values found are $\log {}^*\beta_1 = -7.5$, $\log {}^*\beta_2 = -15.0$, $\log {}^*\beta_3 = -22.7$, $\log {}^*\beta_{4,3} = -19.5$ and $\log {}^*K_{s0} = 17.5$. They refer to fresh precipitates, prepared at room temperature in sodium perchlorate medium with an ionic strength of 1.

In a previous paper[1] a method was described for the determination of the hydrolysis constants of metals from the precipitation borderline in a pM′–pH diagram. This method was applied to cerium(III) and yielded such promising results that further experiments were undertaken for the other lanthanides. In this paper the hydrolysis of samarium(III) will be discussed. Not all the hydrolysis constants of Sm(III) are known, and those published show a remarkable diversity. Moeller[2] reported different values for $\log {}^*\beta_1$; depending on the concentration of the samarium sulphate solution used (0.05–0.001M), he found $\log {}^*\beta_1$ values ranging from -10.7 to -9.1. Baes and Mesmer[3] applied the empirical relation $\log {}^*K_{LnL} = \log {}^*K_{LaL} + b$, which was proposed by Kumok and Serebrennikov,[4] and found $\log {}^*\beta_1 = -7.9$ ($I = 0$), -8.2 ($I = 0.05$) and -9.6 ($I = 3$). Furthermore they reported $\log {}^*\beta_{22} = -13.8$ ($I = 3$) and $\log {}^*K_{s0} = 16.5$ ($I = 0$); the last constant was deduced from considerations about lattice parameters. Guillamont *et al.*[5] determined $\log {}^*\beta_1$ by means of solvent extraction and radiochemical measurements. For lithium perchlorate medium ($\mu = 0.1$) and pH 2.5–5 they found $\log {}^*\beta_1 = -4.4$. Kovalenko *et al.*[6] investigated the composition of samarium hydroxide complexes by an oscillopolarographic method. For solutions containing samarium chloride in concentrations between 2×10^{-4} and $6 \times 10^{-4} M$ they concluded that $Sm(OH)Cl_2$ was precipitated in the pH range 6.30–6.55, and $Sm(OH)_2Cl$ in the pH range 6.65–6.80. In their opinion, solid $Sm(OH)_3$ is formed only at pH ≥ 6.8; $\log {}^*K_{s0} = 16.8$ (20°, $I = 0$). From pH-titrations Meloche and Vrántý[7] calculated $\log {}^*K_{s0} = 21.3$ (20°, $I = 0.1$) from the points in the titration curves corresponding to precipitation of half of the initial samarium perchlorate. Akselrud *et al.*[8] reported the composition $Sm(OH)_2Cl$ for freshly prepared precipitate. After aging for a month it was converted into $Sm(OH)_3$; for this aged precipitate and the experimental conditions 25°, $C_{Sm} = 10^{-4}$–$10^{-1} M$ and pH 6–7, a value of $\log {}^*K_{s0} = 16.4$ was calculated.

The diversity of these results is apparently due to the neglect of the presence of polynuclear hydroxide complexes and to the difference in the experimental conditions used. The ionic strength, the aging of the precipitate, the influence of anions which do not behave indifferently when present in higher concentrations, and the method of precipitate formation undoubtedly play an important role.

In our investigations we found that the most reproducible results were obtained with "fresh precipitates" formed under nitrogen, in a glove-box, analogously to the case of cerium(III).[1] The need to standardize the precipitation procedure is related to the fact that the release of even trace amounts of hydrogen ions in an unbuffered system near pH 7 leads to a large decrease in pH. The gradual release of hydrogen ions occurs because of absorption of CO_2 from the air, delayed precipitation, and delayed formation of soluble (polynuclear) hydroxide complexes. By strict standardization of the precipitation procedure with respect to time and by exclusion of CO_2, values for ${}^*\beta_1$ and ${}^*K_{s0}$ could be established that were consistent with those found by other investigators. Moreover, values for ${}^*\beta_2$, ${}^*\beta_3$ and ${}^*\beta_{4,3}$, absent in existing literature, have been deduced.

THEORY

In previous publications[1,9,10] it has been shown that the borderline of precipitation in the pM′–pH

† Part I: *Talanta*, 1978, **25**, 147.

diagram can be divided into straight-line segments for which the following general formula holds

$$pM'_{max} = (np-q)pH - (p \log {}^*K_{s0} + \log {}^*\beta_{q,p} + \log p) \quad (1)$$

in which ${}^*\beta_{q,p}$ is the overall stability constant of the complex $M_p(OH)_q$, ${}^*K_{s0}$ is the solubility product† and n the charge on the metal ion.

When the precipitation region in the pM'–pH diagram has been established experimentally, the straight-line segments, each with its distinct slope $(np-q)$ can be shifted so that the envelope curve fits the experimental points. From the final position of the lines the stability constants and probable composition of the hydroxide complexes can be deduced.[1]

The following theoretical remarks can be made about the influence of dissolved CO_2 on pH. The equilibrium molar concentrations of the different species derived from CO_2 in air-saturated water[10] are

$$[H_2CO_3] = 10^{-5.0} \quad (2)$$

$$[HCO_3^-] = 10^{-11.35}/[H^+] \quad (3)$$

$$[CO_3^{2-}] = 10^{-21.7}/[H^+]^2 \quad (4)$$

If the normal atmospheric CO_2 pressure ($10^{-3.52}$ atm) is decreased by a factor f through flushing of the glove-box with nitrogen, the concentrations are all decreased by this factor f.

In the pH-range of interest (pH 6–8) the concentration of CO_3^{2-} is negligible relative to $[HCO_3^-]$ and $[H_2CO_3]$. From charge balance it follows that

$$[H^+] = [OH^-] + [HCO_3^-] \quad (5)$$

Multiplication of equation (5) by $[H^+]$ and substitution of equation (3) and $K_w = 10^{-14}$ leads to

$$pH = -\tfrac{1}{2}\log\left(10^{-14} + \frac{10^{-11.35}}{f}\right). \quad (6)$$

From this equation it follows that the deviation from pH 7 (for pure water) caused by dissolved CO_2 becomes negligible for $f > 10^3$. Although strictly holding only for pure water, this inequality still informs us about the extent to which dissolved CO_2 (air) has to be removed from a solution by nitrogen in order to make its contribution to the pH-shift negligible.

Another way in which CO_2 can contribute to a pH-change is by its reaction with the ions Sm^{3+}, $SmOH^{2+}$ and $Sm(OH)_2^+$ to form an insoluble carbonate:

$$2Sm(OH)_i^{(3-i)} + 3H_2O + 3CO_2 \rightarrow \{Sm_2(CO_3)_3\}_{solid} + (6-2i)H^+ + 2iH_2O \quad (7)$$

Hydrogen ions can also be released by an analogous reaction leading to the formation of a basic carbonate. When the CO_2 initially present under air-saturated conditions has been removed by precipitation, absorption of CO_2 from the air will start and cause a slow continuation of reaction (7) (or its analogue). The pH will change gradually if no precautions are taken. It was found experimentally that decrease of the CO_2 pressure by a factor of 100 was sufficient to suppress reaction (7) to such a degree that the pH was acceptably reproducible.

EXPERIMENTAL

Nearly all manipulations were performed in a 1000-litre glove-box, flushed with nitrogen. The solutions in the box were freed from CO_2 by bubbling nitrogen through them. The effectiveness of exclusion of CO_2 was checked by introducing 1 litre of helium into the box and measuring with a helium leakage detector the He concentration of the outlet stream as a function of time. Although at a flushing rate of 0.85 l./sec the factor f should have been $> 10^3$ after 2 hr, more prolonged flushing (> 3 hr) turned out to be necessary, because displacement of the air from inside apparatus and glassware is rather inefficient.

The pH-measurements were made with a glass and calomel electrode system and a Radiometer pH-meter. The calomel electrode was filled with a concentrated solution of sodium chloride to prevent clogging of the asbestos liquid-junction bridge by the precipitation of potassium perchlorate that would have occurred if potassium chloride solution had been used instead. Bates[12,13] and McBryde[14,15] have shown that a glass and calomel electrode system can be calibrated in pC_H units when used with solutions in which an indifferent electrolyte predominates at constant ionic strength. A consistent set of buffer solutions has been prepared for calibration in concentration units by making use of the dissociation constants of phosphoric acid, boric acid and water determined by Baes *et al.*[16–18] The pC_H was measured in our perchlorate medium ($I = 1$) with a precision better than 0.02. This was satisfactory in comparison with the uncertainty in the experimental results.

The samarium solutions were prepared by dissolving commercial 99.9% Sm_2O_3 in 1*M* perchloric acid by heating. The experiments were performed with $10^{-2}M$ samarium stock solutions except for the range $pSm' < 2$, in which case a 0.1*M* solution was used.

Procedure

Add carbonate-free 50% sodium hydroxide solution dropwise to 200–300 ml of samarium perchlorate solution in 1*M* perchloric acid, with vigorous stirring, until a pH of 1 is reached. Add dilute alkali carefully until pH 4 is reached and cool the solution to room temperature. Add dilute alkali until precipitation starts. Remove a 25-ml portion. Add dilute alkali in small portions to the remainder of the solution until the pH has been increased by about 0.2. Remove a second 25-ml portion. Increase the pH again by 0.2 and remove a third 25-ml portion, but finish the three steps within a span of 15 min. Separate the precipitate and solution by decantation after exactly 30 min of aging. Centrifuge the decanted solutions in order to collect residual and colloidal particles. Withdraw aliquots from the tubes, measure the pC_H with a pH-meter calibrated in concentration units and acidify slightly. Keep the solutions for determination of samarium.

Repeat the whole procedure for the next set of three solutions. Proceed until the whole pH-range has been covered. Take the acidified solutions out of the glove box and determine their samarium content by photometric titration with EDTA, with Xylenol Orange as the indicator.[1]

RESULTS AND CONCLUSIONS

The experimental results are plotted in Fig. 1. The uncertainty in the correction to be made for ionic

† According to IUPAC notation[11]

$$\left({}^*\beta_{q,p} = \frac{[M_p(OH)_q].[H]^q}{[M]^p}, \quad {}^*K_{s0} = \frac{[M^{n+}]}{[H^+]^n}\right).$$

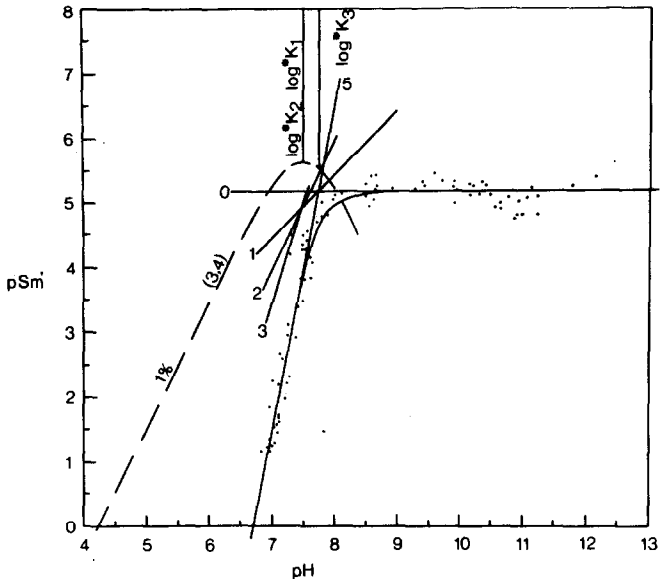


Fig. 1. The solid curve [the borderline of precipitation of $Sm(OH)_3$] has been constructed with the values given in Table 2. The dashed line is the borderline for 1% polycomplexation. The numbers 0, 1, 2, 3 and 5 near the straight lines correspond to the slopes of the straight-line segments approximating the exact envelope curve [equation (8a)–(8e)]. The dots denote the experimental results.

strengths >1 is larger than the uncertainty in the position of the experimental points. Therefore no points have been determined in the region $pSm' < 1$.

The steep part of the borderline of the precipitation region is nearly straight. Regression analysis in the range up to $pSm' = 4.6$ shows that the slope can be estimated as 5.1 ± 0.3. From this value it can be concluded that a polynuclear hydroxide complex has to be present, with a positive charge of at least 5. Although only speculative remarks can be made about the real identity of this species, $Sm_3(OH)_4^{5+}$ is assumed to be the predominant complex for the following reasons. Its charge lies close to the integral value $(3p - q) = 5$ of the slope of the straight-line segment which approximates the envelope curve in that region. Other complexes with a charge of 5+, such as $Sm_2(OH)^{5+}$ and $Sm_4(OH)_7^{5+}$, are much less likely for stereochemical and statistical reasons.[3] In principle a mixture of 2 complexes with charges greater and less than 5+ can also lead to a borderline with a mean slope of 5 and fitting the steep part well, but it is then impossible to fit the bend of the curve to the experimental points in the region pSm' 4.5–5.5, because the envelope curve, which in its steep part is then composed of two intersecting straight-line segments, has an increased curvature in that region, which makes the bend of the envelope curve pass under the experimental points.

The supposition that a polymer of charge 5+ is the only one formed in solution, leads to the following set of equations for the straight-line segments (Table 1).

Assigning equation (8a) to the steep part of the borderline (ranging up to pSm' 4.6) the best fit to the points is obtained with the equation

$$pSm' = 5\,pH - (33.5 \pm 0.1) \qquad (9)$$

which leads to the following relation between the constants:

$$3 \log {}^*K_{s0} + \log {}^*\beta_{4,3} = 33.0 \pm 0.1 \qquad (10)$$

Equation (8e) can be assigned to the horizontal part of the borderline. The best fit corresponds to

$$pSm' = 5.20 \pm 0.02 \qquad (11)$$

Table 1

Equation number	p	q	Slope $(np - q)$	Equation for the borderline segment
8a	3	4	5	$pSm' = 5pH - (3 \log {}^*K_{s0} + \log {}^*\beta_{4,3} + 0.5)$
8b	1	0	3	$pSm' = 3pH - \log {}^*K_{s0}$
8c	1	1	2	$pSm' = 2pH - (\log {}^*K_{s0} + \log {}^*\beta_1)$
8d	1	2	1	$pSm' = pH - (\log {}^*K_{s0} + \log {}^*\beta_2)$
8e	1	3	0	$pSm' = -\log {}^*K_{s3} = -(\log {}^*K_{s0} + \log {}^*\beta_3)$

$${}^*\beta_{q,p} = \frac{[Sm_p(OH)_q] \cdot [H^+]^q}{[Sm^{3+}]^p}; \quad {}^*\beta_{q,1} \equiv {}^*\beta_q \text{ and } [Sm(OH)_3]_{max} = {}^*K_{s3} = {}^*\beta_3 \cdot {}^*K_{s0}.$$

from which can be deduced

$$\log {}^*K_{s0} + \log {}^*\beta_3 = -5.20 \pm 0.02 \qquad (12)$$

If it is assumed that the straight-line segments corresponding to equations (9) and (11) are the only ones contributing to the envelope curve, the following equation holds for this curve:

$$[Sm']_{max} = 10^{-(5pH - 33.5)} + 10^{-5.2} \qquad (13)$$

With this equation an excellent fit is obtained to the experimental points in the rather sharp bend. It means that as the term in equation (13) correspond to $Sm_3(OH)_4^{5+}$ and $Sm(OH)_3$ respectively, the fresh precipitate will be in equilibrium (more or less defined) with these species only. This can be seen as follows. If, together with the precipitate, one (or more) of the species Sm^{3+}, $SmOH^{2+}$ or $Sm(OH)_2^+$ is present in measurable amount, equation (13) has to be extended with the corresponding term. The straight-line segment belonging to this term should contribute to the shape of the envelope curve. The bend of this curve is the first place where such a contribution should become manifest, as can be seen by moving the line segment (with slope 1, 2 or 3) from left to right. As without their contribution the fit of the curve to the experimental points is already excellent, it can be concluded first that there is no contribution of one of the lines corresponding to equations (8b), (8c) or (8d), and secondly that there is a limiting position for the line segments. As the straight-line segments intersect each other at $pH_i = p^*K_i$ the limiting position implies that these constants cannot exceed certain values. In Fig. 1 the envelope curve corresponds to equation (13). The straight-line approximations to this curve [equations (9) and (11)] intersect at pH = 7.74. Different plots have been made with p^*K_i values approaching 7.74. In this way it has been found that the limiting position of the other straight-line segments corresponds to $p^*K_1 = 7.5$, $p^*K_2 = 7.5$ and $p^*K_3 = 7.7$.

Consider now the 1% polycomplex borderline as a measure for the extent of polycomplexation.[1,9,10] The steep left-hand side of this borderline can be approximated by a straight-line segment given by

$$pM_{3,4}^{1\%} = 2pH + \tfrac{1}{2}\{\log {}^*\beta_{4,3} + 2.5\} \qquad (15)$$

Through equations (10) and (12) the value of ${}^*\beta_{4,3}$ is related to the values of the other constants. Thus the extent of the polycomplex region depends upon the p^*K_i values ($i = 1, 2, 3$). As an increase in p^*K_i leads to a decrease of this region, the polycomplex region will be minimal for the limiting set of p^*K_i values already mentioned. Figure 1 is drawn for this limiting situation. Now the question remains whether p^*K_i can adopt lower values. Here we have to rely upon information from other investigators.[2,4] As lanthanide ions are fairly large, hydrolysis does not become appreciable at normal concentrations (10^{-2}–$10^{-3}M$) until fairly high pH values are reached (> 5.5). Actually this sets another limit to the extent of the polycomplex region and hence lower limits to p^*K_i. Correlating this with Fig. 1 it will be obvious that the intervals over which the values of p^*K_i may vary are small. Therefore we assume that Fig. 1 represents a situation which does not deviate much from reality. It can be noted that at the same time we have fulfilled the general rule that the ratio of the consecutive stability constants should be ${}^*K_{i+1}/{}^*K_i \leqslant 1$. Although for an unambiguous establishment of the hydrolysis constants more information is necessary, preferably directly about the polycomplexation itself, we still conclude that the values given in Table 2 can be regarded as useful for describing the hydrolysis of samarium.

Table 2.

$\log {}^*\beta_1 = -7.5$	$\log {}^*\beta_{4,3} = -19.5$
$\log {}^*\beta_2 = -15.0$	$\log {}^*K_{s0} = +17.5$
$\log {}^*\beta_3 = -22.7$	

Baes and Mesmer[3] reported the possibility of formation of $M(OH)_4^-$ species by lanthanides. However, no data have been found in the literature for such species of Sm(III). From our experiments at high pH no conclusions could be drawn as to whether the solubility increases or not. A different experimental method is necessary to obtain significant results at pH above 12.

DISCUSSION

In our opinion it is rather speculative to discuss the errors in the different constants. It is more appropriate to assign an uncertainty of about 0.1 log unit both in pSm' and pH to the position of the calculated precipitation borderline. Comparing our values with the literature data, we noticed that polycomplexation has often been neglected,[2,4,6,7] that interaction with sulphate has not been taken into account[2] or that the adopted extraction model is obviously too simple.[5]

When corrected for differences in ionic strength, our value for $\log {}^*\beta_1$ was found to be in fair agreement with that of Kumok and Serebrennikov,[4] although they used a statistical method, based on data for ligands other than OH^-. Comparing the $\log {}^*K_{s0}$ values, also after correcting for differences in ionic strength, our value ($\log {}^*K_{s0} = 18.4$; $I = 0$) and the one determined by Meloche *et al.*[7] ($\log {}^*K_{s0} = 22.2$; $I = 0$) are significantly higher than those determined by the other authors ($\log {}^*K_{s0} = 16.4$–16.8; $I = 0$). These differences can be attributed to different aging times of the precipitates (Meloche *et al.*[7] 2 min, the other authors 4 hr–1 month, our work 30 min).

A fresh precipitate tends to have a higher solubility then an aged one.[1] It has been concluded that $Sm_3(OH)_4^{5+}$ is the species which is predominantly formed in the polycomplex region. Although this has not been established unambiguously, it is at any rate certain from the steepness of the corresponding part of the precipitation borderline that $Sm_2(OH)_2^{4+}$ is not formed to a measurable extent. So the results of

Kumok and Serebrennikov[4] found by interpolation are questionable.

Summarizing, it can be stated that with the method previously applied to Ce(III) valuable information can be obtained about the occurrence of the various samarium hydroxide species and the magnitude of their stability constants. Further experiments are in preparation for the other lanthanides.

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REFERENCES

1. J. Kragten and L. G. Decnop-Weever, *Talanta*, 1978, **25**, 147.
2. T. Moeller, *J. Phys. Chem.*, 1946, **50**, 242.
3. C. F. Baes, Jr. and R. E. Mesmer, *The Hydrolysis of Cations*, pp. 129–138, 420. Wiley-Interscience, New York, 1976.
4. V. N. Kumok and V. V. Serebrennikov, *Russ. J. Inorg. Chem.*, 1965, **10**, 1095.
5. R. Guillamont, B. Désiré and M. Galin, *Radiochem. Radioanal. Lett.*, 1971, **8**, 189.
6. P. N. Kovalenko, L. T. Azhipa and M. M. Evstifeev, *Russ. J. Inorg. Chem.*, 1966, **11**, 1443.
7. C. C. Meloche and F. Vrátný, *Anal. Chim. Acta*, 1959, **20**, 415.
8. N. V. Aksel'rud and V. B. Spivakovskii, *Russ. J. Inorg. Chem.*, 1960, **5**, 340.
9. J. Kragten, *Talanta*, 1977, **24**, 483.
10. *Idem*, *Atlas of Metal-Ligand Equilibria in Aqueous Solution*, p. 25. Horwood, Chichester, 1978.
11. L. G. Sillén and A. E. Martell, *Stability Constants of Metal–Ion Complexes*, 2nd Ed., Chemical Society, London, 1964.
12. R. G. Bates, *Determination of pH*, 2nd Ed., Ch. 9. Wiley, London, 1973.
13. *Idem*, in *Essays in Analytical Chemistry*, E. Wänninen, ed., p. 23. Pergamon, Oxford, 1977.
14. W. A. E. McBryde, *Analyst*, 1969, **94**, 1118.
15. *Idem*, *ibid.*, 1971, **96**, 739.
16. F. H. Sweeton, R. E. Mesmer and C. F. Baes, Jr., *J. Soln. Chem.*, 1974, **3**, 191.
17. R. E. Mesmer, C. F. Baes, Jr. and F. H. Sweeton, *Inorg. Chem.* 1972, **11**, 537.
18. R. E. Mesmer and C. F. Baes, Jr., *J. Soln. Chem.*, 1974, **3**, 307.

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HANDLING OF ELECTRONIC ABSORPTION SPECTRA WITH A DESK-TOP COMPUTER—II*

CALCULATION OF STABILITY CONSTANTS FROM SPECTROPHOTOMETRIC TITRATIONS

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Summary—A fully automatic system for combined spectrophotometric and pH titrations was described in Part I. Its performance in the titration of weak acids and metal complexes is discussed, along with a computer program for numerical treatment of the data, based on Marquardt's modification of the Newton–Gauss non-linear least-squares method. The deprotonation of *p*-nitrophenol at concentrations of 4×10^{-5} and $4 \times 10^{-6} M$ was studied in order to test the sensitivity. Results identical within the reproducibility of the pH-meter were obtained: $pK^H = 7.00 \pm 0.01$ and 7.02 ± 0.01, respectively. Three complexation reactions were studied: (*1*) the interaction of SCN^- with the Co^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (TMC); five independent experiments gave pK $[CoTMC(SCN)^+ \rightleftharpoons CoTMC^{2+} + SCN^-] = 3.099 \pm 0.003$: (*2*) the deprotonation of the Cu^{2+} complex of 3,7-diazanonanediamide (DANA); five experiments gave pK $(CuDANA^{2+} \rightleftharpoons CuDANAH^+_{-1} + H^+) = 7.14 \pm 0.01$ and pK $(CuDANAH^+_{-1} \rightleftharpoons CuDANAH_{-2} + H^+) = 8.38 \pm 0.01$: (*3*) for the reaction of Cu^{2+} with 1,3,7-triazacyclodecane (L), data from different ligand:metal ratios had to be combined to obtain pK $(CuL^{2+} \rightleftharpoons Cu^{2+} + L) = 16.19 \pm 0.01$, pK $(CuL_2^{2+} \rightleftharpoons CuL^{2+} + L) = 10.30 \pm 0.01$, and pK $(Cu_2L_2(OH)_2^{2+} \rightleftharpoons 2\,CuL^{2+} + 2\,OH^-) = 14.58 \pm 0.03$. Titration curves with a total change in absorbance of as little as 0.03 units could be analysed satisfactorily, extending considerably the useful range of concentrations for spectrophotometric titrations. In combined spectrophotometric/pH titrations the accuracy of the glass electrode is normally the limiting factor. Other equilibrium constants can easily be reproduced with standard errors of less than 0.01 log unit.

Although electronic absorption spectrophotometry is of very broad potential applicability in the determination of equilibrium constants, in practice its use has been limited by the need for very precise absorbance values[1] and numerical treatment of a relatively large amount of raw data with a minimum of simplifications. Several general programs, based on different algorithms, for the calculation of equilibrium constants from spectrophotometric data can be found in the literature. A program by Kankare[2] is based on a direct search method. Feldberg *et al.*[3] have used Sillén's twist matrix method.[4] Leggett and McBryde[5] describe a program based on SCOGS[6] which has been successfully applied to many equilibrium studies. Another Newton–Gauss least-squares refinement program was developed by Lingane and Hugus.[7] Recently, a program using Marquardt's[8] extension of the Newton–Gauss algorithm has been published.[9]

In Part I,[10] we described a fully automatic system for combined spectrophotometric and pH-titrations with on-line digital data acquisition by means of an HP9820 desk-top calculator. The performance of the system was tested critically and absorbance readings with a reproducibility of 0.00012–0.00017 were obtained for chemically stable test solutions. Here we report the use of this set-up in the determination of equilibrium constants for systems of increasing degrees of complexity. The reactions studied were: the deprotonation of *p*-nitrophenol (PNP), the interaction of SCN^- with the Co^{2+} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (TMC), the stepwise deprotonation of the Cu^{2+} complex of 3,7-diazanonanediamide (DANA), and the complexation of Cu^{2+} with 1,3,7-triazacyclodecane (TACD). Computer programs were developed for the calculation of equilibrium constants and molar absorptivities by using a general non-linear least-squares analysis of the Newton–Gauss–Marquardt[8] type. The programs also allow both the original absorption data and the spectra of the individual chemical species, calculated from the final set of parameters, to be plotted. The complete numerical treatment was done on a desk top calculator, HP9821, with fully expanded memory.

EXPERIMENTAL

Materials

TMC,[11,12] DANA.2HCl,[13] and TACD.3HBr,[14,15] (by the tosylate ester method[16]) were synthesized as described in the literature. Standard solutions of $CoTMC(ClO_4)_2$ were obtained from $Co(ClO_4)_2$ and TMC after filtering off excess of Co^{2+} precipitated as $Co(OH)_2$.[17] Amine-buffer

* Part I—*Talanta*, 1979, **26**, 563.

Table 1. Experimental conditions for spectrophotometric titrations

System	Titration mixtures, M		V_o ml	Titrant, ml* $V_{t,1}(\Delta V_1)$	$V_{t,2}(\Delta V_2)$	Wavelengths, nm λ_{max}	λ_{min}	$\Delta\lambda$	No. of batches
p-nitrophenol	CH_3COOH	0.0174	2.4	0.4M NaOH		440	360	10	2
	NaH_2PO_4	0.0174							
	H_3BO_3	0.0174							
	PNP: (*a*)	4×10^{-5}		0.15 (0.01)	0.14 (0.01)				
	(*b*)	4×10^{-6}							
	KCl	0×482							
$CoTMC^{2+}/SCN^-$	morpholine	0.1	2.5	$9.4 \times 10^{-3}M$ NaSCN		340	300	10	5
	$HClO_4$	0.05							
	$CoTMC^{2+}$	2×10^{-4}		0.30 (0.02)	— —				
	$NaClO_4$	0.45							
Cu^{2+}/DANA	DANA.2HCl	0.01	2.0	0.2M NaOH		700	640	10	5
	$CuSO_4$	0.009							
	KCl	0.44		0.24 (0.01)	— —				
	$pH_{initial}$	4–5							
Cu^{2+}/TACD	TACD.3HBr	0.002	2.5	0.05M NaOH		780	540	20	2
	$CuSO_4$ (*a*)	0.0018							
	(*b*)	0.0009		0.30 (0.03)	0.11 (0.01)				
	KNO_3	0.5							

* $V_{t,i}$: total amount of titrant added with increments ΔV_i.

bases were distilled before use. Other analytical grade reagents were used without further purification. All experiments were done at 298 K in doubly distilled water. The ionic strength was adjusted to 0.5. The experimental conditions for the spectrophotometric titrations are summarized in Table 1.

Computer programs

The computer program for on-line data acquisition was described in Part I.[10] A general program has been developed for (*i*) plotting the absorbance data after correction for the baseline, (*ii*) non-linear least-squares calculation of equilibrium constants and molar absorptivities from data at specified wavelengths and plotting of the experimental and calculated titration curves, and (*iii*) calculation and plotting of the absorption spectra of the individual species from the final set of equilibrium constants (weighted mean of results obtained at the different wavelengths). Although the HP9821 desk-top calculator had a fully expanded memory of 1447 registers, space limitations were rather severe and it was necessary to take great care to write the program as concisely as possible. Six hundred registers (roughly 2.5 kbyte) were left for the numerical data and the subroutine describing the equilibrium system. In order to increase the amount of data which could be treated, the program was also divided into three independent parts for tasks (*i*)–(*iii*). Because of extensive use of the same subroutines in all three parts, the effect of splitting is not dramatic, but roughly 100 registers of memory can be saved.

Below we describe these separate programs, rather than the combined one, in some detail.

(*i*) *Plotting of experimental data.* This program is simple in concept. First the data accumulated by the on-line titration system[10] are read in from tape, then the baseline is subtracted from the data and the extremes of the absorbance values are found. The program calls a general plotting subroutine which automatically sets the proper limits and labels the axes. Finally the individual corrected absorbance values are plotted and connected by curves obtained from fourth-order polynominals. Up to 30 curves are identified by the successive use of ten different symbols and solid, broken or dotted lines, respectively.

(*ii*) *Calculation of equilibrium constants and molar absorptivities at specified wavelengths.* After the subroutine describing the chemical system and the data has been read in, the baseline correction is applied and the absorbance values are ordered according to wavelength and rewritten onto the tape in individual data files. The values for equilibrium constants known from previous experiments and estimates for those to be determined are then read in, followed by the number of absorbing species. Next, the program asks for the wavelength to be used in the calculation. Subroutines are called to calculate the concentrations of all absorbing species at each point of the titration curve,* the absorptivities of all species, the residuals in absorbance (difference between experimental and calculated absorbance), and the error-square sum. The latter is printed and compared with the previous one. If the error-square sum remains constant within one part per thousand and some other termination criteria are met (*cf.* Fig. 1), the final values of the equilibrium constants and absorptivities are printed, along with their standard errors. If required, the calculated and experimental absorbances may be printed and/or the titration curve may be plotted. The program then asks for the next wavelength to be used. This part can easily be made fully automatic if the calculation is to be done successively at all wavelengths.

If the termination criteria are not met after the calculation of an error-square sum, the Newton–Gauss–Marquardt[8] non-linear regression analysis routine is called for calculation of better estimates of the equilibrium constants. In cases where sufficiently good estimates for the unknown equilibrium constants are available, the normal Newton–Gauss procedure is used alone in our program, since this is then the most rapid algorithm. A Marquardt correction is applied to the diagonal elements of the curvature matrix (*cf. e.g.*, Bevington[19]) only if divergence occurs. A flow diagram of this part of the program is given in Fig. 1.

(*iii*) *Calculation and plot of absorption spectra of the individual species.* This program is quite similar to (*ii*) except that the non-linear iteration procedure is missing. Calculation of the absorptivities of all species on the basis of the final set of equilibrium constants proceeds automatically from the maximum to the minimum wavelength. The absorption spectra for the individual species are plotted. The final set of absorptivities is stored on tape.

* These subroutines are essentially as described earlier.[18]

RESULTS

As described, equilibrium constants K_λ and their standard errors were calculated at suitable wavelengths λ for each system. Unit weights were assigned to the individual absorbance readings throughout. Weighted means, log K, were obtained from the values of log K_λ, and are compiled in Table 2 along with their standard errors $\sigma(\log K)$. In every case the weights $\sigma_\lambda = \sigma(\log K_\lambda)$ were used in the absolute (σ_a) and the relative (σ_r) form and the larger value is given in Table 2.

$$\sigma_a^2 = 1\Big/\left(\sum_{i=1}^{I} 1/\sigma_{\lambda,i}^2\right) \tag{1}$$

$$\sigma_r^2 = \frac{\sum_{i=1}^{I} (1/\sigma_{\lambda,i}^2)(\log K_{\lambda,i} - \log K)^2}{\left[(I-1).\sum_{i=1}^{I} 1/\sigma_{\lambda,i}^2\right]} \tag{2}$$

I = number of wavelengths.

As indicated in Table 2, the standard deviations in absorbance σ_A for individual titration curves were in general between 0.0002 and 0.0006, close to the intrinsic precision of the titration system.[10] Values of σ_A were between 0.0006 and 0.0018 for $4 \times 10^{-5} M$ PNP and for Cu^{2+}/DANA with higher total changes in absorbance (between 0.3 and 0.8 units), reflecting the uncertainty of the pH readings through the law of error propagation. Equilibrium constants of essentially the same quality were obtained, whether the total change in absorbance was as low as 0.03 or as high as 0.8.

The reproducibility of the titration system was studied with $CoTMC^{2+}/SCN^-$ and Cu^{2+}/DANA, for which the experiment was repeated five times and the variance between results from different batches could be estimated along with the standard errors for log K as obtained from a single experiment. The averages of log K ($\overline{\log K}$) and their standard errors $\sigma(\overline{\log K})$ are included in Table 2 for these two systems.

Individual titration curves for the deprotonation of PNP could be fitted very closely: $\sigma(\log K)$ values of 0.001 and 0.002 were obtained for 4×10^{-5} and $4 \times 10^{-6} M$ PNP, respectively. The latter result is

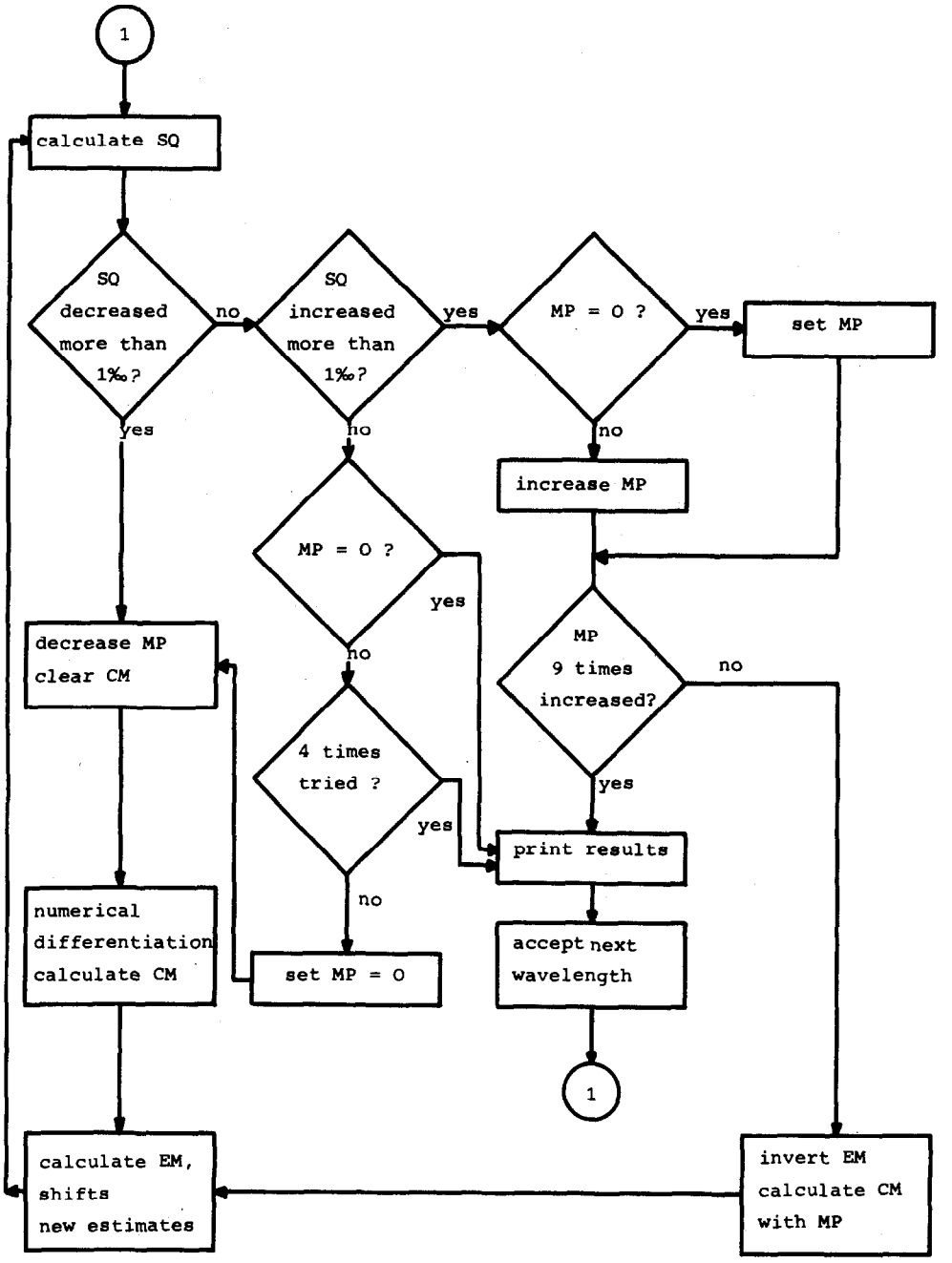


Fig. 1. Flow diagram of the non-linear regression analysis. SQ: Error-square sum, sum of squares of residuals; MP: Marquardt parameter;[8] CM: curvature matrix;[19] EM: error matrix.[19]

remarkable since, depending on the wavelength chosen, the total changes in absorbance were as low as 0.02–0.06, in the experiment with the lower concentration of PNP. Since 30 spectra were recorded per titration, changes in absorbance between two titration steps were typically around 0.001–0.002, and apparently even such small changes could be determined quite accurately.

Probably the main source of error is the glass electrode. The precision of equilibrium constants obtained from combined spectrophotometric and pH-titrations was considered to be ± 0.01 log units at best and no standard errors below this limit are listed for the final results of such experiments. Within the uncertainty expected from the use of the pH-meter the results for 4×10^{-5} and for $4 \times 10^{-6} M$ PNP are identical.

The complexation between $CoTMC^{2+}$ and SCN^- was studied between 340 and 300 nm. Total changes in absorbance were between 0.04 and 0.12 (depending on the wavelength), significantly below the optimum range of the spectrophotometer. From five independent experiments, values of 3.101 ± 0.005, 3.089 ± 0.006, 3.108 ± 0.006, 3.103 ± 0.006, and

Table 2. Results of combined spectrophotometric and potentiometric titrations

Reaction	log K* ($\sigma \times 10^3$)				$\overline{\log K} \pm \sigma$†	$n\lambda$§	np§	$\sigma_A \times 10^4$§
	([PNP] = $4 \times 10^{-5}M$)	([PNP] = $4 \times 10^{-6}M$)						
$PNPH_{-1} + H^+ \rightleftharpoons PNP$	6.999 (1)				7.01 ± 0.01	(7.149)‡	9	30	7–18
$CoTMC^{2+} + SCN^- \rightleftharpoons CoTMC(SCN)^+$	7.016 (2)								
$CuDANAH^+_1 = H^+ \rightleftharpoons CuDANA^{2+}$	3.101 (5)	3.089 (6)	3.108 (6)	3.103 (6)	3.094 (6)	3.099 (3)	(3.07 ± 0.04)‡	5	16	2–6
$CuDANAH_{-2} + H^+ \rightleftharpoons CuDANAH^-_1$	7.161 (9)	7.164 (7)	7.137 (7)	7.142 (4)	7.133 (8)	7.14 ± 0.01	(7.14 ± 0.02)‡	7	26	4–9
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$††	8.375 (6)	8.382 (8)	8.402 (8)	8.372 (7)	8.378 (3)	8.38 ± 0.01	(8.38 ± 0.01)‡	7	26	4–9
$CuL^{2+} + L \rightleftharpoons CuL^{2+}_2$††	16.194 (7)				15.48¶	16.19 ± 0.01	(16.14 ± 0.09)‡	9	49	2–5
$2CuL^{2+} + 2OH^- \rightleftharpoons Cu_2L_2(OH)^{2+}_2$††	10.303 (10)					10.30 ± 0.01	(10.26 ± 0.04)‡	9	49	2–5
	14.582 (30)					14.58 ± 0.03	(14.52 ± 0.09)	9	49	2–5

* Weighted means from results obtained at $n\lambda$ different wavelengths. Mixed constants, with $[H^+] = 10^{-pH}$ and $K_w = [H^+][OH^-] = 1.38 \times 10^{-14}$ are given throughout.
† Because of an estimated uncertainty of 0.01 in the pH-readings a lower limit of 0.01 was set for $\sigma(\overline{\log K})$ in combined spectrophotometric and pH-titrations.
‡ Values from the literature: PNP,[20] extrapolated to zero ionic strength; $CoTMC^{2+}/SCN^-$;[21] Cu^{2+}/DANA;[13] Cu^{2+}/TACD.[15] Ligand deprotonation constants taken from the literature.[13,15]
§ $n\lambda$: number of wavelengths; np: number of points per wavelength; σ_A: range of standard deviations in absorbance.
†† L = TACD.
¶ From Zompa,[22] ionic strength = 0.1 (KNO_3).

3.094 ± 0.006 were obtained for log K ($CoTMC^{2+} + SCN^- \rightleftharpoons CoTMC(SCN)^+$). No significant differences between the experiments were found: $\overline{\log K} = 3.099 \pm 0.003$ with almost identical values for σ_a and σ_r. Thus the overall uncertainty for such complexation reactions, in which no measurement of the pH is involved, is well below 0.01 log unit.

The deprotonation of $CuDANA^{2+}$ to $CuDANAH^+_1$ and to $CuDANAH_{-2}$ was studied at 10-nm intervals between 700 and 640 nm. Formation of $CuDANA^{2+}$ is essentially complete at pH 3 and deprotonation occurs in strongly overlapping equilibria.[13] As shown in Fig. 2, hardly any indication of the presence of a two-step equilibrium is obtained from visual inspection of a titration curve. Although this makes initial estimates of the equilibrium constants somewhat arbitrary, no difficulties were encountered in the refinement process. In fact, the final values were always obtained after two refinement cycles, once the parameters had been calculated at the first wavelength. The time needed for the automatic calculation of one complete experiment for all seven wavelengths is 55 min on the HP9821.

The iteration algorithm is rather insensitive to the quality of the initial estimates for the parameters. With good starting values (within 0.1 log unit), the final results are obtained after three refinements; if both parameters are wrong by one or two orders of magnitude, five and six cycles are needed, respectively. No tendency to divergence was observed even with completely erratic initial guesses.

Standard errors of the equilibrium constants were between 0.003 and 0.009 log unit for results from different wavelengths but a single batch. For reasons discussed above, $\sigma(\overline{\log K})$ was not allowed to be below 0.01 log unit in the final results.

TACD (L) and Cu^{2+} give the complexes CuL^{2+}, CuL^{2+}_2, and $Cu_2L_2(OH)^{2+}_2$ according to results from potentiometric titrations.[15] Since CuL^{2+}_2 and $Cu_2L_2(OH)^{2+}_2$ are formed in essentially the same pH region, data from a single titration curve did not yield reliable values for the corresponding equilibrium constants. Data from two different experiments with different metal:ligand ratios had to be combined. A modification of the standard program was developed which allowed the simultaneous treatment of more than one titration curve. Also, because of the presence of 1:2 and 2:2 complexes, a more complicated subroutine using the Newton–Raphson method for iterative calculation of the concentrations of the complex species had to be applied. This longer subroutine, together with the increased number of data points, completely filled the available memory and the treatment of the data from a single wavelength needed roughly 100 min. Nevertheless, the results agree well with those obtained from purely potentiometric titrations. Log K values were calculated from data obtained between 600 and 780 nm, at 20 nm intervals. While log K ($Cu^{2+} + L \rightleftharpoons CuL^{2+}$) could be determined accurately at all wavelengths, the quality of the

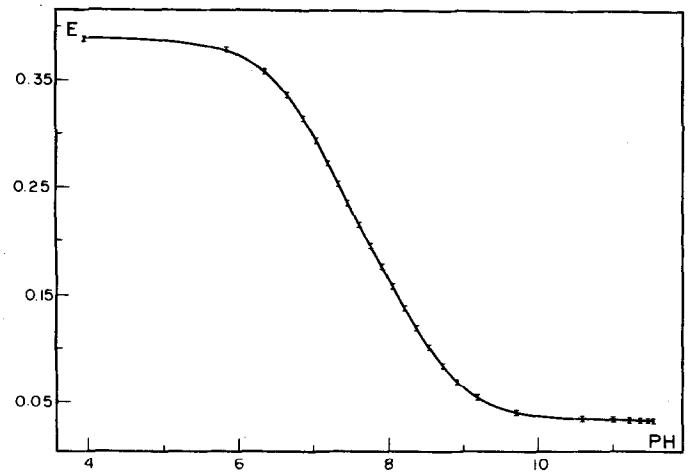


Fig. 2. Titration of $CuDANA^{2+}$ with NaOH. Conditions given in Table 1. λ = 700 nm, error bars = 5σ (absorbance) = 0.002.

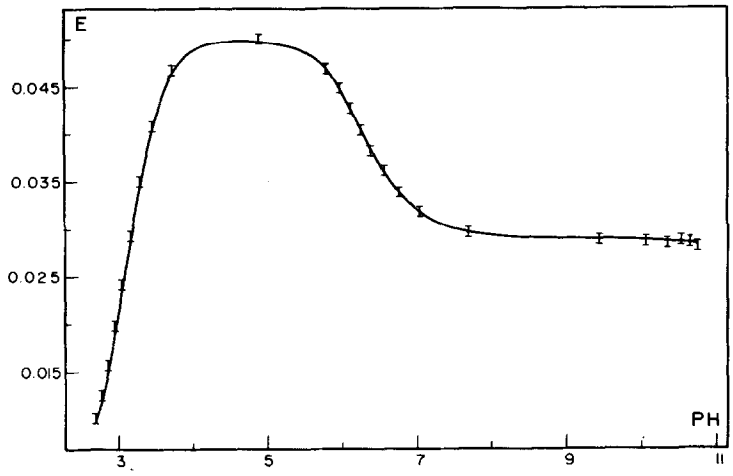


Fig. 3. Titration of Cu^{2+}/TACD with NaOH. TACD = 0.002M, $[Cu^{2+}]$ = 0.0009M, λ = 640 nm, error bars = $2\sigma_A$ = 0.001.

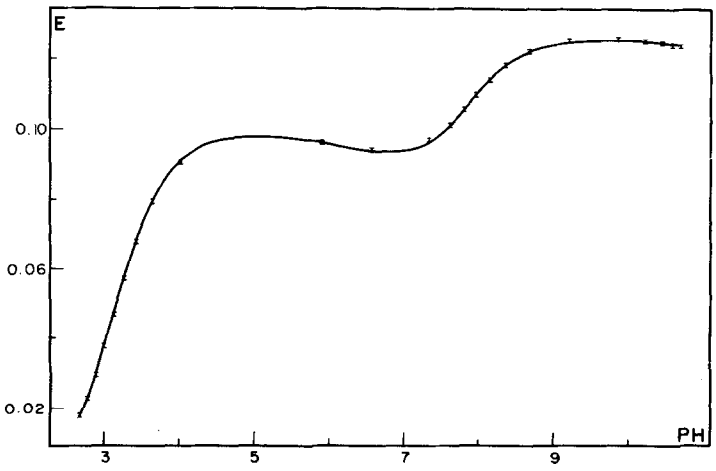


Fig. 4. Titration of Cu^{2+}/TACD with NaOH. TACD = 0.002M, $[Cu^{2+}]$ = 0.0018M, λ = 640 nm, $I = 2\sigma_A$ = 0.001.

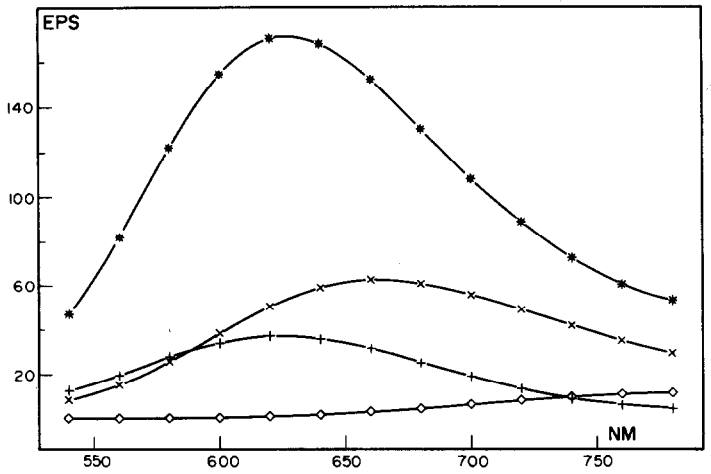


Fig. 5. Absorption spectra for complexes in the system Cu^{2+}/TACD. Molar absorptivities: ◇ Cu_{aq}^{2+}, × CuL^{2+}, + CuL_2^{2+}, *$Cu_2L_2(OH)_2^{2+}$.

results for the other equilibrium constants was strongly wavelength-dependent, since either CuL_2^{2+} or $Cu_2L_2(OH)_2^{2+}$ had absorptivities very close to those of CuL^{2+} at several λ. Titration curves for 640 nm, and Cu^{2+}:ligand ratios of 0.45:1 and 0.9:1 are given in Figs. 3 and 4, respectively.

Although the total changes in absorbance were only 0.035 and 0.1, agreement between experimental and calculated absorbances was quite satisfactory since the standard deviation in absorbance was only 0.0005 or less at all wavelengths. Finally, spectra of the individual species, as calculated from the "best" equilibrium constants, are shown in Fig. 5. Standard errors in molar absorptivity were close to 0.1 $l.mole^{-1}.cm^{-1}$ for CuL^{2+}, 0.2 $l.mole^{-1}.cm^{-1}$ for CuL_2^{2+} and 0.25 $l.mole^{-1}.cm^{-1}$ for $Cu_2L_2(OH)_2^{2+}$ at all wavelengths.

DISCUSSION

The fully automatic system for combined spectrophotometric and potentiometric titrations described previously[10] has a stability and precision such that even small total changes in absorbance of around 0.03–0.05 can be analysed without significant loss in accuracy or reproducibility. A general non-linear least-squares program* was developed for numerical treatment of the data with an HP 9821 desk-top calculator with 1447 registers of memory. For the three complexation systems studied, earlier values from this laboratory were available for comparison, mainly from potentiometric titrations.[13,15,21] As can be seen from Table 2, the new results agreed with the previous ones within their standard errors. In addition, a significant reduction in the standard errors was obtained with the new set-up.

