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1. J. J. LINGANE AND A. M. HARTLEY, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. FEIGL, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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RODD'S CHEMISTRY OF CARBON COMPOUNDS

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Editor: S. COFFEY
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The first part of CHEMISTRY OF CARBON COMPOUNDS appeared in 1951. In all, its 5 volumes and 7500 pages took some 11 years to produce. On completion it was hailed as *"the most comprehensive general textbook of organic chemistry ever to appear in the English language" (Endeavour*, vol. 23, no. 54, 1964)

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 35, No. 2, June 1966

THE DETERMINATION OF ZINC BY SUBSTOICHIOMETRIC ISOTOPE DILUTION

Recently, RŮŽIČKA *et al.* proposed a determination of zinc in highly pure germanium dioxide by a substoichiometric extraction technique. In the present work, the effects on the substoichiometric extraction of equilibrium time, pH and interfering ions were investigated by radioactive tracer techniques and spectrophotometric measurements. The sensitivity of the procedure is limited by the blanks and the addition of oxalate ions can give rise to inaccurate results. The specific activity of ^{65}Zn was also determined by substoichiometric extraction.

C. BALLAUX, R. DAMS AND J. HOSTE,
Anal. Chim. Acta, 35 (1966) 141–147

DETERMINATION OF ZINC IN HIGH PURITY BISMUTH BY THERMAL NEUTRON ACTIVATION

A neutron activation analysis for the determination of zinc in bismuth was developed. After irradiating the samples for 44 days at $4 \cdot 10^{11}$ n/cm^2/sec, zinc was separated quantitatively by hexone extraction and precipitation as quinaldate. The sensitivity of the method was estimated as 0.05 p.p.m. No zinc could be detected in the high purity bismuth samples. An addition method of analysis showed that the precision was 1.2%.

J. I. KIM AND J. HOSTE,
Anal. Chim. Acta, 35 (1966) 148–153

A RAPID RADIOCHEMICAL PROCEDURE FOR INDIUM

A rapid radiochemical procedure was developed for the separation of indium radionuclides from a mixed fission-product solution. An alcoholic pyridine solution is added to a uranium solution containing indium and tin carriers. The resulting tin precipitate is separated from the indium-containing solution by filtering through a cellulose membrane filter. The decontamination factor for tin is $2 \cdot 10^3$. Other fission products are only partially removed. The chemical yield of indium is about 44%, and the time required for the separation is about 10 sec. After the tin-separated indium has decayed, the tin daughters of indium are removed from all the other fission products at a specified time and measured, so that the amount of indium present at the time of the tin precipitation is determined.

D. SAM AND D. L. LOVE,
Anal. Chim. Acta, 35 (1966) 154–161

RAPID RADIOMETRIC DETERMINATION WITH EDTA INVOLVING BACK-TITRATION

(in German)

The principle of back-titration with EDTA is applied to rapid radiometric methods. A suitable vessel for performing the reaction, filtration and count-rate measurement is described. The optimal conditions for the use of solid $^{110m}AgIO_3$ as indicator were studied: the time for solubility-equilibrium of solid silver iodate, the reaction time of EDTA with silver iodate, and the pH-dependence of the silver–EDTA reaction rate. Procedures are given for calibration curves and for rapid radiometric determinations of copper(II), nickel(II), lead(II) and zinc(II). The method is suitable for the range 1–100 μg.

K. MÜLLER,
Anal. Chim. Acta, 35 (1966) 162–168

DETERMINATION OF HYDROGEN, NITROGEN AND OXYGEN IN URANIUM MONOCARBIDE

(in French)

A method is described for the determination of hydrogen, oxygen and nitrogen in uranium monocarbide. Hydrogen and oxygen are determined by the classical or modified "Platinum flux" method at 2000° with a coefficient of variation of 10%. Nitrogen is determined at 2000° by the modification of the "Platinum flux" technique. The results obtained are in agreement with those found by Kjeldahl analysis. The coefficient of variation is about 10%. A procedure for the simultaneous determination of the 3 gases is given.

A. Colombo and G. Serrini,
Anal. Chim. Acta, 35 (1966) 169–180

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH GLYOXIME AND CHLOROFORM EXTRACTION

Palladium(II) reacts with glyoxime in a 1:2 mole ratio to form a yellow water-insoluble chelate, which is soluble in chloroform; the solution has an absorption maximum at 397 mμ. Absorbance measurements at 397 mμ allow determination of the palladium glyoximate in solution. The maximum amount of palladium is extracted at pH 1.0. Platinum(II), iridium(III), gold(III), and phosphate cause some positive interference, and iron(II, III) causes negative interference; the interferences can be eliminated by masking with EDTA. The species extracted has been shown to be identical with that used to prepare the original palladium glyoximate chloroform solution. With EDTA and multiple extractions, the method is satisfactory for the determination of palladium in the presence of other platinum-group elements and many other cations.