No difficulties with convergence[1,23] were encountered in the numerical treatment of the data. For the systems PNP, $CoTMC^{2+}/SCN^-$, and Cu^{2+}/TACD this might be expected since there are no strongly overlapping equilibria. For Cu^{2+}/DANA, the precision of the initial absorbance readings might be decisive.[1] In addition, a highly effective and reliable search procedure is essential if convergence is not to depend on very good initial estimates of the parameters. The time required for lengthy graphical pretreatment of the raw data is, in our opinion, better used for carefully testing the significance of each new parameter introduced into the model describing a chemical system, and for adding as much chemical reasoning as possible when selecting the model.[5,24]

A specific problem of spectrophotometric rather than potentiometric data is, of course, the introduction of additional unknowns in the form of the molar absorptivities. Even if data from different wavelengths are treated successively rather than simultaneously, the number of unknowns is at least doubled relative to that of the same system studied potentiometrically. Three different possible ways of dealing with this problem are described in the literature. (*i*) Absorptivities and equilibrium constants are treated as two different sets of parameters. The computer alternatively calculates the best absorptivities for a given set of equilibrium constants, which is a linear problem and can be solved by simple matrix manipulation, then uses this result to obtain new estimates for the equilibrium constants, and so on, back and forth.[1,23] This method, while avoiding the manipulation of too large matrices, was found to be extremely slow in convergence for overlapping equilibria, probably because of the strong correlation between absorptivities and equilibrium constants in such systems.[7,23] (*ii*) Absorptivities and equilibrium constants are considered to be more or less equivalent parameters and are refined simultaneously.[7] This method needs estimates of both the absorptivities ϵ_j [$j = 1$ to J (number of absorbing species)] and k_i [$i = 1$ to I (number of equilibrium constants)] and the handling of matrices with dimensions $(J + I) \times (J + I)$. We found that convergence

* Listings of the program are available from the authors on request.

was relatively rapid and unproblematic when starting from reasonable estimates. (*iii*) The total number of parameters can effectively be reduced to I, the number of equilibrium constants to be refined,[25] by treating the absorbance and thence the error-square sum not as a function of the ϵ_j values and the k_i values but of the k_i values and the corresponding "best" set of absorptivities $\hat{\epsilon}_j$.

The absorptivities then disappear from the refining process. A closely related algorithm was used in the computer program SQUAD,[5] which is a modification of the well-known general non-linear least-squares program SCOGS.[6] We found this method to be by far the most effective. When it is combined with our own version of the Newton–Gauss–Marquardt algorithm for refinement of the non-linear parameters, the need for good initial estimates seems to be completely abolished and the number of iterations needed seems to depend little on the quality of the estimates, as mentioned above.

The results obtained show that equilibrium constants for simple and relatively complex systems can be obtained from automatic on-line spectrophotometric titrations and non-linear least-squares treatment of the data with a desk-top calculator. The speed of such calculators is, of course, not comparable with that of big computers, but we think that this is offset by the fact that on-line access to big computers is not always available. Slow automatic refinements can easily be done overnight or whenever the calculator is idle. The only problem with our particular calculator is the limited amount of memory (roughly 6 kbyte for programs and data combined), although this did not in fact preclude any of the planned calculations. However, combination of data from many wavelengths is not possible, unless a large amount of reading and writing data from and to tape is done, which would be very time-consuming. With the recent introduction of a new series of inexpensive desk computers with up to 48 kbyte of memory these limitations can be easily overcome and we are confident that the use of such systems will greatly further on-line data acquisition and numerical treatment of spectrophotometric and related data.

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REFERENCES

1. K. Conrow, G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc.*, 1969, **86**, 1025.
2. J. J. Kankare, *Anal. Chem.*, 1970, **42**, 1322.
3. S. Feldberg, P. Klotz and L. Newman, *Inorg. Chem.*, 1972, **11**, 2860.
4. L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1085.
5. D. J. Leggett and W. A. E. McBryde, *Anal. Chem.*, 1975, **47**, 1065.
6. I. G. Sayce, *Talanta*, 1968, **15**, 1397.
7. P. J. Lingane and Z. Z. Hugus, *Inorg. Chem.*, 1970, **9**, 757.
8. D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.
9. R. M. Alcock, F. R. Hartley and D. E. Rogers, *J. Chem. Soc. Dalton*, 1978, 115.
10. G. Hänisch, T. A. Kaden and A. D. Zuberbühler, *Talanta*, 1979, **26**, 563.
11. E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.
12. R. Buxtorf and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1035.
13. T. A. Kaden and A. D. Zuberbühler, *ibid.*, 1974, **57**, 286.
14. H. Koyama and T. Yoshino, *Bull. Chem. Soc. Japan*, 1972, **45**, 481.
15. T. J. Riedo and T. A. Kaden, *Chimia*, 1977, **31**, 220.
16. J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, 1974, **96**, 2268.
17. L. Hertli and T. A. Kaden, *Helv. Chim. Acta*, 1974, **57**, 1328.
18. T. A. Kaden and A. D. Zuberbühler, *Talanta*, 1971, **18**, 61.
19. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969.
20. R. A. Robinson and A. J. Biggs, *Trans. Farad. Soc.*, 1955, **51**, 901.
21. S. Bürki, *Ph.D. Thesis*, Basel, 1977.
22. L. J. Zompa, *Inorg. Chem.*, 1978, **17**, 2531.
23. W. A. E. McBryde, *Talanta*, 1974, **21**, 979.
24. A. Sabatini, A. Vacca and P. Gans, *ibid.*, 1974, **21**, 53.
25. W. H. Lawton and E. A. Sylvestre, *Technometrics*, 1971, **13**, 461.

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DETERMINATION OF BISMUTH IN ORES, CONCENTRATES AND NON-FERROUS ALLOYS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY AFTER SEPARATION BY DIETHYLDITHIOCARBAMATE EXTRACTION OR IRON COLLECTION

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Summary—Two simple, reliable and moderately rapid atomic-absorption methods for determining trace and minor amounts of bismuth in copper, nickel, molybdenum, lead and zinc concentrates and ores, and in non-ferrous alloys, are described. These methods involve the separation of bismuth from matrix elements either by chloroform extraction of its diethyldithiocarbamate (DDTC) complex, at pH 11.5–12.0, from a sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents, or by co-precipitation with hydrous ferric oxide from an ammoniacal medium. Bismuth is ultimately determined, at 223.1 nm, after evaporation of the extract to dryness in the presence of nitric and perchloric acids and dissolution of the salts in 20% v/v hydrochloric acid, or by dissolution of the hydrous oxide precipitate with the same acid solution, respectively. Results obtained by both methods are compared with those obtained spectrophotometrically by the iodide method after the separation of bismuth by DDTC and xanthate extractions.

A current facet of the Canadian Certified Reference Materials Project, sponsored by CANMET, is the certification of zinc, lead and copper sulphide concentrates, CZN-1, CPB-1 and CCU-1, for a number of minor and trace constituents as well as the principal metals. Recently, as part of this project, a spectrophotometric method was developed for determining bismuth, at the μg/g-level, in diverse sulphide ores and concentrates.[1] This method involves the preliminary separation of bismuth by chloroform extraction of its diethyldithiocarbamate (DDTC) complex from a strongly alkaline sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. This is followed by extraction of bismuth as the xanthate and subsequent determination as the iodide. In this work, it was suggested that moderate amounts of bismuth could probably also be readily determined by atomic-absorption spectrophotometry after separation by the relatively specific DDTC extraction step. The need for a reliable atomic-absorption method for determining ≤ 200 μg/g of bismuth in sulphide concentrates was apparent from the high results obtained in the CANMET laboratories for bismuth in CZN-1. It was also evident from the wide range of values (19–120 μg/g) obtained by atomic-absorption methods by other laboratories during the interlaboratory certification programme. Most of these methods involved neither preliminary separation nor preconcentration steps, nor matrix matching in the calibration solutions. This paper describes the application of the DDTC extraction–atomic-absorption finish to ores, concentrates and non-ferrous alloys. It also describes a simpler and more rapid atomic-absorption method based on the separation of bismuth by co-precipitation with hydrous ferric oxide. Results obtained by both methods are compared with those obtained previously by the iodide method.[1]

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EXPERIMENTAL

Apparatus

A Varian Techtron Model AA6 spectrophotometer equipped with a 10-cm laminar-flow, air–acetylene burner, and the conditions recommended by the manufacturer were used for the determination of bismuth.

Reagents

Standard bismuth solution, 1000 μg/ml. Dissolve 0.5000 g of pure bismuth metal in 20 ml of concentrated nitric acid, cool and dilute the solution to 500 ml with water. Prepare a 100-μg/ml solution by diluting 25 ml of this stock solution to 250 ml with water. Prepare the diluted solution fresh as required.

Citric acid–tartaric acid solution, 25% of each acid.

EDTA, disodium salt–sodium hydroxide solution, 12% of each.

Sodium hydroxide, 50% solution.

Potassium cyanide, 20% solution. Prepare fresh as required.

Sodium DDTC, 1% solution. Prepare fresh as required. required.

Iron(III) sulphate solution (1 ml ≡ 10 mg of iron). Dissolve 25 g of ferric sulphate monohydrate in hot water

containing 5 ml of concentrated sulphuric acid, cool and dilute to 500 ml with water.

Ammonia solution 10% v/v.
Hydrochloric acid, 20% v/v.
Sulphuric acid, 50% v/v.
Nitric acid 50% v/v.
Chloroform. Analytical-reagent grade.

Calibration solutions

Add 20 ml of concentrated hydrochloric acid to eight 100-ml standard flasks; then, by burette, add to the first seven flasks 0.5, 1, 2, 3, 5, 7.5 and 10 ml, respectively, of the standard 100-μg/ml bismuth solution. The contents of the last flask constitute the zero calibration solution. If bismuth is separated by co-precipitation with hydrous ferric oxide, add 10 ml of iron(III) sulphate solution to each flask. Dilute each solution to volume with water and mix (Note 1).

Separation of bismuth by extraction of its DDTC complex

Ores and concentrates. Transfer 0.2–0.5 g of powdered sample (Note 2), containing up to approximately 1 mg of bismuth, to a 60-ml zirconium crucible. Add 3 g of sodium peroxide and mix thoroughly (Note 3). Cautiously fuse the mixture over an open flame and maintain it in the molten state for ~30 sec to ensure complete decomposition. Allow the melt to cool, then transfer the crucible to a covered 400-ml Teflon beaker containing ~80 ml of water and 25 ml of 50% sulphuric acid. When the melt has dissolved, remove the crucible after washing it thoroughly with water, then cover the beaker (Note 4) and evaporate the solution to ~75 ml. Remove the cover, add 5 ml of concentrated hydrofluoric acid and evaporate the solution to fumes of sulphur trioxide to remove silica and hydrogen peroxide. Cool, wash down the sides of the beaker with water, evaporate the solution until ~10 ml of sulphuric acid remain (Note 5), then cool to room temperature.

Add ~40 ml of water and 5 or 10 g of sodium chloride (Note 6) to the resulting solution and heat gently to dissolve the sodium salts and lead sulphate. Add 20 ml of 25% citric acid–25% tartaric acid solution, mix (Note 7) and add 50 ml of 12% EDTA–12% sodium hydroxide solution. Using a pH-meter if necessary (Note 8), or a small piece of red litmus paper added to the solution, make the solution alkaline (pH 7–11) with 50% sodium hydroxide solution. Cool the solution to room temperature in a water-bath, then adjust the pH to 11.5–12.0 with 50% sodium hydroxide solution.

Transfer the resulting solution to a 250-ml separatory funnel, add 30 ml of freshly prepared 20% potassium cyanide solution and mix thoroughly. Add 5 ml of freshly prepared 1% sodium DDTC solution, mix, then add 10 ml of chloroform (Note 9), stopper and shake for 1 min. Allow several min for the layers to separate, then drain the chloroform phase into a 150-ml beaker. Extract the aqueous phase twice more, in a similar manner, with 10- and 5-ml portions of chloroform, then wash it by shaking it for ~30 sec with 5 ml of chloroform. Add 10 ml of 50% nitric acid to the combined extracts, heat in a hot water-bath to remove the chloroform, then cover the beaker and add 10 ml of concentrated perchloric acid. Evaporate the solution to fumes of perchloric acid and continue fuming for ~15 min to ensure the complete destruction of organic material. Remove the cover, wash down the sides of the beaker with water and evaporate the solution to dryness. Add sufficient concentrated hydrochloric acid for the concentration in the final solution to be approximately 20% by volume, warm gently to dissolve the salts, transfer the solution to a standard flask of appropriate size (25–100 ml), dilute to volume with water and mix.

Measure the absorbance of the resulting solution, at 223.1 nm, in an oxidizing air–acetylene flame (Note 10). Determine the bismuth content of the solution by relating the resulting value to those obtained concurrently for calibration solutions of slightly higher and lower bismuth concentrations.

Lead-, tin- and copper-base alloys. Depending on the expected bismuth content, transfer 0.2–0.5 g of sample to a 400-ml beaker, cover and add 20 ml of 50% nitric acid. When the dissolution of the sample is complete, add 20 ml of 50% sulphuric acid and heat until the evolution of oxides of nitrogen ceases. Remove the cover, wash down the sides of the beaker with water and evaporate the solution until copious fumes of sulphur trioxide are evolved. Cool to room temperature, add ~40 ml of water and, depending on the amount of lead sulphate present, 5 or 10 g of sodium chloride (Note 6). Heat to dissolve the salts, then proceed with the addition of citric acid–tartaric acid and EDTA–sodium hydroxide solutions, the pH adjustment, the extraction of bismuth DDTC and the subsequent determination of bismuth as described above.

Separation of bismuth by co-precipitation with hydrous ferric oxide

Following the decomposition of ores and mill products and copper-base alloys (Notes 11–13) as described above, and the ultimate evaporation of the solution to fumes of sulphur trioxide, cool and add ~100 ml of water. Add 5 ml of concentrated hydrochloric acid and, if necessary, sufficient iron(III) sulphate solution for at least 100 mg of iron to be present. Cover and heat to dissolve the soluble salts. Add sufficient concentrated ammonia solution to precipitate iron as the hydrous oxide, then add 5 ml in excess and boil the solution to coagulate the precipitate. Allow this to settle, then filter hot (Whatman No. 40 paper) and wash the beaker twice and the paper and precipitate three times with 10% ammonia solution. Discard the filtrate and washings and place a 100-ml standard flask under the funnel. Wash down the sides of the beaker with 40 ml of 20% hydrochloric acid and add the resulting solution to the funnel containing the paper and precipitate. Wash the beaker twice with 20% hydrochloric acid, added from a plastic wash-bottle, and add the washings to the funnel. Wash the paper three times with the acid solution. Discard the paper. Dilute the resulting solution to volume with 20% hydrochloric acid, mix and determine the bismuth content of the solution as described above, but by comparison with absorbance values obtained for calibration solutions containing approximately the same concentration of iron(III).

Notes

1. The calibration solutions should be prepared fresh every week because they are not stable on prolonged standing.

2. Larger samples should not be used unless the volume of EDTA–sodium hydroxide solution that is employed subsequently for masking purposes is increased correspondingly.

3. If the sample contains little, or no, acid-insoluble material, it can be decomposed with acids in a Teflon beaker as follows.

Add 10 ml of 20% v/v bromine–carbon tetrachloride solution, cover and add 15 ml of concentrated nitric acid. Allow the solution to stand for ~15 min, then heat gently to remove the bromine and carbon tetrachloride. Add 20 ml of 50% sulphuric acid, heat gently until the evolution of oxides of nitrogen ceases, then remove the cover and add 5 ml of concentrated hydrofluoric acid. Evaporate the solution to fumes of sulphur trioxide, then proceed as described.

4. The solution should be kept almost completely covered during the initial evaporation, to avoid loss by spray.

5. Low results will be obtained if the solution is evaporated to dryness. If this occurs, add 20 ml each of 50%

sulphuric acid and water, heat to dissolve the salts, then evaporate the solution to fumes of sulphur trioxide and proceed as described.

6. Approximately 10 g of sodium chloride should be used if more than about 250 mg of lead is present. It can be omitted if lead sulphate is absent.

7. If the subsequent DDTC extraction cannot be performed the same day, allow the solution to stand overnight at this point. Addition of the EDTA–sodium hydroxide solution is not harmful except that the EDTA will precipitate from the acidic solution during prolonged standing.

8. A pH-meter is only necessary for highly coloured copper and nickel solutions of low iron content. If an appreciable amount of iron is present, add 50% sodium hydroxide solution until the solution changes colour because of formation of the reddish-brown iron(III)–EDTA complex.

9. Carbon tetrachloride instead of chloroform is not recommended for the extraction of bismuth from solutions containing an appreciable amount of lead. Lead DDTC, which is less soluble in this solvent, precipitates in the organic phase and may interfere mechanically with the extraction of bismuth.

10. Scale expansion (~2.5–5-fold) is recommended for the determination of approximately 1 μg/ml or less of bismuth.

11. This method is not recommended for samples containing more than 50 mg of aluminium, antimony or tin or more than 200 mg of lead.

12. Samples containing more than 1 mg of bismuth can be taken if the final solution is diluted to an appropriate volume with 20% hydrochloric acid and if the calibration solutions contain approximately the same concentration of iron(III).

13. Up to 1 g of sample can be taken if the iron content does not exceed approximately 20% and if large amounts of other elements that form insoluble hydrous oxides (Note 11) are absent. Approximately 4 g of sodium peroxide should be used for the decomposition of 1 g of sample.

RESULTS

Atomic-absorption finish after separation of bismuth by extraction of its DDTC complex

It was shown previously[1] that lead is partly co-extracted into chloroform as the DDTC complex, at pH 11.5–12.0, from a sodium hydroxide medium containing citric acid, tartaric acid, EDTA and potassium cyanide as complexing agents. Tests, in which the extract was ultimately treated with nitric and perchloric acids as described in the proposed method, showed that approximately 14–17 mg of lead are co-extracted, at the 300-mg level, when the recommended amount of sodium DDTC (50 mg) is used. However, up to at least 2000 μg/ml can be present in the final solution taken for analysis without interfering in the determination of bismuth by atomic-absorption spectrophotometry under the proposed conditions. The use of less sodium DDTC to decrease the co-extraction of lead is not recommended. It reduces the rate of complex formation and may result in incomplete extraction of bismuth. Thallium(III) is completely co-extracted as the DDTC complex but up to at least 50 μg/ml will not interfere.

Atomic-absorption finish after separation of bismuth by co-precipitation with hydrous ferric oxide

Co-precipitation procedures, involving the hydrous oxides of lanthanum,[2–5] titanium[6] and zirconium,[7] followed by an atomic-absorption finish, have been used for the separation and determination of bismuth and other elements in sulphide concentrates,[4,5] various metals[2,7] and leach solutions.[6] Iron(III) has also been recommended for co-precipitation purposes,[8,9] and has been used previously by the author for the preliminary separation of arsenic[10] and tellurium[11] from matrix elements in copper, nickel, molybdenum and zinc concentrates before their extraction as xanthates and subsequent spectrophotometric determination. Consequently, it was considered that this separation step, in conjunction with an atomic-absorption finish, should also provide a rapid, simple and reliable method for determining bismuth in diverse ores and concentrates. The use of the other co-precipitants mentioned above was not considered necessary or desirable, where only bismuth is concerned, because most sulphide ores and concentrates usually contain sufficient iron to co-precipitate small amounts of bismuth completely. Furthermore, large amounts of these elements, in conjunction with a large amount of iron, not only increase the metal ion content of the final solution, but also produce a bulky precipitate that is slow to filter and dissolve.

Tests, in which bismuth was separated by co-precipitation with 100 mg of iron(III), as described previously,[10,11] followed by dissolution of the precipitate in 20% hydrochloric acid, yielded complete recovery of 20- and 1000-μg amounts of bismuth. Further tests showed that up to 50 mg (or 500 μg/ml in the final solution) of manganese(II), antimony(V), zirconium, aluminium and tin(IV), which also form insoluble hydrous oxides, will not interfere either in the co-precipitation or in the subsequent determination of bismuth by atomic-absorption spectrophotometry. Larger amounts of tin and antimony cause low results for bismuth because of the slow and incomplete dissolution of the precipitate. A larger amount of aluminium results in a solution that passes very slowly through the filter paper. It also causes slightly high results for bismuth. Up to at least 2000 μg/ml of lead and iron(III), 500 μg/ml of nickel, copper(II), sodium and zinc, 300 μg/ml of molybdenum(VI) and arsenic(V), and 50 μg/ml of indium and thallium(III) can be present in the final solution, without interfering in the determination of bismuth. More than ~2000 μg/ml of lead may result in the precipitation of lead chloride in the solution.

Applications

To test the reliability of the proposed methods, they were applied to the analyses of the CCRMP zinc, lead and copper concentrates, CZN-1, CPB-1 and CCU-1, and to two CCRMP reference ores, MP-1 and PR-1, that have been certified for bismuth. The methods, where applicable, were also applied to certified reference copper-, tin- and lead-base alloys. The results of these analyses are given in Table 1. Except as indicated in the footnotes to Table 1, 0.5-g samples were taken in these tests.

Table 1. Determination of bismuth in CCRMP reference ores and concentrates and in NBS and BCS non-ferrous alloys

Sample	Nominal composition, %	Certified value and range, % Bi	Bi found, %		
			Iodide method	Atomic-absorption spectrophotometry DDTC extraction method	Atomic-absorption spectrophotometry Iron collection method
MP-1 Zinc–tin–copper–lead ore	15.9 Zn, 2.4 Sn, 2.1 Cu, 1.9 Pb, 5.7 Fe, 0.8 As, 19.4 Si, 3.6 Al, 3.4 Ca	0.024 (0.022–0.026)*	0.022	0.023†	0.022‡§
PR-1 Molybdenum ore	39.2 Si, 1.3 Fe, 0.6 Mo, 2.4 Al, 1.4 Ca, 2.0 K	0.111 (0.107–0.114)*	0.107	0.113†	0.109‡
CPB-1 Lead concentrate	64.6 Pb, 4.4 Zn, 8.5 Fe, 17.8 S	0.023 (0.021–0.024)*	0.022‖	0.023‡	0.021‡¶
CZN-1 Zinc concentrate	44.5 Zn, 7.4 Pb, 11.0 Fe, 30.2 S	0.0025[a]	0.0023[b]	0.0023†	0.0022‡§
CCU-1 Copper concentrate	24.7 Cu, 30.7 Fe, 3.2 Zn, 35.6 Si	—	0.0032	0.0036†	0.0037‡
NBS-C1100 Cartridge brass	67.4 Cu, 32.2 Zn	0.0010	0.0011	0.0011	0.0007
NBS-C1101 Cartridge brass B	69.5 Cu, 30.3 Zn	0.0004	0.0004	0.0003	—
NBS-C1102 Cartridge brass C	72.9 Cu, 27.1 Zn	0.0005	0.0006	0.0006	—
NBS-53d Lead-base bearing metal	9.9 Sb, 4.9 Sn	0.135 (0.12–0.143)	0.141	0.145	0.140c
NBS-54D Tin-base bearing metal	88.6 Sn, 7.1 Sb, 3.6 Cu, 0.6 Pb	0.044 (0.037–0.050)	0.048	0.050	—
NBS-127A Solder	30.0 Sn, 0.8 Sb	0.036 (0.031–0.04)	0.039	0.035	—
BCS-178 White metal "B"	84.0 Sn, 7.5 Sb, 4.1 Cu, 3.9 Pb	0.005 (0.003–0.008)[d]	0.0030	0.0038	—
BCS-183/3 Leaded gunmetal	84.5 Cu, 6.7 Sn, 3.3 Zn, 3.4 Pb, 1.5 Ni	0.008 (0.007–0.010)	0.0072	0.0072	0.0068
BCS-207/2 Gunmetal	87.3 Cu, 9.7 Sn, 1.6 Zn, 0.7 Pb	0.04 (0.039–0.048)	0.042	0.045	0.041

* 95% confidence limits of the recommended mean value.
† Sample decomposed by fusion.
‡ Sample decomposed with acids as described in Note 3.
§ 1 g sample taken.
‖ Mean of 10 values ranging from 210 to 221 μg/g.
¶ 0.28 g sample taken.
[a] Consensus mean of 130 results (excluding gross outliers) reported during the interlaboratory certification programme.
[b] Mean of 10 values ranging from 21.2 to 24.4 μg/g.
[c] 0.1 g sample taken.
[d] Certified value based on the 2 results shown in brackets.

DISCUSSION

Table 1 shows that the results obtained for the CCRMP reference ores and concentrates and for the National Bureau of Standards and British Chemical Standards non-ferrous alloys (where applicable) by the two methods, which involve completely different separation procedures, are in excellent agreement with each other, with those obtained previously by the author using the DDTC-xanthate extraction–iodide method,[1] and with the respective certified values. Unfortunately, a consensus value is not available for the CCRMP copper concentrate, CCU-1, because it was not analysed for bismuth during the interlaboratory certification programme. Furthermore, only a consensus value is available for CZN-1 because it could not be certified for bismuth. The precision of the results obtained for CZN-1 by the three methods suggests strongly that the wide range of values obtained in the interlaboratory certification programme is due to uncompensated interelement and/or matrix effects. These effects, as shown by the results obtained by one laboratory (0.0024%), can be minimized by simulating the composition of the sample in the calibration solutions. However, the inherent disadvantage in this method is that it is only applicable to samples in which the approximate content of the predominant matrix elements is known. Similarly, although matrix effects can also be eliminated, to some extent, by using the standard additions method, the results obtained by another participating laboratory (0.0092%), and work by other investigators,[12] has shown that this method is not always reliable.

In the proposed method based on the separation of bismuth by extraction of its DDTC complex, the addition of lead, before the extraction, to eliminate interference from molybdenum and zinc, as described previously,[1] is not necessary. These elements only cause low (unexplained) results for bismuth if it is subsequently stripped from the extract by shaking it with 12*M* hydrochloric acid. Earlier,[1] the author stated that the probable lower limit of this method is about 0.01%. However, this estimate was not based on the use of scale expansion for the determination of bismuth. If an expanded scale is used, the method is suitable for samples containing ~0.0005% or more of bismuth. If desired, this lower limit can be decreased to ~0.0002% if the salts ultimately obtained are dissolved in 2 ml of concentrated hydrochloric acid and the resultant solution is diluted to 10 ml. A method involving the extraction of an analogous bismuth complex, formed with ammonium pyrrolidinedithiocarbamate, into methyl isobutyl ketone, at pH ~ 10.5, from an EDTA–potassium cyanide–citrate medium, followed by the direct atomic-absorption determination of bismuth in the extract has been reported.[13] However, although it has been shown that this method yields excellent results for bismuth in non-ferrous alloys, the proposed method is more suitable for routine work because of the greater stability and ease of preparation of aqueous calibration solutions.

The method based on co-precipitation of bismuth with iron(III) is suitable for samples containing ~0.001% or more of bismuth if a 1-g sample is taken. This lower limit can also be decreased to ~0.0005% if the solution obtained after dissolution of the precipitate is concentrated by evaporation and ultimately diluted to 50 ml. This method is not recommended for samples of high aluminium, tin, antimony and/or lead contents. Both methods are also applicable to nickel and molybdenum ores and concentrates.

REFERENCES

1. E. M. Donaldson, *Talanta*, 1978, **25**, 131.
2. W. Reichel and B. G. Bleakley, *Anal. Chem.*, 1974, **46**, 59.
3. M. Thompson, B. Pahlavanpour, S. J. Walton and G. F. Kirkbright, *Analyst*, 1978, **103**, 705.
4. E. A. Jones, *Natl. Inst. Metallurgy, Johannesburg, Rept.*, No. 1787, 1976.
5. R. V. D. Robért, *ibid.*, No. 1838, 1976.
6. S. J. Royal and K. Dixon, *ibid.*, No. 1795, 1976.
7. M. Malusecka and H. Jedrzejewska, *Chem. Anal. (Warsaw)*, 1976, **21**, 575.
8. *Idem, ibid.*, 1976, **21**, 585.
9. J. D. Mullen, *Talanta*, 1976, **23**, 846.
10. E. M. Donaldson, *ibid.*, 1977, **24**, 105.
11. *Idem, ibid.*, 1976, **23**, 823.
12. J. W. Hosking, K. R. Oliver and B. T. Sturman, *Anal. Chem.*, 1979, 51, 307.
13. H. K. Y. Lau, H. A. Droll and P. F. Lott, *Anal. Chim. Acta*, 1971, **56**, 7.

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EXTRACTION CHROMATOGRAPHY OF NOBLE METALS WITH USE OF MIXTURES OF HYDROCHLORIC AND NITRIC ACID AS MOBILE PHASES

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Summary—The chromatographic behaviour of the platinum metals and gold, silver and copper on paper strips treated with liquid anion-exchangers and eluted with mixtures of HNO_3 and HCl was investigated. It was found that increase of HNO_3 concentration in the acid mixture increases the R_F values more significantly than does that of HCl. The presence of HNO_3 in the development solution prevents the reduction of iridium(IV). The R_F values of the noble metals increase in the order Au(III) < Os(IV) < Ir(IV) < Pt(IV) < Pd(II) < Ru(III) < Rh(III) ~ Ir(III). Several separations of noble metals were carried out on paper strips treated with trioctylamine or quaternary alkylammonium salts, as well as the column separation of the mixture Pt–Pd–Rh. The proposed chromatographic systems seem to be especially useful for the separation of non-volatile noble metals.

The classical separation methods are not always satisfactorily selective for the platinum metals and it is often difficult to obtain the single metals in high purity from their mixtures. Therefore, it is not surprising that a search is made for rapid and more effective separation methods, for analytical and industrial purposes. The most promising separation methods for platinum metals seem to be ion–exchange chromatography and liquid–liquid extraction;[1–8] however, the problem of easy and rapid separation of platinum, palladium, iridium and rhodium has not yet been completely solved. Ion-exchange chromatography has been applied successfully for the separation of noble metals from other metals and from each other and many useful cation- and anion-exchange procedures have been described;[1,4,7,8] however, their use in analytical practice is often limited by incomplete elution (two bands are often formed for the same metal ion, owing to hydrolysis or reduction).[9–11] Further, the chloride complexes of platinum(IV) and iridium(IV) are very strongly retained on anion-exchange resins and can only be eluted with concentrated mineral acid solutions, which makes quantitative analysis of the eluate more difficult.

Extraction chromatography appears to be one of the most promising separation methods for metals,[12] but it has seldom been applied for the separation of noble metals. Pohlandt and Steele[13] separated the non-volatile noble metals on Kel-F treated with tributyl phosphate, by stepwise elution with sulphuric and hydrochloric acid; however, this interesting procedure is rather time-consuming owing to the three successive column separations required. The separation of halide complexes of platinum metals on supports treated with tertiary long-chain amine salts or quaternary alkylammonium salts is difficult owing to the very strong affinity of palladium, platinum, iridium(IV) and osmium(IV) for the stationary phase.[14–16] Amberlite LA-1 hydrochloride seems a more promising liquid anion–exchanger for this purpose,[17,18] but the separation of the chloride complexes of palladium and platinum is unsatisfactory owing to the small differences between their R_F values, and elongated spots are obtained in paper chromatography. A better separation of Pd and Pt is achieved by paper or thin-layer chromatography on supports treated with a mixture of Amberlite LA-1 hydrochloride and tributyl phosphate,[19] but with this system it is impossible to separate iridium from other metals owing to the partial reduction of iridium(IV) to iridium(III) during development with solutions of hydrochloric acid, and iridium(III) forms a single zone with rhodium(III), moving with the solvent front in all chromatographic systems investigated.

The mixtures of eluting agents which are often useful in column ion-exchange separations of metal ion mixtures have been applied in extraction paper chromatography only for some metals in thiocyanate systems.[20–24] It is well known that alkylammonium cations have stronger affinity for nitrate than for chloride;[25,26] the possibility of altering, by addition of nitric acid to the eluent, the R_F values for platinum metals strongly extracted by TOA or quaternary alkylammonium salts, was investigated in the present work. Additionally, the possibility of utilization of paper chromatographic data for column extraction chromatographic separation of the mixture Rh–Pd–Pt with an analogous system was also investigated.

EXPERIMENTAL

Materials

Amberlite LA-1 (Schuchardt, F.R.G.), tri-n-octylamine (Koch-Light, England) and Aliquat 336 (tricaprylmethylammonium chloride; General Mills Chemicals, Inc., U.S.A.) were used as the extractants without further purification. Tri-n-octylbutylammonium nitrate containing 95%

of quaternary ammonium salt was prepared in the manner described previously.[27] The following noble metal compounds, of analytical grade, were used: H_2PtCl_6 30% solution (Mennica Panstwowa, Poland), $(NH_4)_2OsCl_6$ (Johnson-Matthey, England), $PdCl_2$ (POCh, Poland), Na_2IrCl_6 (Pfaltz-Bauer, F.R.G.), $(NH_4)_3IrCl_6$ (Johnson-Matthey, England). The $RhCl_3$aq. (Fluka, Switzerland) and platinum—rhodium alloy containing 10% Rh (Mennica Państwowa, Poland) were of pure grade.

Solutions of noble metals

The samples were usually in the form of 1% w/v noble metal solutions in 6*M* hydrochloric acid. The platinum content was determined gravimetrically[28] and rhodium cerimetrically.[29] More dilute solutions for determination of detection limits were prepared by dilution with a mixture of hydrochloric and nitric acids ($c_{HCl} = 4.5M$; $c_{HNO_3} = 2M$). The platinum–rhodium alloy (18.4 mg) was dissolved in *aqua regia* by heating for 5 hr on the water-bath. The solution was evaporated almost to dryness and the residue treated with 1.5 ml of conc. hydrochloric acid, evaporated again and diluted with conc. hydrochloric acid to a volume of 1.5 ml; 1 ml of this solution contained 1.24 mg of rhodium and 11.44 mg of platinum.

Paper chromatographic procedure

Xylene solutions (0.1*M*) of Aliquat 336, tri-n-octylbutylammonium nitrate and tri-n-octylamine or Amberlite LA-1 salts were used as impregnating solutions. TOA and Amberlite LA-1 were converted into their salts by shaking a 0.1*M* solution of the free base with an equal volume of *aqua regia* diluted 1:8 with distilled water, separating the phases and filtering the organic phase through cellulose. Whatman No. 4 paper strips were passed through the organic solution three times and pressed between two sheets of paper in order to remove the excess of impregnating solution. The paper strips were then air-dried to remove the diluent used for the liquid anion-exchanger. Then 2-μl volumes of solutions of the metals investigated were spotted on the start line of paper strips and the spots were air-dried. Aqueous nitric acid solutions and mixtures of nitric and hydrochloric acids were used as developing solutions. Descending development over a distance of 16 cm required 45–55 min, depending mainly on the acid concentration in the mobile phase.

After development, the paper was air-dried and the metals were detected by spraying the chromatograms with solutions of suitable reagents: 5% stannous chloride in 2*M* hydrochloric acid (Pt, Pd, Au, Rh), followed by 5% potassium iodide in water (Pt, Pd, Au, Rh, Os) or 1% ceric sulphate in water [Ir(III)]. The yellow spots from iridium(IV) were visible on the unsprayed chromatograms.

The detection limits were determined on paper strips treated with Aliquat 336 and eluted with an acid mixture ($c_{HCl} = 4.5M$; $c_{HNO_3} = 2M$) and found to be 0.25 μg (125 ppm of metal in the sample) for Pd, Pt and Au, 0.5 μg for Ir(IV) and Rh and 1 μg for Os(IV). If the concentration is lower than the detection limit, a larger sample should be taken by repetitive spotting. The length of the spot after chromatography depends on the concentration of the sample solution and was found to vary for platinum from 14 mm (250 ppm) to 33 mm (10^4 ppm) and for iridium(IV) from 12 mm (250 ppm) to 17 mm (6×10^3 ppm). It was also found that the spot corresponding to iridium(III) was not formed even when 12 μg of iridium(IV) were placed on the start line.

The volumes of stationary and mobile phases [determined on the basis of the weights of paper strips (*a*) unimpregnated, (*b*) impregnated with TOA salts and (*c*) developed with a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$)] were found to be 0.0906 ml and 2.93 ml, respectively, so the volume ratio of mobile to stationary phase in the paper chromatography was 32.4.

Column chromatographic procedure

Glass tubes (8.2 × 300 mm) were used in this work. Silica gel (0.05–0.2 mm), analytical grade (Merck, F.R.G.), was used as the support for the stationary phase. Tri-n-octylamine was converted into salt form by shaking a 0.4*M* TOA solution in chloroform with an equal volume of a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 2M$). After separation of the phases, the organic phase was filtered through a cellulose filter and 50 ml of the solution were mixed with 40 g of silica gel. The diluent was then evaporated with a vacuum evaporator (Quickfit) on a water-bath. The coated support remained a white, free-flowing powder containing 0.165 g (0.2 ml) of amine salt/g. The dried support (10 g) was then slurried with 40 ml of the eluent ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$), poured into the column, and covered with a Whatman No. 4 cellulose filter. The column height was 250 mm, the dead volume 0.4 ml, the organic phase volume 2 ml and the mobile phase volume 10 ml (determined from the retention volume for nickel, which is not retained). After the column had been washed with 10 ml of the first eluent, 0.6 ml of a synthetic mixture containing 1.98 mg of platinum(IV), 0.995 mg of palladium(II) and 1.033 mg of rhodium(III) in hydrochloric and nitric acids ($c_{HCl} = 2.25M$) $c_{HNO_3} = 3M$) was introduced into the column. Two-step elution under hydrostatic pressure (head of 250 mm) was used for the separation, 1-ml fractions being collected by a fraction collector equipped with a drop-counter. The whole elution needed 280 min at a flow-rate 0.4 ml/min.

Palladium and platinum were determined in single fractions by AAS, with a single-beam (Pye-Unicam) SP 192 atomic-absorption spectrometer. Rhodium was determined in individual fractions or in the total rhodium eluate spectrophotometrically at 500 nm; the calibration graph was based on rhodium(III) solutions in the mixture of acids used as the first eluent.

RESULTS AND DISCUSSION

The R_F values in laminar extraction chromatography depend mainly on the nature of both the organic and aqueous phases. The platinum metals have hitherto been separated on supports treated with Amberlite LA-1 hydrochloride, tributyl phosphate or mixtures of both, and developed with hydrochloric acid. From liquid–liquid extraction data it is known that tertiary long-chain alkylamines and quaternary alkylammonium salts are more selective than primary or secondary high molecular-weight amines[30,31] as extractants for platinum metals in hydrochloric acid. Paper or thin-layer chromatography experiments in chloride, bromide, iodide and thiocyanate systems have indicated that the halide complexes of platinum(IV), palladium(II), iridium(IV) and osmium(IV) are too strongly extracted by tertiary amine salts to permit their separation even at high concentrations of hydrohalic acids in the mobile phase.[14–16,32–34] It is known that decreasing the concentration of extracting agent in the impregnating solution decreases the capacity of the extractant and that at concentrations of extracting agents lower than 0.05*M* elongated spots are usually formed, even with microgram quantities of metals. The other way to alter R_F values is to change the composition of the aqueous mobile phase. Therefore, we first tried to use nitric acid solutions as non-complexing eluents for the platinum metals,

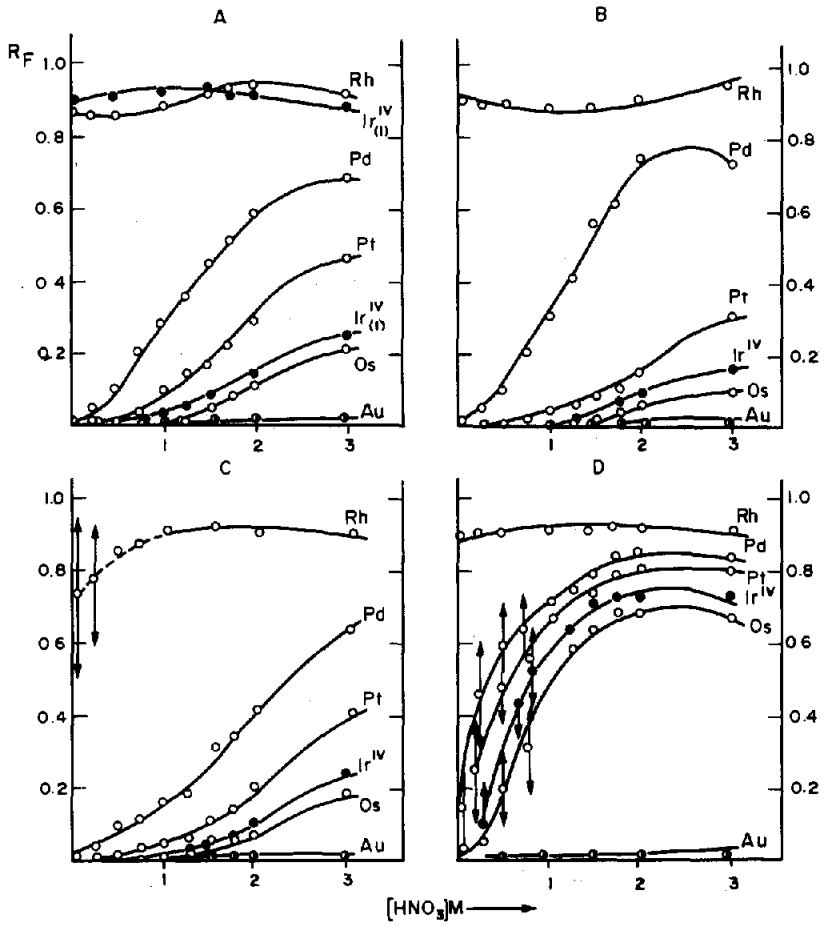


Fig. 1. R_F values of gold(III), osmium(IV), iridium(IV), platinum(IV), palladium(II), rhodium(III) and iridium(III) *vs.* HNO_3 concentration in the developing solution. Constant concentration of HCl = 2.25*M*. Stationary phases: A—TOA hydrochloride, B—Aliquat 336, C-tri-n-octylbutylammonium nitrate, D—Amberlite LA-1 hydrochloride.

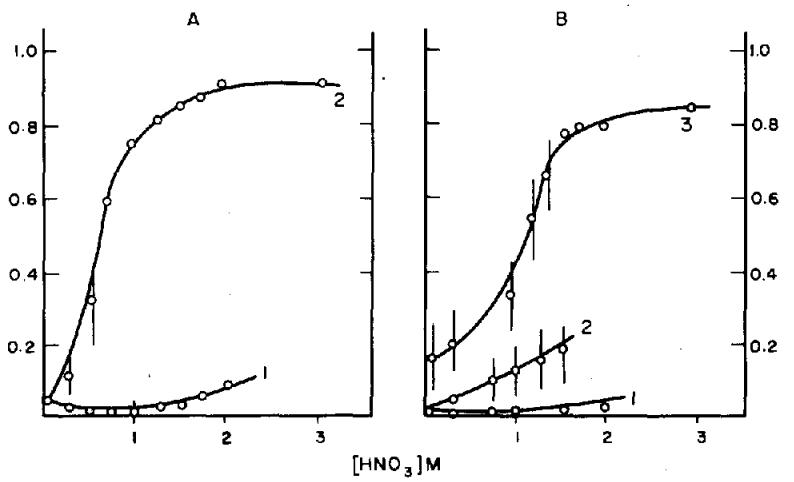


Fig. 2. R_F values of ruthenium(III) *vs.* concentration of HNO_3. Constant concentration of HCl = 2.25*M*. Stationary phases: A—TOA hydrochloride, B—Aliquat 336.

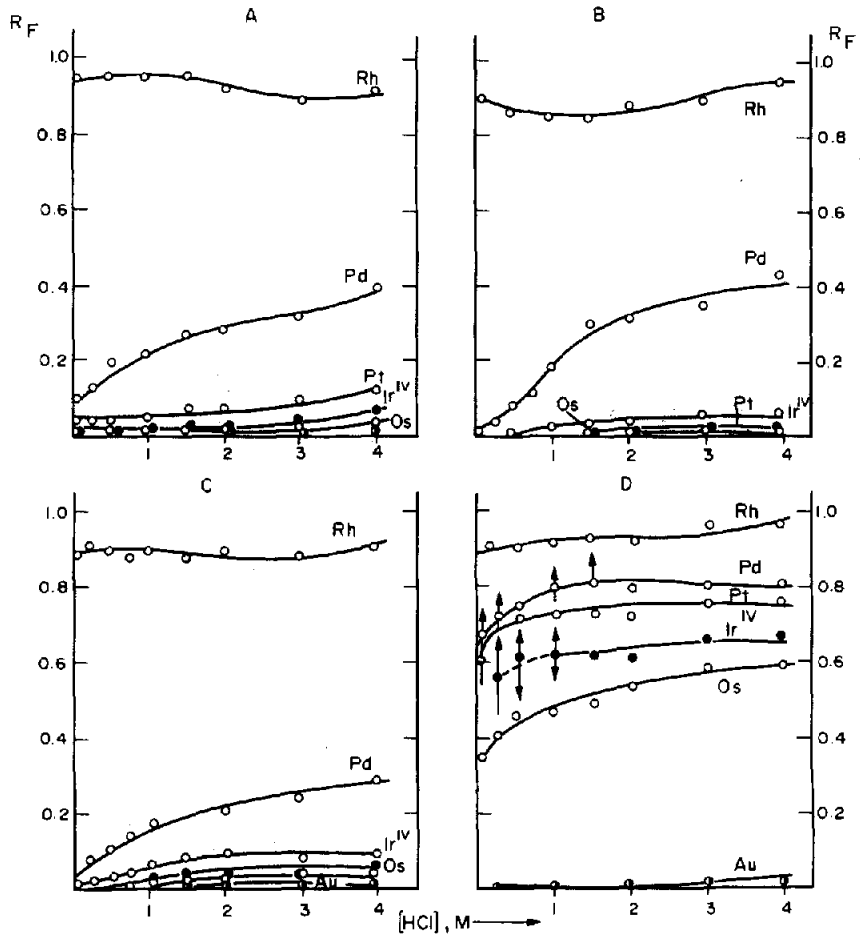


Fig. 3. R_F values of noble metals *vs.* HCl concentration in the mobile phase. Constant HNO_3 concentration = 1*M*. Designations as in Fig. 1.

but they proved unsuitable because elongated spots (comets) were obtained for palladium, platinum and iridium. These are probably due to partial hydrolysis of the chloride complexes of these metals to give aquo-chloro-complexes or hydroxy-chloro-complexes in the absence of chloride ions in the aqueous phase.[1] Double or triple spots were produced by iridium(III), one of which had the R_F value corresponding to iridium(IV). It seems that iridium(III) is partially oxidized to iridium(IV) during the development with nitric acid.

Earlier experiments using the moist paper technique with paper strips impregnated with diluted *aqua regia* and developed with solutions of liquid anion-exchangers in organic diluents, had indicated the possibility of separation of some platinum metals in this chromatographic system.[27] Therefore, we decided to try mixtures of hydrochloric and nitric acid as eluents in the extraction chromatography; the concentrations of the acids in the mobile phase were therefore systematically varied (Figs. 1–5). The results indicated that both acids have a significant influence. Only gold(III) and silver remain at the starting line in all the systems investigated, and rhodium(III) and copper(II) are not extracted and move with the solvent front. Ruthenium(III) forms double spots on paper strips treated with TOA or Aliquat 336 (see Fig. 2) whereas only one spot, moving with the solvent front, is found when Amberlite LA-1 is used as extractant. It seems that at least two complexes of ruthenium are present in the aqueous phase at low chloride concentrations and that only one of them is extracted by TOA or quaternary alkylammonium salts, but neither by Amberlite LA-1.

Iridium(III) is partially oxidized by nitric acid and forms two or three spots, the spot of lowest R_F value corresponding to iridium(IV). On the other hand, only one spot is obtained for iridium(IV) when the nitric acid concentration in the eluent exceeds 1*M* (Fig. 1), in contrast to the result for iridium(IV) in the chloride system.[19] With a constant nitric acid concentration of 1*M* and hydrochloric acid concentrations exceeding 2*M*, a second and just visible spot was formed (on paper strips treated with Aliquat 336 only), having an R_F value corresponding to iridium(III). Similar behaviour of iridium(IV) was also

observed when diluted *aqua regia* was used as mobile phase (Fig. 5), if the total concentration was lower than 1.6*M*; the iridium(IV) was partially reduced to iridium(III), which is not extracted by liquid anion-exchangers. From the results reported for iridium it is evident that the extraction coefficients obtained in various laboratories under somewhat different experimental conditions in batch extraction of this metal by high molecular-weight amines from aqueous hydrochloric acid are often not comparable, since in such experiments the total amount of iridium is usually determined in the aqueous or the organic phase and the oxidation state of the metal is not taken into consideration.[25] On the other hand, the double or triple spots often observed for iridium(IV) in other chromatographic systems[6,35,36] with hydrochloric acid present in the eluent, make the separation of the non-volatile noble metals difficult. Thus the use of mixtures of hydrochloric and nitric acids as eluents in the extraction chromatography of noble metals seems to be useful owing to formation of a single spot for iridium(IV) if the nitric acid concentration is sufficient to prevent reduction of this species.

The R_F values for palladium(II), platinum(IV), osmium(IV) and iridium(IV) increase with increasing concentration of both acids in the developing solution, independent of the liquid anion-exchanger used as stationary phase. The chromatographic results confirm the suggestion that Amberlite LA-1 gives not only the poorest extraction for platinum metals but also the lowest selectivity in comparison with other liquid anion-exchangers used as a stationary phase. At constant concentration of impregnant, and of acid mixture in the mobile phase, the R_F values of platinum(IV), iridium(IV) and osmium(IV) vary with the extractant, increasing in the extractant order Aliquat 336 < tri-n-octylbutylammonium nitrate < TOA < Amberlite LA-1. In contrast, palladium(II) is more strongly extracted by TOA than by Aliquat 336. Sharper separation of the pair Pd–Pt is obtainable on paper strips treated with Aliquat 336, but TOA or tri-n-octylbutylammonium nitrate can also be successfully used for separation of the non-volatile noble

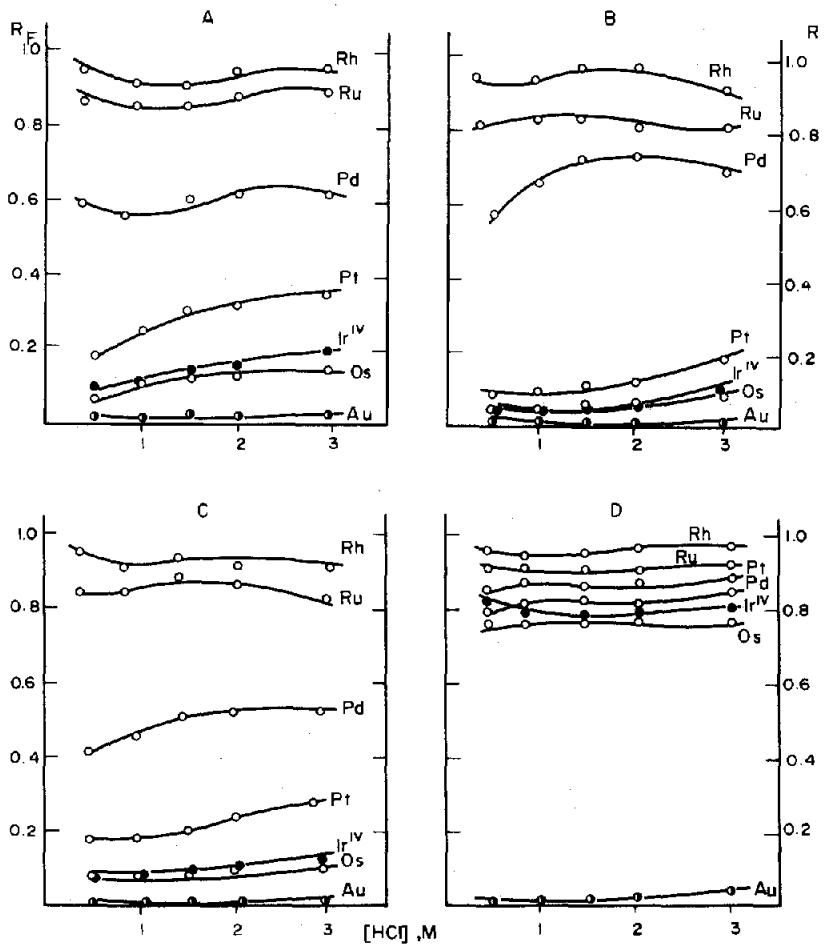


Fig. 4. R_F values of noble metals *vs.* HCl concentration in the mobile phase. Constant HNO_3 concentration = 2.25*M*. Designations as in Fig. 1.

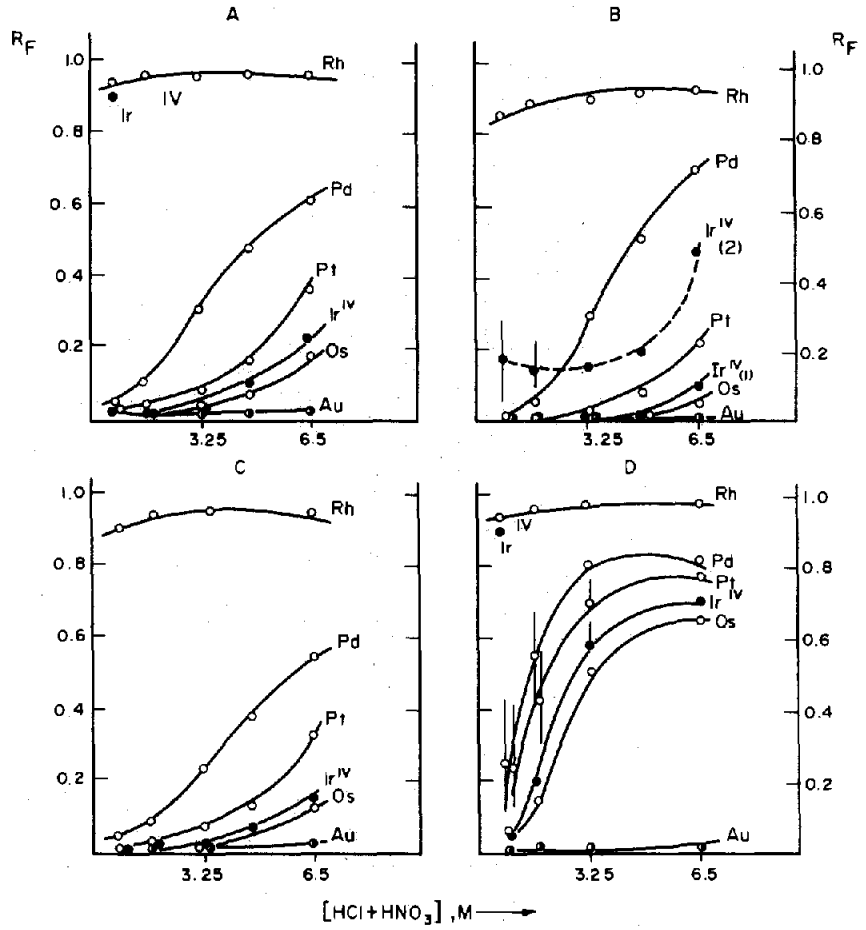


Fig. 5. R_F values of noble metals *vs.* total concentration of HCl and HNO_3 in the mobile phase (obtained by dilution of *aqua regia* with distilled water). Designations as in Fig. 1.

metals if the nitric acid concentration in the mobile phase is high enough, preferably > 1*M*. The affinity of the metals for the stationary phases decreases in the order Au(III) > Os(IV) > Ir(IV) > Pt(IV) > Pd(II) > Ru(III) > Rh(III) ~ Ir(III).

The dependence of R_F on the concentration of nitric or hydrochloric acid (compare Fig. 1 with Figs. 3 and 4) indicates the distinctly stronger eluting properties of nitric acid for platinum metals owing to the affinity of nitrate for the stationary phase being higher than that of chloride.[37,38] The extraction of the platinum metals in the chromatographic systems investigated can thus be described by

$$2(Am^+X^-)_o + MeCl^{2-}_{n+2} \rightleftharpoons [(Am^+)_2MeCl^{2-}_{n+2}]_o + 2X^-$$

where Am^+ denotes the alkylammonium cation and X^- is Cl^- or NO_3^-.

The R_F values in the chromatographic systems investigated and the low dependence of the length of spot on amount of metal offer several possibilities for separating various mixtures of non-volatile noble metals, and some of the separations performed are demonstrated in Figs. 6–8 for synthetic mixtures (containing 1 μg of each metal ion); the qualitative analysis for platinum–rhodium alloy was also successfully performed.

Recommended paper chromatographic procedure

Treat 50 mg of solid sample with 10 ml of *aqua regia* and heat on the water-bath to dissolve, or use an appropriate volume of a liquid sample. Evaporate the solution almost to dryness, add a few ml of concentrated hydrochloric acid and evaporate again. Dissolve the residue and make up to 5 ml with concentrated hydrochloric acid. Spot 2 μl of this solution on a paper strip impregnated with 0.1*M* Aliquat 336 or tri-n-octylamine salt in xylene and dry it. Develop the chromatogram with a mixture of hydrochloric and nitric acids (c_{HCl} = 4.5*M*; c_{HNO_3} = 2*M*) over a distance of 16 cm, dry the paper with a stream of hot air and spray first with 5% stannous chloride in 2*M* hydrochloric acid and then with 5% potassium iodide in water. Control experiments with synthetic solutions containing known amounts of noble metals are recommended. If the concentration of the metal ions in the test solution is lower than the detection limits, a bigger sample must be taken by multiple spotting.

The chromatographic systems recommended

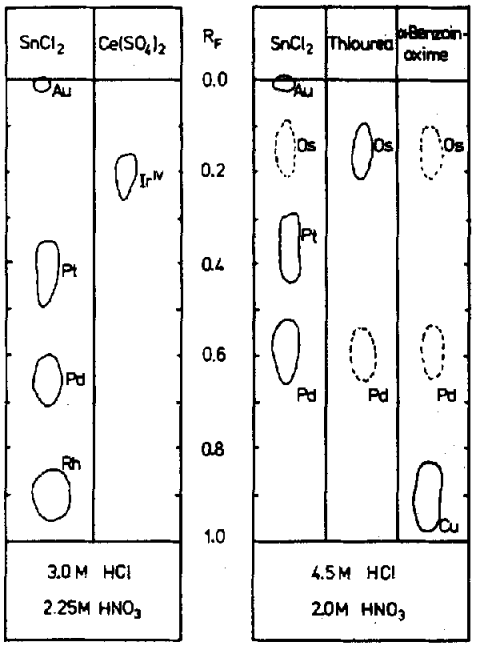


Fig. 6. Examples of chromatographic separation of noble metals on paper strips treated with TOA hydrochloride. The spots were visible after the chromatograms had been sprayed with the reagents mentioned in the upper part of the figure.

(except paper strips treated with Amberlite LA-1) are unsuitable for the separation of osmium and ruthenium; however, these metals can be successfully separated on paper strips treated with tributyl phosphate and developed with 6*M* hydrochloric acid.[18]

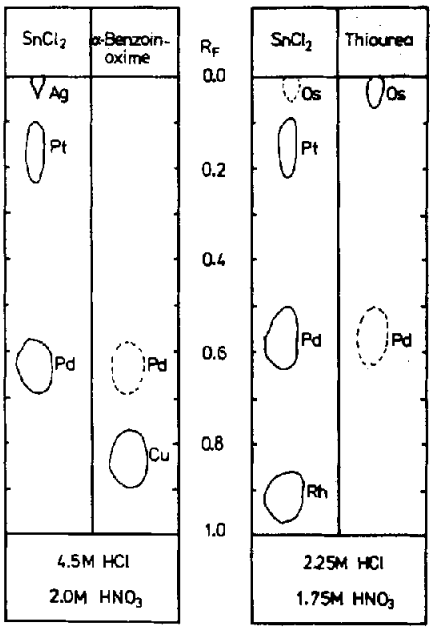


Fig. 7. Examples of chromatographic separation of noble metals on paper strips treated with Aliquat 336.

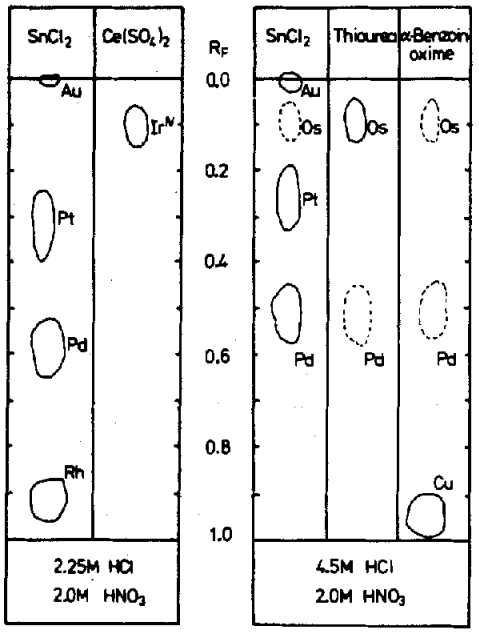


Fig. 8. Examples of chromatographic separation of noble metals on paper strips treated with tri-n-octylbutylammonium nitrate.

The systems proposed require comparatively short developing times (not exceeding 1 hr) owing to the relatively low concentration of acid in the mobile phase.

The results can also be useful in choosing the optimal conditions for column separation of the noble metals because the R_F values are correlated with the retention volumes (v_R) in column chromatography (under analogous experimental conditions) by the following equation[39]

$$\frac{v_R}{v_m} - 1 = \frac{A_m v_s}{A_s v_m}\left(\frac{1}{R_F} - 1\right) = k\left(\frac{1}{R_F} - 1\right)$$

where v_m and v_s denote the volumes of the mobile and stationary phases in the column, respectively, and A_m and A_s are the cross-sectional areas of the mobile and stationary phases in paper chromatography, respectively. In our chromatographic experiments with use of tri-n-octylamine salts as the stationary phase and a mixture of hydrochloric and nitric acids ($c_{HCl} = 2.25M$; $c_{HNO_3} = 3M$) as eluents, the ratios of A_m/A_s and v_s/v_m were found to be 32.4 and 0.2, respectively, so the coefficient k was 6.5. The retention volumes for rhodium and for platinum calculated from the paper chromatographic data and determined in column chromatography, as well as the separation factors for the pair Pd–Rh, are collected in Table 1. An example of column separation of the synthetic mixture containing milligram quantities of platinum, palladium and rhodium is given in Fig. 9. Table 2 reports the results of the determination of these metals (platinum and palladium were determined in single fractions, rhodium was determined in the total

Table 1. Comparison of experimental retention volumes and separation factors S_F for the pair Pd–Rh with those calculated from independent paper chromatographic experiments

	Eluent	Paper chromatography R_F	Paper chromatography $V_{R(calc)}$, ml	Paper chromatography S_F	Column chromatography $V_{R(exp)}$, ml	Column chromatography S_F	$\frac{V_{R(exp)}}{V_{R(calc)}}$
Rh	2.25*M* HCl, 3*M* HNO_3	0.95	13.6	8.9	16	8.8	1.2
Pd		0.68	41		63		1.5
Pd	2.25*M* HCl_1, 2*M* HNO_3	0.58	59.2		88		1.5

Table 2. The determination of rhodium, palladium and platinum after the separation of the synthetic mixture by column chromatography

	Added, *mg*	Found, *mg*
Rh(III)	1.04	1.03
Pd(II)	0.99	0.97
Pt(IV)	1.98	2.01

rhodium eluate). The reported column chromatographic results seem to be promising, so the paper chromatographic data included in this work should be useful in planning column separations of various metal–ion mixtures in analogous chromatographic systems.

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REFERENCES

1. G. I. Ginzburg, N. A. Yezerskaya, I. V. Prokofeeva, N. F. Fedorenko, V. I. Shlenskaya and N. K. Belskii, *Analiticheskaya khimiya platinovikh metallov*, Nauka, Moscow, 1972.
2. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, New York, 1968.
3. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon, London, 1969.
4. A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinhold, London, 1970.
5. P. Markl, *Extraction und Extractions-Chromatographie in der anorganischen Analytik*, Akademische Verlag, Frankfurt, 1972.

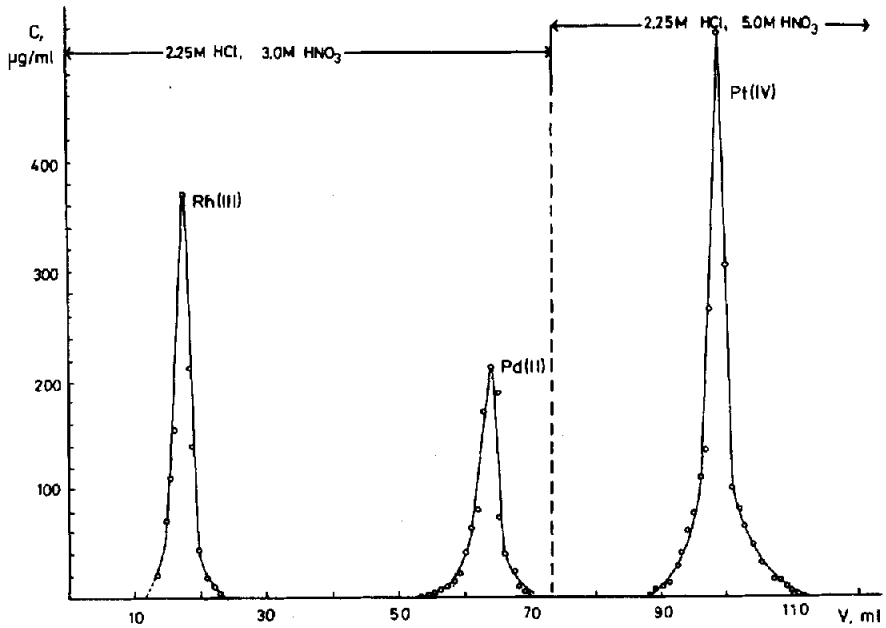


Fig. 9. Separation of Rh(104 μg), Pd(99 μg) and Pt(198 μg). Column: TOA-silica gel, 8.2 × 250 mm; flow-rate 0.4 ml/min.

6. V. Sýkora and F. Dubský, *Sb. Vys. Školy Chem.-Technol. v Praze, Anal. Chem.*, 1974, **H10**, 113.
7. F. E. Beamish, *The Analytical Chemistry of Noble Metals*, Pergamon, Oxford, 1966.
8. F. E. Beamish and J. C. Van Loon, *Recent Advances in the Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1972.
9. E. A. Chuveleva, P. P. Nazarov and K. V. Chnutov, *Zh. Fiz. Khim.*, 1962, **36**, 1022.
10. S. S. Berman and W. A. E. McBryde, *Can. J. Chem.*, 1958, **36**, 835.
11. J. Minczewski, J. Chwastowska and R. Dybczyński, *Trace Analysis, Methods of Separation and Concentration* (in Polish), p. 486. WNT, Warsaw, 1973.
12. T. Braun and G. Ghersini, eds., *Extraction Chromatography*, Elsevier, Amsterdam, 1975.
13. Ch. Pohlandt and T. W. Steele, *Talanta*, 1972, **19**, 839.
14. A. Waksmundzki and S. Przeszlakowski, *Chem. Anal. (Warsaw)*, 1966, **11**, 159.
15. S. Przeszlakowski and E. Soczewiński, ibid., 1966, **11**, 895.
16. S. Przeszlakowski, ibid., 1967, **12**, 1071.
17. S. Przeszlakowski and A. Flieger, *J. Chromatog.*, 1973, **81**, 129.
18. *Idem, Talanta*, 1976, **23**, 844.
19. *Idem, Chem. Anal. (Warsaw)*, 1977, **22**, 431.
20. A. Waksmundzki and S. Przeszlakowski, in K. Macek and I. M. Hais, eds., *Stationary Phase in Paper and Thin Layer Chromatography*, p. 199. Elsevier, Amsterdam, 1965.
21. S. Przeszlakowski, *Chem. Anal. (Warsaw)*, 1967, **12**, 57.
22. C.-C. Chang and H. H. Yang, *Hua Hsueh Hsueh Pao*, 1965, **31**, 182; *Chem. Abstr.*, 1965, **63**, 3601g.
23. *Idem, ibid.*, 1965, **31**, 45; *Chem. Abstr.*, 1965, **63**, 7634d.
24. D. Kennedy and J. S. Fritz, *Talanta*, 1970, **17**, 823.
25. V. S. Shmidt, *Ekstraktsia aminami*, Khimiya, Moscow, 1971.
26. A. S. Kertes, Y. Marcus and Y. Yanir, *Equilibrium Constants of Liquid–Liquid Distribution Reactions, Part 2 Alkylammonium Salt Extractants*, Butterworths, London, 1974.
27. S. Przeszlakowski and A. Flieger, *Chromatographia*, 1978, **11**, 647.
28. A. P. Blackmoore, M. A. Marks, R. P. Barefoot and F. E. Beamish, *Anal. Chem.*, 1952, **24**, 11.
29. O. C. Saxena, *Microchem. J.*, 1968, **13**, 1930.
30. S. N. Ivanova, L. M. Gindin, A. P. Chernyaeva, A. A. Bezzubenko, M. F. Mogilyovkina and L. Ya. Marochkina, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1974, **2**, No. 4, 3.
31. S. N. Ivanova, L. M. Gindin, A. A. Mazurova and L. Ya. Mironova, *Zh. Neorgan. Khim.*, 1967, **12**, 1638.
32. U. A. Th. Brinkman, G. De Vries and E. Van Dalen, *J. Chromatog.*, 1966, **25**, 447.
33. U. A. Th. Brinkman, G. De Vries and H. R. Leene, *ibid.*, 1972, **69**, 181.
34. M. N. Sastri, A. P. Rao and A. R. K. Sarma, *ibid.*, 1965, **19**, 630.
35. J. Michal, *Inorganic Chromatographic Analysis*, Van Nostrand Reinhold, London, 1973.
36. M. P. Volynets, *Tonkosloinaya khromatographia w neorganitcheskom analize*, Nauka, Moscow, 1974.
37. S. Przeszlakowski and R. Kocjan, *Chromatographia*, 1977, **10**, 358.
38. R. Kocjan and S. Przeszlakowski, ibid., 1978, **11**, 96.
39. G. Ghersini and C. Cerrai, in T. Braun and G. Ghersini, eds., *Extraction Chromatography*, p. 366. Elsevier, Amsterdam, 1975.

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ACIDITES ET COMPLEXES DES ACIDES (ALKYL-et AMINOALKYL-) PHOSPHONIQUES—IV

ACIDES AMINOALKYLPHOSPHONIQUES $R^1R^2N(CH_2)_nCR^3R^4PO_3H_2$

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Résumé—Les acides étudiés diffèrent par la longueur de leur chaîne carbonée [$\overset{+}{N}H_3(CH_2)_nPO_3H^-$ avec $n = 1, 2, 3$], la substitution sur l'azote [$R^1R^2\overset{+}{N}HCH_2PO_3H^-$ avec $R^1 = H$; $R^2 = Me$, Et et $R^1 = R^2 = Me$, Et] ou l'encombrement sur le carbone porteur des groupements fonctionnels [$\overset{+}{N}H_3CR^3R^4PO_3H^-$ avec $R^3 = H$; $R^4 = Me$, Et, nPr, iPr, nBu et $R^3 = R^4 = Me$]. Les constantes d'acidité et les constantes globales de stabilité des complexes formés avec Mg(II), Ca(II), Co(II), Ni(II), Cu(II), Zn(II) sont obtenues à l'aide des programmes d'affinements multiparamétriques MUPROT et MUCOMP, appliqués aux données potentiométriques, obtenues à 25°, en milieu 0,1*M* en nitrate de potassium. Dans le cas le plus général, les espèces existantes sont MHA^+, MA, $M(OH)A^-$, MH_2A_2, MHA_2^- et MA_2^{2-} (A^{2-}: forme totalement ionisée du coordinat); l'examen préliminaire des résultats conduit à dégager certaines formes microscopiques prédominantes.

Un travail précédent a permis d'examiner, pour des acides alkylphosphoniques simples, la répercussion de l'acidité du groupement $-PO_3H_2$ sur son pouvoir complexant.[1] Nous avons entrepris, dès 1970, l'évaluation des constantes de stabilité des complexes formés par les acides $NH_2(CH_2)_nCR^3R^4PO_3H_2$ et divers cations parmi Mg(II), Ca(II), Co(II), Ni(II), Cu(II), Zn(II). L'influence de l'allongement de la chaîne carbonée ($R^3 = R^4 = H$; $n = 0, 1, 2$)[2–4] ou de sa ramification ($n = 0$; $R^3 = H$; $R^4 = Me$, Et, nPr, iPr, nBu) ($n = 0$; $R^3 = R^4 = Me$)[5] a été envisagée. Malheureusement, les méthodes de détermination utilisées alors étaient essentiellement basées sur l'exploitation graphique des données expérimentales. Or, cette technique aboutit à des résultats pouvant prêter à contestation et ceci d'autant plus que le nombre de constantes à déterminer est important. Depuis, nous avons réalisé des affinements multiparamétriques qui permettent d'obtenir des constantes d'acidité[6] et de stabilité[7] beaucoup plus fiables. Les valeurs antérieures ont donc été remises en question et soumises à ces ajustements; de plus, des constantes inédites, relatives aux espèces formées avec Mg(II), Ca(II) et certains des acides précédents, ont été déterminées.

Finalement, pour compléter la description du pouvoir complexant de ces composés, l'influence de l'encombrement sur l'azote est examinée, par l'intermédiaire des complexes cuivriques des acides $R^1R^2NCH_2PO_3H_2$ ($R^1 = H$; $R^2 = Me$, Et) ($R^1 = R^2 = Me$, Et).

PARTIE EXPERIMENTALE

Préparations

La plupart des acides aminophosphoniques sont des produits d'origine Calbiochem chromatographiquement purs et utilisés sans purification ultérieure.

Les acides *N*-méthylaminométhylphosphonique et *N*-éthylaminométhylphosphonique proviennent de l'amination de l'acide chlorométhylphosphonique[1] (0,1 mole), par un excès (0,4 mole) de l'amine primaire appropriée, en présence d'une solution de soude (0,3 mole). Il faut opérer en autoclave, vers 100° pendant environ 6 hr. L'évaporation de la solution conduit à un résidu sirupeux qui contient, en plus du composé attendu, les phosphonates $HOCH_2PO_3^{2-}$ et $RN(CH_2PO_3)_2^{4-}$. Le passage du mélange sur résine échangeuse d'ions H^+ permet d'éliminer ces sous-produits qui sont d'abord élués. L'éluat contenant l'acide est recueilli et concentré; l'addition d'éthanol permettant d'isoler l'acide (Rdt. 50–60%).

Les acides *N*,*N*-dialkylaminométhylphosphoniques sont préparés par la méthode proposée par Moedritzer et Irani[8] à partir d'amine secondaire, de formaldéhyde, d'acide orthophosphoreux en présence d'acide chorhydrique. On aboutit à un chlorhydrate d'acide qui est purifié, comme précédemment, par chromatographie sur échangeur d'ions H^+. Les acides sont obtenus par recristallisations dans des mélanges méthanol, acétate d'éthyle (Rdt. 80%).

L'analyse élémentaire de ces produits et leur dosage pHmétrique donnent des résultats en très bon accord avec ceux attendus.[9]

Neutralisations

Les données expérimentales (v, pH) sont obtenues à partir des neutralisations, par la potasse, à 25° en milieu de force ionique "constante",[1] des acides seuls et en présence de cations. La chaîne de mesure potentiométrique est standardisée par les tampons habituels. Le tableau 1 résume

Tableau 1. Récapitulation des conditions expérimentales[a] (force ionique[1] = 0,100 = $[KNO_3] + 3C_M^0$; température de 25°)

Acide XPO_3H_2 X=	Cations M^{2+} M=	C_A^0 constant	C_M^0 constant	Rapports C_A/C_M	Résolution du pH mètre	Résolution de la burette[b]
NH_2CH_2	Cu		2.10^{-3}	0,66; 1; 1,5; 2; 2,5; 3	0,005	0,01
$NH_2CH_2CH_2^s$	Mg, Ca, Co, Ni, Zn	4.10^{-3}		1; 2		
$NH_2CH_2CH_2CH_2^s$ NH_2CHMe^c NH_2CHBu NH_2CHiPr NH_2CMe_2 $MeNHCH_2$	Cu		10^{-3}	0,66; 1; 1,5; 2; 2,5; 3	0,005	0,005
	Mg, Ca[d]	2.10^{-3}		0,2; 0,5; 1		
$EtNHCH_2$ Me_2NCH_2 Et_2NCH_2	Cu	$1,5.10^{-3}$		2; 3	0,001	0,005

Remarques. [a] Les acides non mentionnés n'ont donné lieu qu'à des études de constantes d'acidité. [b] La précision sur le volume est toujours meilleure que la résolution indiquée. [c] Les solutions à neutraliser sont préparées par pesée d'acide et non à partir d'une solution stock. [d] Uniquement dans le cas de l'acide amino-3 propylphosphonique.

les conditions opératoires: pour plus de détails, ainsi que pour la description des courbes de neutralisation obtenues, nous renvoyons aux publications antérieures.[2-5] Cependant nous apporterons quelques compléments relatifs aux précipitations. Il a été vu que les acides phosphoniques forment généralement des phosphonates basiques insolubles $RPO_3Cu.yCu(OH)_2$.[1] Cette précipitation est nettement retardée chez les acides aminophosphoniques mais elle subsiste toujours et correspond encore à un hydroxyphosphonate qui s'enrichit en $Cu(OH)_2$ lorsque le pH croît. Dans les mélanges de Cu(II) et d'acides amino-1 alkylphosphoniques comportant un excès de complexant ($C_A/C_M \geq 2$) la précipitation est imperceptible. Il en va différemment pour les composés substitués sur l'azote où l'apparition de sel basique est d'autant plus avancée que l'encombrement sur l'azote est important: par exemple, avec

Tableau 2. Constantes de stabilité des complexes de l'acide aminométhylphosphonique $\overset{+}{N}H_3CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces	log $\beta_{q/p}(3\sigma)$	Littérature		
			[e]	[f]	[g]
011	HA^-	10,05 (0,02)	10,0	9,97	9,86
021	H_2A	15,44 (0,01$_5$)	15,35	15,29	15,15
031	H_3A^+	15,88	17,2		
111	$MgHA^+$	11,38 (0,02)			
101	MgA	2,03 (0,03)			
111	$CaHA^+$	11,14 (0,03)			
101	CaA	1,71 (0,04)			
111	$CoHA^+$	11,79 (0,02)			12,73
101	CoA	4,45 (0,04)			4,78
122	CoH_2A_2	a			
112	$CoHA_2^-$	16,75 (0,1)			
102	CoA_2^{2-}	8,09 (0,05)			8,79
111	$NiHA^+$	11,69 (0,07)			12,75
101	NiA	5,29 (0,04)		4,94	4,90
122	NiH_2A_2	b			
112	$NiHA_2^-$	16,4 (0,6)			
102	NiA_2^{2-}	8,98 (0,05)		8,5	8,91
111	$CuHA^+$	12,56 (0,02)			13,25
101	CuA	8,12 (0,02)		7,77	7,85
1-11	$Cu(OH)A^-$	c			
122	CuH_2A_2	24,8 (0,2)			26,77
112	$CuHA_2^-$	20,20 (0,06)			
102	CuA_2^{2-}	14,65 (0,04)		14,1	14,06
111	$ZnHA^+$	11,72 (0,06)			12,72
101	ZnA	5,00 (0,08)			5,26
1-11	$Zn(OH)A^-$	d			
122	ZnH_2A_2	23,6 (0,3)			
					(ZnA_2^{2-}: 8,68)

a, b, c, d: avec la précision de nos mesures, la présence de ces complexes s'avère incertaine ($\sigma \sim \beta$); a ($\log \beta_{122} = 22,9$); b ($\log \beta_{122} = 22,6$); c ($\log \beta_{1-11} = -0,4$); d ($\log \beta_{1-11} = -1,9$).

[e]: μ variable ($C_A = 0,1$).[13] [f]: 25°, $\mu = 0,5$ ($NaClO_4$).[14] [g]: 25°, $\mu = 0,1$ ($NaClO_4$).[15]

Tableau 3. Constantes de stabilité des complexes de l'acide amino-2 éthylphosphonique $\overset{+}{N}H_3CH_2CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces[a]	$\log \beta_{qjp}(3\sigma)$	Littérature		
			[d]	[e]	[f]
011	HA^-	11,04 (0,03)	10,8	11,01	10,98
021	H_2A	17,285 (0,02)	17,8	17,98	17,27
031	H_3A^+	18,41	20,25	20,09	
111	$MgHA^+$	12,48 (0,07)			
101	MgA	2,13 (0,07)			
111	$CaHA^+$	12,22 (0,12)			
101	CaA	1,74 (0,13)			
111	$CoHA^+$	12,74 (0,07)			13,91
101	CoA	4,67 (0,06)			4,98
1-11	$Co(OH)A^-$[b]	−4,70 (0,06)			(CoA_2^{2-}: 8,07)
111	$NiHA^+$	12,80 (0,06)			13,90
101	NiA	5,20 (0,05)			5,69
122	NiH_2A_2	25,6 (0,5)			
112	$NiHA_2^-$	18,8 (0,2)			
102	NiA_2^{2-}[c]	10,1 (0,1)			10,50
111	$CuHA^+$	13,75 (0,04)			14,56
101	CuA	8,50 (0,02)			7,52
1-11	$Cu(OH)A^-$	1,04 (0,07)			
122	CuH_2A_2	27,1 (0,2)			29,20
112	$CuHA_2^-$	21,4 (0,2)			
102	CuA_2^{2-}	14,3 (0,5)			14,76
111	$ZnHA^+$	12,99 (0,08)			13,89
101	ZnA	6,16 (0,05)			6,36
1-11	$Zn(OH)A^-$	−1,70 (0,04)			
122	ZnH_2A_2	26,2 (0,2)			
					(ZnA_2^{2-}: 12,46)

[a] une décomposition, même faible, de l'acide de départ perturbe fortement les courbes de neutralisation.

[b] β_{1-11} peut être remplacé par β_{102} {$\log \beta_{102} = 8,5$ (0,3)}, mais l'écart-type σ_r est légèrement supérieur.

[c] β_{102} peut être remplacé par β_{1-11} {$\log \beta_{1-11} = -3,9$ (0,1)}. Dans les cas b et c, les paramètres β_{1-11} et β_{102} sont très fortement corrélés.

[d] μ variable ($C_A = 0,1$).[16] [e] conditions non précisées.[17] [f] 25°, $\mu = 0,1$ ($NaClO_4$).[15]

l'acide *N*,*N*-diméthylaminométhylphosphonique une précipitation est decelée pour $C_A/C_M = 2$; pH = 7,2; taux de neutralisation = 1,6, tandis qu'elle se produit beaucoup plus tôt avec l'acide *N*,*N*-diéthylaminométhylphosphonique ($C_A/C_M = 2$; pH = 6,6; taux de neutralisation = 1,1) rendant alors difficile l'étude des complexes. L'augmentation de la chaîne carbonée des acides ω-aminoalkylphosphoniques diminue l'acidité des solutions: lorsque le nombre d'atomes de carbone croît, la précipitation interfère pour des taux de neutralisation plus faibles.

Tableau 4. Constantes de stabilité des complexes de l'acide amino-3 propylphosphonique $\overset{+}{N}H_3CH_2CH_2CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

qjp	Espèces[a]	$\log \beta_{qjp}(3\sigma)$	Littérature
			[b]
011	HA^-	11,065 (0,04)	10,55
021	H_2A	17,95 (0,03)	17,40
031	H_3A^+	19,58	
111	$MgHA^+$	12,57 (0,05)	
101	MgA	2,01 (0,08)	
111	$CaHA^+$	12,37 (0,05)	
101	CaA	1,68 (0,07)	
111	$CuHA^+$	13,97 (0,05)	14,00
101	CuA	7,15 (0,2)	7,10
1-11	$Cu(OH)A^-$	0,1 (0,2)	
			(CuH_2A_2: 28,27)
			(CuA_2^{2-}: 13,47)

[a] des précipitations prématurées (hydroxydes, phosphonates) rendent les études des complexes difficiles (Cu^{2+}) ou impossibles (Ni^{2+}, Co^{2+}, Zn^{2+}...).

[b] 25°, $\mu = 0,1$ ($NaClO_4$).[15]

RESULTATS

Les tableaux 2 à 6 regroupent les constantes globales des stabilité $\beta_{qjp} = [M_qH_jA_p]/(m^q h^j a^p)$ obtenues à l'aide des programmes d'affinement MUPROT[6] et MUCOMP.[7] Les domaines de confiance 3σ attribués aux β_{qjp} sont généralement plus importants que ceux des affinements classiques, vu le plus grand nombre de paramètres ajustés. Les constantes relatives aux complexes hydroxylés (espèce: log β_{qj0}) utilisées dans les calculs ont été déterminées [$Cu_2(OH)_2^{2+}$ −10,7; $MgOH^+$ −11,9$_5$] ou sont tirées de la littérature[10]

Tableau 5. Constantes de stabilité des complexes des acides amino-1 alkylphosphoniques $\overset{+}{N}H_3CR^3R^4PO_3H^-(H_2A)$, à 25°, en milieu KNO_3 0,1*M*

R^3	R^4	*qjp*	Espèces	log $\beta_{qjp}(3\sigma)$	Littérature	
H	Me	011	HA^-	10,195 (0,025)		
		021	H_2A	15,78 (0,015)		
		031	H_3A^+	16,25		
		111	$MgHA^+$	11,54 (0,06)		
		101	MgA	2,00 (0,08)		
		111	$CuHA^+$	12,82 (0,05)		
		101	CuA	8,50 (0,02)		
		1-11	$Cu(OH)A^-$	−0,1 (1)		
		122	CuH_2A_2	25,9 (0,4)		
		112	$CuHA_2^-$	21,0 (0,1)		
		102	CuA_2^{2-}	15,40 (0,04)		
H	Et	011	HA^-	10,255 (0,02)	10,28 [b]	
		021	H_2A	15,91 (0,01)	16,03	
		031	H_3A^+		17,98	
H	nPr	011	HA^-	10,285 (0,02)	10,32	
		021	H_2A	15,96 (0,01)	16,15	
		031	H_3A^+		18,10	
H	iPr	011	HA^-	10,355 (0,04)	10,45	
		021	H_2A	16,15 (0,02)	16,45	
		031	H_3A^+	16,77	18,49	
		111	$MgHA^+$	11,73 (0,06)		
		101	MgA	2,15 (0,05)		
		111	$CuHA^+$	13,71 (0,02)		
		101	CuA	9,47 (0,01)		
		1-11	$Cu(OH)A^-$	1,7 (0,3)		
		122	CuH_2A_2	26,7 (0,5)		
		112	$CuHA_2^-$	22,53 (0,06)		
		102	CuA_2^{2-}	17,32 (0,05)		
H	nBu	011	HA^-	10,29 (0,03)	10,35	
		021	H_2A	15,99 (0,02)	16,17	
		031	H_3A^+	16,57	18,00	
		111	$MgHA^+$	11,59 (0,07)		
		101	MgA	2,03 (0,05)		
		111	$CuHA^+$	13,25 (0,03)		
		101	CuA	8,97 (0,01)		
		1-11	$Cu(OH)A^-$	0,8 (0,7)		
		122	CuH_2A_2	25,9 (0,6)		
		112	$CuHA_2^-$	21,60 (0,08)		
		102	CuA_2^{2-}	16,27 (0,05)		
Me	Me	011	HA^-	10,31 (0,03)[a]	10,43	10,31 [c]
		021	H_2A	16,115 (0,02)[a]	16,48	16,16
		031	H_3A^+	16,67	18,57	17,81
		111	$MgHA^+$	11,62 (0,07)		
		101	MgA	2,01 (0,06)		14,39 [d]
		111	$CuHA^+$	13,68 (0,08)		8,47
		101	CuA	9,13 (0,03)		28,69
		122	CuH_2A_2	27,25 (0,2)		
		112	$CuHA_2^-$	22,32 (0,09)		
		102	CuA_2^{2-}	16,64 (0,05)		15,29

[a] un autre lot de cet acide donne log β_{011} = 10,27 et log β_{021} = 16,11. La précision des mesures est insuffisante pour pouvoir trancher. Les valeurs retenues sont relatives à l'acide utilisé pour l'étude des complexes.

[b] conditions non précisées.[17] [c] 25°, μ = 0,1 (KCl).[18] [d] 25°, μ = 0,1 (KCl).[19]

Tableau 6. Constantes de stabilité des complexes des acides *N*-alkylaminométhylphosphoniques $R^1R^2\overset{+}{N}H\ CH_2PO_3H^-$ (H_2A), à 25°, en milieu KNO_3 0,1*M*

R^1	R^2	*qjp*	Espèces	log $\beta_{qjp}(3\sigma)$	Littérature
H	Me	011	HA^-	10,912 (0,006)	
		021	H_2A	16,222 (0,005)	
		031	H_3A^+	16,86	
		111	$CuHA^+$	13,325 (0,01)	
		101	CuA	8,29 (0,02)	
		1–11	$Cu(OH)A^-$	0,09 (0,09)	
		122	CuH_2A_2	25,9 (0,15)	
		112	$CuHA_2^-$	20,98 (0,1)	
		102	CuA_2^{2-}	14,59 (0,03)	
H	Et	011	HA^-	11,005 (0,01)	
		021	H_2A	16,341 (0,008)	
		031	H_3A^+	16,87	
		111	$CuHA^+$	13,415 (0,01)	
		101	CuA	7,72 (0,02)	
		1–11	$Cu(OH)A^-$	0,15 (0,06)	
		122	CuH_2A_2	26,31 (0,04)	
		112	$CuHA_2^-$	20,73 (0,05)	
		102	CuA_2^{2-}	13,0 (0,2)	
Me	Me	011	HA^-	11,063 (0,009)	
		021	H_2A	16,247 (0,010)	
		031	H_3A^+	16,70	
		111	$CuHA^+$	13,36 (0,02)	
		101	CuA	7,99 (0,03)	
		1–11	$Cu(OH)A^-$	0,20 (0,07)	
		122	CuH_2A_2	26,08 (0,1)	
		112	$CuHA_2^-$	20,84 (0,1)	
		102	CuA_2^{2-}	13,84 (0,06)	
Et	Et	011	HA^-	11,81 (0,03)	10,32 [a]
		021	H_2A	17,088 (0,03)	18,11
		111	$CuHA^+$	14,12 (0,01)	
		110	CuA	7,46 (0,05)	
		1–11	$Cu(OH)A^-$	−0,02 (0,1)	
		122	CuH_2A_2	27,56 (0,09)	

[a] 25°, $\mu = 1(KNO_3)$.[20]

($CaOH^+$ −12,9; $CoOH^+$ −9,8; $NiOH^+$ −9,3; $ZnOH^+$ −9,8). Les constantes globales de formation de H_3A^+ (β_{031}) sont calculées à partir des constantes d'acidités moyennement fortes déterminées par ailleurs.[12]

Pour simplifier la lecture, les résultats obtenus par d'autres auteurs ont été mis sous forme de constantes globales β_{qjp}. Signalons d'autres déterminations non mentionnées dans les tableaux: elles concernent la complexation de Be(II)[18] et de divers cations[19] par l'acide amino-1 méthyl-1 éthylphosphonique, des alcalinoterreux par les acides amino-2 hydroxy-1 alkyl phosphoniques[21] et de Cr(III) par les acides amino-2 alkylphosphoniques;[22] des études chromatographiques,[23,24] conductimétriques et spectrophotométriques[24] ayant été menées sur les complexes des acides aminoalkylphosphoniques. La comparaison avec les valeurs de la littérature s'avère décevante. En effet, des divergences très importantes sont observées qui ne peuvent être uniquement imputées aux différences de force ionique ou au mode d'expression des constantes (constantes mixtes au lieu de constantes exprimées en concentrations). Leur explication se trouve dans les méthodes de détermination trop sommaires ou dans l'omission d'espèces non négligeables. Il se pourrait également que la pureté des produits soit en cause: elle serait alors capable d'expliquer les écarts observés sur les constantes d'acidité de l'acide amino-2 éthylphosphonique (tableau 3).

DISCUSSION

Le schéma microscopique de dissociation des acides aminophosphoniques est représenté sur la figure 1a. Les constantes d'acidité de l'acide triméthylammonium méthylphosphonique, qui est un zwitterion permanent ($Me_3\overset{+}{N}CH_2PO_3H^-$, log k_{011} = 5,099)[1] et de l'acide diméthylaminométhylphosphonique (log β_{021} − log β_{011} = 5,184) peuvent être considérées comme identiques, compte-tenu de la perturbation provoquée par le méthyle supplémentaire. Cette similitude indique sans ambiguïté que les acides aminophosphoniques sont sous forme dipolaire

$$(H_2A):H\overset{+}{N}—R—PO_3H^-$$

et qu'ils se dissocient pour former ensuite

$$\overset{|}{\overset{+}{H}}N—R—PO_3^{2-}(HA^-).$$

Les formes H_3A^+, HA^- et A^{2-} correspondent donc aux espèces microscopiques encadrées sur la figure 1a.

L'interaction d'un cation M^{2+} avec les formes symbolisées par HA^- et A^{2-} aboutit, dans le cas le plus général, à l'apparition des espèces MHA^+, $M(HA)_2$, $M(HA)A^-$, MA, MA_2^{2-} et $M(OH)A^-$. Nous examinerons plus particulièrement le cas des espèces MHA^+, MA et $M(OH)A^-$, les autres découlant de celles-ci par addition de motifs HA^- et A^{2-}.

Dans le complexe protoné MHA^+ la coordination s'effectue essentiellement par le groupement phosphonate (voir fig. 1b). Comme précédemment, ce choix découle de la comparaison de la stabilité des phosphonates $Me_3\overset{+}{N}CH_2PO_3Cu$ ($\log \beta_{011} = 2{,}18$)[1] et $Me_2\overset{+}{N}HCH_2PO_3Cu$ ($\log \beta_{111} - \log \beta_{011} = 2{,}30$): il fallait d'ailleurs s'y attendre étant donné qu'une proposition considérable de HA^- est sous forme de

$$\overset{|}{\overset{+}{H}}N—R—PO_3^{2-}.$$

Des complexes protonés ont été isolés et étudiés par diverses méthodes spectroscopiques:[25–28] il a été montré que dans ces espèces seuls les atomes d'oxygène du groupement phosphonate échangent des liaisons avec le métal, l'azote étant sous forme ammonium.

Le départ du proton fixé sur l'azote libère la fonction amine et conduit à des espèces du type MA. Ce complexe doit correspondre en réalité à la coexistence des deux formes microscopiques les plus probables: d'une part le chélate où la liaison azote–métal s'ajoute à la liaison phosphonate–métal et d'autre part l'espèce comportant une fonction amine libre (Fig. 1b). Ainsi, la stabilité des complexes des alcalino-terreux et de Ca(II) en particulier est peu améliorée lorsque l'on passe de la complexation par $-PO_3^{2-}$ seul ($1{,}09 < \log \beta_{111} - \log \beta_{011} < 1{,}31$; tableaux 2 à 4) à celle qui ajoute la fonction amine ($1{,}68 < \log \beta_{101} < 1{,}74$). La contribution de $-PO_3^{2-}$ à la stabilité est donc importante. En d'autres termes, MA doit correspondre à deux formes I et II (Fig. 1b), la forme I étant loin d'être négligeable. Ces observations permettent d'expliquer les résultats de Carter *et al.*[29] qui ont déterminé les constantes de stabilité des complexes de Ca(II) avec l'acide nitrilotri(méthylène phosphonique) ($\log \beta_{101} = 6{,}68$) et de son *N*-oxyde ($\log \beta_{101} = 5{,}69$). La faible atténuation de stabilité, non rencontrée chez les aminocarboxyliques correspondants, est explicable si l'on admet, en plus du chélate, l'existence d'une forme où l'azote est libre. Par contre, dans le cas des métaux de transition, un net regain de stabilité est observé lorsqu'on l'on passe de MHA^+ à MA (voir tableaux) traduisant l'intervention d'une liaison azote–métal avec formation d'un chélate (Fig. 1b, forme II). Des études spectroscopiques menées sur des complexes du type MA, ont mis en évidence que le métal était lié à la fois aux atomes d'oxygène du groupement phosphonate et à l'atome d'azote.[28,30] Une forme CuA, où l'amine

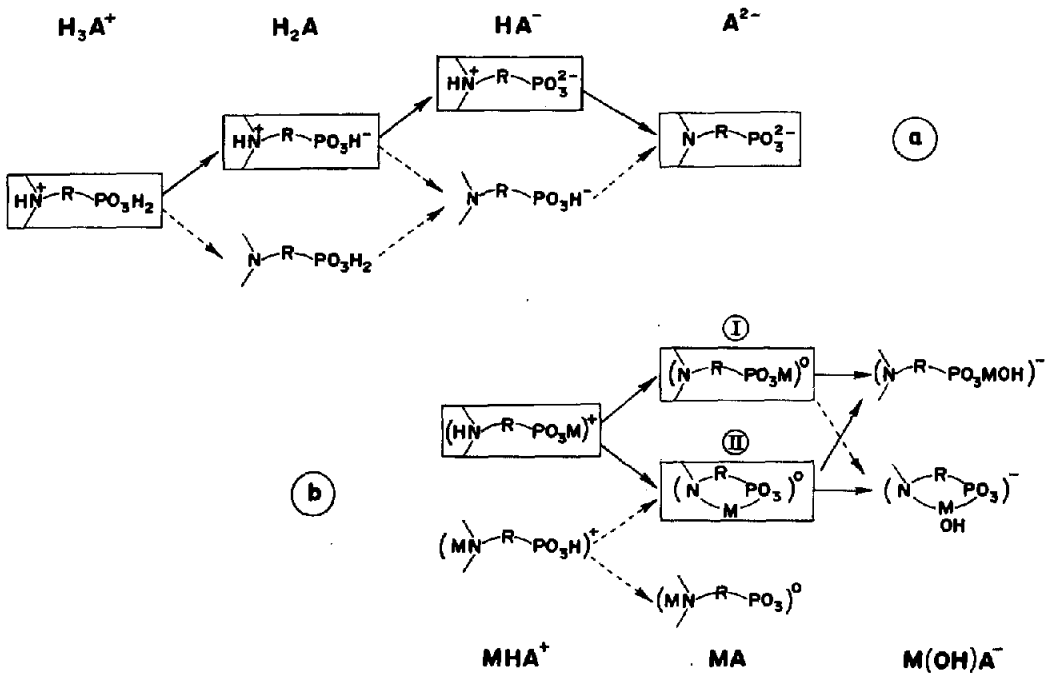


Fig. 1. Schémas microscopiques de dissociation des acides aminoalkylphosphoniques (*a*) et des complexes MHA^+, MA et $M(OH)A^-$ (*b*).

$-NH_2$ n'est pas liée au cuivre a été signalée par Jezowska-Trzebiatowska *et al.*[31] Cependant, vu le pH de travail (HCl 0,05*M*) la fonction amine doit être protonée: ces auteurs ont cru être en présence de CuA, alors qu'il doit s'agir de $CuHA^+$.

Evidemment, le complexe hydroxylé $M(OH)A^-$ résulte de la fixation d'un hydroxyle sur les formes MA précédentes (Fig. 1b). De plus, une rupture du chélate, résultant de la compétition entre l'oxygène de l'hydroxyle et l'azote, est concevable.

Les nombreuses constantes disponibles méritent évidemment une synthèse approfondie qui fera l'objet d'une publication particulière.

REFERENCES

1. M. Wozniak et G. Nowogrocki, *Talanta*, 1979, **26**, 381.
2. M. Wozniak, J. Nicole et G. Tridot, *Chim. Anal. Paris*, 1971, **53**, 512.
3. *Idem, ibid.*, 1972, **54**, 147.
4. *Idem, Analusis*, 1972, **1**, 498.
5. *Idem, Bull. Soc. Chim. France*, 1972, 4445.
6. M. Wozniak et G. Nowogrocki, *Talanta*, 1978, **25**, 633.
7. *Idem, ibid.*, 1978, **25**, 643.
8. K. Moedritzer et R. R. Irani, *J. Org. Chem.*, 1966, **31**, 1603.
9. M. Wozniak, *Thèse*, Lille, 1977.
10. K. B. Yatsimirskii et V. P. Vasil'ev, *Instability Constants of Complex Compounds*, Van Nostrand, Princeton, 1960.
11. M. Micheloni, A. Sabatini et A. Vacca, *Inorg. Chim. Acta*, 1977, **25**, 41.
12. M. Wozniak et G. Nowogrocki, *Bull. Soc. Chim. France*, 1978, 1-153.
13. V. Chavane, *ibid.*, 1948, 774.
14. D. Giron, G. Duc et G. Thomas, *Compt. Rend.*, 1971, **272C**, 1022.
15. H. Sakurai, H. Okumura et S. Takeshima, *Yakugaku Zasshi*, 1976, **96**, 242.
16. P. Rumpf et V. Chavane, *Compt. Rend.*, 1947, **224**, 406.
17. J. P. Berry, A. F. Isbell et G. E. Hunt, *J. Org. Chem.*, 1972, **37**, 4396.
18. N. M. Dyatlova, V. V. Medyntsev, T. Ya. Medved et M. I. Kabachnik, *Zh. Obshch. Khim.*, 1968, **38**, 1065; *J. Gen. Chem. USSR*, 1968, **38**, 1025.
19. N. M. Dyatlova, V. V. Medyntsev, T. M. Balashova, T. Ya. Medved et M. I. Kabachnik, *ibid.*, 1969, **39**, 329; *J. Gen. Chem. USSR*, 1969, **39**, 309.
20. R. P. Carter, R. L. Carroll et R. R. Irani, *Inorg. Chem.*, 1967, **6**, 939.
21. A. V. Serdyukova, A. N. Lazarev, G. M. Baranov et V. V. Perekalin, *Zh. Neorgan. Khim.*, 1975, **20**, 536; *Russ. J. Inorg. Chem.*, 1975, **20**, 299.
22. M. Makles-Grotowska, J. Starosta et W. Wojciechowski, *ibid.*, 1972, **22**, 719; *Russ. J. Inorg. Chem.*, 1977, **22**, 396.
23. M. Darriet, P. Fénot, A. Cassaigne et E. Neuzil, *J. Chromatog.*, 1973, **77**, 239.
24. P. Fénot, *Thèse*, Bordeaux, 1975.
25. M. A. Busch et D. E. Pennington, *Inorg. Chem.*, 1976, **15**, 1940.
26. A. G. Menke et F. Walmsley, *Inorg. Chim. Acta*, 1976, **17**, 193.
27. W. Wojciechowski, A. Arkowska et A. Jablonski, *Zh. Neorgan. Khim.*, 1977, **22**, 94; *Russ. J. Inorg. Chem.*, 1977, **22**, 521.
28. P. Fenot, J. Darriet, C. Garrigou-Lagrange et A. Cassaigne, *J. Mol. Struct.*, 1978, **43**, 49.
29. R. P. Carter, M. M. Crutchfield et R. R. Irani, *Inorg. Chem.*, 1967, **6**, 943.
30. W. Wojciechowski et M. Mackles, *Zh. Neorgan. Khim.*, 1975, **20**, 1015; *Russ. J. Inorg. Chem.*, 1975, **20**, 570.
31. B. Jezowska-Trzebiatowska, H. Szyszuk, A. Antonov, M. Ratajczak et R. Tyka, *Univ. Adama Mickiewicza Poznaniu, Wydz. Mat., Fiz. Chem., [Pr.], Ser. Fiz.*, 1975, **19**, 215; *Chem. Abstr.*, 1976, **85**, 158822.

Summary—The acids under study differed from one another in length of the carbon chain [$\overset{+}{N}H_3(CH_2)_nPO_3H^-$ for n = 1, 2, 3], substitution on the nitrogen atom [$R^1R^2\overset{+}{N}HCH_2PO_3H^-$ for R^1 = H; R^2 = Me, Et and $R^1 = R^2$ = Me, Et] or extent of branching on the carbon atom adjacent to functional groups [$\overset{+}{N}H_3CR^3R^4PO_3H^-$ for R^3 = H; R^4 = Me, Et, nPr, iPr, nBu and $R^3 = R^4$ = Me]. Acidity constants and overall stability constants of complexes formed with Ca(II), Mg(II), Co(II), Ni(II), Cu(II), Zn(II) were obtained with the multiparametric refinement programs MUPROT and MUCOMP, applied to potentiometric data, obtained at 25°, in a 0.1*M* potassium nitrate medium. In the most general case, the existing species are MHA^+, MA, $M(OH)A^-$, MH_2A_2, MHA_2^- and MA_2^{2-}, where A^{2-} stands for the fully ionized ligand; preliminary examination of results points out some predominant microscopic forms.