G. H. Ayres and J. B. Martin,
Anal. Chim. Acta, 35 (1966) 181–189

THIOBENZOYLPHENYLHYDROXYLAMINE: POTENTIAL ANALYTICAL REAGENT

Thiobenzoylphenylhydroxylamine has been prepared and its reactions with metal ions compared to those of its oxygen analogue, benzoylphenylhydroxylamine. Acid dissociation constants and a few formation constants in 1:1 dioxane–water are reported. The thio compound is more reactive, more acidic, and forms chelates of generally greater stability.

G. A. Brydon and D. E. Ryan,
Anal. Chim. Acta, 35 (1966) 190–194

DETERMINATION OF ZIRCONIUM, THORIUM AND SCANDIUM WITH 2,5-DIHYDROXY-1,4-BENZOQUINONE

Zirconium is quantitatively precipitated by 2,5-dihydroxy-1,4-benzoquinone and is separated from scandium in 1 *N* hydrochloric acid solution. Thorium is separated at pH 0.5 from uranium(VI), cerium(IV), lanthanum, yttrium and scandium. Scandium is quantitatively precipitated by this reagent in the pH range 1.4–2.0 and at pH 1.5 equivalent amounts of lanthanum do not interfere; small amounts of yttrium cause interference.

S. P. Singhal and D. E. Ryan,
Anal. Chim. Acta, 35 (1966) 195–199

SIMULTANEOUS DETERMINATION OF PHOSPHORUS, ARSENIC AND GERMANIUM AND THE SEPARATION OF SILICON AND ARSENIC BY SOLVENT EXTRACTION

A simple, rapid, accurate and reliable method for the simultaneous determination of phosphorus, arsenic and germanium as their heteropoly blue complexes is reported. The method involves selective extraction of phosphomolybdic acid at pH 1.0–0.8, and selective extraction of germanomolybdic acid by isooctyl alcohol at pH 0.4, followed by back-extraction of the germanomolybdic acid with water, and reduction of arsenomolybdic acid in the remaining aqueous phase. A rapid and reliable method is also reported for the simultaneous determination of arsenic and silicon by selective extraction of silicomolybdic acid with isooctyl alcohol at pH < 0.4 and the back-extraction of the silicomolybdic acid with water; arsenic is determined in the remaining aqueous phase. The procedure can be applied to the simultaneous determination of phosphorus, arsenic and silicon.

J. Paul,
Anal. Chim. Acta, 35 (1966) 200–205

INTERNAL ELECTROLYSIS FOR THE SEPARATION OF IONS

PART I. SEPARATION AND DETERMINATION OF SILVER, BISMUTH, COPPER AND CADMIUM

The technique of internal electrolysis is recommended for the separation of ions. By proper control of the conditions, *i.e.* by adjustment of pH and by addition of complexing agents, it is possible to separate silver, bismuth, copper and cadmium from each other and from many other ions.

A. K. Majumdar and Sm. Gouri Bhowal,
Anal. Chim. Acta, 35 (1966) 206–211

COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN SELENIUM(IV) AND 1,1′-DIANTHRIMIDE

The complex formation in concentrated sulfuric acid between selenium(IV) and 1,1′-dianthrimide (Di) was studied by spectrophotometry, infrared spectroscopy and chemical analysis. The system was found to contain two species, a Se_2Di complex and a selenium–1,2,7,8-diphthaloylcarbazole complex. The primary complex reaction was assumed to be the formation of the Se_2Di compound; under certain experimental conditions one selenium atom is split off, resulting in the irreversible formation of a carbazole bond. The selenium–1,2,7,8-diphthaloylcarbazole was prepared in the solid state.

F. J. Langmyhr and J. A. Myhrstad,
Anal. Chim. Acta, 35 (1966) 212–219

COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN BORIC ACID AND QUINALIZARIN OR ALIZARIN

The complex formation in concentrated sulfuric acid between boric acid and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) or alizarin (1,2-dihydroxyanthraquinone) was studied by spectrophotometry. Both systems contained only one species, *viz.* a complex between one boric acid and one hydroxyanthraquinone molecules. The reactions of boric acid with hydroxyanthraquinones are discussed and compared with the reaction of boric acid with 1,1′-dianthrimide.

F. J. Langmyhr and A. Holme,
Anal. Chim. Acta, 35 (1966) 220–223

COMPLEX FORMATION AND FLUORESCENCE

PART IV. 8-QUINOLINOL-5-SULFONIC ACID AS A TITRANT FOR BIVALENT CATIONS

8-Quinolinol-5-sulfonic acid can be used in compleximetric titrations by means of a displacement type of titration; a fluorescent weak complex is used to titrate an ion which forms a non-fluorescing stronger complex, the end-point being the appearance of fluorescence. The titration is best performed by an instrumental method. A non-fluorescing weak complex can similarily be used for the titration of a cation which is strongly complexed and fluoresces. By making use of suitable combinations, it is possible to titrate a non-fluorescing complex former and a fluorescing complex former in the same solution.

J. A. Bishop,
Anal. Chim. Acta, 35 (1966) 224–230

THE SIMULTANEOUS ELECTROCHEMICAL DETERMINATION OF CALCIUM AND MAGNESIUM WITHOUT PRIOR SEPARATION. APPLICATION TO BLOOD SERUM AND URINE

(in French)

An important simplification is proposed for the simultaneous electrochemical titration of calcium and magnesium in blood serum and urine. By using platinum wire and mercury electrodes, calcium can be titrated with EGTA and then magnesium with EDTA in the presence of a buffer (pH 10.5) and possibly a citrate–tartrate masking agent. A current due to oxidation of mercury in presence of EGTA or EDTA marks the end-point, and can be read directly or recorded. For blood serum, no preliminary operation is needed; for urine, prior addition of a little silver nitrate makes the method satisfactory.

D. Monnier, G. Delpin and W. Haerdi,
Anal. Chim. Acta, 35 (1966) 231–239

THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM IN SEA WATER

The coprecipitation of chromium from sea water by several precipitates was examined. With hydrous iron(III) oxide a recovery of chromium of $>99\%$ was obtained within the pH range 7.0–9.0 at a chromium level of *ca.* 0.4 μg/l. Chromium was separated from iron by anion exchange and determined spectrophotometrically using diphenylcarbazide. The method showed a precision of ± 0.02 μg Cr/l. Chromium occurs in sea water in the $3+$ oxidation state.

L. Chuecas and J. P. Riley,
Anal. Chim. Acta, 35 (1966) 240–246

A MODIFIED APPARATUS FOR DETERMINATION OF CARBON IN METALS BY THE LOW PRESSURE METHOD

The low pressure method of determination of carbon in metals and alloys was modified to include certain new techniques. An isopentane slush bath dispensed with the use of liquid oxygen and the usual McLeod gauge was replaced by a differential oil manometer, which increased the sensitivity. As little as 5 μg of carbon in $CaCO_3$–quartz standards could be determined with a coefficient of variation of 16.0% which improved to 3.3% at the 100-μg level. The apparatus was used for the determination of carbon in metals such as uranium, zirconium and iron and in steels and cupronickel alloy.

V. T. Athavale, S. P. Awasthi, N. Krishnamachari, M. Sundaresan and M. S. Varde,
Anal. Chim. Acta, 35 (1966) 247–253

A SIMULTANEOUS DTA–GEA–MSA APPARATUS

(Short Communication)

W. W. Wendlandt, T. M. Southern and J. R. Williams,
Anal. Chim. Acta, 35 (1966) 254–255

TITRATION OF IRON(III) AND COPPER WITH EDTA USING N-BENZOYL-N-PHENYLHYDROXYLAMINE AS INDICATOR

(Short Communication)

H. R. Das and S. C. Shome,
Anal. Chim. Acta, 35 (1966) 256–258

CHEMICAL SEPARATION AND DETERMINATION OF SMALL QUANTITIES OF CALCIUM AND MAGNESIUM

(Short Communication)

K. R. Kar and G. Singh,
Anal. Chim. Acta, 35 (1966) 259–261

THE HOMOGENEOUS PRECIPITATION OF LEAD MOLYBDATE

(Short Communication)

G. Newcomb, Jr. and J. J. Markham,
Anal. Chim. Acta, 35 (1966) 261–262

SEPARATION OF SODIUM BY PRECIPITATION WITH HYDROCHLORIC ACID

(Short Communication, in French)

J.-C. Ricq,
Anal. Chim. Acta, 35 (1966) 263–264

THE BEHAVIOUR OF CRYSTAL VIOLET AND METHYL VIOLET IN ANHYDROUS ACETIC ACID MEDIUM·

(Short Communication)

M. Zahradníček, L. Šafařík, S. Štefek and M. Blešová,
Anal. Chim. Acta, 35 (1966) 264–267

CHROMATOGRAPHY OF HALIDE IONS ON THIN LAYERS OF CELLULOSE

(Short Communication)