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EVALUATION OF ACID–BASE TITRATION CURVES OBTAINED BY THE TRIANGLE-PROGRAMMED TITRATION TECHNIQUE IN FLOWING SOLUTIONS

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Summary—Different evaluation techniques for triangle-programmed coulometric acid–base titration curves obtained with various detector systems are compared. In the case of potentiometric detection, hardware differentiation and linearization of the titration curves was investigated. Photometric end-point detection with single or mixed indicators was also studied. It was concluded that among the techniques studied the hardware potentiometric differentiation and the photometric detection with an indicator mixture are the most advantageous.

Many of the mechanized or automatic analysers carry out the determinations with flowing solutions. Most of the segmented or unsegmented flow analysers employ the relation between detector signal and concentration directly for evaluation of the results.[1–3] Ordinary titration to the end-point or the standard-addition method is only occasionally used.[4–6] The reliability of all these methods depends on the stability of the detectors used. It is commonly accepted that an analytical method using complete titration is much more reliable than a direct-relationship method. Recently efforts have been made in various laboratories to combine the simplicity and high rate of analysis of the flow methods with the advantages of the titrimetric methods. These efforts led us to introduce the so-called triangle-programmed titration technique, the theory[7,8] and practice[9–12] of which have been described.

The principle of the technique can be given shortly as follows.

The sample solution of constant concentration C_s is streamed in the flow-through analytical channel of the apparatus at a constant rate, V. At a certain point in the channel a selective reagent is introduced into the flow. After the reagent and sample streams have mixed, any cross-section of the mixed streaming solution is almost completely homogeneous. To carry out the determination a reagent addition-rate *vs.* time program with the shape of an isosceles triangle is used. That is, starting from zero, the reagent addition-rate V_R is increased according to the equation $V_R = nt$ where t = time ($0 < t \leqslant \tau$). After $t = \tau$ the reagent addition rate is decreased to zero according to the equation $V_R = (2\tau - t)n$.

As a result of the reagent-addition program, the reagent–sample mixture ratio in each infinitesimally thin segment of the streaming solution will be different. The fraction of reagent increases continuously as t increases from zero to τ and then it decreases again to zero. In this way the degree of titration first increases from segment to segment and then decreases. If an appropriate detector cell is placed in the flowing solution mixture, the degree of titration can be monitored. Since there is a delay before the infinitesimally thin solution segments of different degrees of titration reach the detector section, there will also be a time delay between achievement of a particular reagent addition-rate and the appearance of the corresponding detector signal. If the reagent addition-rate (V_R) well before the turning point $t = \tau$ exceeds the value which is stoichiometrically equivalent to the sample mass-flow (C_sV), then two separate segments will have a composition corresponding to 100% titration. The recorded detector-signal *vs.* time curve then appears as two titration curves connected to each other as mirror images; from the time period (Q) between the appearance of the equivalence points $t_E(1)$ and $t_E(2)$, the stoichiometry of the titration reaction, the parameters of the reagent addition program and the sample mass-flow, C_sV, the sample concentration can be calculated.

That is for the reaction

$$aS + bR = cP_1 + cP_2 \qquad (1)$$

$$C_s = \frac{2\tau - Q}{(a/bn).V} \qquad (2)$$

as shown elsewhere.[8] From the constants and the value of Q, C_s can be calculated, or it can be determined easily from Q and an appropriate calibration graph.

The coulometric variation of the triangle-programmed titration technique has already proved most satisfactory in practice and applicable to a variety

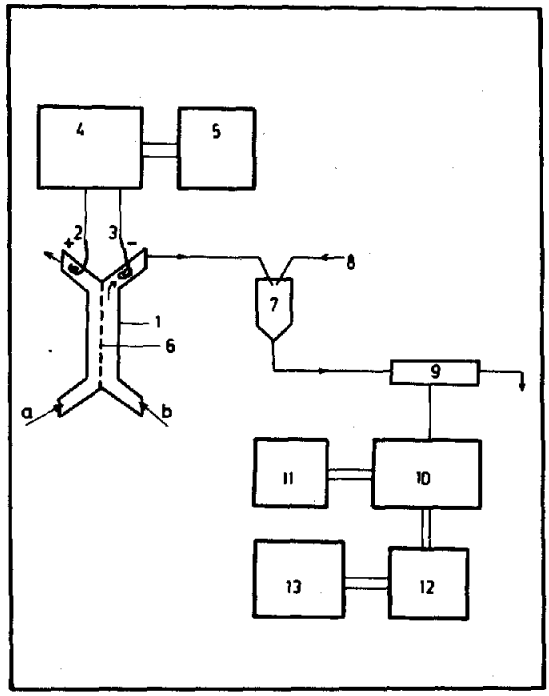


Fig. 1. Experimental set-up for triangle-programmed titrations with electrolytically generated reagents (for details, see text).

of analytical tasks. Various detectors and electrolytically generated titrants have been used in these studies. In continuing our work with this technique our aim is to work out appropriate simple automatic evaluation methods and apparatus, bearing in mind that some types of detector or titration reaction may create special problems in the location of the equivalence point. The aim of the present work was to investigate the applicability of various end-point location and evaluation methods in coulometric triangle-programmed acid–base titrations of flowing solutions.

EXPERIMENTAL

Apparatus

Several types of apparatus used in triangle-programmed titrations have been described in detail elsewhere.[9–12] Parts and units used earlier were employed in constructing the experimental set-up for the present studies.

A schematic view of the apparatus used is given in Fig. 1. The titrant (OH^- ions) was produced in an electrolysis cell (1) which contained two flow-through compartments (a,b) separated from each other. Two platinum-wire spirals (2), (3) served as generator electrodes and were connected to the output of a Radelkis type OH-405 current generator (4) controlled by a Philips type pM 5168 or PAR Model 175) programmer which produced the appropriate single triangle-shaped time program.

The two electrolysis half-cells were in electrical contact since in one section of the cell wall between them there was a window covered with dialysis membrane (6). Potassium nitrate solution (0.1 *M*) was pumped through the two half-cells by a peristaltic pump (LABOR MIM type OL-602). The solution stream passing compartment (a) was fed to waste while the stream leaving the cathodic compartment (b) entered a drip vessel (7) which served as a mixing chamber of small dead-volume. The sample stream (8) was pumped into the mixing chamber at constant rate with a peristaltic pump (LKB Varioperpex 12000). From the drip vessel the mixed stream of reagent-generation solution and sample was passed through the flow-through detector compartment (9) and overflowed to waste. The detector section (10) was provided with a Keithley Type 604 differential electrometer for potentiometric measurements and a Spekol Zeiss spectrophotometer for photometric measurements. A Radelkis type OH-814/1 recorder or occasionally an EMG type TR-1659 digital voltmeter (11), an interface (12) and an EMG type 666 computer (13) completed the apparatus.

Detectors

Three different kinds of detector were used, schematic drawings of which are shown in Fig. 2. The potentiometric detector (a) contains a microcapillary pH-sensitive glass electrode (14) (Radelkis type OP-7431) and a saturated calomel electrode (15): the differential potentiometric detector (b) is made of two microcapillary type glass electrodes and a delay coil (16) inserted between them; for the photometric measurements (c) a flow-through photometric cuvette was used as the detector section.

RESULTS AND DISCUSSION

Potentiometric methods

The theoretical titration curve obtained by the triangle-programmed titration method consists of two symmetrical curves as shown in Fig. 3. This curve results from titration of a strong acid. The left-hand part of the curve, sections A and B, is exactly the same as the conventional potentiometric titration curve. The potential jump gives the equivalence point,

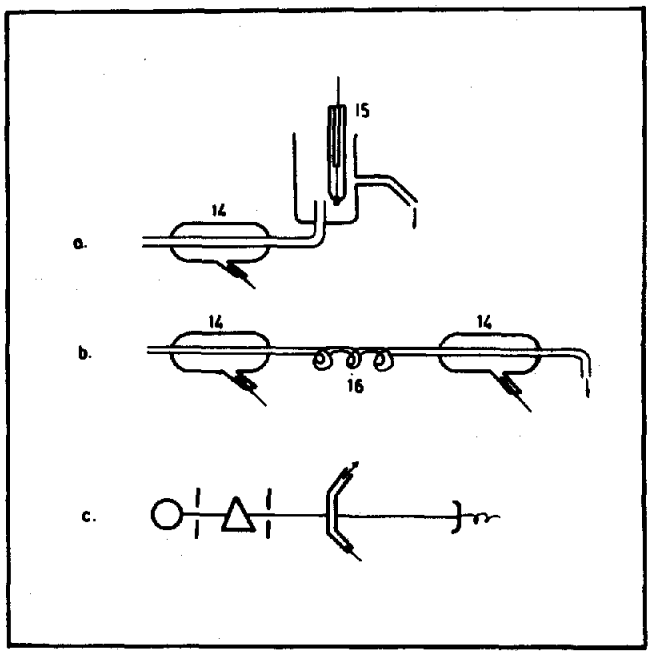


Fig. 2. Detectors used for the triangle-programmed titrations. a, Potentiometric detector. b, Differential potentiometric detector. c, Photometric detector.

i.e., the point where the flux of generated hydroxide ions is exactly the same as the flux of the acid to be determined. After the equivalence point the generating current still increases and the mixed stream contains an excess of hydroxide ions. Once its maximum is reached the generating current is decreased and the amount of generated hydroxide ions also decreases. The equivalence point will be passed again and after the generation program is over, the flow consists of the original acid solution. This second part of the curve, sections C and D, represents the titration of a strong base with a strong acid. The time Q elapsed between the two equivalence points $t_E(1)$ and $t_E(2)$ is linearly dependent on the concentration of the acid as described by equation (2). The experimentally obtained curve for titration of $1 \times 10^{-4}M$ hydrochloric acid is shown in Fig. 4. As can be seen, the curve is not strictly symmetrical. The part which rep-

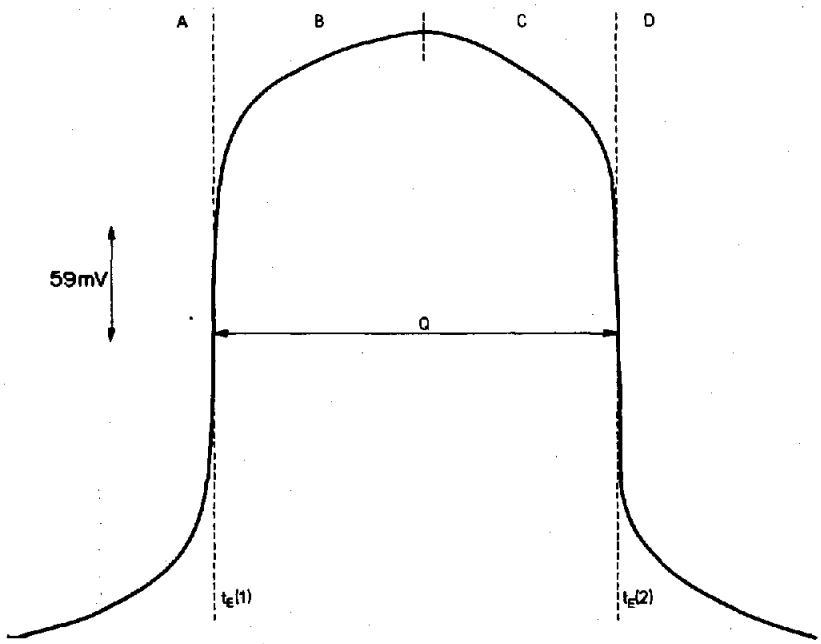


Fig. 3. Theoretical titration curve of a strong acid ($10^{-4}M$).

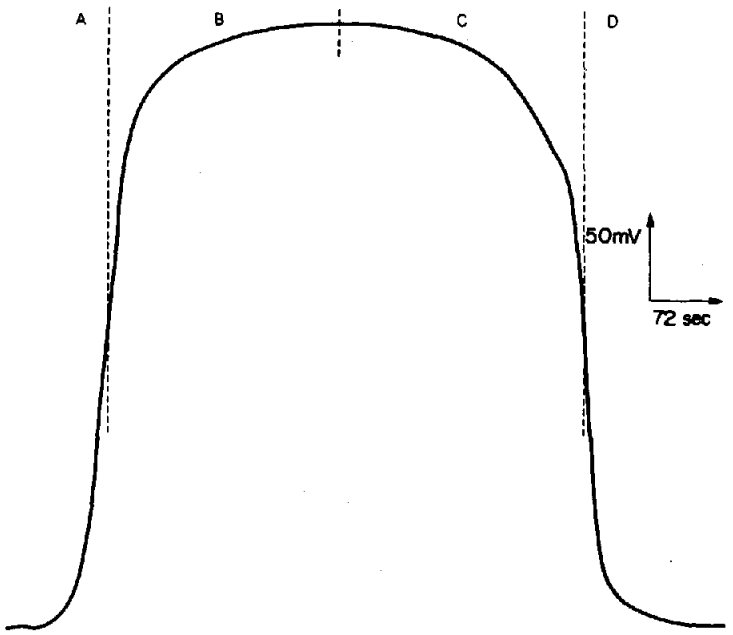


Fig. 4. Potentiometric triangle-programmed titration curve of $10^{-4}M$ hydrochloric acid. $i_{max} = 5$ mA; $2\tau = 130$ sec.

resents the titration of strong base with strong acid, sections C and D, is somewhat distorted because of tailing. Sometimes fluctuations in the measured potential can also be observed on the curve, and this is mostly due to electrical noise and incomplete mixing of the analyte and titrant before the measuring point. The disturbances caused by incomplete mixing can be overcome by employing a more effective mixer or by measuring the potential further away from the point of confluence, but unfortunately this can increase the tailing of the curve and also the time of the analysis.

The equivalence points can be obtained manually from the steepest parts of the potential jumps. However, various methods are available for the automatic evaluation of the titration curves.

Linear transformation of the titration curve

One numerical method for determining the equivalence point is the linear transformation of the titration curve. This method was first introduced by Sørensen[13] and later developed further by Gran[14] and Ingman and Still.[15] The derivation of the linear equation describing the course of the titration of any monobasic acid by the triangle-programmed titration method will be given.

The following equilibria exist in the system:

$$H^+ + A^- \rightleftharpoons HA \qquad K_{HA} = \frac{[HA]}{[H^+][A^-]} \tag{3}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_W = [H^+][OH^-] \tag{4}$$

where K_{HA} is the stability constant of the acid HA and K_w is the ionic product of water. The following balances can be written:

$$C_S = [HA] + [A^-] \tag{5}$$

$$V_R = nt = n([A^-] - [H^+] + [OH^-]) \tag{6}$$

$$V_S = C_S V \tag{7}$$

In the titration of monobasic acids, $a = b$ and at the equivalence point:

$$V_R = V_S \tag{8}$$

$$nt_E = C_S V \tag{9}$$

Combination of equations (3), (5), (6) and (9) gives

$$t_E - t = [H^+]K_{HA}t + \frac{V}{n}([H^+] - [OH^-]) \times (1 + [H^+]K_{HA}). \tag{10}$$

When data from section A in Fig. 3 are evaluated, equation (10) can be approximated to:

$$t_E - t = \frac{V}{n}[H^+]. \tag{11}$$

In section B the mixed stream contains an excess of hydroxide ions and equation (10) can be approximated to:

$$t - t_E = \frac{V}{n}[OH^-] = \frac{V}{n}\frac{K_W}{[H^+]}. \tag{12}$$

If $[H^+]$ is measured potentiometrically, *e.g.*, with a glass electrode, the Nernst equation holds:

$$E = E^0 + S \log [H^+]. \tag{13}$$

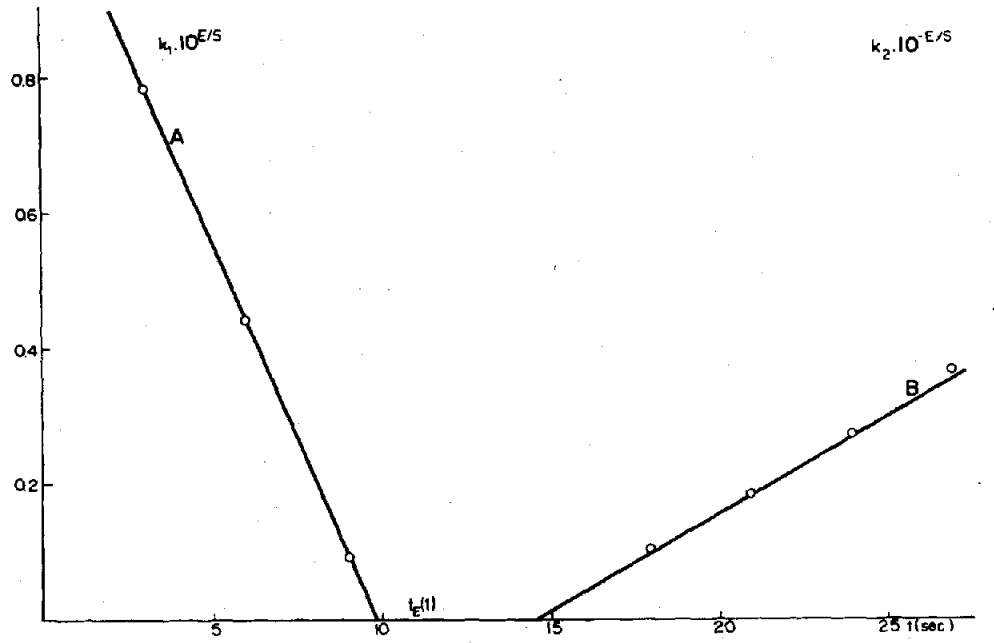


Fig. 5. Linear transformed titration curves obtained when data from Fig. 4 are evaluated by use of equation (11a) for branch A and (12a) for branch B.

If V and n are kept constant, equations (11) and (12) can be expressed as follows:

$$t_E - t = k_1 10^{E/S} \tag{11a}$$

$$t - t_E = k_2 10^{-E/S}. \tag{12a}$$

It is not necessary to know the absolute values of E^0, V, n and K_w because these parameters can be included in the constants k_1 and k_2 which can be arbitrarily chosen. The value of S should be known.

When equations (11a) and (12a) are plotted as functions of t, two straight lines are obtained. These lines theoretically intersect each other on the t-axis at the point t_E. Equation (11a) can be used for sections A and D in the determination of $t_E(1)$ and $t_E(2)$. Equation (12a) is used when data from branches B and C are evaluated for the determination of $t_E(1)$ and $t_E(2)$. This means that theoretically the equivalence points can be obtained automatically in an easy manner. When data from a real titration curve (Fig. 4) are evaluated by the method described, the curves given in Figs. 5 and 6 are obtained. However, as can

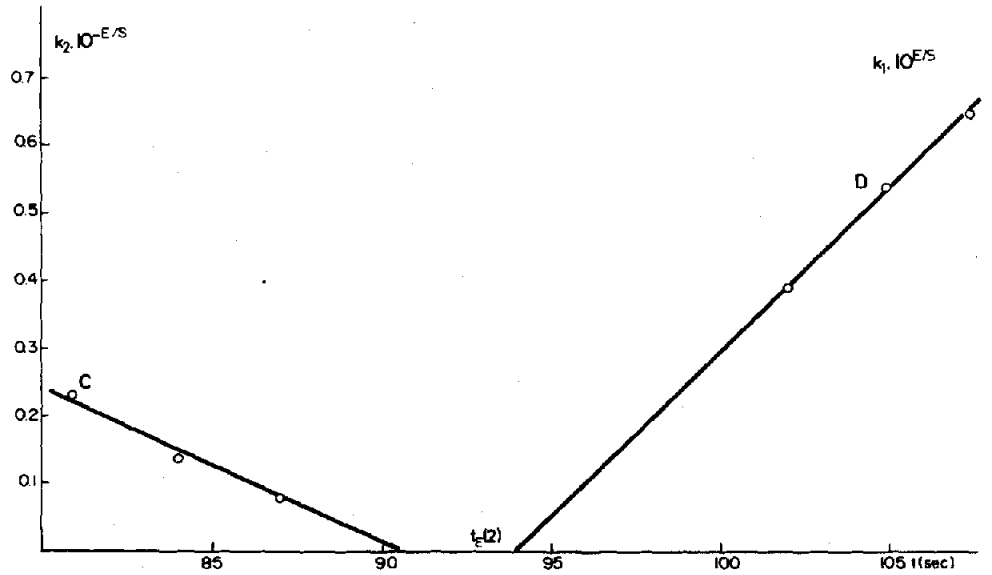


Fig. 6. Linear transformed titration curves obtained when data from Fig. 4 are evaluated with equation (11a) for branch D and (12a) for branch C.

be seen in these figures, neither branches A and B nor C and D intersect each other on the t-axis as in theory they should. The discrepancy is too great to be attributed to interference by carbonate in the flowing solution. The point of intersection of the two lines lies below the t-axis but coincides quite well with the point of the steepest part of the potential jumps in Fig. 4. The time interval corresponding to the distance between the two intersection points with the t-axis can be as much as 1–3% of the total program length (2τ). The smaller the 2τ-value and the lower the concentration of the acid, the longer this time interval. [For example, in titration of $10^{-4}M$ hydrochloric acid by a triangle program with a 95-sec length, the differences of $t_E(1)$ and $t_E(2)$ from the equivalence point were 2.5 and 1.5 sec, but were much shorter than 1% of the program length (95 sec) in the case of $10^{-3}M$ hydrochloric acid.]

The same is true for parts C and D of the titration curve in certain cases (low concentration, small 2τ-value). The branch D, although linear near the t-axis, is curved. This non-linearity is due to the tailing effect and is a drawback as it can make the automatic location of $t_E(2)$ quite difficult. The calibration graph of Q *vs.* concentration is linear.

When a weak acid, *e.g.*, acetic acid, is titrated a different transformation should be used for the linearization. Equation (10) can be approximated to

$$t_E - t = [H^+] K_{HA} t \tag{13}$$

or, if $[H^+]$ is measured potentiometrically:

$$t_E - t = k_3 10^{E/S} t \tag{13a}$$

When equation (13a) is used in the determination of t_E, the absolute starting point of the titration should be known. (In our case, however, t_0 is unknown.) This disadvantage can be overcome by the method for titration of weak acids given by Sørensen in his original paper.[13] Equation (13a) is divided by t and equation (13b) is obtained:

$$\frac{t_E}{t} - 1 = k_3 10^{E/S}. \tag{13b}$$

By plotting $10^{E/S}$ as a function of $1/t$ a straight line will be obtained. The line intercepts the $1/t$ axis at the point $1/t_E$. When t_E is determined in this way, t_0 can be arbitrarily chosen. Equation (13b) can be used to evaluate data from sections A and D. Equation (12a) should be used for sections B and C in the titration of weak acids. When data from a titration of $5 \times 10^{-4}M$ acetic acid Fig. 7 are evaluated by means of equations (13b) and (12a), the curves in Figs. 8 and 9 are obtained. Neither the branches A and B nor C and D give the same t_E. In construction of the calibration line the averages of the two $t_E(1)$ and $t_E(2)$ values are used. As can be seen in Fig. 8 the branch A is not linear but with increasing concentration of the acid, from about $8 \times 10^{-4}M$, the line will be straight. When equation (11a) is used in the evaluation of data from section A in the titration of acetic acid at concentrations less than $8 \times 10^{-4}M$, straight lines are obtained. At low concentrations acetic acid is dissociated to such a degree that the titration can be regarded as virtually a titration of a strong acid. Equation (12a) gives straight lines with data from sections B and C at any concentration. Data from section D give linear plots with equation (13b). Only at concentrations higher than $8 \times 10^{-4}M$ will the line near the equivalence point be curved.

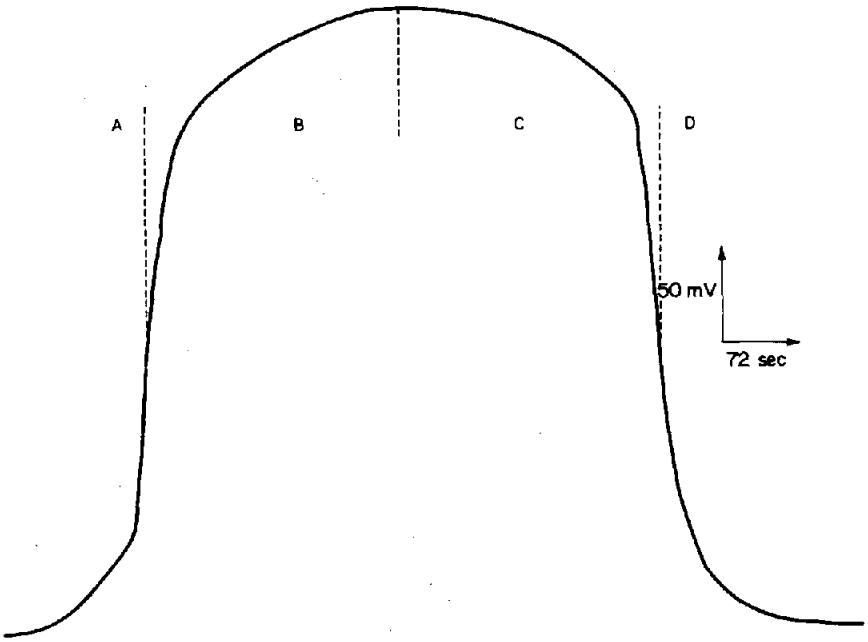


Fig. 7. Potentiometric triangle-programmed titration curve of $5 \times 10^{-4}M$ acetic acid, $i_{max} = 5$ mA; $2\tau = 130$ sec.

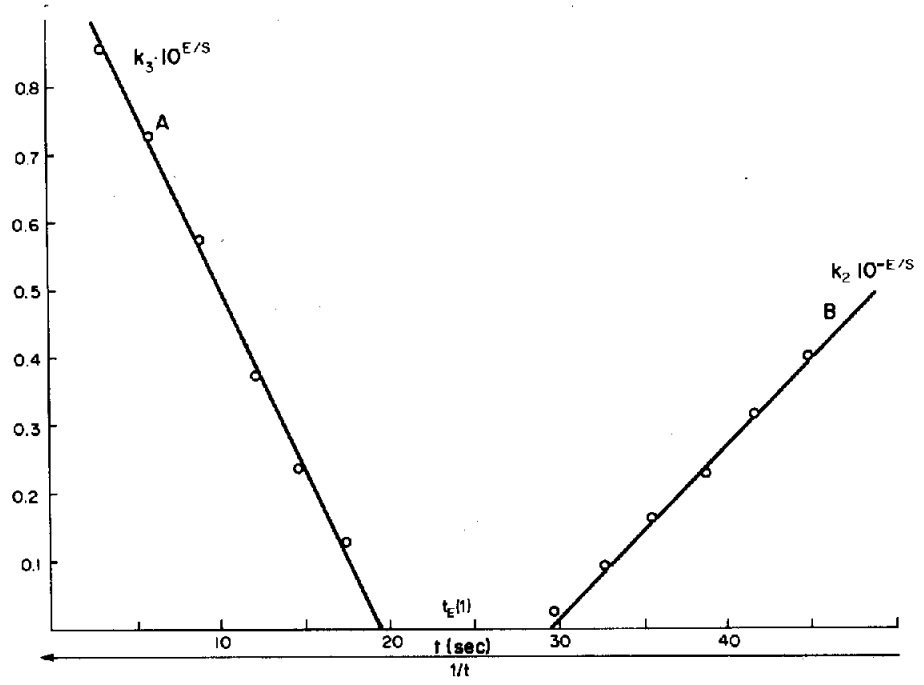


Fig. 8. Linear transformed titration curve obtained when data from Fig. 7 are evaluated with equation (13b) for branch A and (12a) for branch B.

Differentiation of the titration curve

Software method. The equivalence point of the titration can also be determined, as is well known, by differentiating the original $E = f(t)$ curve. The plot of dE/dt *vs.* t forms a peak with t_E at the top. When the second derivative d^2E/dt^2 is plotted as a function of t the curve obtained has two peaks, one on each side of the t-axis. The point where the plot crosses the t-axis between the peaks gives t_E. These methods are used only to locate the inflection point of the original titration curve. In most practical cases, the equivalence point and the inflection point are close enough for such techniques to be unnecessary. From the shape of the titration curves obtained in practice in our method, however, it is obvious that if an automatic software differentiation method is to be used, it must be combined with a curve-smoothing

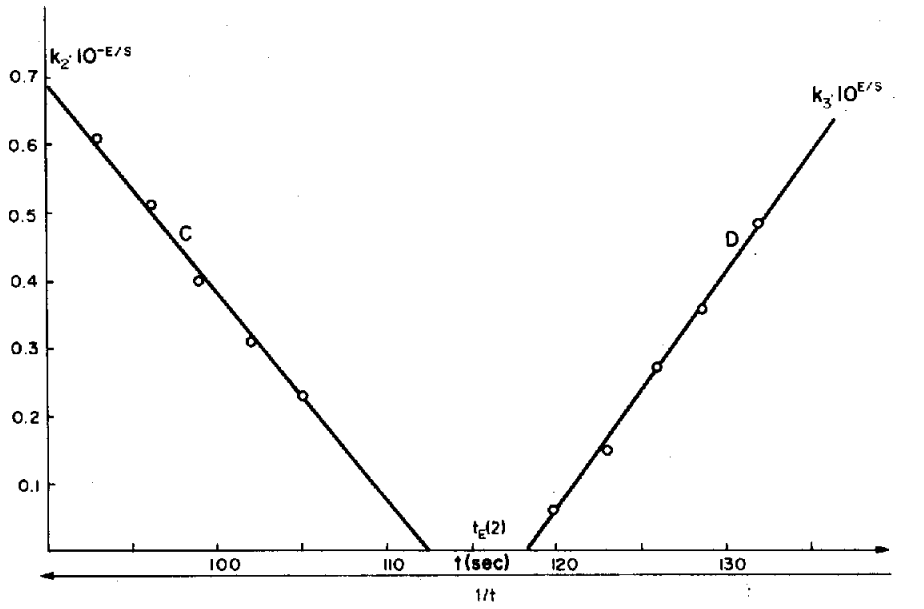


Fig. 9. Linear transformed titration curve obtained when data from Fig. 7 are evaluated with equation (13b) for branch D and (12a) for branch C.

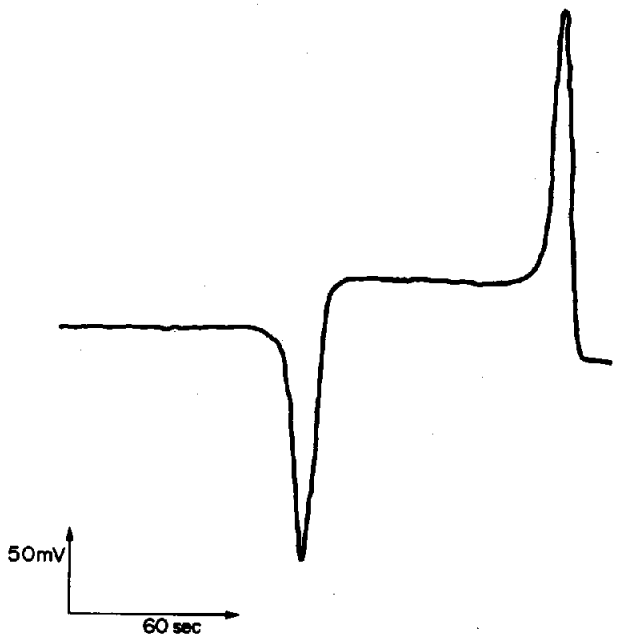


Fig. 10. The hardware differential curve of titration of $4 \times 10^{-4}M$ acetic acid, $i_{max} = 3.75$ mA, $2\tau = 144$ sec.

or curve-fitting procedure. In that way the effects of statistical and electrical noise can easily be eliminated. The curve smoothing or fitting, however, requires considerable off-line computer operation and a computer with considerable memory capacity. The detailed results of our studies of the computerized evaluation of triangle-programmed titrations with software differentiation will be published later.

Hardware method. A differential curve can also be obtained if two electrodes of the same kind are placed an appropriate distance apart in the direction of the flow.[9] By this method the concentration gradient between these two points is measured. The differential curve of the titration of acetic acid obtained by the hardware method is given in Fig. 10. The curve shows well-defined peaks at the two equivalence points. These peaks can easily be automatically located by digital or analogue methods.

Photometric methods

In the triangle-programmed photometric acid–base titrations an indicator is added to the solution to be analysed and the flow goes through a cell where the absorbance is measured. The most common method in batch titrations is to use an indicator which changes colour at the equivalence point. The colour change should be sharp and the measurement should be made at the wavelength of maximal difference between the absorbances of the acid and base forms of the indicator. All acid–base indicators which can be used in normal titrations are suitable.

A method, very attractive for automatic photometric determination of the equivalence point, is given by Mullen and Anton.[16] A mixture of Methyl Red and *m*-Cresol Purple (1.0 mg of each, dissolved in 100 ml of ethanol) is used in the titration of hydrochloric acid. Methyl Red changes from red to yellow over the pH range 4.4–6.2 and *m*-Cresol Purple from yellow to purple over the pH range 7.2–8.8. Between pH 6.2 and 7.2 a solution containing these two indicators is yellow. When a solution of a strong acid is titrated and these two indicators are used, at the equivalence point, there is sharp peak in the absorbance. Before the titration 1 ml of indicator is added to 10 ml of sample (or standard). The experimental curve of such a titration of hydrochloric acid is given in Fig. 11. Peaks are obtained at the two equivalence points $t_E(1)$ and $t_E(2)$. It is obvious that the peaks can conveniently be located automatically. The calibration curve is linear.

Linear transformation of the photometric titration curve

If a single-colour indicator is used for the titration, the evaluation must be based on an appropriate transformation of the titration curve. For example the photometric titration curve can be transformed into a linear plot.[17–19] When the absorbance of the flow-stream is measured, $[H^+]$ can be calculated from the following equation, the usual assumptions being made:

$$[H^+] = \frac{A_{In} - A}{(A - A_{HIn})K_{HIn}} \qquad (14)$$

where K_{HIn} is the stability constant of the indicator, A is the absorbance of the solution, A_{HIn} and A_{In} are the absorbances when the indicator is completely in its acid and base form respectively. For the titration

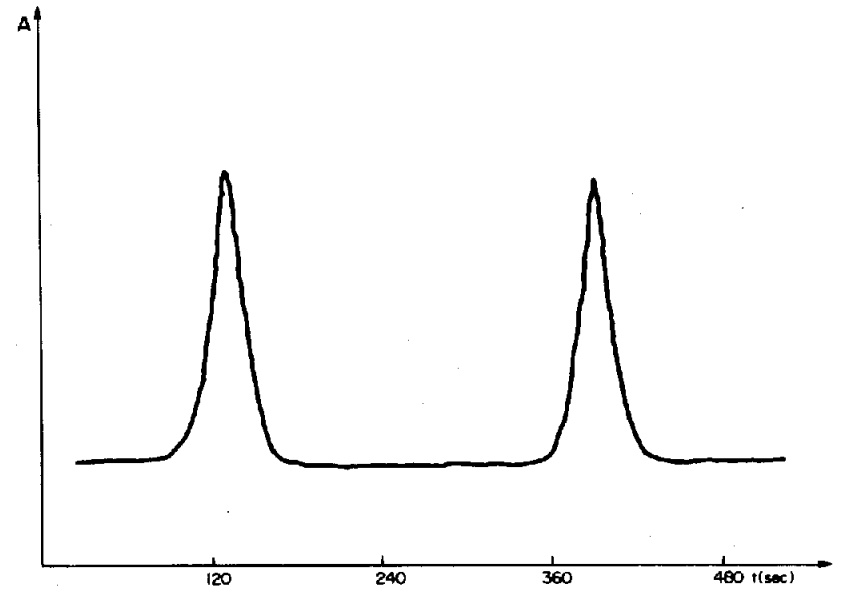


Fig. 11. Triangle-programmed photometric titration curve of 5×10^{-4} *M* hydrochloric acid. A mixture of Methyl Red and *m*-Cresol Purple is used as indicator, $i_{max} = 9.4$ mA; $2\tau = 330$ sec; $\lambda = 565$ nm.

of a strong acid equation (15) is valid:

$$t_E - t = k_4 \frac{A_{In} - A}{A - A_{HIn}} \qquad (15)$$

and when weak acids are titrated, equation (16) can be used:

$$\frac{t_E}{t} - 1 = k_5 \frac{A_{In} - A}{A - A_{HIn}}. \qquad (16)$$

In both cases the indicator should be chosen so that the colour change appears somewhere near the half-titration point. Equations (15) and (16) are valid when parameters n and V are constant. In the titration of a strong acid Quinaldine Red can be used as indicator.[19] Bromocresol Green[19] and *p*-ethoxychrysoidine can be used when acetic acid and other weak acids of similar strength are titrated. In the triangle-programmed titration technique where the equivalence point is passed twice an indicator changing its colour in the alkaline pH region can also be chosen. Phenolphthalein changes its colour in the pH-range

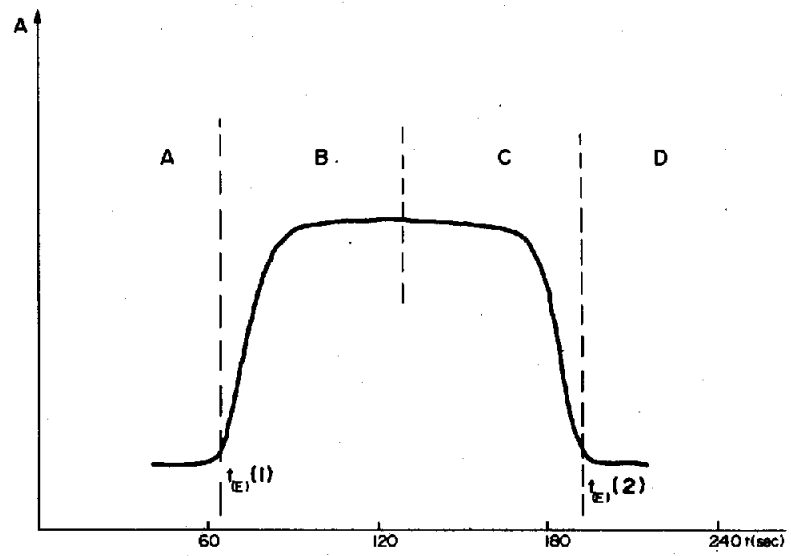


Fig. 12. Triangle programmed photometric titration curve for acetic acid. Phenolphthalein as indicator, $\lambda = 550$ nm; $i_{max} = 9.4$ mA; $2\tau = 120$ sec.

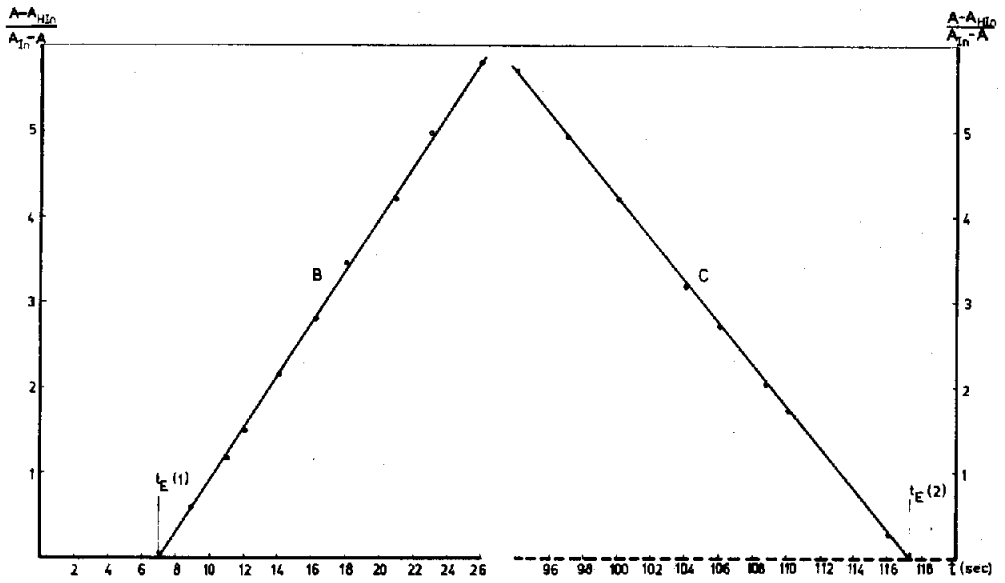


Fig. 13. Linear titration curves obtained when data from Fig. 12 are evaluated with equation (17).

8–10 and can thus be used to determine the equivalence points $t_E(1)$ and $t_E(2)$ from points in sections B and C respectively. Equation (17) should then be used.

$$t - t_E = k_6 \frac{A - A_{HIn}}{A_{In} - A} \qquad (17)$$

A titration curve for $7 \times 10^{-4} M$ acetic acid, obtained with phenolphthalein as indicator is given in Fig. 12. Two of the transformation graphs are shown in Fig. 13. The calibration graph is linear.

DISCUSSION

It is obvious from the results shown, that both potentiometric and photometric methods can be used as detection techniques in triangle-programmed titrations.

The evaluation of the titrations basically relies on accurate location of the two equivalence points, and measurement of the value Q. A calibration curve or calculation then gives the unknown concentration. Various equivalence-point location methods have been investigated. Each has its own advantages and drawbacks. The most serious source of error in the potentiometric methods is the electrical noise, which can sometimes result in failure of the whole method. These errors are avoided in the photometric method, but the choice of a suitable indicator may be difficult. The indicator may also react with the ions generated. This indicator error can be avoided by having the same concentration of indicator both in the standard solution and in the analyte. When the method of linear transformation of the photometric titration curve is used, *i.e.*, equations (15) and (16), the concentration of the indicator should be less than 1% of the concentration of the acid. Equations (15) and (16) have been derived by assuming that only one acid reacts with the hydroxide ions generated. If the concentration of the indicator is too high its reaction with the hydroxide ions cannot be neglected and the solution contains two acids which react with the hydroxide ions. Equations (15) and (16) are then no longer valid, and the lines will not be straight either. The indicator is also often adsorbed on the walls of the tubes and the cell, causing problems when the indicator is changed. In the photometric methods the problems of electrical coupling between the generating and indicating circuits are avoided.

The determination of the equivalence point by the method of linearized plots seems not very attractive in the triangle-programmed titration method. Titration data both before and after the equivalence point are needed in the calculations and different equations should be used for the evaluation of data from different sections of the curve. In the potentiometric methods the tailing effect can also cause some difficulties in the automatic evaluation of data from section D in titration of strong acid, as can be seen in Fig. 6. In titration of weak acids the branch A is slightly curved as can be seen in Fig. 8 and the linearity of the curve also depends on the concentration of the acid and makes the determination of $t_E(1)$ difficult. Sometimes the calibration curve for weak acids is not linear at low concentrations. When the method of linear plots is used in the photometric method the absorbance values A_{In} and A_{HIn} are needed. A_{In} can easily be determined because it is the same as the absorbance of the flow between the two equivalence points. The value of A_{HIn} can be calculated as the average of the absorbance values before and after the titration program. The method of linear plots needs a data collection and storage device and a small computer to perform the calculations.

In the potentiometric method, hardware differentiation seems to be the most advantageous method. It is independent of the character of the acids to be titrated and can be used for both strong and weak acids. Only the appearance of the potential peaks must be determined, which can easily be done automatically. If the acid is very weak a proper potential jump is not obtained and the method cannot be used.

In the photometric method the use of two indicators gives quite an easy and reliable method in the determination of the equivalence points in titration of strong acids. The restriction of the method is perhaps the lack of suitable indicators for the titration of weak acids.

REFERENCES

1. L. Snyder, J. Levine, R. Stoy and A. Conetta, *Anal. Chem.*, 1976, **48**, 942A.
2. Zs. Fehér, G. Nagy, K. Tóth and E. Pungor, *Analyst*, 1974 **99**, 699.
3. D. Betteridge, *Anal. Chem.*, 1978, **50**, 832A.
4. G. H. B. Eeldrink, H. B. Verbruggen, F. A. Jutte, W. J. van Oort and B. Griepink, *Z. Anal. Chem.*, 1976, **280**, 273.
5. W. Jongkind, G. H. B. Eeldrink, H. B. Verbruggen, W. J. van Ooort and B. Griepink, *ibid.*, 1977, **286**, 72.
6. J. M. Ariano and W. F. Gutknecht, *Anal. Chem.*, 1976, **48**, 281.
7. G. Nagy, K. Tóth and E. Pungor, *ibid.*, 1975, **47**, 1460.
8. G. Nagy, Zs Fehér, K. Tóth and E. Pungor, *Anal. Chim. Acta*, 1977, **91**, 87.
9. *Idem, ibid.*, 1977, **91**, 97.
10. *Idem, ibid.*, 1978, **100**, 181.
11. G. Nagy, Z. Lengyel, Zs. Fehér, K. Tóth and E. Pungor, *ibid.*, 1978, **101**, 261.
12. G. Nagy, Zs. Fehér, K. Tóth and E. Pungor, in *Ion-Selective Electrodes*, E. Pungor (ed.) p. 477. Akadémiai Kiadó, Budapest, 1978.
13. P. Sørensen, *Kem. Maanesdsblad*, 1951, **32**, 73.
14. G. Gran, *Analyst*, 1952, **77**, 661.
15. F. Ingman and E. Still, *Talanta*, 1966, **13**, 1431.
16. P. Mullen and A. Anton, *Anal. Chem.*, 1960, **32**, 103.
17. J. Headridge, *Photometric Titrations*, Pergamon, Oxford, 1961.
18. A Johansson and E. Wänninen, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving (eds.) Part I, Vol. 11, p. 7117. Wiley, New York.
19. A. Johansson, *Anal. Chim. Acta*, 1972, **61**, 285.

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THE EFFECT OF TRACE LEVELS OF CYANIDE ON THE FORMATION OF MERCURY–IODIDE COMPLEXES

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Summary—The interference of trace levels of cyanide with the formation of iodo-mercury complexes is made the basis of a method of trace analysis for cyanide. The decrease in absorbance of the iodo-mercury complexes is a linear function of total cyanide concentration up to about $5 \times 10^{-5}M$ in $0.1M$ sodium hydroxide medium when the iodide and mercury total concentrations are $0.05M$ and $3 \times 10^{-5}M$ respectively. Several cyano-mercury complexes are formed simultaneously, and quite a large fraction of the cyanide remains uncomplexed.

Mercury(II) with excess of iodide solution forms the highly stable complexes HgI_2, HgI_3^- and HgI_4^{2-}, the last being the predominant species if the iodide concentration is high enough (*e.g.*, $> \sim 0.01M$). The measurement of the absorbance at 323 nm of the mercuric tetraiodide complex in $1M$ iodide solution has been used for the estimation of ppm concentrations of mercury(II).[1] Cyanide interferes by formation of complex species of the type $Hg(CN)_n^{(n-2)-}$ and mixed-ligand species $Hg(CN)_nI_{(4-n)}$ in neutral media. Penneman and Jones[2] have demonstrated the existence of these complexes by infrared studies. The interference of cyanide is exploited in the method described here (and also by Clyde and Warner[3] in a recent paper†).

The work described here was carried out to identify the conditions favouring the interference of trace levels of cyanide, and to utilize the interference for estimation of trace cyanide.

THEORY

If, in view of the relevant stability constants, we neglect the formation of hydroxo-complexes in presence of excess of iodide, the general reaction between mercury(II) and iodide may be represented by

$$Hg^{2+} + xI^- \rightleftharpoons HgI_x^{(x-2)-} \qquad (1)$$

The overall equilibrium constants for this reaction are given by

$$\beta_x^I = \frac{[HgI_x^{(x-2)-}]}{[Hg^{2+}][I^-]^x} \qquad (2)$$

Mercury(II) also reacts with cyanide:

$$Hg^{2+} + nCN^- \rightleftharpoons Hg(CN)_n^{(n-2)-} \qquad (3)$$

$$\beta_n^{CN} = \frac{[Hg(CN)_n^{(n-2)-}]}{[Hg^{2+}][CN^-]^n}. \qquad (4)$$

The decrease in absorbance, ΔA, of any of the iodo-complexes, will be a function of the iodide, mercury and cyanide concentrations since the first two of these will govern the distribution of iodo-species, and the last two the distribution of cyano-species.

Complications may be caused by the formation of mixed-ligand complexes such as iodo-hydroxo complexes, but in general the effect on the calculated distribution of the mercury species will be comparable with that caused by the uncertainties in the published stability constants for the complexes.

From equations (2) and (4) it is evident that if the iodide concentration is very much greater than that of the mercury and cyanide the change in iodide concentration caused by competitive cyanide complex formation will have practically no effect on the distribution of the mercury iodide complexes. Hence the effect of cyanide can be monitored by measuring the change in concentration of any of the iodo-complexes. Clyde and Warner used the HgI_4^{2-} species, measuring the decrease in its absorbance at 323 nm.

The relationship between this decrease in absorbance and the total cyanide concentration will be a complex function of various factors, but for fixed total iodide and mercury concentrations and a fixed pH will be determined by the stability constants for the cyanomercurate complexes. It follows from the closeness of β_2, β_3 and β_4 for these complexes‡ that all three will be present simultaneously, but $Hg(CN)_2$ will predominate so long as $[CN^-] < \beta_2/\beta_3$, *i.e.*, $< 10^{-4}M$, and $Hg(CN)_4^{2-}$ will not predominate until $[CN^-] > \beta_3/\beta_4$, *i.e.*, $> 10^{-3}M$. Since $[CN^-]$ is here the *free* cyanide concentration, then if the total cyanide is $< 10^{-4}M$, the major species will certainly

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† The present work was in fact completed in 1976, and the delay in publication is due entirely to the insistence of the referee and Editor-in-Chief that the theory be explored as thoroughly as possible [Ed.].

‡ $\log \beta_2 = 34.5$, $\log \beta_3 = 38.5$, $\log \beta_4 = 41.6$.

be $Hg(CN)_2$. However, as the cyanide concentration increases, the relative proportions of the higher cyanide complexes will also increase. It follows that the relationship between cyanide concentration and decrease in absorbance will not be a linear function of the cyanide concentration, though it may approximate to one over a certain concentration range.

The work described here was therefore a systematic investigation of the effect of varying the conditions, with a view to finding the optimum set.

EXPERIMENTAL

Reagents

Analytical grade chemicals were used where possible.

Mercury(II) stock solutions, $5 \times 10^{-3}M$ (1000 ppm). Mercuric oxide (1.08 g) and potassium iodide (16.6 g) dissolved in distilled water and diluted to 1 litre or mercuric chloride (1.355 g) dissolved in distilled water and made up to 1 litre.

Potassium iodide solution, 1.0M.

Cyanide stock solution, $3.85 \times 10^{-3}M$ (1000 ppm). Potassium cyanide (2.50 g) dissolved in 100 ml of 1.0*M* sodium hydroxide and diluted to 1 litre; standardized weekly by titration with 0.05*M* silver nitrate.[4]

All working solutions, made from the stock solutions by suitable dilution and mixing, were 0.1*M* in sodium hydroxide unless otherwise stated.

Procedure

Solutions of the required composition were prepared by suitable dilution and mixing of the stock solutions, and the absorbances were measured at the appropriate wavelengths.

The maximum total concentrations employed were: cyanide $6.2 \times 10^{-5}M$; mercury(II) $5 \times 10^{-5}M$; iodide 0.1*M*; sodium hydroxide 0.1*M*. Hence, the ionic strength of the reaction medium never exceeded 0.2 (but was mostly less than 0.15), and all the free cyanide was in ionic form as CN^-.

DISCUSSION OF RESULTS

Iodo-mercury complexes

Provided the free iodide concentration in the sample solution, $[I^-]_s$ is practically the same as that in the reference, $[I^-]_r$, two peaks are obtained in the spectrum (Fig. 1), the peaks shifting towards shorter wavelengths with decreasing iodide concentration, especially the peak at ~270 nm. In this work the reference solutions were therefore always matched in iodide concentration with the test solutions.

Both peaks must be assigned to the HgI_4^{2-} complex, because the molar absorptivity would be of the order of 10^7 l.mole^{-1}.cm^{-1}, *i.e.*, about 100 times the commonly accepted theoretical maximum, if the sole absorbing species were HgI_3^- (see below for equilibrium concentrations of the species). The shift in wavelength with decrease in iodide concentration may indicate that HgI_3^- absorbs in the same regions as HgI_4^{2-}, since lower iodide concentration favours formation of HgI_3^- (the two species should be in equi-

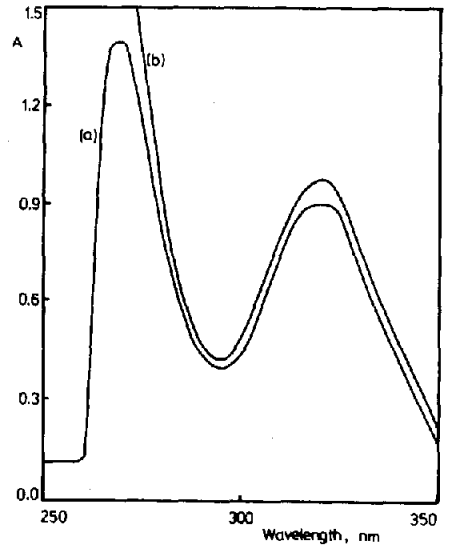


Fig. 1. Spectra of iodo-mercury complexes in 0.1*M* potassium iodide medium, measured against (a) 0.1*M* potassium iodide and (b) water.

molar ratio when $[I^-] = \beta_3/\beta_4 = 10^{26}/10^{30} = 10^{-4}M$).* The apparent molar absorptivity also changes with iodide concentration (Fig. 2); this and the wavelength shift could be due to a structural change in the solvent or to an ionic strength effect and the change in the distribution of the complexes.

Cyanide interferences

The cyanide interference, as measured in terms of reduction ΔA in the absorbance of the mercury iodide complexes, increases with decreasing iodide concentration as expected from the theory (Fig. 3). A limiting factor in obtaining higher ΔA values with a fixed amount of cyanide is that the absorbance of the mercury iodide complexes decreases sharply as the iodide concentration falls below 0.1*M*. The iodide concentration range where maximum absorbance readings A_0 may be obtained in the absence of cyanide, together with large absorbance depressions ΔA in the presence of cyanide, is 0.02–0.1*M*. For this reason the cyanide interference was studied largely in the iodide concentration range 0.005–0.1*M*. Both peaks behave alike towards cyanide interference; the sharper peak (at 265–278 nm) was used to study the effects of cyanide.

Cyanide interference is greatly enhanced in strongly basic conditions. For example, no absorbance depression is observed in neutral or $10^{-4}M$ hydroxide medium until the cyanide–mercury molar ratios are above 2.0 and 1.0, respectively. On the other hand, with alkali concentrations above $10^{-2}M$ in the medium, there is depression of the absorbance with cyanide–mercury mole ratios from 0.2 to 2.0. The best ΔA values are obtained in 0.05–0.1*M* hydroxide medium. Cyanide interference in such basic media is essentially linear in effect up to a cyanide–mercury mole ratio of about 2 (Fig. 4), except when the iodide

*The stability constants quoted in the literature vary considerably. The values used here have been rounded off and are used mainly for illustrative purposes.

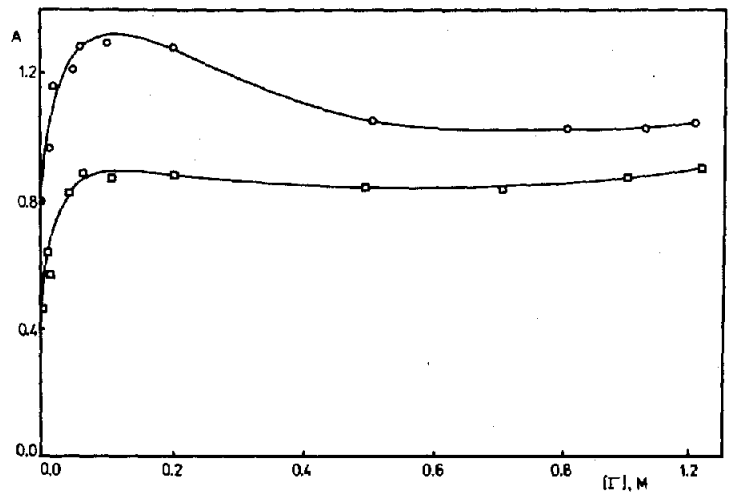


Fig. 2. Absorbance of iodo-mercury complex, as a function of iodide concentration, measured at (a) 268–273 nm and (b) 323 nm.

concentration is below about 0.03*M*. The slopes of plots of ΔA (or A) against cyanide concentration increase only slightly with decreasing iodide concentration.

Clyde and Warner[3] stated that the absorbance decreased at pH 11 and attributed this to abstraction of mercury(II) from the iodo-complex by the hydroxide. As they do not specify *which* absorbance decreases, the statement is not very helpful, but as the ratio $[HgI_4^{2-}]/[Hg(OH)_2]$ should be equal to $\beta_{HgI_4}[I^-]^4/\beta_{Hg(OH)_2}[OH^-]^2 \sim 10^{30}/(10^{22} \times 10^{-6}) \sim 10^{14}$ for $[I^-] = 1.0M$ and pH 11 (the conditions used by Clyde and Warner), this explanation seems improbable. Figure 4 shows that even at pH 13, with 0.05*M* iodide, the mixed-ligand species $Hg(CN)_2OH$ is only a minor component of the system; the ratio of $[HgI_4^{2-}]/[Hg(OH)_2]$ under these conditions should still be of the order of 10^5, so it seems likely that they mean that the absorbance decreases more at pH 11 in the presence of cyanide, which could be explained by the fact that the cyanide should be almost completely in the ionic form at this pH. These authors also stated that varying the pH between 5 and 9 had no effect, but again they do not make it clear whether the pH refers to that of the sample being tested or the final solution. The fact that they obtained a linear calibration curve for $[CN^-]_{total}/[Hg^{2+}]_{total}$ ratios ranging up to 10:1, when compared with the findings in the present paper, seems to indicate that the cyanide was in fact protonated to some extent. From $pK = 9.2$ for

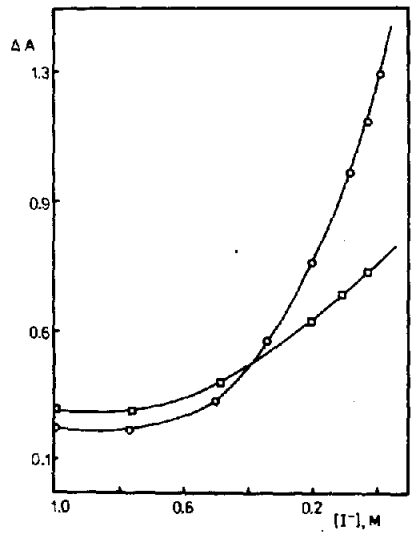


Fig 3. Absorbance depression ΔA as a function of iodide concentration ($5 \times 10^{-5}M$ Hg, 1.94×10^{-4} CN^-), measured at (a) 268 nm and (b) 323 nm.

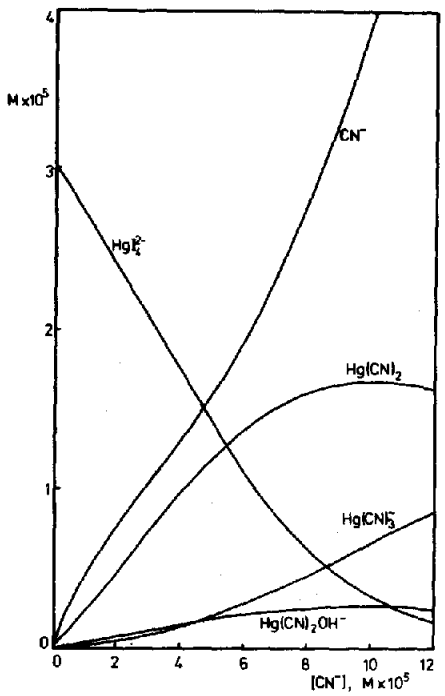


Fig. 4. Distribution of various species as a function of total cyanide concentration ($3 \times 10^{-5}M$ Hg, 0.05*M* I^-, 0.1*M* OH^-).

HCN, it would be expected that at pH 9 just over half the uncomplexed cyanide would be in protonated form and at pH 7 over 99% would be present as HCN. This may also help to account for their observation that if the mercury concentration was doubled from $2.0 \times 10^{-4}M$ to $4 \times 10^{-4}M$ there was a profound effect on the absorbance decrease on addition of cyanide, but again there is a lack of clarity in their paper. The caption to their Fig. 1 does not say whether these values refer to the total mercury concentration in the solution measured, or the concentration of the reagent added. If the latter is the case, it is difficult to see how use of $5 \times 10^{-4}M$ mercury(II) reagent (as in the procedure) could work; if the former, the lower concentration used is already ten times that used in the procedure, and increasing it may simply result in a decreased slope for the calibration curve. From the absorbances and molar absorptivity quoted it can be deduced that the concentrations refer to the reagent. A simplified calculation based on the assumption that HgI_4^{2-} and $Hg(CN)_2$ are the only complexes formed shows that under Clyde and Warner's conditions the ratio $[HgI_4^{2-}]/[Hg(CN)_2] = \beta_{HgI_4}[I^-]^4/\beta_{Hg(CN)_2}[CN^-]^2$ exceeds 1 when $[CN^-] < 10^{-2.25}$, and 100 when $[CN^-] < 10^{-3.25}$. Clyde and Warner's Fig. 1 indicates that with the $4.0 \times 10^{-4}M$ reagent there is no formation of cyanide complexes until the cyanide concentration is at least $2.1 \times 10^{-4}M$ (or $[CN^-] > 10^{-3.7}M$), in agreement with this.

The values of n for $Hg(CN)_n$ (which range between 2.0 and 2.2) calculated from the slopes of plots of log ΔA *vs.* log $[CN]_{total}$ on the simplifying assumption that only one complex is formed, indicate that the major cyanomercurate complex in 0.03–0.06M iodide medium is $Hg(CN)_2$.

A HALTAFALL calculation of the distribution of the various species in the solution (Table 1) confirms this observation for the conditions finally selected for the determination: $Hg(CN)_2$ is formed predominantly, especially at the lower concentrations of cyanide. $Hg(CN)_4^{2-}$ is the cyanide complex with the lowest concentration. The species next in importance to $Hg(CN)_2$ is $Hg(CN)_3^-$. The ratio $[Hg(CN)_3^-]$: $[Hg(CN)_2]$ increases with increasing cyanide concentration, and $[Hg(CN)_2]$ passes through a maximum. It is interesting that a large fraction of the cyanide remains uncomplexed. The contribution of the mixed-ligand species $Hg(CN)_2OH^-$ is comparatively small. Most importantly, however, the concentration of HgI_4^{2-} decreases linearly as the cyanide concentration increases up to about $6 \times 10^{-5}M$.

It is this last feature that is the basis for the measurement of trace quantities of cyanide. Advan-

Table 1. HALTAFALL calculation of equilibrium concentrations for $3 \times 10^{-5}M$ Hg, $0.05M$ I^-, $0–12 \times 10^{-5}M$ CN^- (total concentrations) in $0.1M$ NaOH medium

Total $[CN^-]$, $10^{-5}M$	$\log[HgI_2]$	$\log[HgI_3^-]$	$\log[HgI_4^{2-}]$	$\log[CN^-]$	Constants used
0	−7.720	−6.922	−4.525	—	
1	−7.759	−6.961	−4.564	−5.316	
2	−7.817	−7.019	−4.621	−5.107	
3	−7.884	−7.086	−4.689	−4.978	$\log\beta_{Hg(CN)_2} = 34$
4	−7.962	−7.163	−4.766	−4.877	$\log\beta_{Hg(CN)_3} = 38$
5	−8.050	−7.252	−4.854	−4.789	$\log\beta_{Hg(CN)_4} = 41$
6	−8.151	−7.352	−4.955	−4.707	$\log\beta_{HgI_2} = 24$
7	−8.265	−7.466	−5.069	−4.628	$\log\beta_{HgI_3} = 26$
8	−8.391	−7.593	−5.195	−4.551	$\log\beta_{HgI_4} = 30$
9	−8.528	−7.729	−5.331	−4.476	$\log\beta_{Hg(CN)OH} = 14$
10	−8.670	−7.871	−5.473	−4.403	$\log\beta_{Hg(CN)_2OH} = 20$
11	−8.812	−8.013	−5.616	−4.334	
12	−8.951	−8.152	−5.754	−4.270	

Total $[CN^-]$, $10^{-5}M$	$\log[Hg(CN)_2]$	$\log[Hg(CN)_3^-]$	$\log[Hg(CN)_4^{2-}]$	$\log[Hg(CN)OH]$	$\log[Hg(CN)_2OH^-]$
0	—	—	—	—	—
1	−5.687	−7.003	−9.219	−6.971	−6.487
2	−5.327	−6.434	−8.441	−6.820	−6.127
3	−5.136	−6.113	−7.991	−6.758	−5.936
4	−5.012	−5.888	−7.665	−6.735	−5.811
5	−4.924	−5.713	−7.401	−6.736	−5.724
6	−4.862	−5.569	−7.176	−6.755	−5.662
7	−4.819	−5.447	−6.975	−6.790	−5.619
8	−4.791	−5.342	−6.793	−6.840	−5.591
9	−4.777	−5.253	−6.628	−6.901	−5.577
10	−4.773	−5.176	−6.479	−6.970	−5.573
11	−4.778	−5.112	−6.346	−7.044	−5.578
12	−4.789	−5.059	−6.229	−7.119	−5.589

tage is taken of the relation between ΔA and the cyanide concentration, and the relatively large slopes of the plots, allowing the determination of cyanide concentrations as low as 0.1 μg/ml in suitably alkaline iodide solution.

Determination of cyanide

From a burette add 25-ml aliquots of a solution 0.1*M* in potassium iodide, $6 \times 10^{-5}M$ in mercury(II) and 0.1*M* in sodium hydroxide, to ten 50-ml standard flasks. In eight of the flasks place various volumes from 0 to 14 ml of 5-ppm cyanide solution in 0.1*M* sodium hydroxide. To the other two flasks add different volumes of the unknown cyanide solution, made 0.1*M* in sodium hydroxide. Make all the solutions up to the mark with 0.1*M* sodium hydroxide and mix them. Read the absorbances at 268 nm, against 0.05*M* potassium iodide in 0.1*M* sodium hydroxide. Read the cyanide contents of the sample from a calibration curve of A (or ΔA) *vs.* cyanide concentration in ppm or mole/l.

The only disadvantage is the interference from other heavy metals. This is common with most methods of cyanide analysis. On the other hand, the technique is very fast compared with other chemical methods; it is reasonably sensitive, and the interference which is usually observed in neutral solutions from traces of organic compounds such as aldehydes, methanol and acids, is eliminated by use of the alkaline medium.

REFERENCES

1. A. J. Pappas and H. B. Powell, *Anal. Chem.*, 1967, **39**, 579.
2. R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, 1961, **20**, 19.
3. D. D. Clyde and M. A. Warner, *Analyst*, 1978, **103**, 648.
4. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., pp. 74–75, 271–273. Longmans, London, 1968.

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SHORT COMMUNICATIONS

ANALYTICAL BEHAVIOUR OF POLY(VINYL ACETATE) AND ITS HYDROLYSIS PRODUCTS WITH IODINE

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(*Received* 21 *December* 1978. *Revised* 21 *May* 1979. *Accepted* 25 *May* 1979)

Summary—Formation of the red complex between poly(vinyl acetate) and iodine in the presence of iodide is quantitatively independent of the method by which the polymer is prepared. In contrast, the amount of complex formed in the case of partly hydrolysed products of poly(vinyl acetate) depends strongly on the source of this polymer and may vary from sample to sample by as much as a factor of five, while the use of different hydrolysis methods gives rise to even greater differences in the amount of complex formed by the products. The determination of partly hydrolysed poly(vinyl acetate) through the red iodine complex is recommended only when the standard polymer sample and the unknown have been prepared in the same batch. Details of these systems are discussed.

Complexation of poly(vinyl acetate) (PVAc) with iodine in the presence of iodide has been demonstrated as a method for the determination of this polymer.[1] In a development of the method, the absorbance of the red complex at 510 nm (A) yielded accurately linear calibration curves, $A = 0.022c$, for the concentration range c = 25–100 mg of polymer per litre of final solution in the case of two polymers of different molecular weight obtained from the same source.[2] Certain partly hydrolysed products of PVAc also form a red complex,[3–7] but no systematic investigation has been reported, as far as we are aware, of the suitability of this complex as the basis of an analytical method. Moreover, the quantity of red complex formed by certain partly hydrolysed products appears to depend on the method of hydrolysis used,[8–14] as this may influence the length and frequency of the block sequences of acetate and alcohol groups along the polymer molecular chains.[7,15] We have felt the need, therefore, first to test pure PVAc samples obtained from all common sources to establish whether or not the sensitivity of red complex formation can vary at all with the source of the polymer. Then the same polymers have been hydrolysed to an extent within the range of commercial interest and the sensitivity of the partly hydrolysed products for red complex formation has been determined to assess the analytical potential of the procedure for these products.

EXPERIMENTAL

PVAc samples were obtained from all the known commercial sources, and three specimens were prepared in the laboratory (Table 1). The degree of hydrolysis of the products resulting from hydrolysis[7] of the PVAc samples was determined as previously described[7,16] (Table 2). Methanol was of reagent grade, and other reagents were of analytical grade unless otherwise stated. The procedures used are given below. Details of preliminary exploration are omitted.

The pure PVAc samples were each tested as follows.[1,2] In each of ten 10-ml standard flasks were placed 5 ml of 0.0212M methanolic iodine solution. Suitable aliquots of 0.03035M methanolic PVAc solution were added (molarity based on the vinyl acetate segment of molecular weight 86.09), and the volume was made up to 10 ml with methanol (a blank containing no polymer was also prepared). One ml of each of these solutions was diluted to 25 ml with 0.0169M aqueous potassium iodide with very gentle swirling to avoid partially precipitating the colloidal red complex. After 1 hr, the spectra of the solutions, which had a poly(vinyl acetate) concentration up to 0.000486M, were measured in 1-cm cells at 20 ± 0.2° with a Unicam SP500 or SP700 spectrophotometer, with the blank solution in the reference beam.

The Aldrich PVAc sample was hydrolysed by three distinct methods[7] to within the range 91 ± 1 mole% of hydroxyl groups, and accurately linear calibration curves were established for iodine complex formation in test solutions of the products as follows. Ten solutions were made up in 50-ml standard flasks from suitable aliquots of aqueous polymer solution (80–90% hydrolysed PVAc does not dissolve in methanol) diluted to 20 ml with distilled water and mixed with aqueous iodine/iodide solution and water to give final total concentrations of 0.0002M iodine and 0.0054M iodide. The ranges of polymer concentration were varied in proportion to their sensitivity to iodine complex formation. Spectra were scanned as before, and absorbances per concentration unit (mg/l.) at λ_{max} are recorded in Table 2.

Nine of the pure PVAc samples were reliably hydrolysed by methoxide-catalysed trans-esterification in methanol[7] to within the range 81 ± 1 mol%, and test solutions of the products were compared as follows. Fifty ml of solution were made up in standard flasks as above, to give final total concentrations of 0.0015M iodine, 0.0045M iodide and 0.01M polymer. Results are in Table 2.

Table 1. Absorption coefficients for iodine complexes formed at 20°C by poly(vinyl acetate) from various sources, with 0.000423*M* iodine and 0.0162*M* potassium iodide in 4% methanol–water mixture

Source of polymer	Molecular weight*	Absorption coefficient†
Hopkin & Williams	33×10^3	2.45
BDH	45×10^3	2.18
Koch-Light	45×10^3	2.24
Aldrich	70×10^3	2.28
Solution polymerization‡	70×10^3	2.43
BDH	160×10^3	2.28
K & K	160×10^3	2.25
UV radiation‡	160×10^3	2.32
Fisons	260×10^3	2.23
Suspension polymerization‡	1050×10^3	2.13
Monsanto§	500×10^3	2.2 (ref. 2)

* Approximate viscosity average.
† For λ_{max} 520 nm; $10^2 \times$ absorbance/polymer concentration (in mg/l.).
‡ Polymer prepared in the laboratory.
§ Gelva V7 and V100 polymers.[2]

Table 2. Absorption coefficients for iodine complexes formed at 20°C by partly hydrolysed poly(vinyl acetate) polymers with iodide and potassium iodide in water

Source of PVAc	Method of hydrolysis	λ_{max}, *nm*	Absorption coefficient*
(*a*) *Results for* 81 *mol*% *hydrolysed PVAc*†			
Aldrich	Trans-esterification	490	0.22
Hopkin & Williams	Trans-esterification	490	0.18
UV radiation	Trans-esterification	500	0.16
K & K	Trans-esterification	500	0.14
Koch-Light	Trans-esterification	490	0.14
BDH 160000	Trans-esterification	495	0.14
Suspension polymerization	Trans-esterification	495	0.11
BDH 45000	Trans-esterification	500	0.06
Solution polymerization	Trans-esterification	510	0.05
(*b*) *Results for* 91 *mol*% *hydrolysed PVAc*‡			
Aldrich	Saponification	485	0.13
Aldrich	Trans-esterification	485	0.05
Aldrich	Acid equilibration	485	0.0015

* Defined as in Table 1.
† With 0.0015*M* iodine and 0.0045*M* potassium iodide.
‡ With 0.0002*M* iodine and 0.0054*M* potassium iodide.

RESULTS AND DISCUSSION

The absorption coefficients shown in Table 1 for complex formation by the ten pure PVAc samples studied have the mean value 2.28 and standard deviation 0.10 (confirming the generality of the result previously recorded[2]). However, there is probably a tendency for increases in molecular weight (MW) to cause a slight decrease in the coefficients. Nevertheless, the general agreement between the results establishes that with a calibration curve prepared with any pure PVAc polymer as standard, the reported method may be applied to the determination of an unknown sample of PVAc with an expectation of an error of not more than 10%.

The absorption coefficients shown in Table 2 for the hydrolysed PVAc products, on the other hand, show wide discrepancies. We are surprised that the coefficients in group (*a*) are spread by a factor as great as five, because we have been at pains to carry out the hydrolysis as uniformly as possible, and this suggests that the method of preparation of the PVAc from its monomer may in some way influence the structure of the hydrolysed products and their ability to complex with iodine. There is a rough correlation between the absorption coefficient and λ_{max} but not between the coefficient and MW. When different hydrolytic methods are deliberately used, as for group (*b*), and other variables in the system are kept uniform, the range of absorption coefficients is even greater. Whilst the individual results were generally reproducible (within $\pm 2\%$)[2] and satisfactory linear relationships between absorbance and concentration of polymer were observed, it is clear that the use of the red iodine complex for the determination of hydrolysed PVAc polymers must be subject to gross

errors unless a pure sample of the particular polymer to be determined can be used as a standard.

The results in Table 1 and Table 2(*a*) were obtained with the use of iodine and iodide concentrations sufficient to ensure complete formation of the complex.[1,2] Thus, when the iodide and iodine concentrations were reduced by a factor of 4, the absorption coefficients in Table 1 were reduced by only *ca.* 10%. The coefficients for the hydrolysed polymers were slightly sensitive to iodide concentration, the optimum value of this being *ca.* 0.005*M*. Addition of 0.05*M* sodium chloride to the test solutions had no appreciable effect. In order to verify a Beer's law relationship for the polymer hydrolysed by acid equilibration, Table 2(*b*), a lower iodine concentration was used so that the broad maximum of the complex centred at 485 nm should not be swamped by the wing of the intense iodine absorption band with $\lambda_{max} \sim 460$ nm.[3]

REFERENCES

1. S. Hayashi, C. Kawamura and M. Kakayama, *Bull. Chem. Soc. Japan*, 1962, **11**, 1309.
2. J. G. Pritchard and F. T. Serra, *Talanta*, 1973, **20**, 541.
3. J. G. Pritchard and D. A. Akintola, *ibid.* 1972, **19**, 877.
4. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, 3rd Ed., Vol. III, p. 54. Van Nostrand, London, 1953.
5. L. G. Tebelev and N. A. Silkina, *Dokl. Akad. Nauk SSSR*, 1965, **161**, 1096.
6. S. Hayashi, C. Kawamura and M. Takayama, *Bull. Chem. Soc. Japan*, 1970, **43**, 537.
7. D. P. Joshi and J. G. Pritchard, *Polymer*, 1978, **19**, 427.
8. I. Sakurada, *Gohsei Seni Kenkyu*, 1942, **1**, 213.
9. S. Hayashi, C. Nakamo and T. Motoyama, *Kobunshi Kagaku*, 1964, **21**, 304; 1965, **22**, 358.
10. R. K. Tubbs, *J. Polymer Science A-1*, 1966, **4**, 623.
11. K. Noro, *Brit. Polymer J.*, 1970, **2**, 128.
12. M. Shiraishi, *ibid.*, 1970, **2**, 135.
13. M. Shiraishi and K. Toyoshima, *ibid.*, 1973, **5**, 419.
14. S. Hayashi, T. Michichiro, I. Keneko and N. Hojo, *Makromol. Chem.*, 1975, **176**, 3221.
15. S. Hayashi, C. Nakano and T. Motoyama, *Kobunshi Kagaku*, 1963, **20**, 303.
16. H. O. Triebold and L. W. Aurand, *Food Composition and Analysis*, pp. 160–165. Van Nostrand, Princeton, 1963.

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A SENSITIVE COLORIMETRIC METHOD FOR ESTIMATION OF ASCORBIC ACID

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Summary—The reaction of ascorbic acid with ammonium molybdate to give molybdenum blue was investigated and used for microestimation of the vitamin in the pure state, dosage forms and plasma. The proposed method couples sensitivity (as little as 2 μg/ml can be determined) and specificity since no interference was found in the presence of common reducing sugars, antioxidants and degradation products of the vitamin. Recovery varied from 98.9 to 102.3% ± 0.2–0.5%.

Various methods have been reported for the estimation of ascorbic acid. The most widely used are the colorimetric or spectrophotometric methods depending on the reactions with 2,6-dichloroindophenol,[1,2] diazotized 4-methoxy-2-nitroaniline,[3,4] 2,4-dinitrophenylhydrazine,[5] 4-nitrobenzenediazonium fluoroborate,[6] dimethoxyquinone,[7] 2,3,5-triphenyltetrazolium chloride,[8] and phenylhydrazinium chloride.[9] A highly specific microfluorometric method is based on the reaction of dehydroascorbic acid with *o*-phenylenediamine, with a borate blank.[10] Titrations with iodine,[11] 2,6-dichloroindophenol,[12,13] and *N*-bromosuccinimide[14,15] have been reported. Differential pulse polarography has been used.[16] Ascorbic acid has also been determined as its molybdophosphate complex.[17]

Ammonium molybdate can be used for detection of ascorbic acid in paper chromatography,[18] and the present work was undertaken to examine factors influencing this reaction. The optimum conditions found were used to establish a method suitable for determining ascorbic acid in pharmaceutical dosage forms and in plasma.

EXPERIMENTAL

Reagents

Ammonium molybdate, freshly prepared 10% aqueous solution; 10% w/v sulphuric acid; 10% trichloroacetic acid solution; lactose, dextrin, starch, magnesium stearate, sodium metabisulphite, vitamins B_1, B_2, B_6, D, E, K; nicotinic acid, nicotinamide, folic acid, calcium pantothenate; rutin; calcium gluconate; copper sulphate solution; 1*M* sodium hydroxide. Stock standard ascorbic acid solution, freshly prepared in pure water; working standard prepared by dilution, to contain 0.1–0.5 mg of ascorbic acid per ml.

General procedure

Transfer 1 ml of sample solution containing 0.1–0.5 mg of ascorbic acid to a 50-ml standard flask, add 2 ml of 10% sulphuric acid and 4 ml of ammonium molybdate solution; mix and leave for 1 hr. Dilute with water to the mark and mix. Measure at 730 nm against a reagent blank prepared in the same manner but without the ascorbic acid. This blank should remain colourless for several days. Construct a calibration curve by using different concentrations (0.1–0.5 mg/ml) of ascorbic acid to develop the colour and diluting to obtain 2–10 μg/ml in the final system.

Analysis of tablets

Take a portion of the powdered tablets equivalent to 25 mg of ascorbic acid, extract it with water, filter into a suitable standard flask, then make up to volume with water. Transfer an aliquot into a suitable standard flask and apply the general procedure.

Analysis of preparations in ampoules

Dilute the contents of the ampoule to a suitable standard volume with water, and apply the general procedure to an aliquot.

RESULTS AND DISCUSSION

Development of the procedure

Preliminary experiments showed that the reaction is dependent on the ratio of sulphuric acid to ascorbic acid, the optimum being 0.2–0.4% w/v sulphuric acid in a solution containing 2–10 μg/ml concentration of the vitamin (Table 1).

For 2–10 μg of the vitamin per ml, the ammonium molybdate concentration should lie in the range 0.7–0.8% w/v in the solution measured (Table 1).

Raising the temperature accelerates the colour development, the same colour intensity being reached in 10 min at 85° and 60 min at 20°. However, interference from other reducing agents such as lactose becomes significant at higher temperature. Therefore, room temperature (20–25°) is recommended, the optimum time being 60 min (Fig. 1).

The blue colour formed is stable for about 20 hr under the specified conditions. The absorbance maxi-

Table 1. The effect of concentration of reagents on the intensity of the colour developed with ascorbic acid

Sulphuric acid, 10% *w/v* Volume, *ml*†	*A**	Ammonium molybdate, 10% *w/v* Volume, *ml*§	*A**
1.0	0.165	1.0	0.010
1.8–2.2	0.285	2.0	0.050
3.0	0.150	3.0	0.195
4.0	0.065	4.0	0.285
5.0	No colour	5.0	0.280
		6.0	Precipitation

* *A* = absorbance for 5-μg/ml ascorbic acid; average of three determinations.
† Plus 4 ml of 10% ammonium molybdate solution.
§ At a fixed sulphuric acid level of 0.4% w/v.

mum is at 720–750 nm and Beer's law is obeyed over the range 2–10 μg/ml.

Specificity of the method

Some excipients commonly added to dosage forms were found not to interfere. The recovery of ascorbic acid in the systems studied was 100.0–100.8 ± 0.1–0.4% (Table 2). The recovery was not affected even in the presence of a relatively high lactose content (1:1 ratio to ascorbic acid). The possible interference of some pharmaceuticals likely to be formulated with vitamin C has been also studied; the results are shown in Tables 2 and 3. Rutin, vitamins B_1, B_2, B_6, D, E, K, nicotinic acid, nicotinamide, folic acid and calcium pantothenate all gave no interference.

The specificity of the method for determining ascorbic acid in the presence of its decomposition products was also evaluated. Aqueous solutions of ascorbic acid which had been kept at 85° in presence of copper ions at pH 8.0 for varying periods of time were analysed. The results (Table 4) suggest that the method is suitable for monitoring the rate or degree of oxidation of the vitamin.

Determination of vitamin C in dosage forms and plasma

The results obtained are shown in Table 3. Recovery for vitamin C tablets was 98.9–102.3 ± 0.2–0.7% compared to 101.0–103.5 ± 0.8% obtained by the B.P. method.

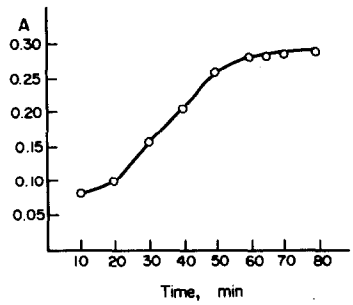


Fig. 1. The effect of time on the colour intensity (5.0-μg/ml ascorbic acid at 20°).

Table 2. Determination of 10 mg of ascorbic acid in presence of excipients, minerals and other substances usually incorporated in ascorbic acid preparations

Substance	Taken, *mg*	Ascorbic acid recovery, %*
Dextrin	5.0	100.0 ± 0.1
Magnesium stearate	5.0	100.0 ± 0.1
Lactose	10.0	100.6 ± 0.2
Starch	10.0	100.1 ± 0.1
Sodium metabisulphite	10.0	100.2 ± 0.3
Calcium gluconate	50.0	101.0 ± 0.4
Ergocalciferol	0.1	100.7 ± 0.2
Folic acid	2.0	100.4 ± 0.1
Pyridoxine, HCl	2.0	100.2 ± 0.1
Riboflavine	5.0	100.1 ± 0.3
Rutin	5.0	100.8 ± 0.3
Thiamine, HCl	10.0	100.1 ± 0.1
α-Tocopherol	10.0	100.2 ± 0.2
Menadione	10.0	100.5 ± 0.1
Calcium pantothenate	25.0	100.6 ± 0.2
Nicotinic acid	50.0	100.0 ± 0.4
Nicotinamide	50.0	100.1 ± 0.1

* Average of 5 results.

Table 3. Determination of ascorbic acid in pure form and different pharmaceutical preparations by the ammonium molybdate method, compared with the B.P.1973 method

Sample	Ammonium molybdate method Taken mg	Mean recovery %†	B.P.1973 Taken mg	Mean recovery, %†	F_{calc}§	Spiked samples (10 mg of ascorbic acid) mean recovery, %†
Pure ascorbic acid	25.0	99.2 ± 0.4	100.0	101.0 ± 0.5	1.56	
Tablets						
(1) 500 mg*	25.0	99.6 ± 0.6	100.0	102.6 ± 0.6	1.00	100.1 ± 0.2
(2) 500 mg*	25.0	98.9 ± 0.7	100.0	103.0 ± 0.5	1.96	100.0 ± 0.3
(3) 150 mg*	25.0	99.5 ± 0.7	100.0	102.6 ± 0.5	1.96	100.2 ± 0.1
(4) 160 mg*	25.0	100.8 ± 0.2	100.0	103.5 ± 0.8	16	100.0 ± 0.2
Ampoules						
(5) 500 mg*	25.0	102.3 ± 0.4	100.0	103.3 ± 0.6	2.25	100.0 ± 0.4
(6) 500 mg*	25.0	101.9 ± 0.5	100.0	102.8 ± 0.7	1.96	101.2 ± 0.5
Human plasma (4 ml + 10 mg of ascorbic acid)						102.5 ± 0.6

* Nominal content

† Average of 6 experiments.

§ F_{theory} 5.05.

(1) Cebion, Merck; (2) Redoxon, Roche; (3) Supradyn, Roche; (4) Ruta-C 60, Kahira; (5) Cevital, Nile; (6) Calcium C, Sandoz.

Table 4. Measurement of oxidation rate of 5-μg/ml ascorbic acid solution

Time, *min*	Absorbance
5.0	0.16
10.0	0.12
20.0	0.10
30.0	0.07
60.0	0.06
120.0	0.05
300.0	0.01

Experiments on human plasma spiked with vitamin C gave a recovery of 101.5 ± 0.6%. The plasma was treated with trichloroacetic acid[19] before addition of a spike of ascorbic acid and application of the method.

As shown by Table 3, the recommended method compares favourably with the B.P. 1973 method. An advantage is the sensitivity; as little as 50 μg can be determined. The method is therefore suitable for single-dose assay where the level of the vitamin is low.

REFERENCES

1. L. P. Pepkowitz, *J. Biol. Chem.*, 1943, **151**, 405.
2. W. B. Robinson and E. Stotz, *ibid.*, 1945, **160**, 217.
3. M. Schmall, C. W. Pifer and E. G. Wollish, *Anal. Chem.*, 1953, **25**, 1486.
4. M. Schmall, C. W. Pifer, E. G. Wollish, R. Duschinsky and H. Gainer, *ibid.*, 1954, **26**, 1521.
5. J. J. Roe and C. A. Kuether, *Science*, 1942, **95**, 77.
6. K. Istvan and F. Gustane, *Acta Pharm. Hung.*, 1967, **37**, 127.
7. M. Eldawy, A. S. Tawfik and S. Elshabouri, *Anal. Chem.*, 1975, **47**, 461.
8. H. M. Hashmi, A. S. Adil, A. Viegas and I. Ahmad, *Mikrochim. Acta*, 1970, 457.
9. N. Wahba, D. A. Yessa and R. S. Labib, *Analyst*, 1974, **99**, 397.
10. M. J. Deutsch and C. E. Weeks, *J. Assoc. Offic. Agr. Chem.*, 1965, **48**, 1248.
11. *British Pharmacopoeia 1973.*
12. *The United States Pharmacopeia*, 19th rev., 1975, pp. 36, 37.
13. *Official Methods of Analysis of the AOAC*, 12th Ed., pp. 175, 176. Association of Official Analytical Chemists, Washington, D.C., 1975.
14. M. Z. Barakat, M. F. A. El-Wahab and M. H. ElSadr, *Anal. Chem.*, 1955, **27**, 536.
15. D. F. Evered, *Analyst*, 1960, **85**, 515.
16. J. B. Johnson, M. J. McCaffrey and S. H. Rubin, to be published, see S. H. Rubin, E. De Ritter and J. B. Johnson, *J. Pharm. Sci.*, 1976, **65**, 964.
17. A. De Vleeschauwer, W. Deschacht and H. Hendrickx, *Mededel, Landbouwhogeschool Opzoekingsstat. Staat Gent*, 1961, **26**, 149; *Anal. Abstr.*, 1962, **9**, 4950.
18. J. Herrmann and M. Zobel, *Z. Lebensmitt.-Untersuch.*, 1962, **116**, 477; *Anal. Abstr.*, 1962, **9**, 4951.
19. H. Varley, *Practical Clinical Biochemistry*, p. 631. Interscience, New York. 1969.

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SENSITIVE SPECTROPHOTOMETRIC METHOD FOR TRACE AMOUNTS OF URANIUM

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Summary—A sensitive spectrophotometric method for the determination of uranium with Pyrogallol Red (PGR) and cetyltrimethylammonium bromide (CTAB) is described. The sensitivity of the colour reaction between uranium and Pyrogallol Red is greatly increased in the presence of cetyltrimethylammonium bromide. The blue ternary complex (λ_{max} 580 nm) has composition 1:2:4 [U(VI):PGR:CTAB] at pH 5.6. Beer's law is obeyed over the range 19.0–0.24 ppm of uranium and the molar absorptivity is 3.3×10^4 l.mole^{-1}.cm^{-1} at 620 nm. A tentative structure for the ternary complex is suggested. A simple method is suggested for evaluation of stability constants of such ternary complexes.

Pyrogallol Red (PGR) forms a violet chelate with the uranyl ion.[1,2] Other metallochromic indicators widely used for the spectrophotometric determination of uranium(VI) include PAR,[3] PAN,[4] Eriochrome Cyanine R[2] and Chromazurol S.[5,6] These colour reactions are not specific, and the sensitivity is also not adequate, especially for very small quantities of uranium(VI). In our preliminary observations it was found that the sensitivity of the uranium(VI)–PGR reaction is increased by addition of cetyltrimethylammonium bromide, owing to formation of a blue ternary complex in the pH range 4–7. There is also less interference from foreign ions. We have therefore explored the analytical value of this complex. The spectrophotometric methods proposed for evaluation of formation constants of ternary complexes are tedious and in only a few systems[7] have the formation constants of ternary complexes of surfactants been determined. We therefore propose a new simple procedure for determining such stability constants. It should be specially useful in the case of outer-sphere complexes.

EXPERIMENTAL

Reagents

A stock solution of uranyl nitrate was prepared and standardized gravimetrically by the oxine method. Working solutions were prepared by appropriate dilution. A stock solution of PGR (0.001*M*) was prepared by dissolving the required amount in 25 ml of methanol and diluting to 250 ml with redistilled water. Solutions of CTAB were prepared by dissolving the calculated amounts in hot redistilled water and cooling. Acetate buffer solutions were prepared from 0.2*M* sodium acetate and 0.2*M* acetic acid. All chemicals used were analytical-reagent grade.

RESULTS AND DISCUSSION

All experiments were done at room temperature 25° ± 1°. The total volume of the mixtures was kept at 25 ml. The order of addition of the reactants had no significant effect on the absorbance and stability of the colour, but in the studies described, the order of addition was PGR, buffer, uranyl nitrate and CTAB.

Spectral characteristics

Figure 1 shows the absorption spectra of solutions containing PGR, PGR and CTAB, PGR and UO_2^{2+}, and PGR, UO_2^{2+} and CTAB at pH 5.6. The wavelengths of maximum absorption were 530, 560, 540 and 580 nm respectively. The formation of the ternary complex is indicated by a pronounced bathochromic shift in the spectrum and a marked increase in absorbance in comparison with the binary chelate. A solution containing PGR and CTAB absorbs strongly at 580 nm but at longer wavelengths, *e.g.*, 610 and 620 nm, the absorbances of PGR and PGR–CTAB solutions are practically negligible. This is the reason for the increased sensitivity. The absorption spectra of PGR and the binary chelate solutions are almost parallel at wavelengths longer than 530 nm and so the spectrophotometric method based on the binary chelate is not sensitive.

The absorption spectra of PGR in presence of a twentyfold molar ratio of CTAB were recorded over the pH range 1.9–8.6 (Fig. 2). At between pH 6.0 and 3.3, λ_{max} is 560 nm, and outside this range gradually shifts towards the λ_{max} of PGR. For solutions containing PGR and increasing amounts of CTAB λ_{max} gradually shifts to 560 nm, becoming constant when the CTAB:PGR mole-ratio is $\geq$4:1 (Fig. 3).

Mixtures at various pH-values and containing UO_2^{2+}, PGR and CTAB in the ratio 1:2:10 were prepared and the absorption spectra were recorded (Fig. 4). The ternary complex has a constant λ_{max} at pH between 1.6 and 6.8, but the absorbance is constant only between pH 5.1 and 6.4.

Composition of the complex

The UO_2^{2+}:PGR ratio in the ternary complex was established as 1:2 by the continuous variations[8] and

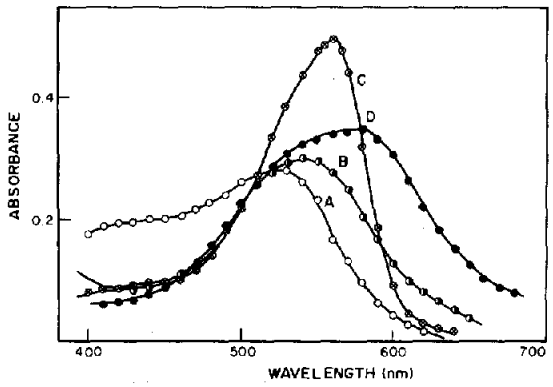


Fig. 1. *A*, PGR ($2 \times 10^{-5}M$); *B*, PGR ($2 \times 10^{-5}M$); UO_2^{2+} ($1 \times 10^{-5}M$); *C*, PGR ($2 \times 10^{-5}M$); CTAB ($4 \times 10^{-4}M$); *D*, PGR ($2 \times 10^{-5}M$), UO_2^{2+} ($1 \times 10^{-5}M$), (CTAB ($4 \times 10^{-4}M$); pH 5.6.

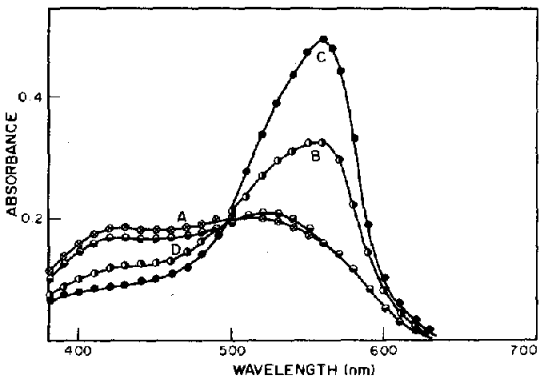


Fig. 2. PGR ($2 \times 10^{-5}M$), CTAB ($4 \times 10^{-4}M$); pH 1.9 (*A*), 3.3 (*B*), 5.6 (*C*), 8.6 (*D*).

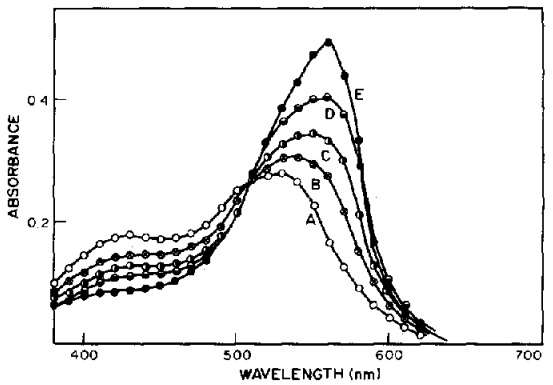


Fig. 3. PGR ($2 \times 10^{-5}M$); CTAB $2 \times 10^{-5}M$ (*A*), $4 \times 10^{-5}M$ (*B*), $6 \times 10^{-5}M$ (*C*), $8 \times 10^{-5}M$ (*D*), $1 \times 10^{-4}M$ (*E*), pH 5.6.

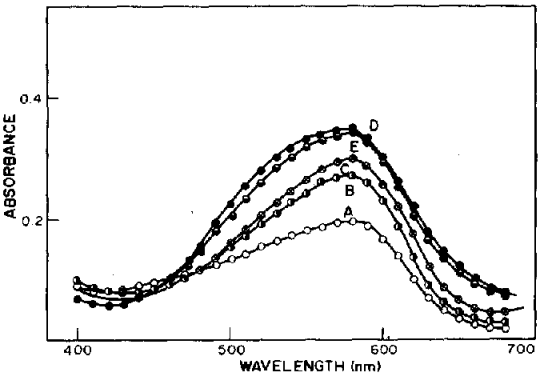
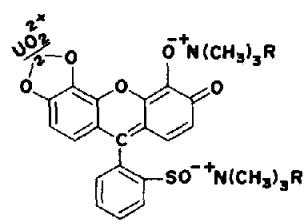


Fig. 4. PGR ($2 \times 10^{-5}M$); UO_2^{2+} ($1 \times 10^{-5}M$); CTAB ($4 \times 10^{-4}M$); pH 1.6 (*A*), 3.4 (*B*), 3.8 (*C*), 5.5 (*D*), 6.3 (*E*).

mole-ratio[9] methods in the presence of a suitable excess of CTAB. The proportion of cetyltrimethylammonium ions in the complex was determined by measuring the absorbances of mixtures containing UO_2^{2+} and PGR in the ratio 1:2 and different amounts of CTAB, and plotting the absorbances against amount of CTAB. It was found that a fourfold (molar) ratio of CTAB to complex is required for maximum colour formation. The complex is thus formulated as UO_2 $(PGR)_2(CTA)_4$.

The uranyl ion usually has co-ordination number four, which appears to be satisfied by two PGR molecules. The CTA cations would in any event be unlikely to react with the $UO_2^{2+}(PGR)_2$ chelate at the metal co-ordinating centre, and the ternary complex thus probably has the following structure:



Evaluation of stability constants

When only solution equilibria involving changes in the outer sphere have to be considered, *i.e.* in systems where the inner-sphere complexes are inert, the same experimental and calculation methods can be applied as in the case of the study of successive complex formation.[10] The ternary complex forms in a stepwise manner and can be described in terms of the following equations (charges omitted):

$$M + 2PGR \overset{k_1}{\rightleftharpoons} M(PGR)_2 \qquad (1)$$

$$M(PGR)_2 + 4CTA \overset{k_2}{\rightleftharpoons} M(PGR)_2(CTA)_4 \qquad (2)$$

$$K_1 = \frac{[M(PGR)_2]}{[M][PGR]^2} \qquad (3)$$

$$K_2 = \frac{[M(PGR)_2(CTA)_4]}{[M(PGR)_2][CTA]^4} \qquad (4)$$

The overall formation constant $\beta = K_1 K_2$. K_1 and K_2

are evaluated separately by the mole-ratio method and the expressions

$$K_1 = \frac{c_1(1-\alpha_1)}{\alpha_1 c_1(2\alpha_1 c_1)^2} \quad (5)$$

$$K_2 = \frac{c_2(1-\alpha_2)}{\alpha_2 c_2(4\alpha_2 c_2)^4} \quad (6)$$

where α_1 and α_2 are the degrees of dissociation of $M(PGR)_2$ and $M(PGR)_2(CTA)_4$ respectively, and c_1 and c_2 are the analytical concentration of UO_2^{2+} and the actual concentration of $M(PGR)_2$ respectively. The results are given in the following table.

c_1, M	α_1	log K_1	c_2, M	α_2	log K_2	log β = log K_1K_2
2×10^{-5}	0.043	12.64	1×10^{-5}	0.103	22.48	35.12

Photometric determination

For calibration, solutions (25 ml) were prepared containing a fixed amount of PGR, different amounts of uranyl nitrate solution and a constant suitable excess of CTAB, and adjusted to pH 5.6 with acetate buffer. The absorbances at 620 nm were plotted against the amount of uranyl nitrate. Beer's law was obeyed over the range 19.0 to 0.24 ppm of uranium. The molar absorptivity was found to be 3.3×10^4 $l.mole^{-1}.cm^{-1}$ at 620 nm. The relative standard deviation was 1.1% for 5 ppm of uranium. Chloride, nitrate, acetate Pt(IV), Rh(III) and Th do not interfere even in large excess. In determination of 5 ppm of uranium, the following ions interfere at the levels (ppm) given in brackets: ClO_4^-(3), PO_4^{3-}(4), SO_4^{2-}, Cu^{2+}(5), Fe^{2+}, MoO_4^{2-}, WO_4^{2-}, Ni^{2+}, Co^{2+}, VO^{2+}(6), Cr(VI) (8), In^{3+}, Ru^{3+}(9), Hg^{2+}, Ca^{2+}, Pd^{2+}(10), Cd^{2+}(11), Ga^{3+}, Zn^{2+}, Sr^{2+}(12), Y^{3+}, Al^{3+}(13), La^{3+}, Ba^{2+}, Hf^{4+}(14), Sm^{3+}(15).

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REFERENCES

1. J. Horak and A. Okáč, *Collection Czech. Chem. Commun.*, 1968, **33**, 304.
2. O. Prakash, J. R. Verma and S. P. Mushran, *Chim. Anal. (Paris)*, 1970, **52**, 655.
3. L. Sommer, V. M. Ivanov and H. Novotná, *Talanta*, 1967, **14**, 329.
4. E. Gagliardi and B. Ilmaier, *Mikrochim. Acta*, 1968, 1259.
5. L. Sommer, *Collection Czech. Chem. Commun.*, 1970, **35**, 794.
6. S. N. Sinha and A. K. Dey, *Indian J. Chem.*, 1963, **1**, 70.
7. V. Svoboda and V. Chromý, *Talanta*, 1966, **13**, 237.
8. P. Job, *Ann. Chim. (Paris)*, 1928, **9**, 113.
9. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
10. M. T. Beck, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold, London, 1970.

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ANALYTICAL DATA

PROTONATION CONSTANT OF SOME SULPHA-DRUGS IN DIOXAN WATER MEDIUM

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Summary—The dissociation constants of some sulpha-drugs have been determined potentiometrically in 10–50% (v/v) dioxan–water media at 25° at ionic strength 0.1*M* ($NaClO_4$). Correlation of mole fraction of dioxan and p*K* gives a straight line. The p*K* values do not vary linearly with reciprocal of the dielectric constant of the medium at high percentage of dioxan.

In continuation of our studies on the sulpha-drugs,[1,2] the dissociation constants of sulphanilamide and its derivatives have been determined in 10–50% dioxan–water media at 25° and ionic strength (μ) 0.1*M* ($NaClO_4$). The effect of dielectric constant and temperature on the p*K* values has also been studied. Since the sulpha-drugs are insoluble in water the data for aqueous media are computed from the linear plot of p*K* *vs.* mole fraction of dioxan.