L. S. Bark, R. J. T. Graham and D. McCormick,
Anal. Chim. Acta, 35 (1966) 268–270

AN IMPROVED METHOD FOR THE DETECTION AND ESTIMATION OF MICRON-SIZED SULFATE PARTICLES: CORRECTION

(Short Communication)

J. P. Lodge, Jr. and E. R. Frank,
Anal. Chim. Acta, 35 (1966) 270–271

THE DETERMINATION OF ZINC BY SUBSTOICHIOMETRIC ISOTOPE DILUTION

C. BALLAUX, R. DAMS AND J. HOSTE
Institute for Nuclear Science, Ghent University, Ghent (Belgium)
(Received November 1st, 1965)

Růžička and Starý[1] and Suzuki[2,3] have described a substoichiometric isotope dilution technique. In substoichiometric isotope dilution the determination of the specific activities can be replaced by a measurement of the relative activities. The amount of the element to be determined is then given by the relation:

$$x = y\left(\frac{A_1}{A_2} - 1\right) \tag{1}$$

where x = the amount of the element to be determined; y = the known amount of the element in the standard solution; A_1 = the activity of the standard solution and A_2 = the activity of the unknown solution.

The separation of zinc by means of a dithizone extraction in the presence of interfering ions, requires the addition of a masking agent. Diethanoldithiocarbamate was suggested by Starý and Růžička[4], as this reagent forms crystalline precipitates with many metal ions but not with zinc. In the present work, the influence on the substoichiometric extraction, of the equilibrium time and of the acidity of the solution was investigated. To control the reproducibility, increasing amounts of zinc were extracted with the same substoichiometric amount of dithizone. By means of radioactive isotopes a critical study was made of the interferences of cobalt, lead, silver, copper, iron, mercury, indium, gold, germanium, arsenic and oxalate ions.

The specific activity of a ^{65}Zn solution was also determined by substoichiometric extraction and zinc was determined in highly pure germanium dioxide.

EXPERIMENTAL

Apparatus

Counting technique. Integral γ-counting in a 2 ″ × 1¾″ well-type NaI(Tl) detector. β-Counting with an end-window G.M. tube (thickness 2 mg/cm^2).

Spectrophotometer. Beckman D.U. spectrophotometer with 1.00 cm Corex-cuvettes.

pH-meter. Radiometer 22.

Tracers

Most of the radioisotopes were produced by neutron irradiation in the BR-1 reactor (Table I). A ^{210}Pb solution was obtained carrier-free from the Radiochemical Centre, Amersham, England.

Reagents

Diphenylthiocarbazone (dithizone). A.R., dissolved in carbon tetrachloride (A.R.); only freshly prepared solutions were used.

Diethanoldithiocarbamate. 3 g of diethanolamine and 1.75 g of carbon disulfide (A.R.) were mixed in 60 ml of absolute methanol (A.R.).

Hydrochloric acid (A.R.) and *ammonia* (A.R.) were purified by isopiestic distillation.

TABLE I

DATA FOR RADIOISOTOPES USED

Element	*Isotope*	$T_{\frac{1}{2}}$[5]	*Irradiation*[5]
Co	^{60}Co	5.2 y	β^-, γ
Pb	^{210}Pb	22 y	β^-, γ
Ag	^{110m}Ag	270 d	β^-, γ
Cu	^{64}Cu	12.8 h	EC, β^-, β^+, γ
Fe	^{59}Fe	45.1 d	β^-, γ
Hg	^{203}Hg	48 d	β^-, γ
In	^{114m}In	49 d	γ
Au	^{198}Au	2.7 d	β^-, γ
Ge	^{77}Ge	12 h	β^-, γ
As	^{76}As	26.5 h	β^-, β^+, γ
Zn	^{65}Zn	245 d	β^-, γ

Buffer-masking solution. 5 ml of diethanoldithiocarbamate solution and 45 ml of ammonium chloride 0.1 N–ammonia buffer (pH, 8–9) were mixed. To remove the last traces of zinc, this solution was extracted with dithizone dissolved in carbon tetrachloride.

All other reagents were of A.R. grade.

Procedure

To 10 ml of the unknown zinc solution (x µg), add 4 ml of the buffer-masking solution and a standard solution containing radio-zinc (y µg). Adjust the pH of the solution to 8 ± 0.5 with ammonia and 1 N hydrochloric acid. Extract the solution with 5 ml of carbon tetrachloride containing a substoichiometric amount of dithizone.

After shaking for 5 min, separate the organic phase. At the same time, extract the standard solution, containing 4 ml of buffer-masking solution, with the same substoichiometric amount of dithizone. Measure the activity of 4 ml of the organic phase of the unknown and standard solutions (A_2 and A_1). The amount of zinc can be calculated from eqn. (1).