EXPERIMENTAL

The sulpha-drugs were used as received from the manufacturers. Dioxan was purified and stored as described by Vogel.[3] Doubly distilled water was used. Chemically pure sodium perchlorate was used to keep the ionic strength constant.

A Systronic pH-meter, type 322, was calibrated at pH 4.0 and 9.2 with potassium hydrogen phthalate and borax buffers. The U_H correction (Van Uitert and Haas[4]) was applied to the measurements.

Potentiometric titrations of, (*i*) 2.0 ml of 0.05*M* perchloric acid and (*ii*) 2.0 ml of 0.05*M* perchloric acid + 5.0 ml of 0.02*M* sulpha-drug with 0.05*M* carbonate-free sodium hydroxide were performed as described earlier.[5] The initial total volume was 50.0 ml and the desired dioxan–water composition was maintained throughout. The ionic strength was kept at 0.1*M* with 1.0*M* sodium perchlorate. An inert atmosphere was maintained inside the titration cell by passage of oxygen-free nitrogen presaturated with the solvent. Before the titration was started the contents of the titration vessel were adjusted to the desired temperature, in a thermostat.

RESULTS AND DISCUSSION

The Irving and Rossotti method[6] was used for calculation of $\bar{n}_H$ values from the titration curves (*i*) and (*ii*), and the dissociation constant, p*K*, was found by the Bjerrum half-integral method.[7] The values are also calculated by using the formula:

$$pK = pH + \log \frac{\bar{n}_H}{1 - \bar{n}_H}$$

and by plotting a graph of pH *vs.* $\log\bar{n}_H/(1 - \bar{n}_H)$. The values obtained are all in good agreement. The average values are reported in Table 1.

The p*K* value found for sulphanilamide is slightly higher than that reported earlier,[8] possibly because of the different experimental conditions.

Table 1. Dissociation constant (p*K*) of sulpha-drugs at 25 ± 0.2°C in dioxan–water media

Compound	Dioxan, % *v/v* 0*	10	20	30	40	50	*m*
Sulphanilamide	10.60	10.82	11.06	11.36	11.75	12.22	9.50
Sulphafurazole	6.15	6.45	6.70	7.10	7.52	8.10	11.20
Sulphadiazine	6.35	6.65	6.96	7.31	7.82	8.41	11.74
Sulphamethoxy pyridazine	6.75	7.02	7.30	7.68	8.12	8.70	11.08
Sulphamerazine	6.90	7.15	7.40	7.75	8.14	9.68	10.22
Sulphathiazole	7.12	7.40	7.72	8.08	8.50	9.10	11.43
Sulphaphanazole	7.50	7.72	8.05	8.40	8.80	9.32	10.52
Sulphamethizole	7.72	7.95	8.25	8.68	9.00	9.55	10.66
Sulphadimidine	7.75	8.00	8.31	8.58	9.06	9.56	10.30
Sulpha dimethoxine	8.05	8.32	8.60	8.97	9.38	9.91	10.80
Sulphapyridine	8.35	8.60	8.91	9.24	9.62	10.21	10.45
n_2	0.000	0.023	0.050	0.083	0.123	0.174	—
$1/\epsilon$	0.0127	0.0146	0.0165	0.0193	0.0235	0.0303	—

* By extrapolation (= *C* in equation $pK = mn_2 + C$).

The effect of change in dielectric constant

The degree of dissociation of an acid depends on the dielectric constant (ϵ) of the medium. In a solvent of low dielectric constant the electrostatic force between the ions is increased, which facilitates the formation of molecular species and should increase the pK value (Table 1) as reported earlier.[9,10] The dielectric constant decreases with increase in dioxan concentration in the mixtures used here.[11]

The change in pK mole fraction of dioxan (n_2) gave a linear plot obeying the relationship $pK = mn_2 + C$, where m and C are the slope and intercept (pK value at 0.0% dioxan) respectively. The values of m and C are reported in Table 1. The pK values do not vary linearly with the reciprocal ($1/\epsilon$) of the dielectric constant of the medium at high percentage of dioxan.

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REFERENCES

1. K. Lal, *Acta. Chim. (Budapest)*, 1978 (accepted); *Chem. Era*, 1978 (accepted).
2. K. Lal and S. P. Gupta, *Acta Ciencia Indica*, 1978, **4**, 242.
3. A. I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd Ed., p. 177. Longmans, London, 1956.
4. L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 1953, **75**, 451.
5. K. Lal and S. P. Gupta, *Ind. J. Chem.*, 1976, **14A**, 260; *Rev. Chim. (Romania)*, 1976, **27**, 657.
6. H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1953, 3397; 1954, 2904.
7. J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, Haase, Copenhagen, 1957.
8. P. H. Bell and R. O. Roblin, Jr., *J. Am. Chem. Soc.*, 1942, **64**, 2905.
9. M. Giulio, *Electrochemistry, Principles, Practices and Applications*, p. 80. Elsevier, Amsterdam, 1963.
10. A. Gemant, *J. Chem. Phys.*, 1942, **10**, 723.
11. Y. K. Agrawal and S. G. Tandon, *Talanta*, 1972, **19**, 700.

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DETERMINATION DES CONSTANTES D'EQUILIBRE CONDITIONNELLES ET DES CONSTANTES DE VITESSE DES REACTIONS ENTRE LE SELENIUM(IV) ET CINQ ORTHODIAMINES AROMATIQUES

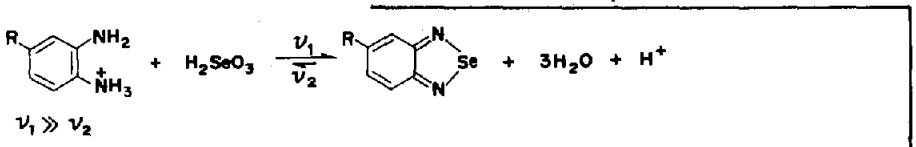
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Résumé—La détermination des constantes d'équilibre conditionnelles et des constantes de vitesse, à diverses valeurs de pH, des réactions entre le sélénium(IV) et cinq orthodiamines aromatiques a permis de mettre en évidence une réaction principale, d'ordre II, qui implique la participation sélective de l'espèce monoprotonée de l'orthodiamine et de l'acide sélénieux non dissocié. L'ion monohydrogénosélénieux ou l'espèce diprotonée de l'orthodiamine peuvent prendre part à une réaction parallèle selon une cinétique plus lente. Les produits de réaction sont très stables.

Le sélénium, à l'étage d'oxydation IV, est susceptible de réagir avec des orthodiamines aromatiques pour donner un benzosélénadiazole, souvent appelé piazsélénole, utilisable pour la détermination analytique du sélénium.[1,2]

Le mécanisme réactionnel proposé empiriquement implique la participation de l'espèce monoprotonée de l'orthodiamine et de l'acide sélénieux non dissocié selon la rèaction:[3,4]



$v_1 \gg v_2$

Poursuivant nos travaux antérieurs relatifs à la détermination des constantes d'ionisation de certaines diamines aromatiques[5] et de leurs dérivés séléniés,[1] ce travail sera consacré, dans un premier temps, à la détermination spectrophotométrique des constantes d'équilibre des réactions entre le sélénium(IV) et cinq orthodiamines aromatiques, en opérant dans des conditions bien définies de température, force ionique et pH. Par la suite, nous établirons, pour chaque dérivé, une valeur de pH pour laquelle la vitesse de réaction est maximale, en suivant les variations des constantes de vitesse en fonction du pH.

PARTIE EXPERIMENTALE

Réactifs

Orthodiamines étudiées. L'orthophénylènediamine (PD) et ses dérivés 4-méthyl (4-CH_3-PD), 4-chloro (4-Cl-PD), 4,5-dichloro (4,5-diCl-PD) et 4-nitro (4-NO_2-PD). Ces dérivés ont été obtenus, purifiés et conservés selon un mode opératoire décrit précédemment;[5] ils ont été utilisés sous forme de dichlorhydrate, sauf le dérivé nitré qui a été employé sous forme dibasique. La pureté des produits a été vérifiée par dosage potentiométrique des chlorures. Les solutions de travail ($5 \cdot 10^{-4} M$) ont été préparées par dissolution d'une quantité adéquate du produit dans de l'eau bidistillée.

Acide sélénieux (Baker PA). La solution de travail ($5 \cdot 10^{-4} M$) a été préparée par dilution, à l'aide d'eau bidistillée, d'une solution mère ($10^{-2} M$) dont le titre a été vérifié par iodométrie.

Détermination spectrophotométrique des constantes d'équilibre

Méthode de Job.[6] A partir des solutions de travail placées dans des burettes, on réalise, dans des ballons jaugés de 100 ml, une série de mélanges de même concentration molaire totale en diamine et en sélénium, soit $10^{-4} M$, mais différents par la proportion relative de leurs divers constituants. La force ionique de toutes les solutions est fixée à $0{,}1 M$ à l'aide de perchlorate de sodium et le pH est ajusté à 1,5 au moyen de solutions $2 M$ d'acide perchlorique et d'hydroxyde de sodium. L'absorption de ces mélanges, placés dans un bain thermostatique à 25°, est mesurée par rapport à un réactif blanc, à une longueur d'onde précisée ci-après, jusqu'à valeur constante.

Méthode combinée de Budĕšinskỳ[3,7–9] *et de Klausen et Langmyhr.*[10] A partir des solutions de travail, on réalise une série de mélanges ayant, cette fois, la même concentration en diamine et en sélénium et des solutions de comparaison, toujours de concentration égale en diamine et en sélénium, mais dont la concentration molaire totale est de moitié plus petite. On opère dans les mêmes conditions que précédemment. L'absorption des solutions de comparaison est, en plus, mesurée dans des cellules de quartz de 2 cm pour le calcul de la constante selon la méthode de Klausen et Langmyhr.

Méthode de Budĕšinskỳ et Svec.[11] Le calcul de la constante se base sur les résultats de la méthode de Job (excès en sélénium) et de la méthode de Budesinsky (concentration équivalente en sélénium et en diamine).

La constante d'équilibre s'exprime selon l'équation:

$$K = \frac{[PIS]}{(H_2SeO_3 - [PIS])(Diamine - [PIS])}$$

[PIS] = concentration en piazsélénole à l'équilibre, H_2SeO_3 et Diamine = concentrations initiales en acide sélénieux et en diamine.

Détermination des constantes de vitesse en fonction du pH

On mesure l'absorption en fonction du temps de solutions équimoléculaires ($5 \cdot 10^{-5} M$) en sélénium et en orthodiamine, dont le pH a été ajusté à une valeur comprise entre 3,5 et 0,3. On opère dans les mêmes conditions que ci-avant.

La constante de vitesse d'une réaction d'ordre II s'exprime selon l'équation:

$$k = \frac{1}{t} \frac{x}{a(a - x)}$$

a = concentrations initiales en acide séléniéux et en diamine (égales),
x = quantité de substance ayant réagi après un temps t.

RESULTATS ET DISCUSSION

Détermination des constantes d'équilibre conditionnelles

Pour chaque dérivé, à l'exception du 4-NO_2-PD, il est aisé, en suivant l'évolution spectrale UV-visible au cours du temps de réaction entre les orthodiamines et le sélénium (à 25°, pH 1,5 et μ_i 0,1M), de sélectionner une longueur d'onde où l'absorption du dérivé sélénié formé est maximale tandis que celle de l'orthodiamine ou de l'acide sélénieux est nulle.

L'étude spectrale permet, en outre, de noter l'apparition d'un certain nombre de points isosbestiques; ceux-ci figurent au tableau 1 qui mentionne également les diverses caractéristiques spectrales observées dont l'interprétation a été donnée précédemment.[1,5]

La méthode spectrophotométrique de détermination des constantes d'équilibre à été préférée aux autres techniques, en raison des avantages qu'elle présente dans le cas particulier de la réaction étudiée.[12]

La figure 1 reprend le tracé expérimental d'une courbe de Job correspondant à l'orthophénylènediamine; l'allure de la courbe est analogue pour tous les autres dérivés. La présence d'un maximum à la valeur 0,5 de la fraction molaire en sélénium et en diamine et l'absence d'inversions de la convexité ou

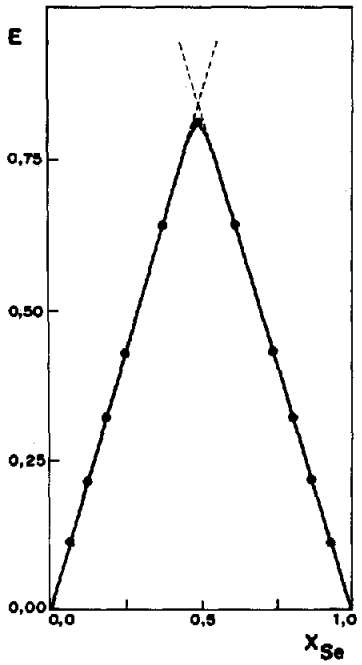


Fig. 1. Courbe de Job obtenue pour la réaction entre le sélénium(IV) et l'orthophénylènediamine (concentration totale $10^{-4} M$, 25°, pH 1,5 et μ_i 0,1M).

de parties concaves de la courbe expérimentale permet d'établir que le produit de réaction est de composition 1:1 et du type AB.[13,14] Les résultats obtenus en utilisant le tracé des tangentes de la courbe de Job figurent au tableau 2 dont l'examen indique qu'à la valeur de pH considéré, le produit de réaction est très stable. Signalons aussi que, à 25° et à pH 1,5, un temps très long (souvent deux semaines) est requis pour que la réaction soit complète.

Nous avons tenté d'obtenir des valeurs plus précises des constantes d'équilibre conditionnelles en utilisant d'autres techniques:[3,7–11] les valeurs auxquelles ces dernières ont conduit figurent au tableau 2; elles sont parfaitement compatibles entre elles mais aucune différence statistiquement valable ne peut être établie entre la stabilité des piazsélénoles obtenus. Dans tous les cas, la très grande stabilité des dérivés séléniés a nécéssairement conduit a des valeurs peu précises.

Tableau 1. Principales caractéristiques spectrales notées lors de l'étude UV-visible de la réaction entre le sélénium(IV) et les cinq diamines aromatiques (25°, pH 1,5, et μ_i 0,1M)

Dérivé	Diamine pure λ_{max}, *nm* Bande ^1L_a	Bande ^1L_b	Piazsélénole λ_{max}, *nm* Bande $\pi \rightarrow \pi^*$	Points isosbestiques, *nm*
4-CH_3-PD	232	282	335	225,5, 241, 263, 293
PD	230	280	332,5	217, 242, 261, 290,5
4-Cl-PD	236	287	338	227, 250, 269, 296,5
4,5-diCl-PD	242	299	347	231,5, 261, 267, 306
4-NO_2-PD	361	—	344	356

Tableau 2. Détermination des constantes d'équilibre conditionnelles des réactions entre le sélénium(IV) et cinq diamines aromatiques (25°, pH 1,5 et μ_i 0,1*M*)

Dérivé	$\lambda_{analytique}$ nm	Job	log *K** Buděšínský	Klausen et Langmyhr	Buděšínský et Svec
4-CH_3-PD	335	6,6	6,3	6,2	6,4
PD	332,5	7,4	7,1	7,1	7,3
4-Cl-PD	338	7,0	6,8	6,8	6,8
4,5-diCl-PD	347	6,9	6,7	6,7	6,8
4-NO_2-PD	375	7,5	6,7	6,8	7,3

* Chaque valeur représente la moyenne d'au moins 6 essais.

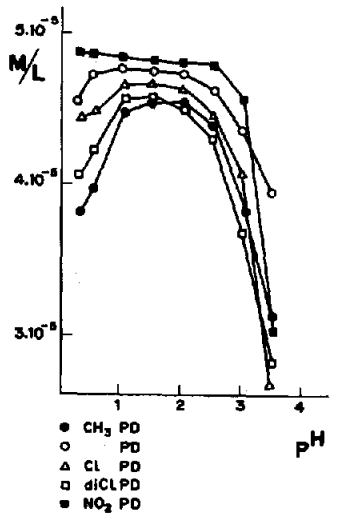


Fig. 2. Quantité en môle par litre de piazsélénole formé à l'équilibre au départ d'une solution équimoléculaire ($5 \cdot 10^{-5} M$) en diamine et en sélénium(IV) à 25°.

Il faut remarquer qu'il est malaisé de tenir compte des coefficients de réaction secondaire car, comme nous le montrons dans la suite du travail, plusieurs espèces réagissantes contribuent à la réaction dont le mécanisme apparaît alors plus complexe que celui déjà suggéré par deux auteurs.[15,16] En outre, signalons que, simultanément à la réaction étudiée, une dégradation de l'orthodiamine, très limitée en milieu acide peut se produire; sa nature et son importance sont peu connues.

En ce qui concerne le dérivé 4-NO_2, il n'a pas été possible de sélectionner une longueur d'onde où seul le piazsélénole formé absorbe; nous avons été contraints de travailler à une longueur d'onde où l'absorption de la diamine est grande par rapport à celle du piazsélénole. Ayant déterminé les coefficients d'extinction spécifique de la diamine et du piazsélénole, à la longueur d'onde et au pH considéré, nous avons pu calculer la quantité de piazsélénole formé à tout instant.

Determination des constantes de vitesse et de l'ordre de la réaction

Les réactions des cinq diamines avec le sélénium ont été suivies au cours du temps, à 25° et à des valeurs de pH variant de 0,3 à 3,5.

A la lecture de la figure 2 qui illustre le résultat de ces évolutions on constate que la zone de pH située entre 1 et 2 est optimale pour l'équilibre de la réaction directe en ce qui concerne les cinq dérivés.

La variation de pH entre 0,3 et 3,5 n'entraîne aucune modification appréciable du spectre UV-visible des piazsélénoles dont les coefficients d'extinction spécifique restent donc inchangés.[1]

Si des différences significatives dans la valeur des constantes d'équilibre ne peuvent être notées dans la zone de pH située entre 1 et 2, il n'en est pas de même pour la vitesse de la réaction qui est fortement influencée par l'acidité du milieu réactionnel.

Nous avons déterminé l'ordre et la constante de vitesse de la réaction par la méthode classique d'intégration; pour tous les dérivés, pendant environ 24 h,

Tableau 3. Valeur des constantes de vitesse d'ordre II (k), en fonction du pH pour les cinq réactions étudiées

Dérivé	pH 3,5	3,0	2,5	k, $l \cdot mole^{-1} \cdot sec^{-1}$ 2,0	1,5	1,0	0,5	0,3
4-CH_3-PD	0,15	0,33	0,67	0,90	0,82	0,38	0,11	0,07
	0,01 (10)*	0,01 (10)	0,02 (10)	0,02 (10)	0,02 (10)	0,01 (10)	0,02 (10)	0,02 (10)
PD	0,12	0,34	0,69	1,10	1,22	0,93	0,33	0,19
	0,01 (14)	0,01 (14)	0,01 (14)	0,01 (14)	0,02 (14)	0,01 (14)	0,01 (14)	0,01 (14)
4-Cl-PD	0,11	0,44	0,87	1,26	1,50	1,42	1,03	0,76
	0,01 (8)	0,01 (8)	0,02 (8)	0,01 (8)	0,02 (8)	0,01 (8)	0,01 (8)	0,02 (8)
4,5-diCl-PD	0,12	0,34	0,92	1,48	1,71	1,74	1.57	1,43
	0,03 (8)	0,03 (8)	0,03 (8)	0,03 (8)	0,02 (8)	0,03 (6)	0,04 (6)	0,06 (6)
4-NO_2-PD	0,02	0,08	0,35	0,61	0,67	0,68	0,73	0,74
	0,01 (10)	0,01 (16)	0,02 (20)	0,02 (20)	0,02 (20)	0,02 (18)	0,04 (16)	0,02 (8)

* L'écart étalon (nombre d'essais).

la constante de vitesse répond parfaitement à l'équation d'une constante de réaction chimique d'ordre II pour laquelle les concentrations des corps réagissants sont égales. Cette constatation confirme celle d'autres auteurs concernant le diaminonaphtalène[15] et le 4-CH_3-PD.[15] Le tableau 3 mentionne la valeur expérimentale des constantes de vitesse d'ordre II.

L'examen de ce tableau montre clairement que la valeur maximale de la constante de vitesse est déplacée vers des pH plus acides au fur et à mesure que la basicité de la diamine diminue.

Ayant déterminé les valeurs des constantes d'ionisation des diamines[3] et connaissant celles de l'acide sélénieux,[15,16] il nous a été possible de tracer les graphiques de distribution des espèces en fonction du pH: pour chaque dérivé, la valeur maximale de la constante de vitesse d'ordre II correspond à un pH où la quantité relative en acide sélénieux non dissocié et en diamine monoprotonée est la plus grande. La diminution de la valeur des constantes de vitesse lorsque les pH sont plus élevés est due à la diminution de la quantité d'acide sélénieux non dissocié (se transformant progressivement en monohydrogénosélèniure); la diminution en milieu plus acide est due à l'abaissement de la concentration en espèce monoprotonée (qui se transforme alors en diprotonée).

Il semble donc qu'il se produit, dans un premier temps, une réaction principale entre l'acide sélénieux non dissocié et la diamine monoprotonée; des réactions parallèles impliquant d'autres espèces ioniques se passent simultanément mais les constantes de vitesse de celles-ci sont beaucoup plus faibles et ne perturbent pas, dans un premier stade, la valeur de la constante de vitesse déterminée expérimentalement. Parmi les espèces réagissant plus lentement se trouvent l'anion monohydrogénosélèniure (explique la réaction du 4-NO_2-PD aux pH moins acides) et la forme diprotonée de la diamine (explique la réaction du 4-CH_3-PD en milieu plus acide). La réaction avec la forme dibasique de la diamine peut, selon toute vraisemblance, être exclue.

Enfin, il nous a été possible d'établir des relations entre la somme de deux constantes $\sigma_m + \sigma_p$ de Hammett[17–19] et les constantes de vitesse à un pH donné. Toutefois, le dérivé 4-NO_2-PD s'écarte totalement des tracés; nous ne pouvons, jusqu'à présent, expliquer ce phénomène.

BIBLIOGRAPHIE

1. J. Nève, M. Hanocq et L. Molle, *Talanta*, 1979, **26**, 15.
2. J. Nève et M. Hanocq, *Anal. Chim. Acta*, 1977, **93**, 85.
3. B. Buděšínský, *Z. Physik. Chem. (Frankfurt)*, 1971, **76**, 310.
4. P. Cukor et F. Lott, *J. Phys. Chem.*, 1965, **69**, 3232.
5. J. Nève et M. Hanocq, *Anal. Lett.*, 1977, **10**, 133.
6. P. Job, *Ann. Chim. (Paris)*, 1928, **9**, 113.
7. B. Buděšínský, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1345.
8. *Idem, Z. Anal. Chem.*, 1972, **258**, 186.
9. *Idem, Anal. Chem.*, 1975, **47**, 560.
10. K. S. Klausen, *Anal. Chim. Acta*, 1969, **44**, 377.
11. B. Buděšínský et J. Svec, *Z. Physik. Chem. (Frankfurt)*, 1970, **73**, 7.
12. H. S. Rossotti, *Talanta*, 1974, **21**, 809.
13. K. S. Klausen et F. J. Langmyhr, *Anal. Chim. Acta*, 1968, **40**, 167.
14. *Idem, ibid.*, 1968, **28**, 335.
15. L. Barcza, *Mikrochim. Acta*, 1964, 136.
16. T. Kawashima, *Sci. Rep. Kagoshima Univ.*, 1972, **21**, 57.
17. L. P. Hammett, *Trans. Farad. Soc.*, 1938, **34**, 156.
18. H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.
19. C. G. Swain et E. C. Lupton, *J. Am. Chem. Soc.*, 1968, **90**, 4328.

Summary—The conditional equilibrium and rate constants, at various pH values, of the reaction between selenium(IV) and five aromatic orthodiamines, were determined. A main reaction of second order occurs first between the monoprotonated species of the diamine and the non-dissociated selenious acid. The hydrogen selenite ion and the diprotonated diamine can also react but more slowly. The reaction products are very stable.

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PAPERS RECEIVED

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ERRATUM

In the paper by S. J. Haynes, *Talanta*, 1978, **25**, 85, the following corrections should be made.
Page 86, footnotes to Table 1, for "ferric thiocyanate spectrophotometric method" read "zirconium–Eriochrome Cyanine R spectrophotometric method"

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LOUIS GORDON MEMORIAL AWARD

The Editorial Board and Publisher of *Talanta* take great pleasure in announcing that the Louis Gordon Memorial Award for the best-written paper published in *Talanta* in 1977 is made to Iwao Tsukahara, Furukawa Electric Co. Ltd., Tokyo, for his paper "Extraction–spectrophotometric determination of traces of gold in copper, silver, lead, blister copper, copper concentrate and anode slime with 4,4'-bis(dimethylamino)-thiobenzophenone" (*Talanta*, 1977, **24**, 633).

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PUBLICATIONS RECEIVED

Chemical Analysis of Additives in Plastics: T. R. CROMPTON, 2nd Ed., Pergamon, Oxford, 1977. Pp. xii + 366. £15.25; $27.50.

This new edition is said in the preface to be about twice the length of the first, reflecting the continued growth of the literature since the first edition appeared in 1970. It certainly gives a well organized coverage of a widely scattered range of problems and techniques, from the normal analytical problems associated with determination of a known substance in a variety of matrices, to the much more difficult one of identifying and determining one or several unknown components of a complex mixture in which most of the components may be of similar chemical composition. Thus chromatographic and spectroscopic methods are heavily relied on, and modern techniques such as head-space analysis are coming into play. The text is illustrated with almost 180 figures and 90 tables.

Potentiometric Water Analysis: D. MIDGLEY and K. TORRANCE, Wiley, New York, 1978. Pp. xi + 409.

Written by two authors who are expert practitioners in the field covered, this is a thoroughly workmanlike book, starting with a lucid account of the background theory, the apparatus and ancillary equipment, the techniques, errors, and likely difficulties, and going on to a systematic account of the applications, listing the electrodes and methods available, the details of the method, the necessary statistical information on performance, and a useful section on tracing faults. This book should be on the reference shelf of all laboratories using ion-selective electrodes or doing water analysis.

Principles of Field Ionization and Field Desorption Mass Spectrometry: H. D. BECKEY. Pergamon, Oxford, 1977. Pp. xv + 335.

Since the author published his first book on the subject at the beginning of the 1970's there has been a great increase in interest in the techniques associated with field ionization. Several commercial organizations have produced field ionization sources and these have been used by mass spectrometrists to study a wide range of organic and inorganic compounds. This book is an attempt to summarize the advances in both theory and practice which have taken place in the intervening period. The material is collected under five headings dealing with the theory of field ionization and field desorption, experimental techniques, high field surface chemistry, the decomposition of ions in the gas phase and the applications of the technique to analytical chemistry. There is an interesting discussion on the design of ion sources and the production of suitable emitters and on the relationship between this form of mass spectrometry and the field microscopy from which it was developed. The chapter describing ion decomposition includes sections dealing with the rates of unimolecular decomposition of ions and with the elucidation of the mechanisms by which they decompose. Most analytical chemists will be surprised by the wide range of problems to which this new and growing technique has been applied. Both qualitative and quantitative studies are described and the coverage includes such diverse investigations as the analysis of heavy petroleum fractions and the determination of the structures of drug metabolites. The book is recommended to all practising mass spectrometrists and to those analytical chemists using physical methods in the solution of their problems.

Physical Chemistry: P. W. ATKINS, Oxford University Press, Oxford, 1978. Pp. xvi + 1018. £15.00 hardback; £7.95 paperback.

This book is a joy to read, and in its general approach to what is probably the most difficult part of chemistry for students inevitably reminds the reader of Hinshelwood's classic "The Structure of Physical Chemistry". The general pattern is to state what is going to be done in the section, to do it with a clear exposition of the meaning, the difficulties and the applications, and then to ask some questions about it. There are numerous worked examples to show the technique of problem solving and the more important bits of information are collected into "boxes", shaded to make them readily distinguishable. Anyone having difficulty with physical chemistry is strongly recommended to buy a copy at once.

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EDITORIAL

PERGAMON PRESS—STATEMENT ON THE NEW U.S. COPYRIGHT LAW FOR EDITORS, AUTHORS AND CONTRIBUTORS

In 1978 a new Copyright Law became effective in the U.S. and one of the results is that journals published by Pergamon Press will be asking authors for copyright on each article. How this has come about and why it is important to all of us, requires an explanation.

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Therefore, journals require a transfer of copyright in order to allow for a continuation of the methods that have been used in the past for the dissemination of scientific information. Thus, a transfer of copyright agreement for each article will be required of each author. The author will continue to hold all other traditional rights. For example, there are proprietary rights other than copyright such as patent rights; by definition, these are not transferred. We mention this explicitly since many people confuse patent rights with copyright. It will continue to be an explicit part of our permissions policy that anyone who wishes to *reprint* charts, graphs, etc. from an article will need only the author's permission. For reprinting complete articles, permission of the publisher *only* is required.

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Correlation between chromatographic parameters and connectivity index in liquid–solid chromatography: WOJCIECH MARKOWSKI, TADEUSZ DZIDO and TERESA WAWRZYNOWICZ. (11 *January* 1978)

Determination of silver in irons and steels by atomic-absorption spectrometry with an induction furnace: Direct analysis of solid samples: ABDULLAH M. AZIZ-ALRAHMAN and JAMES B. HEADRIDGE. (16 *January* 1978)

A rapid and selective method for direct gravimetric determination of vanadium(V) and its application to alloy steel and some rocks. BIJOLI KANTI PAL, SATI PRASANNA DAS THAKUR and BIRENDRA K. MITRA. (16 *January* 197°)

A non-linear least-squares approach for the refinement of all parameters involved in acid–base titrations: GIUSEPPE ARENA, CARMELO RIGANO, ENRICO RIZZARELLI and SILVIO SAMMARTANO. (17 *January* 1978)

Indirect potentiometric determination of hydrazine, isoniazid, sulphide and thiosulphate with a chloramine-T ion-selective electrode: M. A. KOUPPARIS and T. P. HADJIIOANNOU. (18 *January* 1978)

Interactions of tetrathionate with sulphite and sulphide: O. H. TUOVINEN. (23 *December* 1977)

Determination of chromium in low-alloy steels by atomic-absorption spectrophotometry: L. P. PANDEY, A. GHOSE, P. DASGUPTA and A. S. RAO. (23 *January* 1978)

Solvent extraction of metals with hydroxamic acids: F. VERNON and J. H. KHORASSANI. (26 *January* 1978)

Estimation of metallic iron in rusted sponge-iron: Dissolution of iron oxides by bromine/methanol: R. J. COSSTICK and P. C. NANCARROW. (30 *January* 1978)

Titrimetric determination of dissolved oxygen in waste water: G. SIVA REDDY, S. C. SOUNDAR RAJAN and Y. KRISHNA REDDY. (30 *January* 1978)

Determination spectrophotométrique des constantes d'acidité de quelques 2,1,3-benzoselenadiazoles (biazselenoles): Étude de leurs relations avec certaines fréquences de vibration infra-rouge et les constantes de substitution de Hammett: J. NEVE, M. HANOCQ and L. MOLLE. (31 *January* 1978)

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PAPERS RECEIVED

Untersuchungen zur Atomspektroskopischen Spurenanalyse in $A^{III}B^{V}$-Halbleiter-Mikroproben—III: Untersuchungen zur Schichtabtrennung und zur Spurenanalyse in dünnen GaAs-Schichten: I. R. SCHELPAKOWA, I. G. JUDELEWITSCH, S. A. SOLTAN, O. I. SCHTSCHERBAKOWA, K. DITTRICH and R. ZSCHOCKE. (2 *November* 1977)

Co-crystallization with 1-(2-pyridylazo)-2-naphthol and X-ray fluorescence for trace metal analysis of water: MICHEL G. VANDERSTAPPEN and RENÉ E. VAN GRIEKEN. (22 *November* 1977)

The atomic-absorption determination of beryllium in geologic materials by use of electrothermal atomization: E. Y. CAMPBELL and F. O. SIMON. (31 *October* 1977)

Die Potenzreihenentwicklung als empirisches mathematisches Modell bei der Analyse von Eisen und Silicium in Blei-Schachtofenschlacke mittels Röntgenfluoreszenz: G. SANNER. (23 *November* 1977)

Analytical evaluation of the derivatives used in equilibrium calculations: I. NAGYPÁL and I. PÁKÁ. (23 *November* 1977)

Sodium tetrachloroferrate as dehydrating agent: M. SALEEM, ASLAM M. KHAN and M. SHAHID. (24 *November* 1977)

Transport phenomenon through an iron(III) hydrous oxide membrane: *R. K. Gulati, Sat Paul Arora, J. S. Tyagi* and W. U. MALIK. 29 *November* 1977)

Indirect polarographic estimation of palladium: P. B. KALAPURNA. (30 *November* 1977)

Redox titrations—II: Location of inflection points of titration curves for homogeneous redox reactions: ATTE MERETOJA, OLAVI LUKKARI and ERKKI HAKOILA. (1 *December* 1977)

Paper extraction-chromatography of noble metals with use of mixtures of hydrochloric and nitric acid as mobile phases: S. PRZESZLAKOWSKI and A. FLIEGER. (1 *December* 1977)

Determination of mercury by isotope-dilution mass spectrometry with extraction: KOZO MATSUMOTO, YOUICHE KUNO and TSUGIO TAKEUCHI. (6 *December* 1977)

Effect of electrolytes on the solubility of benzoyltrifluoroacetone: Y. YOSHIMURA and N. SUZUKI. (6 *December* 1977)

Titrimetric determination of some organic compounds with bromine chloride: KRISHNA K. VERMA, ASHUTOSH SRIVASTAVA, JAMEEL AHMED and SAMEER BOSE. (7 *December* 1977)

A general spray reagent for the detection of pesticides on thin-layer plates: J. C. KOHLI, V. B. SOOD and K. S. SANDHU. (8 *December* 1977)

Direct photometric determination of cobalt(II) with *N*-methylaminothioformyl-*N'*-phenylhydroxylamine: S. P. MATHUR, R. S. THAKUR, C. S. BHANDARI and N. C. SOGANI. (8 *December* 1977)

Dosages thermométriques de quelques substances a intérêt pharmaceutique derivées du noyau phénothiazine par une solution d'hydroxyde de sodium: Enthalpie de neutralisation, enthalpie et entropie d'ionisation du chlorhydrate de prométhazine: J. L. BURGOT. (17 *August* 1977)

Dosages thermométriques de quelques diacides organiques, en milieu aqueux: Mise en evidence de la neutralisation successive des deux groupes acides de forces voisines: J. L. BURGOT. (17 *August* 1977)

Formation and thermodynamic properties of Ag(I) complexes with $S_2O_3^{2-}$, thiourea and SCN^- as ligands: DOMENICO DE MARCO, ATHOS BELLOMO and ALESSANDRO DE ROBERTIS. (9 *December* 1977)

Properties and construction of reagents for inorganic photometric analysis on the basis of azo dyes: A. T. PILIPENKO and L. I. SAVRANSKY. (12 *December* 1977)

Spectrophotometric titration of zirconium in siliceous materials: K. F. SUGAWARA, YAO-SIN SU and W. R. STRZEGOWSKI. (13 *December* 1977)

Thin-layer chromatography of organic sulphates, phosphates and nitrates: T. OKUMURA. (13 *December* 1977)

Electrochemical stripping determination of traces of copper, lead, cadmium and zinc in zirconium metal and zirconium dioxide: KAREL ŠTULÍK, PŘEMYSL BERAN, JAN DOLEŽAL and FRANTIŠEK OPEKAR. (13 *December* 1977)

***N*-Substituted phenothiazines as redox indicators in bromometry**: H. SANKE GOWDA and S. AKHEEL AHMED. (13 *December* 1977)

Spectroscopic studies of the metal complexes of ethylenediaminetetra-acetic acid in aqueous solution: A. A. MCCONNELL, R. H. NUTTALL and D. M. STALKER. (15 *December* 1977)

Bestimmung kleiner Nitrit- und Nitratkonzentrationen in 0.1 bis 16 molaren wässrigen Ammoniaklösungen: KLAUS RÖHL, SIEGFRIED SCHÖNHERR and RICHARD SCHRADER. (16 *December* 1977)

Studies on extraction of zirconium(IV) by quaternary ammonium halides from hydrochloric acid solutions and its separation from hafnium(IV): I. S. EL-YAMANI, M. Y. FARAH and F. A. ABD EL-ALEIM. (19 *December* 1977)

Stability and distribution studies of Sn(IV) and Cr(III) arsenophosphates: Separations of metal ions: K. G. VARSHNEY and ASIF A. KHAN. (19 *December* 1977)

Masking of manganese in relation to stepwise complexometric determination of calcium, magnesium and manganese: B. C. SINHA and S. DASGUPTA. (19 *December* 1977)

Information efficiency of analytical methods: KLAUS DANZER and KAREL ECKSCHLAGER. (19 *December* 1977)

Simultaneous determination of oxygen and mercury in inorganic and organic mercury compounds: KEIKO OHSAWA, SHOJI MIWA, TAKEO KURIKI and KAZUO IMAEDA. (23 *December* 1977)

Determination of dissolved oxygen in water: S. A. RAHIM and S. H. MOHAMED. (23 *December* 1977)

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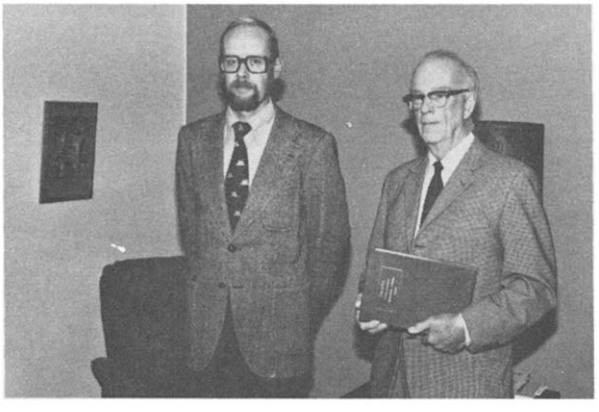
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Dr. D. BETTERIDGE presenting the Louis Gordon Memorial Award for 1976 to Professor F. NYDAHL.



At the presentation (left to right: A. BENGTSSON, Professor B. NYGARD, Professor A. JOHANSSON, Professor F. NYDAHL, D. BETTERIDGE and Professor J. RUZICKA).



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PAPERS RECEIVED

Polarographic reduction of some 5-arylazopyrimidines: R. N. GOYAL and SUDHA TYAGI. (2 *February* 1978)

Determination of the salting coefficients of benzoyltrifluoroacetone: Y. YOSHIMURA and N. SUZUKI. (6 *February* 1978)

Cation-exchange studies of eleven metal ions in DMSO–HCl, DMSO–HNO_3, acetone–HCl and acetone–HNO_3 systems: A selective separation of bismuth from numerous metal ions: MOHSIN QURESHI, RAM GOPAL VARSHNEY and ISHTIAQ ALI. (7 *February* 1978)

The silver salt of *N*-chloro-4-methylbenzene sulphonamide as a new oxidimetric reagent: RANGASWAMY, H. S. YATHIRAJAN and D. S. MAHADEVAPPA. (8 *February* 1978)

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Comparaison de trois méthodes de dosage du cuivre par analyse statistique: MICHEL ARNAC and JEAN-PIERRE CHANUT. (3 *February* 1978)

Radiotracer study of the dissolution of amalgams: I. MÁDI. (14 *February* 1978)

Spectrophotometric determination of nickel by adsorption of its α-furildioxime complex on naphthalene: MASATADA SATAKE, YUKIO MATSUMURA and TAITIRO FUJINAGA. (15 *February* 1978)

Amperometric determination of Ag(I), Au(III), Hg(II) and Pd(II) with thiosalicylamide: A. BASU, M. MAZUMDAR and S. C. SHOME. (16 *February* 1978)

Colorimetric reagents for alkali metal ions based on crown-ether complex formation—I: 4′-Picrylaminobenzo-15-crown-5: MAKOTO TAKAGI, HIROSHI NAKAMURA and KEIHEI UENO. (20 *February* 1978)

Absorption of nitrogen dioxide in organic solvents: NORIKO SHINOZUKA, MASAKI KARAYAMA and SHIGEO HAYANO. (21 *February* 1978)

Gas chromatographic investigation of volatile oxides and hydroxides of Tc, Re, Ru, Os and Ir—I: Investigation by isothermal gas-chromatography: A. STEFFEN and K. BÄCHMANN. (1 *February* 1978)

Gas chromatographic investigation of volatile oxides and hydroxides of Re, Tc, Os, Ru and Ir—II: Thermochromatographic investigations: A. STEFFEN and K. BÄCHMANN. (1 *February* 1978)

A rapid method for the estimation of glutamic acid with chloramine-T: S. N. KATGERI, D. S. MAHADEVAPPA and H. M. K. NAIDU. (21 *February* 1978)

Ring–air technique[a] An alternative to the ring-oven technique: R. D. DAVIES and V. PRETORIUS. (21 *February* 1978)

Determination of HOD by infrared spectrophotometry: B. I. AL-ALI and J. R. MAJER. (22 *February* 1978)

A note on the calculation of acid–base titration curves and their equivalence points: ÅKE OLIN and BO WALLÉN. (23 *February* 1978)

Benzohydroxamic acid as a reductometric titrant: Determination of manganese in ores and alloys: M. K. AHMED and C. SUBHA RAO. (24 *February* 1978)

Tin(II) sulphate as a new reductimetric titrant—direct titration of thallium(III) using ion-pair and redox indicators: S. R. SAGI and M. S. PRASADA RAO. (24 *February* 1978)

Equilibria of chromium(III) complex formation with Semi-Xylenol Orange: T. YOSHINO, S. MURAKAMI and M. ISHIHARA. (24 *February* 1978)

Specificity of a new colour reaction of chloramine-T with the carbonyl group: K. L. BAJAJ and K. L. AHUJA. (24 *February* 1978)

Accurate determination of sulphur in steels and alloys by isotope-dilution mass spectrometry: KAZUO WATANABE. (28 *February* 1978)

A new graphical method for differentiating mono and polynuclear complexes and for determining their stability constants: D. V. GONZÁLEZ GARCÍA, A. ARREBOLA RAMÍREZ and M. ROMÁN CEBA. (28 *February* 1978)

Ion-exchanger colorimetry—III: Microdetermination of zinc in water: KAZUHISA YOSHIMURA, HIROHIKO WAKI and SHIGERU OHASHI. (28 *February* 1978)

Analytical aspects of absorption spectroelectrochemistry at a platinum electrode—I: Study of metal ions: J. F. TYSON and T. S. WEST. (6 *March* 1978)

Effect of acids on the determination of cobalt by atomic-absorption spectrometry: MOSTAFA M. EMARA, NAZIK A. FARID, MONIR M. ALI and ABD EL-AZIZ GHAARIB. (7 *March* 1978)

Determination of thioureas by reaction with phenacyl bromide: NEELAM KHANNA and K. S. BOPARAI. (7 *March* 1978)

Semimicro spectrophotometric determination of nitroglycerine in propellants by use of 2,4-xylenol: GEORGE NORWITZ and PETER N. KELIHER. (27 *February* 1978)

Spectrophotometric determination of *p*-dimethylaminocinnamaldehyde on the microgram scale: SAIDUL ZAFAR QURESHI and NIZAM AHMAD. (7 *March* 1978)

Oxidation of some sugars with ammonium hexanitratocerate(IV) in nitric acid medium: I. C. SHUKLA. (7 *March* 1978)

Acidités et complexes des acides (alkyl- et aminoalkyl-) phosphoniques—I: Détermination potentiométrique des constantes d'acidité par affinement multiparamétrique. Prise en compte de l'impureté carbonate: MICHEL WOZNIAK and GUY NOWOGROCKI. (20 *December* 1977)

Extraction of molybdenum and other elements as trithiocarbonates: V. YATIRAJAM and USHA AHUJA. (9 *March* 1978)

Determination of metallic iron in a mixture of lime, calcium sulphide and pyrrhotite: V. S. SASTRI. (10 *March* 1978)

The determination of zinc in blast furnace flue dusts: A. HITCHEN and G. ZECHANOWITSCH. (21 *February* 1978)

Spectrophotometric determination of the pseudo-halide 1,2,3,4-thiatriazol-5-thiolate, $CS_2N_3^-$: EDUARDO A. NEVES and DOUGLAS W. FRANCO. (13 *March* 1978)

Sequential testing as an efficient screening method for interferences in routine analysis as applied to atomic-absorption spectrometry with flame and graphite furnace atomization: W. WEGSCHEIDER, G. KNAPP and H. SPITZY. (14 *March* 1978)

Spectrophotometric determination of vanadium as V(III) (*o*-phenanthroline thiocyanate, after extraction of V(III) thiocyanate with ethyl acetate: V. YATIRAJAM and S. P. ARYA. (14 *March* 1978)

Extractive separation and spectrophotometric determination of tungsten as ferrocyanide: V. YATIRAJAM and SUDERSHAN DHAMIJA. (16 *March* 1978)

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PAPERS RECEIVED

Extraction and simultaneous spectrophotometric determination of vanadium(IV) and (V) with 2-hydroxyacetophenoneoxime: T. SREENIVASULU REDDY and S. BRAHMAJI RAO. (28 August 1979)

Spectrophotometric method for the determination of microgram quantities of aluminium(III) with 2,4-dihydroxyacetophenone iso-nicotinoyl hydrazone (RPINH): G. ABDUL HUQ and S. BRAHMAJI RAO. (28 August 1979)

Extraction and simultaneous spectrophotometric determination of iron(II) and copper(II) in steel, brass and nickel-silver with quinoline-2-aldehyde thiosemicarbazone: D. V. KHASNIS and V. M. SHINDE. (28 August 1979)

Water analysis by spark-source mass-spectrometry after preconcentration on activated carbon: BRUNO M. VANDERBORGHT and RENÉ E. VAN GRIEKEN. (28 August 1979)

New titrants for perchlorate and fluoroborate: WALTER SELIG. (28 August 1979)

Studies on the extraction of some metal oxinates: Influence of the oxine medium on the extraction of Ni(II) and Co(II) oxinates: V. PANDU RANGA RAO, Y. ANJANEYULU, A. M. S. RAJU, P. SASI SEKHAR and R. RAMABRAHMA SASTRY. (30 August 1979)

Determination of nitrate and nitrite with ascorbic acid: N. RUKMINI, V. S. N. P. KAVITHA and K. RAMA RAO. (30 August 1979)

The extraction of iridium and platinum from organic solvents by polyurethane foam: R. A. MOORE and A. CHOW. (24 May 1979)

Colorimetric determinations based on the formation of hydroxamic acids: J. BARTOS. (25 September 1979)

Approaches used in deducing Schubert's ion-exchange equations: HUGO ZUNINO and GERARDO GALINDO. (13 September 1979)

Thermal decomposition of chemotherapeutic preparations and expectorants: ALEKSANDER RADECKI and MAREK WESOŁOWSKI. (27 September 1979)

Determination of microgram amounts of copper by peak paper chromatography: BHAJAN SINGH and PRITAM SINGH THIND. (28 September 1979)

Determination of tin in ores, iron, steel and alloys by atomic-absorption spectrophotometry after separation by extraction as the iodide: ELSIE M. DONALDSON. (1 October 1979)

A statistical approach to the study of simple stepwise equilibria: SELMAN A. BERGER and SAMUEL M. GRAFF. (3 October 1979)

Method of analysis for lorazepam: N. M. SANGHAVI and Y. V. BAILUR. (4 October 1979)

The binding of trace amounts of lead(II), copper(II), cadmium(II), zinc(II) and calcium(II) to soil organic matter: J. A. MARINSKY, A. WOLF and K. BUNZL. (18 September 1979)

Analytical applications of thio-, seleno, and telluroethers—IX: Spectrophotometric studies on the behaviour of β-ethylthioethylenethioglycollate ion in aqueous Ni(II) and Cu(II) solutions: LUIZ R. M. PITOMBO, MORENA P. PETERS and MARIA DO CARMO MEDEIROS. (7 September 1979)

Analytical applications of thio-, seleno-, and telluroethers—X: Potentiometric determination of the successive stoichiometric constants of Ni(II) and Cu(II) complexes with β-ethylthioethylenethioglycollate ion: LUIZ R. M. PITOMBO, MARIA DO CARMO MEDEIROS and MORENA P. PETERS. (7 September 1979)

Biamperometric determination of thymol with dichloramine-T as oxidimetric titrant in acetic acid media: B. K. KAPOOR and T. B. SINGH. (10 September 1979)

A new general method for the sensitive and selective detection of organic acids: H. S. RATHORE, S. K. SHARMA and K. KUMARI. (11 September 1979)

Spectrophotometric determination of bismuth after separation by adsorption of its 2-mercaptobenzothiazole complex on naphthalene: MASATADA SATAKE. (12 September 1979)

Spectrophotometric determination of bismuth after separation by adsorption of its 2-mercaptobenzothazole complex on naphthalene: MASATADA SATAKE. (12 September 1979)

Determination des constantes d'acidité de diacides moyennement forts: A. VERBERT, G. NOWOGROCKI and M. WOZNIAK. (21 May 1979)

Liquid–liquid extraction of thorium in malonate solution with liquid anion-exchangers: MADHURI A. SAWANT and S. M. KHOPKAR. (17 September 1979)

Inductively coupled-plasma optical emission spectrometry: Application to the determination of molybdenum, cobalt and boron in soil extracts: J. L. MANZOORI. (18 September 1979)

A rapid determination of brass composition and plating weight on brass-plated steel wire and cord by X-ray fluorescence spectrometry: R. L. M. VAN LINGEN. (20 September 1979)

Absorption spectrophotometry: J. R. MAJER and A. S. P. AZZOUZ. (3 September 1979)

High-voltage paper electrophoresis of keto-steroids as xanthydrazones: STANISŁAW PŁAZA. (3 September 1979)

Analytical aspects of absorption spectroelectrochemistry at a platinum electrode—II: Quantitative basis and study of organic compounds: J. F. TYSON and T. S. WEST. (3 September 1979)

Stability constants of ethylenediamine complexes with copper(II), cadmium(II) and zinc(II) in *N,N*-dimethylformamide: MAKOTO AIHARA, HIROSHI MATSUO and KIYOKO YAMAMOTO. (4 September 1979)

The present status and future of room-temperature phosphorimetry: E. LUEYEN-BOWER, J. L. WARD, G. WALDEN and J. D. WINEFORDNER. (6 September 1979)

An investigation of methods for the analysis of zinc concentrates for their total fluoride contents: D. S. RUSSELL, H. B. MACPHERSON and V. P. CLANCY. (7 September 1979)

Gas chromatography and gas chromatography–mass spectrometry of organosulphur compounds and other labile molecules: MICHAEL THOMPSON and MIRIAM STANISAVLJEVIĆ. (7 September 1979)

Identification of metabolites of phencyclidine by gas chromatography/mass spectrometry: J. B. ADDISON. (20 August 1979)

Determination of orthophosphate with a silver-sensitive electrode: E. J. DUFF and J. L. STUART. (8 October 1979)

Analytical applications of ESCA to samples in powder form: KICHINOSUKE HIROKAWA and MASOAKI OKU. (9 October 1979)

Spectrophotometric determination of ruthenium and osmium as ruthenate and osmate: Differential determination of ruthenium in some of its compounds: Z. MARCZENKO, M. BALCERZAK and S. KUŚ. (9 October 1979)

Determination of methyltestosterone in tablets by (A) an ion exchange–spectrophotometric and (B) a solvent extraction–spectrophotometric method: B. D. HOSANGADI and C. M. FARIAS. (10 October 1979)

Mixed-ligand copper(I) complexes with aliphatic amines and 2-aminophenol or 2-amino-5-nitrophenol: A. K. SINHA and G. C. PANDEY. (10 October 1979)

Analytical applications of DEAPG as gravimetric reagent—I: Estimation of Hg(II): R. K. UPADHYAY and A. P. TEWARI. (10 October 1979)