Substoichiometric extraction as a function of extraction time and pH

Amounts of 101.7 µg of zinc in 10 ml of solution were shaken with 5 ml of $3 \cdot 10^{-4}$ M dithizone in carbon tetrachloride for varying periods of time. After dilution, the extinctions of the organic phase were measured spectrophotometrically at $\lambda_{\text{max.}} = 535$ mµ. From the results presented in Fig. 1, it appears that equilibrium was reached after shaking for 5 min.

To determine the influence of the pH on the extraction, a series of 10-ml solutions containing 2.86 μg of zinc (46.342 counts/min) were extracted with 5 ml of 10^{-5} M dithizone at different acidities. The results of the activity measurements of the organic layers are shown in Fig. 2. In the pH region 7.3 to 9.0 a maximal zinc extraction was obtained.

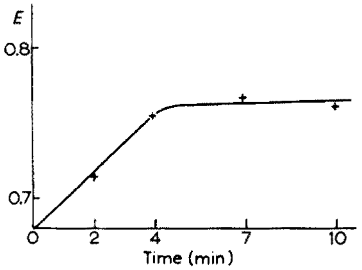

Fig. 1. Extraction as a function of extraction time.

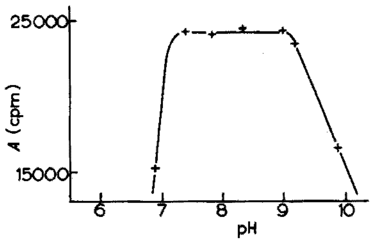

Fig. 2. Extraction as a function of pH.

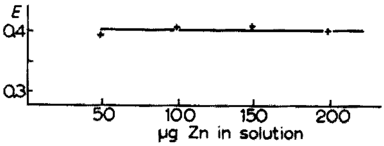

Fig. 3. Reproducibility of the substoichiometric extractions.

Reproducibility of substoichiometric extractions

Solutions with varying concentrations of zinc were extracted with the same substoichiometric quantity of dithizone (10 ml of 10^{-4} M). The results shown in Fig. 3 were obtained spectrophotometrically. It appears that the extracted amount of zinc is only determined by the quantity of dithizone added.

Interferences

In the presence of large amounts of cobalt, lead, silver, copper, iron, mercury, indium, gold, germanium and arsenic, 50.86 μg of zinc were separated by a substoichiometric extraction (5 ml of 10^{-4} M dithizone). The extraction of the interfering

TABLE II

INTERFERENCES

Element	*mg added*	*Stability constant of dithizone complex*[1]	% *Extraction*
Co	1.222	10^{13} (Ref. 6)	< 0.02
As	1.25	—	0.02
Pb	2.40	17	0.04
Ag	1.03	$4 \cdot 10^7$; $9 \cdot 10^8$	0.04
Cu	1.04	$3.6 \cdot 10^9$; $3 \cdot 10^{10}$	0.09
Fe	20.0	—	0.1
Hg	2.8	$5.7 \cdot 10^{26}$; $7.1 \cdot 10^{26}$	0.15
In	1.12	$6.9 \cdot 10^4$	0.3
Au	0.02	—	0.55
Ge	400	—	< 0.002
Zn	0.05	$5 \cdot 10^2$	—

metals was examined by means of radioactive tracer solutions. The fractions of the radioactive isotopes, separated with the organic layer, are given in Table II. It appears that the interference due to these ions is negligible.

Determination of zinc by substoichiometric isotope dilution analysis

Zinc solutions containing 101.7 μg of zinc, and standard solutions containing 110.0 μg of radio-zinc, were extracted with 5 ml of dithizone solution ($2 \cdot 10^{-4} M$).

For the verification of the results, the aqueous phases were extracted once more. The mean value found (100.6 μg of zinc) was in good agreement with the expected value. Because only low activities were measured, the standard deviation of the mean value of the results given in Table III is rather high.

TABLE III

ANALYSIS OF ZINC SOLUTIONS

		A_1 *(counts/min)*	A_2 *(counts/min)*	x *(μg)*	Δ μg
I	1 extraction	848	441	101.5	+0.6
II	1 extraction	1363	715	99.7	−0.9
	2 extractions	1153	621	94.2	−6.7
III	1 extraction	1473	750	106.4	+5.8
	2 extractions	1152	613	96.7	−3.9
	3 extractions	1165	595	105.4	+4.8
Mean value				100.6 ± 3.8	−1.1

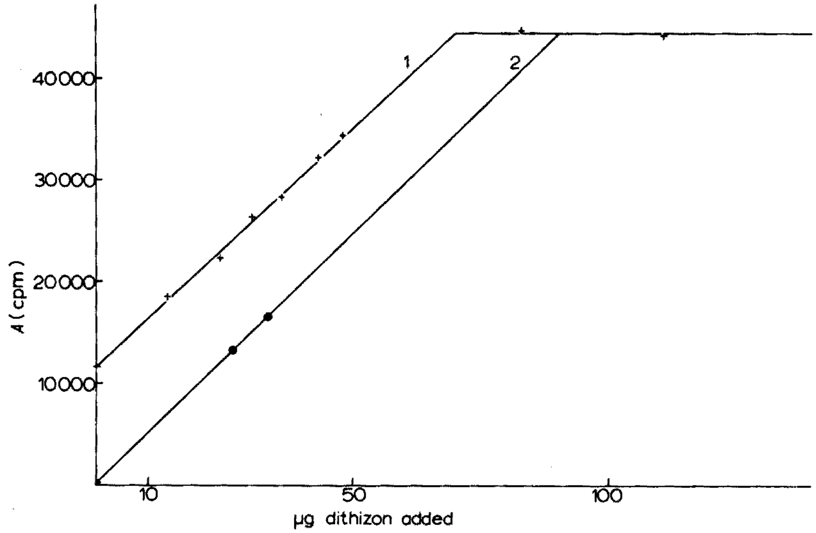

Fig. 4. Determination of the specific activity of the ^{65}Zn solution.

Determination of the specific activity of a ^{65}Zn solution

After the addition of 4 ml of buffer-masking solution, a series of 10-ml portions of ^{65}Zn solutions (52.442 counts/min) was extracted with increasing amounts of dithizone dissolved in 5 ml of carbon tetrachloride. When an equivalent quantity of dithizone was added, the total ^{65}Zn activity passed into the organic phase. As can be seen from Fig. 4, curve 1, even when no dithizone was added, 10.168 counts/min of ^{65}Zn were extracted. The buffer-masking solution, prepared as given by STARÝ AND RŮŽIČKA[4], thus contained dithizone, introduced into the water–methanol phase when the buffer-masking solution was purified by dithizone extraction. The amount of dithizone present in 4 ml of the buffer-masking solution, as calculated from Fig. 4, represents 24.5 μg dithizone. This amount limits RŮŽIČKA AND STARÝ's substoichiometric isotope dilution method to the determination of 3 μg of zinc. This dithizone can easily be back-extracted from the buffer-masking solution with carbon tetrachloride. The results shown as curve 2 were obtained after the addition of a buffer-masking solution which had been extracted with pure carbon tetrachloride. It is apparent that no activity was extracted when no dithizone was present. The dithizone solution was standardised spectrophotometrically with a standard zinc solution.

Determination of zinc in germanium dioxide

RŮŽIČKA *et al.*[7] determined zinc in germanium dioxide by substoichiometric activation analysis. This procedure involves the dissolution of the sample in 8 *N* sodium hydroxide. From our experiments, it appeared that different varieties of germanium dioxide could not be dissolved even by the action of hot concentrated sodium hydroxide solutions. It was necessary to fuse the sample with solid sodium hydroxide or carbonate. This fusion, carried out in a platinum crucible with purified sodium carbonate, introduced a blank value of about 1 μg. The method also necessitated the addition of oxalate ions to keep the germanium in solution. This possible interference was also studied. To 10-ml portions of ^{65}Zn solutions (51.9 μg) were added 35 mg of ammonium oxalate. The zinc was extracted with a substoichiometric amount of dithizone (5 ml of 10^{-4} *M*). At the same time, identical solutions, free of oxalate, were extracted with the same amount of dithizone.

TABLE IV

EXTRACTION IN THE PRESENCE OF OXALATE IONS

Activity extracted without oxalate (counts/min)	2020	7539	7589	8018	9037
Activity extracted, oxalate present (counts/min)	1859	7007	6971	7416	8373
% deviation	7.9	7.1	8.1	7.5	7.4

The results (Table IV) indicate that the oxalate ions prevented a quantitative dithizonate formation.

CONCLUSIONS

(*1*) The substoichiometric determination of zinc by isotope dilution analysis and by activation analysis as proposed by RŮŽIČKA *et al.*[4,7] can lead to inaccurate results because of the solubility of the dithizone in the buffer-masking solution. This solubility limits the sensitivity of the method to the determination of 3 μg of zinc. The dissolved dithizone can be back-extracted with carbon tetrachloride. The fact that in the presence of oxalate ions the reaction between dithizone and zinc is not stoichiometric must also be taken into account.

(*2*) Some varieties of germanium dioxide cannot be dissolved in 8 *N* sodium hydroxide and must be fused with sodium hydroxide or carbonate. Alternatively, they could be dissolved in a pressure tube at 150° with 12 *N* hydrochloric acid followed by evaporation as chloride or extraction of the matrix with carbon tetrachloride.