Volume 25, 1978

SUBJECT INDEX

Acids, Carboxylic, Selective detection . . . 235
—, Organic, Iodometric determination . . . 400
Acid–base titration curves, Calculation of . . . 720
Acidity constants, of alkyl- and aminoalkylphosphonic acids . . . 633
Alkalimetric determination of thiols . . . 291
Alkylphosphonic and aminoalkylphosphonic acids, acidity constants . . . 633
————, Stability constants of complexes . . . 643
Aluminium, Determination by spark-source mass-spectrometry . . . 73
Amines, Primary aromatic, Colorimetric determination . . . 290
2-Amino-4-aryl-5-phenylazothiazoles, Investigation of substituent effects . . . 111
Ammonium ion, Novel colour reactions for . . . 423
Analytical chemistry and Joseph Louis Gay-Lussac . . . 611
—, error, Critical examination . . . 325
—, methods, Information efficiency of . . . 725
Anders Ringbom, Essays in memory of . . . No. 1, II
Anion-exchanger, liquid, for separation of U(IV) . . . 599
Antidepressants, Titration with iodine monochloride . . . 349
Arsenic, by FAAS . . . 160
3-Arylazo-3-bromopentane-2,4-diones, polarography of . . . 421
Atomic-absorption spectrophotometry (AAS), Analysis of single garnet crystals . . . 317
————, Control of the time constant . . . 705
————, Detection limits for elements . . . 435
————, Determination of chromium in low-alloy steels . . . 482
————,— of Hg(II) . . . 563
————,— of Mg, Fe and Mn in glass . . . 573
————,— of manganese . . . 287
————, Line interferences . . . 441
————, Use of commercial hollow-cathode lamps . . . 223
————, Flameless, Determination of arsenic . . . 160
————,—,— of beryllium . . . 251
————,—,— of selenium . . . 167
————,—,— of Se(IV) and Se(VI) in water . . . 15
————,—,— of silver . . . 413
————,—,— of trace elements in GaAs . . . 243, 249

Benzodiazepines, Cyclohexene-substituted . . . 209
Benzoyltrifluoroacetone, Salting coefficients of . . . 489
Beryllium, Determination by FAAS . . . 251
—,—, Gravimetric . . . 203
—, Extraction by quaternary ammonium halides . . . 704
Bismuth, Determination, Spectrophotometric . . . 131, 691

Cadmium, Contamination of biological samples . . . 173
—, Determination in Zr metal and Zr oxide . . . 363
Calcium, Determination, Complexometric . . . 693
—,— in serum . . . 541
—, Ion-pair extraction . . . 91
Calculation of acid–base titration curves . . . 720
Catalytic analysis, Selectivity of . . . 123
— reaction of rhenium, Application in analysis . . . 383
Cerium(III), Hydroxide complexes of . . . 147
Chalcopyrite ores, Oxidation of . . . 345
Chemical phase analysis, for kyanites . . . 269
Chemiluminescence in solution, Recent analytical developments . . . 377
Chlorine and fluorine, Determination with ion-selective electrodes . . . 85
Chromatography, Gas, Determination of organomercury(II) compounds . . . 299
—,—, of volatile metal oxides and hydroxides . . . 551, 677
Chromium, Determination by AAS . . . 482
—,— by ion-exchanger colorimetry . . . 103
Chromium(III), Determination, Spectrophotometric . . . 484
— arsenophosphate, for ion-exchange separation of metal ions . . . 528
Citric acid, Determination, Semiquantitative . . . 235
Cobalt(II), Spectrophotometric determination . . . 592

Co-crystallization with 1-(2-pyridylazo)-2-naphthol, and X-ray fluorescence, for metals in water 653
Colorimetry, Ion-exchanger, Determination of zinc . . . 579
—, Precision, for elemental microanalysis . . . 183
Colour reactions, Novel, for ammonium ion . . . 423
Complexes, Calculation of distribution diagrams . . . 511
—, Mononuclear, Apparent formation constants . . . 447
Computer program, for distribution diagrams of complexes . . . 511
Concentration and determination of organic pollutants in water . . . 659
Copper, Contamination of biological samples . . . 173
—, Determination in Zr metal and Zr oxide . . . 363
—,—, Spectrophotometric . . . 165, 685
Copper(II), Complexes with proline-containing sorbent . . . 493, 499
—, Determination, Spectrophotometric . . . 544
Copyright, Statement on new U.S. law . . . No. 4, I
Coulometry, of Fe(III)–Solochrome Violet RS system . . . 461
Cyanide, Titration with silver nitrate . . . 137, 143

Derivatives used in equilibrium calculations . . . 549
Detection limits, in AAS . . . 435
Di-acids, Organic, Thermometric titration . . . 233
Dissociation constants, of L-proline-containing sorbent . . . 493
Dissolution, of tantalum pentoxide . . . 232
Drugs, Luminescence properties of . . . 46
Drying of iron ores for chemical analysis . . . 169

Electrode, Carbon-paste, Determination of theophylline . . . 221
—, Ion-selective, Chloramine-T . . . 477
—,——, for Ca and K in serum . . . 541
—,——, for F and Cl . . . 85
—,——, for nitrogen . . . 398
—, Membrane, Chromium ferrocyanide . . . 521
—, Mineral-graphite, for vanadium oxides . . . 116
—, Solid, Behaviour in pulse voltammetry . . . 151
Elemental microanalysis, by precision colorimetry . . . 183
Elements, Refractory, in uranium . . . 665
—, Trace, in GaAs . . . 243
Emission spectrography, Determination of refractory elements in uranium . . . 665
Equation, for sampling constant . . . 731
Equilibrium calculation, Analytical evaluation of derivatives . . . 549
Equivalence point, Confidence interval in linear titrations . . . 593
Extraction, Ion-pair, of Na, K and Ca . . . 91
—, of beryllium by quaternary ammonium halides . . . 704
—, of Cr(III) and Rh(III) with oxine . . . 484
—, of hafnium with 4-methyl-3-pentene-2-one . . . 395
—, of Hg(II) with 5-(4-pyridylnonane) . . . 563
—, of potassium by flow-injection method . . . 295
—, of zinc with 5-(4-pyridyl)nonane . . . 371
—, of Zn(II) with 1-(2-pyridylazo)-2-naphthol and non-ionic surfactant . . . 585
—, of zirconium with quaternary ammonium halides . . . 714
—, Solvent, of Ga(III) . . . 109
Extraction-polarography of metal complexes of dithio-acid derivatives . . . 263

Ferrocyanide, Titration, with membrane electrode . . . 531
Fire-assay preconcentration of gold and Pt metals . . . 257
Fluoride, Catalytic titration of . . . 113
Fluorimetry, Determination of potassium . . . 295
Fluorine and chlorine, Determination with ion-selective electrodes . . . 85
Formation constants, Apparent, of mononuclear complexes . . . 447

Gallium, Spectrophotometric determination . . . 685
Gallium(III), Solvent extraction . . . 109
Gamma-ray spectrum analysis, Program for . . . 21
Garnet crystals, Composition by AAS . . . 317
Gay-Lussac, Joseph Louis, and analytical chemistry . . . 611
Gold, Extraction with di-n-octyl sulphide . . . 163
—, Spectrographic determination . . . 257

Hafnium, Extraction and separation from zirconium . . . 523
—, Separation from zirconium . . . 395
Hexacyanoferrate(II), Titration with silver nitrate . . . 137, 143
HOD, Determination in biological fluids . . . 607
Hollow-cathode lamps, Commercial, use in AAS . . . 223

Hydrazine, Titration with ion-selective electrode . . . 477
Hydroxide complexes of cerium(III), Stability constants . . . 147

IDENT, Radioisotope identification subroutine to SAMPO . . . 21
Inflection points of titration curves, Location of . . . 557
Information efficiency of analytical methods . . . 725
Iodide, Determination with potassium dichromate and sodium vanadate . . . 50
Ion-exchange, Membranes, Inorganic . . . 157
——, Properties of Sn(IV) and Cr(III) arsenophosphates . . . 528
Ion-exchanger colorimetry, Determination of chromium . . . 103
———,— of zinc . . . 579
Iron, Determination, Titrimetric . . . 54, 357
— and iron(II), Determination, Titrimetric . . . 311
—, in glass, Determination by AAS . . . 573
—, Metallic, Determination in minerals . . . 702
—,—, Estimation in sponge iron . . . 486
Iron(III), Complex with Solochrome Violet RS . . . 461
—, EDTA chelate, Thermometric studies . . . 97
Iron-containing samples, Dissolution in phosphoric acid . . . 275
— ores, Drying conditions by coulometry . . . 169
— oxides, Dissolution by bromide/methanol . . . 486
Isoniazid, Titration with ion-selective electrode . . . 477

Karl Fischer reagents, Reaction rates with water . . . 229
Kyanites, Chemical phase analysis of . . . 269

Lead, Determination in Zr metal and Zr oxide . . . 363
—, Sorption by solids . . . 727
Line interferences, in AAS . . . 441
Louis Gordon Memorial Award . . . No. 1, I, No. 8, I
Luminescence properties of drugs . . . 46

Magnesium, Determination by AAS . . . 573
—,—, Complexometric . . . 693
Manganese, Determination by AAS . . . 287
—,———, in glass . . . 573
—,—, Complexometric . . . 693
—,—, with benzohydroxamic acid . . . 708
—, Masking with potassium cyanide . . . 693
Mass-spectrometry, Isotope-dilution, Determination of mercury . . . 701
—, Spark-source, Calibration for aluminium and its alloys . . . 73
Matrix, Ammoniacal solutions, Determination of nitrite and nitrate . . . 535
—, Biological materials, Contamination by Cu and Cd . . . 173
—,——, Determination of HOD . . . 607
—,——,— of selenium . . . 167
—,——,— of vanadium . . . 352
—, Brass and bronze, Determination of Sn(IV) . . . 284
—, Coal and coke, Determination of nitrogen . . . 398
—, Copper concentrates, Determination of Fe(III) . . . 54
—, Environmental samples, Determination of arsenic . . . 160
—, Flue dust, Determination of zinc . . . 673
—, GaAs, Determination of trace elements . . . 243
—, Geological materials, Determination of gold and Pt metals . . . 257
—,——,— of beryllium . . . 251
—,——,— of manganese . . . 287
—,——,— of rhenium . . . 569
—, Glass, Analysis by AAS . . . 573
—, Granite rocks, Determination of F and Cl . . . 85
—, Iron and steels, Determination of silver . . . 413
—,— ores, Determination of iron . . . 311, 357
—, Mining effluents, Determination of polythionates and thiosulphate . . . 79
—, Molybdenum, Determination of nitrogen . . . 195
—, Non-ferrous alloys, Determination of bismuth . . . 131
—, Ores and alloys, Determination of manganese . . . 708
—,— concentrates, Determination of bismuth . . . 131
—, Pharmaceutical preparations, Determination of pyrazolones . . . 119
—, Plasma, Determination of theophylline . . . 221
—, Propellants, Determination of nitroglycerine . . . 521
—, Semiconductors, Determination of trace nitrogen . . . 41
—, Serum, Determination of Ca and K . . . 541
—, Siliceous materials, Titration of zirconium . . . 669
—, Silver compounds and alloys, Determination of silver . . . 418

—, Sponge iron, Determination of metallic iron . . . 486
—, Steels, Determination of chromium . . . 482
—,—,— of silicon . . . 226
—, Thiols, Determination of water . . . 282
—, Titanium, Determination of nitrogen . . . 505
—, Tungsten, Determination of nitrogen . . . 195
—, Uranium, Determination of refractory elements . . . 665
—, Water, Determination of anionic surfactants . . . 279
—,—,— of chromium . . . 103
—,—,— of dissolved oxygen . . . 519, 480
—,—,— of organic pollutants . . . 659
—,—,— of selenium . . . 15
—,—,— of trace metals . . . 653
—,—,— of zinc . . . 579
—, Zirconium metal and zirconium oxide, Determination of Cu, Pb, Cd and Zn . . . 363
— effects, Determination of Mn by AAS . . . 287
Mebendazole, Titration of . . . 716
Membranes, for conductometric titration . . . 9
—, Ion-exchange, Inorganic . . . 157
Mercury, Determination by isotope-dilution mass-spectrometry . . . 701
Mercury(II), Extraction and determination by AAS . . . 563
—, Reaction with Cadion A and Cadion 2B . . . 546
Metals, Complexes with dithio-acid derivatives . . . 263
—,— with EDTA, Spectroscopy of . . . 425
—, Extraction with hydroxamic acids . . . 410
—, in water, by co-crystallization and X-ray fluorescence . . . 653
— oxides and hydroxides, Gas chromatographic study . . . 551, 677
Methylmercury(II), Complex with EDTA . . . 215
Microanalysis, Elemental, by precision colorimetry . . . 183
Microwave oven, Drying of sulphide-bearing materials . . . 181

Neutron activation analysis, Determination of rhenium . . . 569
Nickel, Adsorption of α-furildioxine complex on naphthalene . . . 718
—, Spectrophotometric determination . . . 544, 718
—, Ternary complexes with citric acid and 2,2′-bipyridyl . . . 177
Nitrate, Determination of traces . . . 535
Nitrite, Determination of traces . . . 535
p-Nitroaniline–formaldehyde polymer, Electrochemical study . . . 402
Nitrogen, Determination by ion-selective electrode . . . 398
—,— in $A^{III}B^{V}$ semiconductors . . . 41
—,— in Mo and W . . . 195
—,— in titanium . . . 505
— and oxygen, Desorption from iron surfaces . . . 383
Nitroglycerine, Spectrophotometric determination . . . 521

Opipramol, Spectrophotometric determination . . . 710
Organic compounds, Titration with bromine chloride . . . 469
Organomercury compounds, Determination by gas chromatography . . . 299
——, Determination with cysteine . . . 405
Oxygen, in water, Complexometric determination . . . 519
—,——, Titration of . . . 480
— and nitrogen, Desorption from iron surfaces . . . 383

Palladium, Complex with EDTA, Stability constant . . . 239
—, Extraction with di-n-octyl sulphide . . . 163
—, Spectrophotometric determination . . . 533, 544
Pergamon Press—Statement on new U.S. copyright law . . . No. 4, I
Phenols, Selective detection . . . 235
Phenothiazine derivatives, Spectrophotometric determination . . . 710
——, Thermometric titration . . . 339
Photometry, Inorganic, with azo dyes . . . 451
Platinum, Extraction with di-n-octyl sulphide . . . 163
—, Spectrophotometric determination . . . 416
— metals, Spectrographic determination . . . 257
Polarographic reduction of 3-aryl-3-bromopentane-2,4-diones . . . 421
Polarography, of 2-amino-4-aryl-5-phenylthiazoles . . . 111
—, of Fe(III)–Solochrome Violet RS system . . . 461
—, of metal complexes with dithio-acid derivatives . . . 263
—, Pulse, Determination of pyrazolone derivatives . . . 119
—,—,— of silicon . . . 226
Pollutants, Organic, Determination in water . . . 659
Polythionates and thiosulphate, Determination, acidimetric . . . 79
Potassium, Determination by ion-selective electrode . . . 541

—,— by microextraction and fluorimetry . . . 295
—, Ion-pair extraction . . . 91
Promethazine, Enthalpy of neutralization . . . 339
—,— and entropy of ionization . . . 339
Pyrazolone derivatives, Determination by pulse polarography . . . 119

Radioisotope identification and mass determination in gamma-ray analysis . . . 21
Reaction rate, between water and Karl Fischer reagents . . . 229
Reagent, 4-Amino-3-methyl-5-mercapto-1,2,4-triazole for silver . . . 418
—, Ammonium 1-pyrrolidinecarbodithioate, for Se(IV) and Se(VI) . . . 15
—,——, for W(VI) . . . 696
—, Azo dyes, for inorganic photometry . . . 451
—, *N*-Benzylbenzohydroxamic acid, for vanadium . . . 352
—, 2,2′-Bipyridyl and citric acid, Ternary complexes with Ni(II) and Zn(II) . . . 177
—, Bis(dialkylthiophosphoryl)- and bis(diarylthiophosphoryl)-disulphides, for palladium . . . 533
—, Bromamine-T, New oxidimetric titrant . . . 525
—, Bromine chloride, for titration of organic compounds . . . 469
—,—, methanol, for dissolution of iron oxides . . . 486
—, Cadion A and Cadion 2B, for Hg(II) . . . 546
—, Chloramine-T, for phenothiazines and opipramol . . . 710
—, Cysteine, for organomercury compounds . . . 405
—, Dicyclohexyl-18-crown-6, for extraction of Na, K and Ca . . . 91
—, Diethyldithiocarbamate, for Se(IV) and Se(VI) . . . 15
—, Diethylenetriaminepenta-acetic acid, for bismuth . . . 691
—, Di-n-octyl sulphide, for extraction of Au, Pd and Pt . . . 163
—, 1,5-Diphenylcarbohydrazide, for chromium . . . 103
—, Dithio-acid derivatives, for complexes with metals . . . 263
—, Dithizone, for Se(VI) and Se(VI) . . . 15
—, EDTA, Complex with Fe(III) . . . 97
—,—,— with metals . . . 425
—,—,— with methylmercury(II) . . . 215
—,—,— with palladium . . . 239
—, Furoin thiosemicarbazone, for Ni(II), Pd(II) and Cu(II) . . . 544
—, α-Furildioxime, complex with nickel . . . 718
—, Hexamethylphosphoramide, for extraction of rhenium . . . 597
—, Hydrazine, for condensation with salicylaldehyde . . . 241
—, Hydroxamic acids, for extraction of metals . . . 410
—,——, for titration of manganese . . . 708
—, *N*-Hydroxy-*N*,*N*′-diphenylcinnamamidine, for V(V) . . . 698
—, 2-(*o*-Hydroxyphenyliminomethyl)pyridine, for metals . . . 59
—, 2-Hydroxy-1-naphthaldoxime, for Ti(IV) . . . 354
—, Iodide, for bismuth . . . 131
—, Iodine monochloride, for titration of tranquilizers and antidepressants . . . 349
—, Long-chain amines, for extraction of zirconium and hafnium . . . 523
— ?-Mercapto-3-(2-furyl)propenoic acid, for titanium . . . 56
—, ′-Methylaminothioformyl-*N*′-phenylhydroxylamine, for Co(II) . . . 592
—, 4-Methyl-3-pentene-2-one, for extraction of hafnium . . . 395
—, Monothiobenzoylmethane, for extraction of Ga(III) . . . 109
—, Oxine, for Cr(III) and Rh(III) . . . 484
—, Phenacyl bromide, for thioureas . . . 591
—, Phenylbenzene sulphazide, for selenium . . . 44
—, 2-(Phenyliminomethyl)pyridine, for metals . . . 59
—, 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one, for Cu and Ga . . . 685
—, Phosphoric acid, for dissolution of Fe-containing samples . . . 275
—,——, for iron . . . 311
—, Potassium cyanide, for masking of manganese . . . 693
—,— dichromate, for iodide . . . 50
—, 1-(2-Pyridylazo)-2-naphthol, for extraction of Zn(II) . . . 585
—, 5-(4-Pyridyl)nonane, for extraction of Hg(II) . . . 563
—,—,—— of zinc . . . 371
—, Quaternary ammonium halides, for extraction of beryllium . . . 704
—, Remacrylblau B and Remacrylrot 2BL, for anionic surfactants . . . 279
—, Sodium nitrilotriacetate, as complexing agent . . . 143
—,— oxinate, for beryllium . . . 203
—,— tetrachloroferrate, as dehydrating agent . . . 596
—,— vanadate, for iodide . . . 50
—, Solochrome Violet RS, for Fe(III) . . . 461
—, Thiobenzoylacetone, for copper . . . 165
—, Thiohydantoin derivatives, for metals . . . 331
—, Thiosemicarbazones and semicarbazones, Review . . . 619
—, Thorium nitrate, for fluoride . . . 113
—, *N*-*o*-Toluyl-*N*-*o*-tolylhydroxylamine, for Sn(IV) . . . 284
—, Trifluoperazine dihydrochloride, for platinum . . . 416

—, Xenon trioxide, as oxidant . . . 1
—, 2,4-Xylenol, for nitroglycerine . . . 521
Review, Analytical applications of thiosemicarbazones and semicarbazones . . . 619
—, Determination of tungsten . . . 61
—, Gas chromatographic determination of organomercury(II) compounds . . . 299
Rhenium, Determination in geological materials . . . 569
—, Extraction and spectrophotometric determination . . . 597
—, New catalytic reaction . . . 389
Rhodium(III), Spectrophotometric determination . . . 484

Salicylaldehyde, Condensation with hydrazine . . . 241
Salting coefficients, of benzoyltrifluoroacetone . . . 489
Sampling constant equation . . . 731
Selectivity of catalytic methods . . . 123
Selenium, by FAAS . . . 167
—, Separation and determination . . . 44
Selenium(IV) and Se(VI), by FAAS . . . 15
Signal comparison parameter, for Zeeman background-corrected spectrometers . . . 723
Silicon, Determination by pulse polarography . . . 226
Silver, Determination by FAAS . . . 413
—,—, Gravimetric . . . 418
Sodium, Ion-pair extraction . . . 91
— oxalate, Drying and decomposition . . . 603
Sorbent, L-proline-containing, Complexes with Cu(II) . . . 493, 499
Spectroscopy, Infrared, for determination of HOD . . . 607
—, Mass, Isotope-dilution, Determination of mercury . . . 701
—, X-ray fluorescence, for trace metals in water . . . 653
—,— photoelectron, Application to surface analysis . . . 383, 539
Spot tests, for carboxylic acids, ureas, phenols and critic acid . . . 235
Stability constants, of hydroxide complexes of Ce(III) . . . 147
——, of complexes of alkyl- and aminoalkylphosphonic acids . . . 643
——, of copper(II)–L-proline complexes . . . 499
——, of metal complexes with 2-(phenyliminomethyl)pyridine and 2-(*o*-hydroxyphenylimino-methyl)pyridine . . . 59
——, of Pd–EDTA complex . . . 239
Sulphide, Titration with ion-selective electrode . . . 477
— bearing materials, Drying in microwave oven . . . 181
Sulphite and sulphide, Interactions with tetrathionate . . . 408
Surface analysis, by X-ray photoelectron spectroscopy . . . 539
Surfactants, Anionic, Spectrophotometric determination . . . 279

Talanta Advisory Board . . . No. 4, III
Tantalum pentoxide, Dissolution of . . . 232
Target, Al–Ti, for X-ray photoelectron spectroscopy . . . 539
Tetrathionate, Interactions with sulphite and sulphide . . . 408
Theophylline, Determination in plasma . . . 221
Thermochromatography, of volatile metal oxides and hydroxides . . . 677
Thermometry, of Fe(III)–EDTA chelate . . . 97
Thiols, Alkalimetric determination . . . 291
Thiosulphate and polythionates, Determination in mining effluents . . . 79
—, in the Wollack procedure, Analysis and kinetics . . . 359
—, Titration with ion-selective electrode . . . 477
Thiourea, Determination by precipitation of Hg(II) sulphide . . . 52
—,— with phenacyl bromide . . . 591
Tin(IV), Gravimetric determination . . . 284
— arsenophosphate, for ion-exchange separation of metal ions . . . 528
Titanium, Determination, Colorimetric . . . 56
—,—, Gravimetric . . . 354
Titration, Acidimetric, of thiosulphate and polythionates . . . 79
—, Catalytic, of fluoride . . . 113
—, Chelatometric, of iron . . . 311
—, Conductometric, Calculation of curves . . . 137
—,—, with HCl . . . 9
—, Coulometric, of water in iron ores . . . 169
—, Iodometric, of organic acids . . . 400
—, Karl Fischer, of water in thiols . . . 282
—, Linear, Confidence interval of equivalence point . . . 593
—, Oxidimetric, with Bromamine-T . . . 525
—, Potentiometric, Calculation of curves . . . 137
—,—, of EDTA complex with methylmercury(II) . . . 215
—,—, of ferrocyanide . . . 531
—,—, of hydrazine, isoniazid, sulphide, and thiosulphate . . . 477

—,—, of organomercury compounds . . . 405
—, Pressurometric . . . 1
—, Redox, of iron . . . 311
—, Spectrophotometric, of zirconium . . . 669
—, Thermometric, of organic di-acids . . . 233
—,—, of phenothiazine derivatives . . . 339
— curves, Acid–base, Calculation of . . . 720
——, of homogeneous redox reactions . . . 557
Tranquilizers, Titration with iodine monochloride . . . 349
Tungsten, Determination, Review of methods . . . 61
Tungsten(VI), Determination, Ultraviolet spectrophotometry . . . 696

Uranium(IV), Separation with liquid ion-exchanger . . . 599
Ureas, Selective detection . . . 235

Vanadium, Spectrophotometric determination . . . 352
Vanadium(V), Spectrophotometric determination . . . 698
— oxide, Determination, Voltammetric . . . 116
——, High-temperature analytical uses . . . 185
Voltammetry, Pulse, Behaviour of solid electrodes . . . 151
—,—, Determination of theophylline . . . 221
—, Stripping, for determination of Cu, Pb, Cd and Zn . . . 363

Water, Determination in iron ores . . . 169
—, Karl Fischer titration . . . 282
—, Reaction rate with Karl Fischer reagents . . . 229
Wollack procedure, for thiosulphate, Analysis and kinetics . . . 359

Zeeman background-corrected spectrometers, Signal comparison parameter . . . 723
— effect, Applications to analytical AAS . . . 223, 435, 441
Zinc, Determination, by ion-exchanger colorimetry . . . 579
—,—, in flue dusts . . . 673
—,—, in Zr metal and Zr oxide . . . 363
Zinc(II), Extraction with 1-(2-pyridylazo)-2-naphthol and non-ionic surfactant . . . 585
—,—— 5-(4-pyridyl)nonane . . . 371
—, Ternary complexes with citric acid and 2,2′-bipyridyl . . . 177
Zirconium, Extraction and separation from hafnium . . . 523
—,— with quaternary ammonium halides . . . 714
—, Separation from hafnium . . . 714
—, Spectrophotometric titration . . . 669

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NOTICE

FA-Amsterdam; International Conference on Flow Analysis. 11–13 September 1979, Amsterdam, The Netherlands

A three day conference on Flow Analysis will be held in Amsterdam. The programme will cover a wide and representative selection of current research on all aspects of flow analysis. The topics will be as follows.

Instrumentation design for flow analysis.
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A first announcement and a preliminary registration form are available from the secretariat:

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PUBLICATIONS RECEIVED

Validation of the Measurement Process: J. R. DEVOE, ACS Symposium Series No. 63. American Chemical Society, Washington D.C., 1977. pp. vii + 207. $20.00

This book contains a useful collection of papers for the analytical chemist who is concerned about the accuracy and precision of his results. The topics covered are Statistical control of measurement processes, Testing basic assumptions in the measurement process, Systematic error in chemical analysis, Role of reference materials and reference methods, Optimization of experimental parameters, and Components of variation in chemical analysis. A novel concept discussed is the Analysis of blunders, which aims to be a basis for improving results by finding the causes of errors, instead of ignoring "outliers".

Chemometrics: Theory and Application: B. R. KOWALSKI, ACS Symposium Series No. 52. American Chemical Society, Washington D.C., 1976. pp. viii + 288. $21.00.

The introduction to this book gives a definition of *Chemometrics* as "the development and application of mathematical and statistical methods to extract useful chemical information from chemical measurements". It seems to me that a large number of chemists could have been called "chemometricians" long ago, had the term been invented. New terminology, and, even worse, jargon, does much to obscure useful information from the reader, and there is a great deal of both here. Nevertheless, there is much that is useful. Most of us will want to know "How to Avoid Lying with Statistics", and most of the other papers have something to offer. If only all the authors had been able to present their material with the clarity and lucidity of Meites and Shai!

Computer-Assisted Organic Synthesis: W. T. WIPKE and W. J. HOWE, ACS Symposium Series No. 61. American Chemical Society, Washington D.C., 1977. pp. vii + 239. $21.00.

It is not easy to represent organic chemical structures in computer-readable form, and to represent reactions is a formidable task. This collection of papers presented at an ACS symposium held in New York in 1976 describes some of the attempts that have been made to do this, and much more. The ultimate aim is to have the computer devise complete synthetic routes by examining all the alternatives for each step and choosing the best overall scheme. However, it would appear that it will be some time before the majority of organic chemists can make use of computer assistance. The final paper, by Eakin and Warr of ICI, describes the only scheme simple enough to be likely to be widely used in the immediate future. This book will certainly give organic chemists something to think about.

Minicomputers and Large Scale Computations: P. LYKES, ACS Symposium Series No. 57. American Chemical Society, Washington D.C., 1977. pp. xi + 239. $21.50.

This collection of papers from a joint ACS/Chemical Institute of Canada meeting held in Montreal in 1977 describes a wide range of applications of minicomputers to problems which would normally be tackled only with a large computer, such as M.O. calculations, X-ray crystallography, statistical mechanics, chemical kinetics, molecular dynamics, quantum chemistry *etc.* The book is most likely to be useful to chemists who are actually contemplating using a minicomputer for some application, but it raises important points about the economics of computing, which should be read by users of large computers. Many of the projects described were carefully costed, and the minicomputer was generally found to be more cost-effective than a large computer.

Developments in Biodegradation of Hydrocarbons—1: R. J. WATKINSON (ed.), Applied Science Publishers, London, 1978. pp. x + 232. £16.00.

This would appear to be the first volume in a series devoted to developments in science, but it is not clear whether further volumes dealing specifically with hydrocarbon degradation are contemplated. The book consists of seven separate reviews, each written by a different author or authors. They are concerned with the metabolism of hydrocarbons by micro-organisms and the effect of this interaction on the structure and behaviour of the micro-organisms. Metabolic pathways and genetic engineering are discussed, but the coverage is not confined to purely academic topics. There are sections dealing with the destruction of hydrocarbons in a marine environment and with the deterioration of hydrocarbon products on industrial sites. The book provides an introduction to a subject which is acquiring an ever increasing importance and will be of interest to a wide range of scientists working in such diverse disciplines as fuel technology, biochemistry, bacteriology and analytical chemistry.

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ANNOUNCEMENT

FEDERATION OF EUROPEAN CHEMICAL SOCIETIES (FECS)

WORKING PARTY ON ANALYTICAL CHEMISTRY (WPAC)

EUROPEAN ANALYTICAL COLUMN 1

According to a resolution at the seventh meeting of the WPAC/FECS in Davos, 22 May 1977, the minutes of the WPAC-meetings will be published in short form by the national analytical member societies in order to provide better information on the activities of this working party.

The WPAC consists at the moment of 28 members representing 23 national societies of 17 European countries. The chairman is Prof. H. Malissa, Technical University of Vienna. WPAC activities are directed towards the practical needs of analytical chemistry in the European context, such as the organization of the Euroanalysis conferences, the discussion of standardization in environmental analysis and the treatment of educational problems in analytical chemistry.

At the seventh meeting of the WPAC, special consideration was given to the organization of the Euroanalysis III conference in Dublin, 20 - 25 August 1978 and the preparation of the Euroanalysis IV conference in Helsinki, 1981. Like the preceding Euroanalysis meetings in Heidelberg (1972) and Budapest (1975), Euroanalysis III will emphasise both pure and applied aspects of analytical chemistry. The programme has been designed to appeal to the widest possible audience - from scientists engaged in the use of analytical techniques in problem solving to those involved in research and development of analytical techniques. The conference will, therefore, present an excellent opportunity for participants to learn about research work being carried out in the laboratories of the member states of the Federation and its practical application in many countries throughout the world.

The scientific programme will consist of invited plenary and keynote lectures, contributed papers, poster sessions, round table discussions and panel discussions.

The round table discussions will be devoted to two further main activities of the WPAC: standardization in environmental analysis [Standard Reference Materials, (SRM) and Standard Reference Criteria (SRC)] and education in analytical chemistry. Invited plenary and keynote lecturers will describe their ideas and act as discussion starters.

The creation of a special discussion group on SRM was proposed by Prof. Malissa at the Davos meeting. Practical work has already been done in establishing a dust SRM, by laboratories in Austria, Hungary, Yugoslavia and Germany.

The aim of the round table discussion on education in analytical chemistry is to create a European model for teaching analytical chemistry in such a way that the growing demands of technology, medicine and environmental research can be met by analytical chemists graduating from European universities. This should not necessarily mean that "classical analytical chemistry" should be abandoned but certainly that modern methods of analysis have to be included in the teaching plan of some universities. In order to find the best model every member country will present two posters on the actual and the "optimal" situation in its teaching of analytical chemistry. In two special lectures the needs of industry and of government will be discussed.

At the Davos meeting it was furthermore resolved to support the creation of a "European Museum of Analytical Chemistry" to collect, conserve and demonstrate valuable prototypes of pioneering analytical instrumentation and original publications.

Colleagues who are interested in cooperating in the fields described above are kindly requested to contact the secretary of the WPAC:

Prof. Dr. R. KELLNER
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A 1060 Wien

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PUBLICATIONS RECEIVED

Chemical Analysis of Organometallic Compounds, Volume 5: T. R. CROMPTON. Academic Press, London, 1977. Pp. xii + 432. £24.00.

This volume, the final one in the series, covers the analysis of organic compounds of Cr, Mo, W, U, Se, Te, Mn, Fe, Co, Ni, platinum group metals, Al and Zn. As before, many detailed procedures are given, so that the text can usefully be employed as a laboratory manual. The great deficiency of this series is that it has taken so long to appear in print. In the section on Al and Zn, which repeats much of the material from a previous book (now out of print) by the author, the most recent reference was published in 1973. In the rest of the book, the most recent reference was published in 1970 [apart from one (1973) reference to a manufacturer's hand-out]. It is a pity that the author did not make some attempt to update the text; seven years is a very long time in chemistry. It is ironic that one of the most outstanding omissions is a paper on analysis of organoselenium compounds published in 1974 by one of the Series Editors.

Liquid Chromatography Detectors: R. P. W. SCOTT. Elsevier, Amsterdam, 1977. Pp. vii + 248. $34.50.

This constitutes Volume 11 of the Journal of Chromatography Library series of monographs dealing with various aspects of chromatography. Liquid chromatography was one of the earliest of the techniques to be developed and was soon superseded by other more rapid and convenient forms of chromatography. Renewal of interest was aroused by the development of high-pressure techniques and of sensitive universal detectors with high sensitivity. The book discusses the behaviour and performance of various types of detectors and their application in liquid chromatography. The factors which control sensitivity and reproducibility are examined and the various types of detectors are reviewed. The essentially practical nature of the treatment commends it to all analytical chemists involved in the separation, identification and quantitation of small samples and complex mixtures.

Handbook of Air Pollution Analysis: R. PERRY and R. J. YOUNG (eds.), Chapman & Hall, London, 1977. Pp. xiv + 506. £20.00.

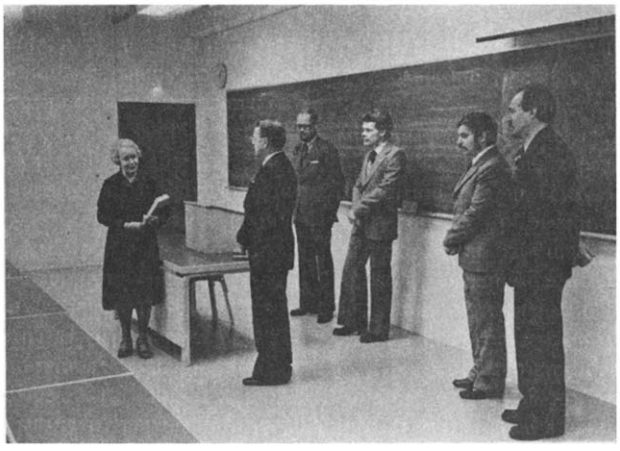
This is an advanced treatise which deals not only with the methods of analysis available for monitoring various forms of air pollution, but also with the associated problems of sampling and interpretation of the final analytical data. The material is divided into nine separate chapters, each constituting an authoritative monograph on a particular aspect of the subject, although there is an excellent system of cross-referencing to topics common to several chapters. There are separate sections which describe the analysis of hydrocarbons, halogenated compounds, metals and pollutants containing nitrogen and sulphur. Of particular interest, however, are the detailed accounts of sampling methods, the examination of particulate matter, the design of remote monitoring systems and the planning of an air-pollution study. The book is well written and clearly indexed and will be of the greatest value to all practising analytical chemists, but more particularly, to those involved in atmospheric monitoring and public-health engineering.

Electrical Phenomena at the Biological Membrane Level: E. ROUX (ed.), Elsevier, Amsterdam, 1977. Pp. xv + 565. £65.50.

This is a collection of some 40 papers delivered at the 29th International Meeting of the Société de Chimie Physique held at Orsay on 12–15 October 1976. These papers are broadly concerned with the applications of the ideas and methods of physical chemistry to the problems associated with electrical phenomena occurring at biological interfaces and membranes. There is extensive use of model systems which may involve the production of synthetic membranes in attempts to explain the production and transmission of charge across membranes. The book will be of interest to the cell biologist concerned with such fields as conduction along nerves, mechanism of vision, the transfer of electrons between macromolecules of biological significance and the role of electronic conductance in photosynthesis. There is also much here to be recommended for study by the biochemist and biophysicist.

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ANALYTICAL CHEMISTRY: ESSAYS IN MEMORY OF ANDERS RINGBOM



Presentation of "Analytical Chemistry: Essays in Memory of Anders Ringbom" to Mrs. Astrid Ringbom by Professor Wänninen at Åbo Akademi, Finland, on 29 September. (Left to right: Mrs. Ringbom, Professor Wänninen, Professor Ingman, Dr. Still, Dr. Harju, Dr. Skrifvars).

Talanta, Vol. 25, pp. ii–iv. Pergamon Press, 1978. Printed in Great Britain.

PUBLICATIONS RECEIVED

Dithizone: H. M. N. H. IRVING. The Chemical Society, London, 1977. Pp. iv + 106. £7.25, $14.50.

What a pleasure to have for review a book that is written by a master of the English language, an all-rounder in chemistry, and a mathematician and linguist, in short by a polymath. All who have occasion to use dithizone will find this volume as essential as the solvent for the reagent, and will be grateful to its author for such a masterly survey in such short compass. If the publishers had made the price match the value then only the rich could have afforded it; as it is, they jave made a sufficiently good try for the average customer to recommend its purchase to the library instead of buying it himself.

Pyrolysis–Gas Chromatography: R. W. MAY, E. F. PEARSON and D. SCOTHERN. The Chemical Society, London, 1977. Pp. vii + 109. £7.20, $14.40.

This review of the application of gas chromatographic identification of pyrolysis products as an aid to identification and analysis of materials would be much more useful if it had an index, but there is none to be found, so unless the reader constructs his own, he must either learn the general arrangement of the textual matter or rely on luck to find the information he wants. This omission detracts from the value of what is otherwise a very useful survey, and makes the price seem even less excusable.

Accuracy in Spectrophotometry and Luminescence Measurements: R. MAVRODINEANU, J. I. SHULTZ and O. MENIS (eds.). NBS Special Publication 378, U. S. Department of Commerce, Washington, 1973. Pp. VII + 255. $4.50

This review of the report of a conference held in 1972 may seem rather late in appearing, but in fact the report, though published in 1973, has only just arrived. It is none the less welcome for the delay, as its contents will always be useful, giving a clear indication of what is possible and what is not in measurements based on the intensity of light. It should be compulsory reading for all practitioners in the field and also for all editors handling publication of the resulting contributions. At the price it is truly remarkable value for money, and everyone can afford his own copy.

Standardization in Spectrophotometry and Luminescence Measurements: K. D. MIELENZ, R. A. VELAPOLDI and R. MAVRODINEANU (eds.). NBS Special Publication 466. U. S. Department of Commerce, Washington, 1977. Pp. VII + 150. $5.25.

This report of the workshop seminar on standardization, held in November 1975, forms a companion volume to the one on accuracy (see above), and is equally to be recommended to all workers in this field. The two can be bought for less than the price of a bottle of indifferent wine in certain restaurants, and are certainly of lasting and far greater value. For expert advice on how to do it and how to avoid mistakes, consult this book before doing the standardization.

Analytical Chemistry: Essays in Memory of Anders Ringbom: ERKKI WÄNNINEN (Editor-in-Chief). Pergamon, Oxford, 1977. Pp. xiv + 607. £27.50, $50.00.

This volume of essays was conceived by friends and colleagues of the late Professor Ringbom as a memorial to an outstanding analytical chemist who had a profound influence on teaching and research in the subject. It takes the form of invited papers on both the theory and practice of analytical chemistry, and offers a wide-ranging and varied insight into modern thought on teaching and research in analytical chemistry. It can be recommended to all chemists with a general interest in their subject.

Solvent Extraction Chemistry: TATSUYA SEKINE and YUKO HASEGAWA. Dekker, New York, 1977. Pp. xii + 919. SFr. 240.

This text, about equally divided between theory and applications, written by two well-known practitioners in the field, will be welcomed by all chemists engaged in solvent extraction work. There are over 7000 references, occupying about a third of the total number of pages. Perhaps it would be too much to hope for a selection of recommended methods in a book of this nature, but it would have been helpful if the text had at least indicated the types of sample for which particular methods had been used. The preface says that the literature was covered up to the end of Volume 76 of *Chemical Abstracts* (1972) but internal evidence from the lists of references shows some extension up to late 1974. It is a little disappointing that the coverage is not more nearly up to date, but perhaps it is inevitable in a book of this nature. Nevertheless, the book gives very complete coverage of the field in general and should prove a most useful source of information.

Analysis of Paper (2nd Ed.): B. L. BROWNING (ed.), Dekker, New York, 1977. Pp. viii + 366. SFrs. 110.

The publishers say that "Manufacturers of paper and paperboard, suppliers of components or of additives introduced into paper, converters and printers, purchasers and users of paper, librarians, forensic investigators—everyone concerned with the properties, behavior, and applications of paper will find this book a valuable source of information.", and I fully endorse this statement: I believe that students of analytical chemistry would also find this book of great interest. The book gives a great deal of very readable background information for the non-specialist, but it also succeeds in including detailed procedures for a very wide range of determinations. It starts with a general discussion of analytical methods, and a very important chapter on the problems of sampling. Methods are included for detection and determination of moisture, fibres, lignin, rosin size, starch, proteins, coatings, waxes and oils, fillers, dyes, acidity and alkalinity, biological control agents, wet strength agents, and many other components. The final chapter is on "Paper in Forensic Science".

Ion Exchange and Solvent Extraction: A Series of Advances, Volume 7: J. A. MARINSKY and Y. MARCUS, Dekker, New York, 1977. Pp. xvi + 294. SFr. 106.

The subjects of this Volume are "Interphase mass transfer of chemical reactions with crosslinked polystyrene", by G. Schmuckler and S. Goldstein, "Influence of polymeric matrix structure on performance of ion-exchange resins" by V. A. Davankov, S. V. Rogozhin and M. P. Tsyurupa, "Spectroscopic studies of ion-exchangers", by C. Heitner-Wirguin, "Ion-exchange materials in natural water systems", by M. M. Reddy and "The thermal regeneration of ion-exchange resins", by B. A. Bolto and D. E. Weiss. The first three chapters are mainly of theoretical interest at present, but the fourth will be of interest to environmental chemists, and the fifth describes a very important development in commercial water purification.

Ion-Selective Electrodes: E. PUNGOR (ed.), Akadémiai Kiadó, Budapest, 1977. Pp. 263. £9.30.

This book consists of texts of papers presented at a Symposium held at Matrafured, Hungary, 18–21 October 1976. The authors include W. Simon, W. E. Morf, J. D. R. Thomas, E. Pungor, K. Tóth, B. P. Nikolskii and numerous other well-known names. The text has been produced fron camera-ready copy provided by the authors, so the style of presentation is rather uneven, but perhaps the relatively low price will compensate for this. Much interesting new work in the ever-expanding field of ion-selective electrodes in described, and useful accounts of the discussion on each paper, and of the closing Panel Discussion, are included.

Analysis of Drugs and Metabolites by Gas Chromatography–Mass Spectrometry, Volume 1, **Respiratory Gases, Volatile Anesthetics, Ethyl Alcohol, and Related Toxicological Materials**: B. J. GUDZINOWICZ and M. J. GUDZINOWICZ, Dekker, New York, 1977. Pp xii + 223. SFr. 78.

This book is very much more useful than its misleading title suggests, since most of the text is concerned with normal gas-chromatographic methods, not with GC–MS ones, although, of course, as pointed out by the authors, most of the methods would be readily adaptable for use with GC–MS equipment. Comprehensive reviews are given of the determination of respiratory gases, volatile anaesthetics, ethyl alcohol and related toxicological materials, and background information on the biological effects of the materials is also included. Detailed descriptions of experimental procedures are given for the most useful methods, and many typical chromatograms are illustrated. The precision, accuracy and sensitivity of the procedures are discussed.

Assay of Drugs and Other Trace Compounds in Biological Fluids: E. REID (ed.), North-Holland, Amsterdam, 1977. Pp. x + 253. $26.75, Dfl. 65.00.

This book, which resulted from a "Techniques Forum" held in September 1975 at the Wolfson Bioanalytical Centre of the University of Surrey, attempts to serve as a general guide-book to the development of microanalytical methods for determination of trace amounts of known substances in biological media. The major part of the text discusses general principles, with particular reference to instrumental methods for the final determination step, general analytical strategy, and sample preparation. The remainder is devoted to "analytical case histories" of methods of assay for particular substances. Also included are summaries of the discussion which took place at the "Forum", along with some useful editorial comments.

Non-Aqueous Solutions—5 (Leeds, 1976): J. B. GILL (Ed.), Pergamon, Oxford, 1977. Pp. 124, £13.

The Plenary and Section lectures presented at the Leeds Conference on Non-Aqueous Solutions in 1976 are reprinted from *Pure & Appl. Chem.*, 1977, **49**, 1–124. The majority of the papers are concerned with either kinetics or spectroscopy in conventional solvents or molten salts.

Liquid Chromatography of Polymers and Related Materials (Chromatographic Science Series, Vol. 8): J. CAZES (Ed.), Dekker, New York 1977. Pp. VIII + 192. SFrs. 65.00.

This is a collection of the 13 papers presented in 1976 at the First International Symposium on Liquid Chromatographic Analysis of Polymers and Related Materials. The authors are from a variety of American companies. The contents cover a range of topics and a variety of materials. Although the papers are brief there is a lot of information therein, and all concerned with the analysis of polymers will find them of interest.

Applications of Ion-Selective Membrane Electrodes in Organic Analysis: G. E. BAIULESCU and V. V. COSOFRET. Horwood, Chichester, 1977. Pp. 235. £16.00.

This is a lengthy review of the impact of ion-selective electrodes on organic analysis. It demonstrates that they have boosted titrimetric procedures following decomposition of the sample, e.g., thio compounds, and that they have also extended the range of possible determinations, such as the direct measurement of penicillin with an enzyme electrode. It has all the strengths of a review—wide, up to date coverage—and the defects—an uncritical approach and superficial treatment. Most readers, and especially those who value a guide to the competing claims of the experts, will find the work a valuable addition to the analytical literature.

Handbook of Analysis of Synthetic Polymers and Plastics: J. URBAŃSKI, W. CZERWIŃSKI, K. JANICKA, F. MAJEWSKA and H. ZOWALL, Horwood, Chichester, England, 1977. Pp. 494. £25.00, US $49.50.

It is always a pleasure to find a book, such as this, in which a lot of useful information is presented so lucidly. The authors wear their collective learning lightly to give an account of the major techniques employed for the analysis of polymers and to describe procedures for the detailed analysis of virtually all the plastics and polymers which are commercially available. The proportions of these parts (general: particular) are 1:2 respectively. Both chemical and physical methods are discussed with emphasis being given to basic chemical tests, infrared spectroscopy and chromatography. Many infrared spectra are given throughout the text. Unfortunately, the quality of the spectra emphasises the improvements in spectroscopy which have taken place in the last five years and which are not mentioned, e.g., ^{13}C NMR. Such omissions are inevitable in a long work in translation, but the surprising absence of thermal analysis must be an editorial decision. Despite these shortcomings, it remains a most valuable work, especially for the analyst

with the occasional requirement to analyse a plastic or polymer. He will find clear procedures for the initial classification, confirmation of identity and quantitative determination as well as relevant background information on the material in question.

Das Arbeiten mit ionenselektiven Elektroden, 2nd Ed.: KARL CAMMANN, Springer-Verlag, Berlin, 1977. Pp. XII + 227. DM 76, US $33.50.

This revised and expanded edition of a well-known work in its field will be welcomed by all who work with or are interested in ion-selective electrodes. Besides the background theory and description of construction and function of the electrodes themselves, there is a full treatment of the analytical techniques which use the electrodes, and a brief but wide-ranging review of their application in scientific research and technology.

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EDITORIAL

PERGAMON PRESS—STATEMENT ON THE NEW U.S. COPYRIGHT LAW FOR EDITORS, AUTHORS AND CONTRIBUTORS

In 1978 a new Copyright Law became effective in the U.S. and one of the results is that journals published by Pergamon Press will be asking authors for copyright on each article. How this has come about and why it is important to all of us, requires an explanation.

Traditionally, a transfer of copyright from authors to the publisher or society owning a journal was assumed to be implicit in the process of submitting a manuscript and getting it refereed and accepted for publication. In each journal issue, a copyright notice was printed and was taken to apply to the journal issue as a whole and to each article in it separately. Armed with this understanding, the publisher could not only publish the journal but could distribute reprints of separate articles, authorize others to reprint selectively or cover-to-cover, negotiate translation rights, authorize indexing and abstracting services to use material from the journals, authorize free fair-use copying by individuals and libraries, produce and market microform editions of the journals, etc. All of this has been done successfully by Pergamon in the spirit of actively advancing and diffusing the knowledge contained in its journals.

The new 1978 U.S. Copyright Law changes the situation in at least three important respects. First, it vests statutory copyright in each individual article with the authors of that article, or with their employers in the case of a "work made for hire". This copyright can now be transferred only in a formal written manner. The submission of a manuscript for publication without a formal transfer gives the publisher only the right to publish it as part of the entire issue of the journal in printed and other formats.

The second major change in the U.S. law: The copyright of a journal issue which the publisher registers formally with the Register of Copyrights and which he prints on the inside of the front cover of the journal, under the new law, applies only to the issue as a whole and not to the articles separately. In order for an article to be covered separately, a copyright notice will have to appear on the first page of the article and this requires a transfer of copyright to Pergamon from the author. Otherwise, for each future republication use, each of the original authors would have to give written permission. This would be extremely cumbersome and would clearly inhibit the whole current information distribution system.

The third major change in the U.S. law affecting journals is a much more rigorous definition of the conditions under which libraries may make photographic copies. Individuals or non-profit libraries acting for them will still be free to make copies of articles for their use in research and teaching. However, for commercial libraries and microfilm services the limits of copying are severe; without clear authorization from the copyright holder, distribution through these channels simply cannot legally take place. This obstructs the information distribution system.

Therefore, journals require a transfer of copyright in order to allow for a continuation of the methods that have been used in the past for the dissemination of scientific information. Thus, a transfer of copyright agreement for each article will be required of each author. The author will continue to hold all other traditional rights. For example, there are proprietary rights other than copyright such as patent rights; by definition, these are not transferred. We mention this explicitly since many people confuse patent rights with copyright. It will continue to be an explicit part of our permissions policy that anyone who wishes to *reprint* charts, graphs, etc. from an article will need only the author's permission. For reprinting complete articles, permission of the publisher *only* is required.

Finally, the author retains the right to use the article in his or her future works—for example to include it in a reprint volume. Naturally, authors as individuals will also have fair-use privileges for research and teaching. These points will be covered in the new copyright notice published in the cover of the journal. A form for transfer of copyright agreement will also appear at the end of each issue, and in the interests of economy of time, authors are requested to sign a photocopy of it and send it together with the manuscript when they submit a paper for publication.

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We hope authors will understand the necessity of our taking action to protect copyright of the material published in our journals, and thereby achieve maximum dissemination of their work.

Robert Maxwell
Publisher

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PUBLICATIONS RECEIVED

Laboratory Handbook of Chromatographic and Allied Methods: edited by O. MIKEŠ, Horwood, Chichester, 1979. Pp. 764. £38.50.

In the reviewer's opinion there are too many books on chromatography and related methods. An earlier book edited by Mikeš had numerous competitors. Each book should justify its existence. This new one does. It is not a second edition of the previous manual but a refreshingly modern book which within its wide range deals clearly and in reasonable depth with equipment and materials readily available in the West. The book describes not only the principles involved but gives examples of applications and how to select and improve methods. Chromatography is still partly an art, or skill, and a particularly attractive feature of this book is that the experience of the contributors is revealed in the way they deal with minor handling techniques, and with other, at first sight apparently trivial, matters all of which in fact largely determine whether or not a chromatographic method will be found to be successful. The book is large and for many users should be on its own self-sufficient, but it is impossible, and in this field impractical and undesirable, for any text to seek to be comprehensive. Reference is made to specialist texts.

The topics covered include theories of chromatographic and related methods, applications of partition, adsorption, ion-exchange, gel, affinity and gas chromatography and techniques of column, paper, thin-layer and other types of chromatography. There are chapters on electromigration and countercurrent distribution, and the book ends with a useful review of the literature and a list of United Kingdom suppliers of materials and equipment. The chapters vary in style and scope but overall the coverage is good. In such a large book it is not surprising that there are a few outdated terms and typographical errors. The historical introductions are interesting and well-balanced. The book is indeed what its predecessor claimed to be, namely a laboratory, or bench, manual and in that appropriate guise it will prove of considerable value for reference and browsing. It is an excellent guide through the jungle of competing techniques, chromatographic reagents and suppliers, and will be of some help in assisting in decisions about the most suitable commercially available equipment. Both the novice, and the already experienced worker, will benefit from the expertise displayed.

K. C. B. WILKIE

Modern Methods for Trace Element Analysis: M. PINTA, Ann Arbor Science, Ann Arbor, Michigan, 1978. Pp. xii + 492. £18.60.

This text offers a useful introduction to the application of some selected analytical techniques to trace element analysis. The techniques included are fluorimetry, emission spectroscopy, atomic-absorption spectrometry, atomic-fluorescence spectrometry, X-ray fluorescence spectrometry and activation analysis. For each topic, the theory is discussed briefly, then the apparatus and operational procedures are discussed, and finally a wide selection of practical methods is given. References to the original literature are extensive. The chapters on atomic-absorption methods, which include extensive discussion of non-flame methods, will be particularly useful to the newcomer to modern routine trace analytical practice. In his introduction, the author tries to justify the omission of several important modern techniques, including electrochemical stripping methods, differential-pulse polarography, ion-selective electrodes, and spark-source mass spectrometry: it would have been preferable if he had merely stated that he did not propose to discuss them.

I found that the printers' setting of the equations in the text sometimes made them barely comprehensible: no italic characters were used, and minus signs, en-rules and em-rules all came out looking like hyphens.

MARY MASSON

Analysis with Ion-Selective Electrodes: J. VESELÝ, D. WEISS and K. ŠTULÍK, Horwood, Chichester, 1978. Pp. 240. £16.

The core of this book is a 100-page review of applications of ion-selective electrodes up to 1976–77. A wide range of analyses are covered in outline, but one would have to go to the original reference (there are 839 in this section) before attempting anything that was not straightforward. The discussions of selectivity and other properties of ISEs are thorough and there are useful hints for masking or removing interferences. Given the purpose of the book, a little too much space is given to experimental electrodes and it is not made clear which forms of ISE are readily available and from which manufacturer. Another weakness is that the authors seem to have little faith in ISEs for trace analysis: in this area the reference list is less than comprehensive.

The first half of the book is a sound general introduction to the subject. Chapter 1 describes the theory briefly but at the right level. Chapter 2 is very good on electrode construction (although the air-gap electrode is misunderstood), reference electrodes and aspects of intrumentation. Chapter 3 deals adequately with calibration, known addition methods, and Gran plots; the section on continuous measurements, being brief and narrowly-based, is not of the same standard.

The cost per page is comparatively high, especially in view of the poor paper and printing. It is, however, a useful compilation for anyone wishing to devise or modify a method and on that basis the price is by no means outrageous. The text is clearly written and well illustrated and the book's merits far outweigh any defects I have pointed out.

DEREK MIDGLEY

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PUBLICATIONS RECEIVED

Laboratory Handbook of Chromatographic and Allied Methods: edited by O. MIKEŠ, Horwood, Chichester, 1979. Pp. 764. £38.50.

In the reviewer's opinion there are too many books on chromatography and related methods. An earlier book edited by Mikeš had numerous competitors. Each book should justify its existence. This new one does. It is not a second edition of the previous manual but a refreshingly modern book which within its wide range deals clearly and in reasonable depth with equipment and materials readily available in the West. The book describes not only the principles involved but gives examples of applications and how to select and improve methods. Chromatography is still partly an art, or skill, and a particularly attractive feature of this book is that the experience of the contributors is revealed in the way they deal with minor handling techniques, and with other, at first sight apparently trivial, matters all of which in fact largely determine whether or not a chromatographic method will be found to be successful. The book is large and for many users should be on its own self-sufficient, but it is impossible, and in this field impractical and undesirable, for any text to seek to be comprehensive. Reference is made to specialist texts.

The topics covered include theories of chromatographic and related methods, applications of partition, adsorption, ion-exchange, gel, affinity and gas chromatography and techniques of column, paper, thin-layer and other types of chromatography. There are chapters on electromigration and countercurrent distribution, and the book ends with a useful review of the literature and a list of United Kingdom suppliers of materials and equipment. The chapters vary in style and scope but overall the coverage is good. In such a large book it is not surprising that there are a few outdated terms and typographical errors. The historical introductions are interesting and well-balanced. The book is indeed what its predecessor claimed to be, namely a laboratory, or bench, manual and in that appropriate guise it will prove of considerable value for reference and browsing. It is an excellent guide through the jungle of competing techniques, chromatographic reagents and suppliers, and will be of some help in assisting in decisions about the most suitable commercially available equipment. Both the novice, and the already experienced worker, will benefit from the expertise displayed.

K. C. B. WILKIE

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I found that the printers' setting of the equations in the text sometimes made them barely comprehensible: no italic characters were used, and minus signs, en-rules and em-rules all came out looking like hyphens.

MARY MASSON

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The cost per page is comparatively high, especially in view of the poor paper and printing. It is, however, a useful compilation for anyone wishing to devise or modify a method and on that basis the price is by no means outrageous. The text is clearly written and well illustrated and the book's merits far outweigh any defects I have pointed out.

DEREK MIDGLEY

Talanta. Vol. 26, pp. iii–iv
Pergamon Press Ltd., 1979. Printed in Great Britain

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DEREK MIDGLEY

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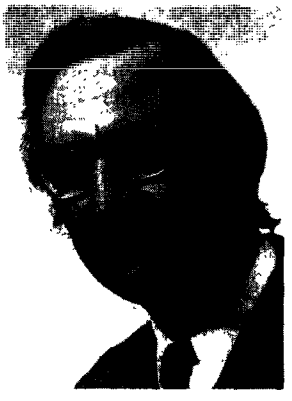
The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

H. KRAGTEN
S. P. PERONE
G. WERNER

They also wish to record their sincere thanks for the help given by

J. F. K. HUBER
F. BERMEJO-MARTINEZ
S. SIGGIA

who retire from the Advisory Board.



Born in Amsterdam in 1932 Dr. Johannes Kragten graduated in physical chemistry at the University of Amsterdam in 1957. After five years of teaching practical physics to lower graduates and spending one year in biophysics research he set up a service group in analytical chemistry at the solid-state physics laboratory of this University. He specialized in accurate analysis of small metal samples, especially by means of photometric complex-formation titrations and received his doctorate in 1971 on theoretical considerations on the influence of metal–indicator complex formation on the accuracy. He is author of 20 research papers and contributed to the Memorial Publication for the late Anders Ringbom (1977). Studies on reliability and accuracy in complexometry, separations and atomic-absorption spectroscopy have led to a theory of the relation between accuracy of analysis and manipulations with metal solutions, for which purpose he compiled with the aid of a computer an atlas of diagrams dealing with side-reactions and hydroxide solubility: *Atlas of Metal-Ligand Equilibria in Aqueous Solution* (1978). Dr. Kragten is treasurer of the Analytical Section of the Royal Dutch Chemical Society. He was on the Management Committee of the International Conference on Magnetism In Amsterdam 1976. As a member of the inter-university advisory committee for developmental co-operation he recently visited South East Asia and since then has been involved in 15 projects on genetics, pedology, zootechnics, metallurgy, microelectronics, instrumental organic chemistry, solid-state physics, corrosion and analytical chemistry.



Professor Sam Perone was born in Rockford, Illinois, and attended Rockford College, where he obtained a B.A. in 1959 and was named to Phi Beta Kappa. He pursued graduate work in analytical chemistry at the University of Wisconsin, where he was awarded fellowships from the Woodrow Wilson Foundation and the National Science Foundation before completing his Ph.D. work in 1962. He joined the faculty of Purdue University in September, 1962, where he currently holds the rank of Professor of Chemistry and is Head of the Analytical Chemistry Division. Professor Perone has published over 70 research articles in the areas of electroanalytical chemistry, photoelectrochemistry and computerized methods for chemical analysis, and has co-authored a textbook, *Digital Computers in Scientific Instrumentation* (1973), and a laboratory manual *Digital Electronics and Laboratory Computer Experiments* (1975). He developed an NSF-supported summer institute on computerized instrumentation for scientists and engineers which was presented annually at Purdue from 1968 to 1974. In 1970, he was awarded a NATO Senior Postdoctoral Fellowship for study at the Eidg. Technische Hochschule. Zürich, Switzerland. He is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma, and he is a member of the editorial board of the journal *Computers and Chemistry*. Professor Perone is vice-chairman of ASTM Committee E-31 on Computerized Laboratory Systems, a member of the ACS Committee on Computers in Chemical Education, and currently serving as Alternate Councilor for the Analytical Division of the American Chemical Society.



Prof. Gerhard Werner is 45 years old and graduated in chemistry (Diplomchemiker) in 1957, obtaining his doctor's degree (Dr. rer. nat.) in 1961 and becoming Doctor of Sciences (Dr. sc.) in 1971. He is now Professor of Analytical Chemistry and head of the Analytical Centre of Karl-Marx-University, Leipzig, German Democratic Republic. His research interests include separation methods, especially ion-exchange, extraction chromatography and solvent extraction of the rare-earth elements, trace analysis and application of ion-selective electrodes. He has authored and co-authored 4 books (text-book and laboratory manual on electrochemistry and electrolytic equilibria, separation methods and catalytic methods of analysis, which will appear shortly) and numerous research papers. His main activities in education have been the establishment of an extended analytical curriculum at his university and lecturing in postgraduate analytical curricula. In 1974 he founded the annual "Analytiktreffen" of the Karl-Marx-University.

LIST OF CONTENTS

JANUARY

Louis Gordon Memorial Award I
Analytical Chemistry: Essays in memory of Anders Ringbom II
A. R. Blanchette and D. J. Curran: Pressurometric titrations with xenon trioxide as oxidant 1
Lucretia Ghergari and Candin Liteanu: Conductometric titration with indicating resistance. IV. The use of membranes with some organic and inorganic acids as active components for HCl titration in a highly conducting medium 9
Toshihiko Kamada, Tatsuhiko Shiraishi and Yuroku Yamamoto: Differential determination of selenium (IV) and selenium (VI) with sodium diethyldithiocarbamate, ammonium pyrrolidinedithiocarbamate and dithizone by atomic-absorption spectrophotometry with a carbon-tube atomizer 15
W. Carder, T. D. Mac Mahon and A. Egan: IDENT. A radioisotope-identification sub-routine for use with the gamma-ray spectrum analysis program SAMPO. 21

Short Communications
K. Dittrich und G. Abel: Emissionsspektrographische Bestimmung von Stickstoffspuren über die Cyanbandenemission in $A^{III}B^{V}$-Halbleitern 41
J. K. Diwan and K. Satyanarayana: Analytical application of phenylbenzene sulphazide in separation and determination of selenium 44
J. N. Miller, D. L. Phillipps, D. Thorburn Burns and J. W. Bridges: The luminescence properties of some anti-inflammatory and antipyretic drugs 46
N. Krishna Murty and K. Rama Rao: Determination of iodide with potassium dichromate and sodium vanadate in the presence of acetone 50
A. Cygański: Determination of some organic thio-compounds by precipitation of mercuric sulphide from mercury (II) ammine complexes. II. Determination of thiourea and some of its derivatives 52
V. S. Sastri: A rapid titrimetric determination of iron in copper concentrates and copper-bearing leach solutions 54
A. Izquierdo et J. Calmet: Identification et détermination colorimétrique du titane avec l'acide 2-mercapto-3(2-furyl)propenoïque 56

Annotation
F. Capitán, F. Salinas and L. F. Capitán-Vallvey: Stability constants of complexes formed by some metal ions with 2-(phenyliminomethyl)pyridine and 2-(*o*-hydroxyphenyliminomethyl)pyridine 59

Papers Received i
Publications Received ii

FEBRUARY

J. J. Topping: **Talanta Mini-Review:** Analytical methods for the determination of tungsten 61
E. van Hoyl, F. Adams and R. Gijbels: Sensitivity calibration for the spark-source mass-spectrometric analysis of aluminium and its alloys 73
R. Makhija and A. Hitchen: Determination of polythionates and thiosulphate in mining effluents and mill circuit solutions 79
S. J. Haynes: Joint determination of fluorine and chlorine in granitic rocks with ion-selective electrodes. . . . 85
M. Jawaid and F. Ingman: Ion-pair extraction of Na^+, K^+ and Ca^{2+} with some organic counter-ions and dicyclohexyl-18-crown-6 as adduct-forming reagent 91
K. Doi: Thermometric studies on the Fe(III) EDTA chelate 97
K. Yoshimura and S. Ohashi: Ion-exchanger colorimetry. II. Microdetermination of chromium in natural waters 103

Short Communications
B. N. Prabhu and S. M. Khopkar: Solvent extraction of gallium(III) as the mono-thiodibenzoylmethane complex 109
W. U. Malik, R. N. Goyal and R. Jain: Quantitative treatment of substituent effects in the polarographic investigations of some potential antineoplastic 2-amino-4-aryl-5-phenylazothiazoles. 111
F. F. Gaál, B. F. Abramović and V. D. Canić: Determination of fluoride with thorium nitrate by catalytic titration 113
O. A. Songina: The mineral-graphite electrode and its application to the analysis of vanadium oxides . . . 116
C. Pelinard, E. Nivaud et P. Boucly: Comportement électrochimique des anti-inflammatoires dérivés de la pyrazolone: application au dosage dans les médicaments 119

Papers Received i
Publications Received ii

MARCH

M. Otto, H. Mueller and G. Werner: Selectivity of catalytic methods of determination 123
Elsie M. Donaldson: Spectrophotometric determination of bismuth in concentrates and non-ferrous alloys by the iodide method after separations by diethyldithiocarbamate and xanthate extraction 131
Jan Asplund: Titration of cyanide and hexacyanoferrate(II) with silver nitrate. I. Calculation of titration curves for potentiometric and conductometric titration 137

JAN ASPLUND: Titration of cyanide and hexacyanoferrate(II) with silver nitrate—II. Determination of sodium cyanide and sodium hexacyanoferrate(II) in a complexing agent . . . 143
J. KRAGTEN and L. G. DECNOP-WEEVER: Hydroxide complexes of cerium(III) . . . 147
J. W. DIEKER, W. E. VAN DER LINDEN and H. POPPL: Behaviour of solid electrodes in normal and differential pulse voltammetric methods . . . 151

Short Communications
S. K. SRIVASTAVA, A. K. JAIN, SUSHMA AGRAWAL and RAJ PAL SINGH: Studies with inorganic ion-exchange membranes . . . 157
K. OHTA and M. SUZUKI: Electrothermal atomic-absorption spectrometry of arsenic and its application to environmental samples . . . 160
M. MOJSKI: Extraction of gold, palladium and platinum from chloride, bromide and iodide solution with DI-n-Octyl sulphide (DOS) in cyclohexane . . . 163
M. V. R. MURTI and S. M. KHOPKAR: Extraction and spectrophotometric determination of copper with thiobenzoylacetone (3-mercapto-1 phenylbut-2-en-1-one) . . . 165
M. ISHIZAKI: Simple method for determination of selenium in biological materials by flameless atomic-absorption spectrometry using a carbon-tube atomizer . . . 167
T. YOSHIMORI, T. ASANO and T. HARADA: Coulometric investigation of the drying conditions of high-grade iron ores for chemical analysis . . . 169
R. G. SMITH, JR: Sources of copper and cadmium contamination in small biological samples . . . 173

Analytical Data
P. G. DANIELE, G. OSTACOLI and P. AMICO: Mixed complexes of Ni^{2+} or Zn^{2+} and citric acid with 2,2'bipyridyl in aqueous solution . . . 177

Annotations
H. F. STEGER, E. MARK and L. E. DESJARDINS: The drying of sulphide-bearing materials in a microwave oven: A caveat . . . 181
E. DEBAL and R. LEVY: Use of precision colorimetry for elemental microanalysis . . . 183

APRIL

Editorial . . . I
Talanta Advisory Board . . . III
B. NEBESAR: The high-temperature analytical uses of vanadium(V) oxide . . . 185
E. GRALLATH und H. M. ORTNER: Bestimmung von Stickstoff in Refraktärmetallen – I. Molybdän und Wolfram . . . 195
A. M. HUNDEKAR, P. UMAPATHY and D. N. SEN: Gravimetric determination of beryllium with sodium oxinate . . . 203
J. VOLKE, M. M. ELLAITHY and O. MANOUŠEK: A spectrophotometric and polarographic investigation of three new cyclohexene-substituted benzodiazepines . . . 209
M. JAWAID: Potentiometric studies of complex formation between methylmercury(II) and EDTA . . . 215

Short Communications
J. W. MUNSON and H. ABDINE: Determination of theophylline in plasma by oxidation at the stationary carbon-paste electrode . . . 221
G. F. MURPHY and R. STEPHENS: Applications of the Zeeman effect to analytical atomic spectroscopy—V. Use of commercial hollow-cathode lamps . . . 223
A. G. FOGG and A. A. OSAKWE: Assessment of a new method for the differential pulse polarographic determination of silicon in steel . . . 226
A. CEDERGREN: Reaction rates between water and some modified rapidly-reacting Karl Fischer reagents . . . 229
M. QURESHI, H. S. RATHORE and J. S. THAKUR: A simple method for dissolution of tantalum pentoxide . . . 232
J. L. BURGOT: Dosages thermometriques de quelques diacides organiques, en milieu aqueux: mise en evidence de la neutralisation successive des deux groupes acides de forces voisines . . . 233
MD. N. AKHTAR, H. S. RATHORE and M. QURESHI: Selective detection of carboxylic acids, ureas and phenols and semiquantitative determination of citric acid by capillary solid-state spot-tests . . . 235

Annotations
J. KRAGTEN: The stability constant of Pd-EDTA . . . 239
E. C. OKAFOR: On the condensation of salicylaldehyde with hydrazine . . . 241
Papers Received . . . i
Notes for Authors . . . iii
Copyright Form . . . v

MAY

I. R. SCHELPAKOWA, I. G. JUDELEWITSCH, S. A. SOLTAN, O. I. SCHTSCHERBAKOWA, K. DITTRICH und R. ZSCHOCKE: Untersuchungen zur atomspektroskopischen Spurenanalyse in $A^{III}B^{V}$-Halbleiter-Mikroproben – III. Untersuchungen zur Schichtabtrennung und zur Spurenanalyse in dünnen GaAs-Schichten . . . 243
E. Y. CAMPBELL and F. O. SIMON: Atomic-absorption determination of beryllium in geological materials by use of electrothermal atomization . . . 251

A. M. HARRIS, J. B. LENGTON and F. FARRELL: Spectrographic determination of gold and platinum metals in geological and other materials by fire-assay preconcentration . . . 257
V. F. TOROPOVA, R. G. K. BUDNIKOV and N. A. ULAKHOVICH: Electrochemical properties of metal complexes of dithio-acid derivatives and their application in extraction polarography . . . 263
D. N. TEWARI: Chemical phase-analysis for kyanites . . . 269

Short Communications
N. JORDANOV, B. NIKOLOVA and I. HAVEZOV: Composition of phosphoric acid solutions obtained when orthophosphoric acid is used as solvent for iron-containing samples by heating: the influence of nitric acid, sulphuric acid and iron(III) . . . 275
ST. JANEVA and R. BORISSOVA-PANGAROVA: Extractional spectrophotometric determination of anionic surfactants in waters with Remacrylblan B and Remacrylrot 2BL . . . 279
H. J. FRANCIS JR. and D. D. PERSING: Determination of water in thiols by Karl Fischer titration . . . 282
B. K. PAL, B. K. MITRA and S. CHATTOPADHYAY: Selective gravimetric method for direct determination of tin(IV) with *N*-*o*-toluoyl-*N*-*o*-tolylhydroxylamine and its application to brass and bronze analyses . . . 284
R. F. SANZOLONE and T. T. CHAO: Matrix effects on the determination of manganese in geological materials by atomic-absorption spectrophotometry under different flame conditions . . . 287
S. BELAL, EL SAYED, A. EL NENAEY and S. A. SOLIMAN: Colorimetric determination of some pharmaceutical primary aromatic amines . . . 290
B. C. VERMA and S. KUMAR: Alkalimetric determination of mercaptans through trithiocarbonic acid formation 291

Preliminary Communication
K. KINA, K. SHIRAISHI and N. ISHIBASHI: Ultramicro extractions and fluorimetry based on the flow-injection method . . . 295
Publications Received . . . i
Announcement . . . ii
Copyright Form . . . iii

JUNE

J. A. RODRIGUEZ-VAZQUEZ: **Talanta Mini-Review:** Gas-chromatographic determination of organomercury(II) compounds . . . 299
T. MIZOGUCHI and H. ISHII: Analytical applications of condensed phosphoric acid—I. Determination of ferrous and total iron in iron ores after decomposition with condensed phosphoric acid . . . 311
K. AMETANI: Compositional analysis of single crystals of flux-grown magnetic garnets by atomic absorption spectrophotometry . . . 317
W. E. HARRIS: A critical examination of analytical error . . . 325
M. T. MONTAÑA GONZÁLEZ, J. L. GÓMEZ ARIZA, F. PINO and R. GARCIA VILLANOVA: Derivatives of 2-thiohydantoin as spectrophotometric analytical reagents . . . 331
J. L. BURGOT: Dosages thermométriques de quelques substances à intérêt pharmaceutique dérivées du noyau phénothiazine par une solution d'hydroxyde de sodium: enthalpie de neutralisation, enthalpie et entropie d'ionisation du chlorhydrate de prométhazine . . . 339

Short Communications
G. H. FAYE: Spectrophotometric method for assessing oxidation of chalcopyrite-bearing ores and concentrates 345
Y. A. BELTAGY, A. S. ISSA and M. S. MAHROUS: Pharmaceutical analysis of some tranquillizers and antidepressants with iodine monochloride . . . 349
R. R. NANEWAR and U. TANDON: Spectrophotometric determination of vanadium in biological materials with *N*-benzylbenzohydroxamic acid . . . 352
R. SESHADRI NAIDU and R. RAGHAVA NAIDU: 2-Hydroxy-1-naphthaldoxime as an analytical reagent for titanium(IV) . . . 354
OM. P. BHARGAVA, A. ALEXIOU and W. GRANT HINES: Rapid method for total iron determination in iron ores, sinter and related materials without use of mercury compounds . . . 357
W. P. KILROY: Thiosulphate in the Wollak procedure—analysis and kinetics in acidic formaldehyde medium 359
Talanta Mini-Reviews . . . i
Copyright Form . . . iii

JULY

K. ŠTULÍK, P. BERAN, J. DOLEŽAL and F. OPEKAR: Electrochemical stripping determination of traces of copper, lead, cadmium and zinc in zirconium metal and zirconium dioxide . . . 363
M. IQBAL, M. A. QURESHI and M. EJAZ: Liquid–liquid extraction of zinc from aqueous thiocyanate solutions with 5-(-4-pyridyl)nonane in benzene . . . 371
D. B. PAUL: Recent analytical developments using chemiluminescence in solution . . . 377
F. HONDA and K. HIROKAWA: Desorption of oxygen and nitrogen from iron surfaces. Application of X-ray photoelectron spectroscopy to surface analysis . . . 383
N. JORDANOV, M. PAVLOVA and S. STEFANOV: A new catalytic reaction of rhenium and its analytical application 389

Short Communications
S. KALYANARAMAN and S. M. KHOPKAR: Solvent extraction separation of hafnium with 4-methyl-3-pentene-2-one 395
K. J. DOOLAN and C. B. BELCHER: Nitrogen determination in coal and coke with an ammonia electrode . . . 398
S. N. NEMA and R. M. VERMA: Iodometric microdetermination of certain organic acids 400
V. B. AGRAWAL: Electrochemical studies of p-nitroaniline-formaldehyde polymer 402
H. DAOUD, A. BILLABERT et M. HAMON: Dosage de quelques dérivés organomercuriels par la cystéine . . . 405
O. H. TUOVINEN: Interactions of tetrathionate with sulphite and sulphide 408
F. VERNON and J. H. KHORASSANI: Solvent extraction of metals with hydroxamic acids 410
A. M. AZIZ-ALRAHMAN and J. B. HEADRIDGE: Determination of silver in irons and steels by atomic-absorption spectrometry with an induction furnace: direct analysis of solid samples 413
H. SANKE GOWDA and K. S. JAGADEESH: Rapid spectrophotometric determination of platinum with trifluoperazine dihydrochloride 416
R. V. GADAG and M. R. GAJENDRAGAD: 4-amino-3-methyl-5-mercapto-1,2,4-triazole as a gravimetric reagent for determination of silver in silver compounds, alloys and complexes 418

Analytical Data
R. N. GOYAL and S. TYAGI: Polarography of some 3-arylazo-3-bromopentane-2,4-diones 421

Preliminary Communication
H. W. YUROW and I. MASTER: Novel colour reactions for ammonium ion in acidic solution 423
Papers Received i
Publications Received iii
Notice iv
Copyright Form v

AUGUST

Louis Gordon Memorial Award I
A. A. MCCONNELL, R. H. NUTTALL and D. M. STALKER: Spectroscopic studies of the metal complexes of ethylenediaminetetra-acetic acid in aqueous solution 425
R. STEPHENS: Applications of the Zeeman effect to analytical atomic spectroscopy—VI. A comparison of some experimental and theoretical detection limits 435
R. STEPHENS and G. F. MURPHY: Applications of the Zeeman effect to analytical atomic spectroscopy—VII. Line interferences 441
G. GALINDO and H. ZUNINO: Some limiting factors of the ion-exchange equilibrium method for determining apparent formation constants of mononuclear complexes 447
A. T. PILIPENKO and L. I. SAVRANSKY: Properties and construction of azo-dye reagents for inorganic photometric analysis 451
A. G. FOGG and J. E. LEWIS: A polarographic and coulometric study of the iron(III)-solochrome violet RS system 461
K. K. VERMA, A. SRIVASTAVA, J. AHMED and S. BOSE: Titrimetric determination of some organic compounds with bromine chloride 469

Short Communications
M. A. KOUPPARIS and T. P. HADJIOANNOU: Indirect potentiometric determination of hydrazine, isoniazid, sulphide and thiosulphate with a chloramine-T ion-selective electrode 477
G. SIVA REDDY, S. C. SOUNDAR RAJAN and Y. KRISHNA REDDY: Titrimetric determination of dissolved oxygen in waste water 480
L. P. PANDEY, A. GHOSE, P. DASGUPTA and A. S. RAO: Determination of chromium in low-alloy steels by atomic-absorption spectrophotometry 482
B. K. PURI and M. GAUTAM: Spectrophotometric determination of chromium(III) and rhodium(III) after extraction with oxine into molten naphthalene 484
R. J. COSSTICK and P. C. NANCARROW: Estimation of metallic iron in rusted sponge-iron: dissolution of iron oxides by bromine methanol 486

Analytical Data
Y. YOSHIMURA and N. SUZUKI: Determination of the salting coefficients of benzoyltrifluoroacetone 489
Papers Received i
Publications Received ii
Copyright Form iii

SEPTEMBER

YU. A. ZOLOTAREV, A. A. KURGANOV and V. A. DAVANKOV: Potentiometric determination of the dissociation constants of an asymmetric sorbent containing L-proline, and the stability constants of its Cu(II) complexes 493
YU. A. ZOLOTAREV, A. A. KURGANOV, A. V. SEMECHKIN and V. A. DAVANKOV: Determination of stability constants of fixed-site complexes of copper(II) ions and of sorbed copper-L-proline complexes with an asymmetric resin containing L-proline groups 499

SEPTEMBER—*continued*

E. Grallath und D. Hirschfeld: Bestimmung von Stickstoff in Refraktärmetallen – II. Titan 505
F. Aullas, B. Tyburce et M. Rumeau: Mise au point d'un programme de calcul des diagrammes de répartition des complexes à force ionique variable 511

Short Communications
S. A. Rahim and S. H. Mohamed: Determination of dissolved oxygen in water 519
G. Norwitz and P. N. Keliher: Semimicro spectrophotometric determination of nitroglycerine in propellants by use of 2,4-xylenol 521
I. S. El-Yamani, M. Y. Farah and F. A. Abd El-Aleim: Co-extraction and separation of zirconium and hafnium by long-chain amines from sulphate media 523
C. G. R. Nair, R. Lalithakumari and P. I. Senan: Bromanine-T as a new oxidimetric titrant 525
K. G. Varshney and A. A. Khan: Stability and distribution studies on Sn(IV) and Cr(III) arsenophosphates: separations of metal ions 528
A. K. Jain, S. K. Srivastava, S. Agrawal and R. P. Singh: Use of chromium ferrocyanide membrane electrode in the potentiometric titration of ferrocyanide with metal ions 531
A. N. Shishkov and Hr. G. Malakova: Disulphides of dithiophosphinic acids as analytical reagents—I. Extractive spectrophotometric determination of palladium with some bis(dialkylthiophosphoryl)- and bis(diarylthiophosphoryl)disulphides 533
K. Röhl, S. Schönherr und R. Schrader: Bestimmung kleiner Nitrit- und Nitratkonzentrationen in Wässrigen Ammoniaklösungen 535
K. Hirokawa and M. Oku: Application of an Al–Ti alloy target in surface analysis by X-ray photoelectron spectroscopy 539
R. W. Cattrall and K.-T. Fong: Serum calcium and potasium determination by the split membrane ion-selective electrode technique 541
C. K. Bhaskari and S. Devi: Furoin thiosemicarbazone as an analytical reagent for nickel(II), palladium(II) and copper(II) 544
Gr. Popa, A. F. Dănet and M. Popescu: Spectrophotometric study of the reaction of Hg(II) with Cadion A and Cadion 2B 546

Annotation
I. Nagypál, J. Páka and L. Zékány: Analytical evaluation of the derivatives used in equilibrium calculations 549
Papers Received i
Publications Received ii
Copyright Form iii

OCTOBER

A. Steffen and K. Bächmann: Gas chromatographic study of volatile oxides and hydroxides of Tc, Re, Ru, Os and Ir—I. Investigation by isothermal gas chromatography 551
A. Merilõja, O. Lukkari and E. Hakoila: Redox titrations—II. Location of inflection points of titration curves for homogeneous redox reactions 557
S. Ahmed, W. Dil, S. A. Chaudhri and M. Ejaz: Extraction of mercury(II) from aqueous thiocyanate solutions with 5-(4-pyridyl)nonane in benzene, and its subsequent atomic-absorption spectrometric determination . 563
A. Gharib and D. F. C. Morris: Determination of rhenium in geological materials by radio-chemical neutron-activation analysis 569
T. Catterick and C. D. Wall: Rapid analysis of small glass fragments by atomic-absorption spectroscopy 573
K. Yoshimura, H. Waki and S. Ohashi: Ion-exchanger colorimetry—III. Microdetermination of zinc in water 579
H. Watanabe and H. Tanaka: A non-ionic surfactant as a new solvent for liquid–liquid extraction of zinc(II) with 1-(2-pyridylazo)-2-naphthol 585

Short Communications
N. Khanna and K. S. Boparai: Determination of thioureas by reaction with phenacyl bromide 591
S. P. Mathur, R. S. Thakur, C. S. Bhandari and N. C. Sogani: Direct photometric determination of cobalt(II) with *N*-methylaminothioformyl-*N'*-phenylhydroxylamine 592
C. Liteanu, I. Rică and V. Liteanu: On the confidence interval of the equivalence point in linear titrations 593
M. Saleem, A. M. Khan and M. Shahid: Sodium tetrachloroferrate as a dehydrating agent 596
M. Mitra and B. K. Mitra: Liquid–liquid extraction of a rhenium thiocyanate complex with hexamethylphosphoramide and direct spectrophotometric determination in the organic phase 597
M. B. Dalvi and S. M. Khopkar: Analytical applications of a liquid anion-exchanger for the separation of uranium(VI) in malonate solution 599

Annotations
T. Yoshimori, Y. Asano, Y. Toriumi and T. Shiota: Investigation on the drying and decomposition of sodium oxalate 603
B. I. Al-Ali: Determination of HOD by infrared spectrophotometry 607
Erratum i
Notice ii

NOVEMBER/DECEMBER

F. SZABADVÁRY: Joseph Louis Gay-Lussac (1778–1850) and analytical chemistry 611
R. B. SINGH, B. S. GARG and R. P. SINGH: Analytical applications of thiosemicarbazones and semicarbazones: a review 619
M. WOZNIAK et G. NOWOGROCKI: Acidités et complexes des acides (alkyl- et aminoalkyl-) phosphoniques—I. Détermination potentiométrique des constantes d'acidité par affinement multiparamétrique: prise en compte de l'impureté carbonate 633
M. WOZNIAK et G. NOWOGROCKI: Acidités et complexes des acides (alkyl- et aminoalkyl-) phosphoniques—II. Affinement multiparamétrique applique aux complexations suivies par potentiométrie 643
M. G. VANDERSTAPPEN and R. E. VAN GRIEKEN: CO-crystallization with 1-(2-pyridylazo)-2-naphthol, and X-ray fluorescence, for trace metal analysis of water 653
R. C. CHANG and J. S. FRITZ: Concentration and determination of trace organic pollutants in water 659
A. G. I. DALVI, C. S. DEODHAR, T. K. SHESHAGIRI, M. S. KHALAP and B. D. JOSHI: Determination of refractory elements in U_3O_8 by carrier distillation emission spectrography 665
K. F. SUGAWARA, Y.-S. SU and W. R. STRZEGOWSKI: Spectrophotometric titration of zirconium in siliccous materials 669
A. HITCHEN and G. ZECHANOWITSCH: Determination of zinc in blast furnace flue dusts 673
A. STEFFEN and K. BÄCHMANN: Gas chromatographic study of volatile oxides and hydroxides of Re, Tc, Os, Ru and Ir—II. Thermochromatographic investigations 677
M. Y. MIRZA: Studies on extraction of Cu(II), Ga(III), In(III) and Tl(III) with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one. Separation and spectrophotometric determination of copper and gallium 685

Short Communications

P. NENOVA, D. KANTCHEVA and B. KARADAKOV: Spectrophotometric determination of bismuth with diethylenetriaminepenta-acetic acid 691
B. C. SINHA and S. DASGUPTA: Masking of manganese in relation to stepwise complexometric determination of calcium, magnesium and manganese 693
Y. YAMAMOTO, H. MURATA and S. UEDA: Ultraviolet spectrophotometric determination of tungsten(VI) with ammonium 1-pyrrolidinecarbodithioate 696
K. K. DEB and R. K. MISHRA: *N*-hydroxy-*N*,*N'*-diphenylcinnamamidine (HDPCA) as a new reagent for extractive separation and photometric determination of vanadium(V) 698
K. MATSMOTO, Y. KUNO and T. TAKEUCHI: Determination of mercury by extraction and isotope-dilution mass spectrometry 701
V. S. SASTRI: Determination of metallic iron in a mixture of lime, calcium sulphide and pyrrhotite 702
I. S. EL-YAMANI and E. N. ABD EL-MESSIEH: Studies on extraction of beryllium from thiocyanate solutions by quaternary ammonium halides 704
C. D. WALL and T. CATTERICK: A simple method for improving control of the time constant in recording transient signals in atomic-absorption spectrometry 705
M. K. AHMED and C. SUBBA RAO: Benzohydroxamic acid as a reductometric titrant determination of manganese in ores and alloys 708
A. S. ISSA, Y. A. BELTAGY and M. S. MAHROUS: Spectrophotometric determination of some phenothiazine derivatives and opipramol with chloramine-T 710
I. S. EL-YAMANI, M. Y. FARAH and F. A. ABD EL-ALFIM: Studies on extraction of zinconium by quaternary ammonium halides from hydrochloric acid media and its separation from hafnium 714
A.-A. M. WAHBI and S. ONSY: Determination of mebendazole 716
M. SATAKE, Y. MATSUMURA and T. FUJINAGA: Spectrophotometric determination of nickel after separation by adsorption of its α-furildioxime complex on naphthalene 718
Å. OLIN and B. WALLÉN: A note on the calculation of acid-base titration curves and their equivalence points 720

Annotations

R. STEPHENS: A signal-comparison parameter for Zeeman background-corrected spectrometers 723
K. DANZER and K. ECKSCHLAGER: Information efficiency of analytical methods 725
W. F. PICKERING: Analytical aspects of lead sorption by solids 727

Letter to the Editor

C. O. INGAMELLS: A further note on the sampling constant equation 731
Papers Received i
Copyright Form iii

Talanta, Vol 25, p iv.
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NOTICE

THE PITTSBURGH CONFERENCE

MARCH 1979

The 1979 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held 5–9 March 1979 at the Cleveland Convention Center, Cleveland, Ohio, USA. Symposia have been organized as described below:

(1) (2) Liquid Chromatography for Environmental Regulatory Requirements
(3) Practical Applications of Glass Capillary Columns in Gas Chromatography
(4) Problems and Solutions in Capillary Gas Chromatography
(5) Ion Chromatography
(6) Photoacoustic Spectroscopy
(7) Laboratory Systems Management
(8) Microcomputers/Microprocessors and Process Control Automation
(9) New Surface Analysis Techniques
(10) Trace Analysis in Characterization of Materials
(11) Environmental Analysis of Water and Sediment
(12) Inductively Coupled Plasma Emission
(13) Symposium on Biomedical Aspects
(14) New Analytical Techniques on the Horizon
(15) 1979 Awards Symposium (Spectroscopy Society of Pittsburgh, Society for Analytical Chemists of Pittsburgh, Hasler Award, Dal Nogare Award)
(16) Fourier Transform/Computer Dispersive Groups Symposium
(17) ASTM E-42—New Surface Analysis Instrumentation
(18) ASTM E-31—Computerized Laboratory Systems
(19) Coblentz Award Symposium

General papers *are not* restricted to the symposia topics. Papers may be contributed in all areas of the disciplines of Analytical Chemistry and Applied Spectroscopy. In 1978, over 600 papers were submitted for the Technical Programme.

Those authors wishing to present papers in the 1979 Pittsburgh Conference Technical Programme should submit three (3) copies of a 300-word abstract to:

Mrs. Linda Briggs
1979 Pittsburgh Conference
437 Donald Road
Pittsburgh, PA 15235
U.S.A.

The abstract should be complete and show: the title of the paper and the name of the author(s), the organization(s) in whose laboratory the work was done, and the addresses(es). The *complete* mailing address of each author, including the department and any other mailing code, must be given. The name of the author who will present the paper must be underlined. The abstract page must be signed and dated in verification that the paper and all material therein has not been published or previously presented.

The *final date* for receipt of abstracts is *August* 29, 1978. Abstracts received after this date cannot be guaranteed consideration for inclusion in the 1979 Technical Programme.

In 1978, the Modern Laboratory Equipment presented at the Conference totalled about 362 exhibitors occupying approximately 800 booths and 17 seminar rooms in which was displayed the latest equipment available for Analytical Chemistry and Spectroscopic work. Anyone desiring to reserve exhibit space or to obtain additional information regarding the 1979 Exposition should contact:

Mr. Allen J. Sharkins
Exposition Chairman
1979 Pittsburgh Conference
P.O. Box 2128
Lower Burrell, PA 15068
U.S.A.

Solvent Extraction in Flame Spectroscopic Analysis: M. S. CRESSER, Butterworths, London, 1978. Pp. x + 200. £15.00.

As one would be entitled to expect of a monograph of only 200 pages costing as much as this one, the book is well produced and proof-read, pleasant to handle and to read.

In content I found it disappointing; the author has set out to produce "an introduction with a strong practical bias", yet only 61 pages of the 200 are on applications. Of the remainder, there are a total of 50 pages listing over 1000 references, 795 of which refer to applications. The remaining pages are devoted to the theory of AAS, AFS and AES, the theory of solvent extraction and one good chapter on the practicalities of solvent extraction procedures. There is no fault to find with the theoretical discussion, but I question the necessity for its inclusion in a practical handbook when so much of it is common knowledge or readily available already. For example, the contamination of samples during grinding is a danger common to all trace analysis, and has no special relevance to solvent extraction/flame spectroscopy.

The longest chapter is on applications, and to my mind suffers from a lack of critical appraisal of the work referenced and from the attitude expressed in the first two lines. They refer to an analyst "wishing to apply solvent extraction/flame spectroscopy to a particular sample", presumably for its own sake; of the 56 elements covered, reading the author's own comments suggests that nearly half would be better determined by a different technique. The lack of criticism has led to inconsistencies even within sections; under arsenic, the first reference is to "detection limits of 0.1 $\mu g\ ml^{-1}$ (or worse)", and 25 lines later to "an excellent detection limit of 0.07 $\mu g\ ml^{-1}$".

I would also have very much liked to see some recommendations based on Dr. Cresser's own wide experience of solvent extraction, rather than the mere blanket reporting of large numbers of systems to be found in the literature. Most of us use this type of monograph for guidance, and it is lacking.

Overall, I would not buy the book at this price; as an analyst I would prefer to use a text on solvent extraction procedures in general and to decide for myself whether a flame finish would be advantageous or not.

R. C. ROONEY

AUTHOR INDEX

Abd El-Aleim F. A., 523, 714
Abd El-Messieh E. N., 704
Abdine H., 221
Abel G., 41
Abramović B. F., 113
Adams F., 73
Agrawal S., 157, 531
Agrawal V. B., 402
Ahmed J., 469
Ahmed M. K., 708
Ahmed S., 563
Akhtar Md. N., 235
Al-Ali B. I., 607
Alexiou A., 357
Ametani K., 317
Amico P., 177
Asano T., 169
Asano Y., 603
Asplund J., 137, 143
Aulas F., 511
Aziz-Alrahman A. M., 413

Bächmann K., 551, 677
Belal S., 290
Belcher C. B., 398
Beltagy Y. A., 349, 710
Beran P., 363
Bhandari C. S., 592
Bhargava Om. P., 357
Bhaskare C. K., 544
Billabert A., 405
Blanchette A. R., 1
Bopari K. S., 591
Borissova-Pangarova R., 279
Bose S., 469
Boucly P., 119
Bridges J. W., 46
Budnikov R. G. K., 263
Burgot J. L., 233, 339

Calmet J., 56
Campbell E. Y., 251
Canić V. D., 113
Capitán F., 59
Capitán-Vallvey L. F., 59
Carder W., 21
Catterick T., 573, 705
Cattrall R. W., 541
Cedergren A., 229
Chang R. C., 659
Chao T. T., 287
Chattopadhyay S., 284
Chaudhri S. A., 563
Cosstick R. J., 486
Curran D. J., 1
Cygański A., 52

Dalvi A. G. I., 665
Dalvi M. B., 599
Daoud H., 405
Dănet A. F., 546
Daniele P. G., 177
Danzer K., 725
Dasgupta P., 482
Dasgupta S., 693
Davankov V. A., 493, 499
Deb K. K., 698
Debal E., 183
Decnop-Weever L. G., 147
Deodhar C. S., 665
Desjardins L. E., 181
Devi S., 544
Dieker J. W., 151
Dil W., 563
Dittrich K., 41, 243
Diwan J. K., 44
Doi K., 97
Doležal J., 363
Donaldson E. M., 131
Doolan K. J., 398

Eckschlager K., 725
Egan A., 21
Ejaz M., 371, 563
Ellaithy M. M., 209
El Nenaey A., 290
El Sayed., 290
El-Yamani I. S., 523, 704, 714

Farah M. Y., 523, 714
Farrell F., 257
Faye G. H., 345
Fogg A. G., 226, 461
Fong K.-T., 541
Francis H. J. Jr., 282
Fritz J. S., 659
Fujinaga T., 718

Gaál F. F., 113
Gadag R. V., 418
Gajendragad M. R., 418
Galindo G., 447
Garcia Villanova R., 331
Garg B. S., 619
Gautam M., 484
Gharib A., 569
Ghergariu L., 9
Ghose A., 482
Gijbels R., 73
Gómez Ariza J. L., 331
Goyal R. N., 111, 421
Grallath E., 195, 505

Hadjiioannou T. P., 477
Hakoila E., 557
Hamon M., 405
Harada T., 169
Harris A. M., 257
Harris W. E., 325
Havezov I., 275
Haynes S. J., 85
Headridge J. B., 413
Hines W. G., 357
Hirokawa K., 383, 539
Hirschfield D., 505
Hitchen A., 79, 673
Honda F., 383
Hundekar A. M., 203

Ingamells C. O., 731
Ingman F., 91
Iqbal M., 371
Ishibashi N., 295
Ishii H., 311
Ishizaki M., 167
Issa A. S., 349, 710
Izquierdo A., 56

Jagadeesh K. S., 416
Jain A. K., 157, 531
Jain R., 111
Janeva St., 279
Jawaid M., 91, 215
Jordanov N., 275, 389
Joshi B. D., 665
Judelewitsch I. G., 243

Kahn A. A., 528
Kalyanaraman S., 395
Kamada T., 15
Kantcheva D., 691
Karadakov B., 691
Keliher P. N., 521
Khalap M. S., 665
Khan A. M., 596
Khanna N., 591
Khopkar S. M., 109, 165, 395, 599
Khorassani J. H., 410
Kilroy W. P., 359
Kina K., 295
Koupparis M. A., 477
Kragten J., 147, 239
Krishna Murty N., 50
Krishra Reddy Y., 480
Kumar S., 291
Kuno Y., 701
Kurganov A. A., 493, 499

Lalithakumari R., 525
Lengton J. B., 257
Levy R., 183
Lewis J. E., 461
Liteanu C., 9, 593
Liteanu V., 593
Lukkari O., 557

Mac Mahon T. D., 21
Mahrous M. S., 349, 710
Makhija R., 79
Malakova Hr. G., 533
Malik W. U., 111
Manoušek O., 209
Mark E., 181
Master I., 423
Mathur S. P., 592
Matsmoto K., 701
Matsumura Y., 718
McConnell A. A., 425
Meretoja A., 557
Miller J. N., 46
Mirza M. Y., 685
Mishra R. K., 698
Mitra B. K., 284, 597
Mitra M., 597
Mizoguchi T., 311
Mohamed S. H., 519
Mojski M., 163
Montaña González M. T., 331
Morris D. F. C., 569
Mueller H., 123
Munson J. W., 221
Murata H., 696
Murphy G. F., 223, 441
Murti M. V. R., 165

Nagypál I., 549
Nair C. G. R., 525
Nancarrow P. C., 486
Nanewar R. R., 352
Nebesar B., 185
Nema S. N., 400
Nenova P., 691
Nikolova B., 275

Nivaud E., 119
Norwitz G., 521
Nowogrocki G., 633, 643
Nuttall R. H., 425

Ohashi S., 103, 579
Ohta K., 160
Okafor E. C., 241
Oku M., 539
Opekar F., 363
Olin A., 720
Onsy S., 716
Ortner H. M., 195
Osakwe A. A., 226
Ostacoli G., 177
Otto M., 123

Páka I., 549
Pal B. K., 284
Papa Gr., 546
Pandey L. P., 482
Paul D. B., 377
Pavlova M., 389
Pelinard C., 119
Persing D. D., 282
Phillipps D. L., 46
Pickering W. F., 727
Pilipenko A. T., 451
Pino F., 331
Popescu M., 546
Poppe H., 151
Prabhu B. N., 109
Puri B. K., 484

Qureshi M., 232, 235, 371

Raghava Naidu R., 354
Rahim S. A., 519
Rama Rao K., 50
Rao A. S., 482
Rathore H. S., 232, 235
Rîcă I., 593
Rodriguez-Vazquez J. A., 299
Röhl K., 535
Rumeau M., 511

Saleem M., 596
Salinas F., 59
Sanke Gowda H., 416
Sanzolone R. F., 287
Sastri V. S., 54, 702
Satake M., 718
Satyanarayana K., 44
Savransky L. I., 451
Schelpakowa I. R., 243
Schönherr S., 535
Schrader R., 535
Schtscherbakowa O. I., 243
Semechkin A. V., 499
Sen D. N., 203
Senan P. I., 525
Seshadri Naidu R., 354
Shahid M., 596
Sheshagiri T. K., 665
Shiota T., 603
Shiraishi K., 295
Shiraishi T., 15
Shishkov A. N., 533
Simon F. O., 251
Singh R. B., 619
Singh R. P., 157, 531, 619
Sinha B. C., 693
Siva Reddy G., 480
Smith R. G. Jr., 173
Sogani N. C., 592
Soliman S. A., 290
Soltan S. A., 243
Songina O. A., 116
Soundar Rajan S. C., 480
Srivastava A., 469
Srivastava S. K., 157, 531
Stalker D. M., 425
Stefanov S., 389
Steffen A., 551, 677
Steger H. F., 181
Stephens R., 223, 435, 441
Strzegowski W. R., 669
Štulík K., 363
Su. Y.-S., 669
Subba Rao C., 708
Sugawara K. F., 669
Suzuki M., 160
Suzuki N., 489
Szabadváry F., 611

Takeuchi T., 701
Tanaka H., 585
Tandon U., 352
Tewari D. N., 269
Thakur J. S., 232
Thakur R. S., 592
Thorburn Burns D., 46
Topping J. J., 61
Toriumi Y., 603
Toropova V. F., 263
Tuovinen O. H., 408
Tyagi S., 421
Tyburce B., 511

Ueda S., 696
Ulakhovich N. A., 263
Umapathy P., 203

van der Linden W. E., 151
Vanderstappen M. G., 653
van Greiken R. E., 653
van Hoye E., 73
Varshney H. G., 528
Verma B. C., 291
Verma K. K., 469
Verma R. M., 400
Vernon F., 410
Volke J., 209

Wahbi A.-A. M., 716
Waki H., 579
Wall C. D., 573, 705
Wallen B., 720
Watanabe H., 585
Werner G., 123
Wozniac M., 633, 643

Yamamoto Y., 15, 696
Yoshimori T., 169, 603
Yoshimura K., 103, 579
Yoshimura Y., 489
Yurow H. W., 423

Zechanowitsch G., 673
Zékány L., 549
Zolotarev Yu. A., 493, 499
Zschocke R., 243
Zunino H., 447

Talanta. Vol. 26. p. v
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ERRATA

In the paper by D. Klockow, G. F. Graf and J. Auffarth, *Talanta*, 1979, **26**, 733, the term "ppM" (parts per milliard) should be replaced wherever it occurs, by the term "ppm" (parts per million) as originally written by the authors, and the definition of ppM given in the "Reagents" section on p. 734 should be deleted.

The title of the paper by R. N. Reddie and D. E. Peters, *Talanta*, 1979, **26**, 389, should read:

AN EVALUATION OF METHODS OF ANALYSIS FOR ALKYLAMINO-OXOMETHANE SULPHONATES