(*3*) The accuracy and the reproducibility of the determination depends on the specific activity of the ^{65}Zn tracer. A high specific activity can be obtained by a deuteron irradiation of high purity copper. The specific activity can easily be determined by substoichiometric extraction.

(*4*) If zinc is to be determined in a highly pure matrix, the introduced blank limits the sensitivity of the isotope dilution method. A substoichiometric activation analysis must be preferred in this case.

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SUMMARY

Recently, RŮŽIČKA *et al.* proposed a determination of zinc in highly pure germanium dioxide by a substoichiometric extraction technique. In the present work, the effects on the substoichiometric extraction of equilibrium time, pH and interfering ions were investigated by radioactive tracer techniques and spectrophotometric measurements. The sensitivity of the procedure is limited by the blanks and the addition of oxalate ions can give rise to inaccurate results. The specific activity of ^{65}Zn was also determined by substoichiometric extraction.

RÉSUMÉ

Récemment, RŮŽIČKA et ses collaborateurs ont proposé un dosage de zinc dans un dioxyde de germanium de grande pureté, à l'aide d'une technique d'extraction substoéchiométrique. Les auteurs ont examiné l'influence du temps, du pH et d'ions gênants sur cette extraction, à l'aide de traceurs radioactifs et de mesures spectrophotométriques. On a également déterminé l'activité spécifique de ^{65}Zn.

ZUSAMMENFASSUNG

Kürzlich schlugen RŮŽIČKA u.a. eine Bestimmung von Zink in hochreinem Germaniumdioxid mit Hilfe einer substöchiometrischen Extraktionstechnik vor. In der vorliegenden Arbeit wurden die Einflüsse des pH-Wertes und störender Ionen mit der radioaktiven Tracertechnik und spektralphotometrischen Messungen untersucht. Die spezifische Aktivität von ^{65}Zn wurde mit der substöchiometrischen Extraktion bestimmt.

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DETERMINATION OF ZINC IN HIGH PURITY BISMUTH BY THERMAL NEUTRON ACTIVATION

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As appears from the surveys of BOCK-WERTHMANN[1-3], activation analysis of zinc in various samples has been investigated by many workers. From these bibliographies it can be seen that only 2 workers have dealt with zinc in bismuth samples[4,5]. These papers are however not available to the general public.

As a non-destructive analysis of traces of zinc in bismuth is not practical, a separation procedure had to be developed. Various methods have already been applied for this purpose, *e.g.* precipitation as zinc mercury thiocyanate[6-13] or zinc quinaldate[7,14,15], organic solvent extractions[16-19], ion exchange[14,20,21] and the use of a column on which dithizone is retained with an organic solvent on cellulose acetate[22]. The applicability of these methods is of course predominantly dependent upon the properties of the matrix and the zinc quantity to be determined. Accordingly, a special investigation seemed necessary for the determination of traces of zinc in a bismuth matrix.

In a first step the matrix itself was precipitated as bismuth oxychloride, whereas other impurities were scavenged to a certain extent. Zinc was then extracted with hexone and stripped into the aqueous phase with dilute ammonia. Precipitation with quinaldic acid finally gave a highly specific radiochemical separation with an excellent recovery. The accuracy of the established procedure was tested by an addition method. The obtained sensitivity was 0.05 p.p.m.

Although zinc was not even qualitatively detectable in the samples, experiments with synthetic samples showed that the procedure established is adequate for the determination of the zinc traces in high purity bismuth.

NUCLEAR DATA

From the nuclear data (Table I) it is seen that after thermal neutron activation of zinc, 5 nuclides are available for determining this element. The small value for the isotopic abundance as well as the small activation cross-section of ^{70}Zn restricts the use of ^{71m}Zn and ^{71}Zn. If a rapid chemical separation is possible, working near the irradiation place, ^{69}Zn is the most useful nuclide, as the activation cross-section is satisfactory and a good saturation factor after a short irradiation can be obtained. Since this work was not performed under these conditions, ^{69}Zn could not be used. The selection was thus restricted to ^{69m}Zn or ^{65}Zn.

The chemical separation and the transportation time required under the present working conditions decreased the activity of ^{69m}Zn far below the activity strength

TABLE I

NUCLEAR DATA

Target nuclide	*% Abundance*	*Act. σ (barn)*	*Isotope produced*	*Half life*	*Radiation and energy (MeV)*
^{64}Zn	48.89	0.44	^{65}Zn	245 d	β^+: 0.324 (1.5%) γ : 1.110 (44%)
^{68}Zn	18.56	1.0 0.097	^{69}Zn ^{69m}Zn	52 m 13.8 h	β^-: 0.897 γ : 0.438
^{70}Zn	0.62	0.085	^{71}Zn	2.2 m	β^-: 2.4 γ : 0.12, 0.51, 0.90, 1.09
			^{71m}Zn	3 h	β^-: 1.5 γ : 0.38, 0.49, 0.61

at the end of irradiation. For this reason ^{65}Zn was chosen, even though a long irradiation time was required to produce an adequate activity.

SEPARATION TECHNIQUE

As the sample size was quite large (2 g), the bismuth was first precipitated as bismuth oxychloride by diluting the solution[23,24]. It was found that many trace elements were more or less scavenged into the precipitate, *e.g.* copper, selenium, gold, mercury, polonium, antimony, silver, etc. (a long irradiation of the sample produces ^{210}Po nuclide, the daughter of ^{210m}Bi). The coprecipitation of zinc was determined with ^{65}Zn. The results are shown in Table II.

TABLE II

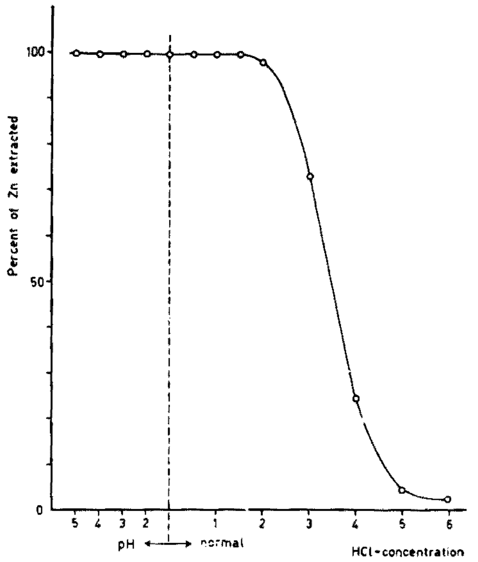
COPRECIPITATION OF ZINC

Experiment no.	*Zn carrier added (mg)*	*Activity[a] added (counts/min)*	*Activity of filtrate (counts/min)*	*% of Zn in filtrate*
1	30	1190	1204	100.0
2	20	35200	33600	95.5
3	10	35500	34300	96.5
4	0	41100	40800	99.5

[a] Specific activity is *ca.* 10^3 counts/min/μg of zinc.

Many methods are known for liquid–liquid extraction of zinc[16–19,25,26]. None of these methods is however specific and a subsequent separation step is required. To achieve an easy stripping of zinc from the organic phase, a hexone extraction of the thiocyanate in hydrochloric acid was chosen[27]. Zinc thiocyanate was quantitatively extracted into hexone in hydrochloric acid from pH 5 up to 1.5 *N* hydrochloric acid. The extractability as a function of the pH is shown in Fig. 1.

After extraction, the organic phase was stripped with ammonium hydroxide. It was found that the ammonium hydroxide concentration for a quantitative stripping depended on the hydrochloric acid concentration used in the previous extraction. Hence, if zinc was extracted at a certain acidity, quantitative stripping was possible with a somewhat higher ammonium hydroxide concentration. The experimental results are shown in Fig. 2.



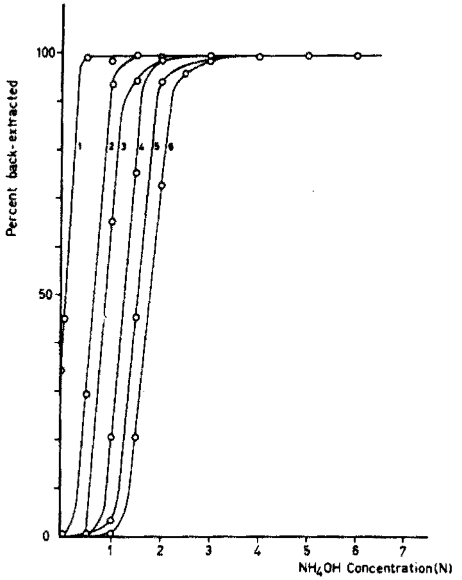


Fig. 1. Extractability of zinc thiocyanate into methyl isobutyl ketone.

Fig. 2. Back-extraction of zinc. HCl concentration of previous extraction: (1) 0.01 N; (2) 0.5 N; (3) 1.0 N; (4) 1.5 N; (5) 2.0 N; (6) 3.0 N.

As a final step in the separation of zinc, the zinc quinaldate precipitation is often used[7,14,15,28]; this gave satisfactory results as far as yield and decontamination were concerned.

EXPERIMENTAL

Sampling and irradiation

A sample of approximately 2 g was taken from three kinds of bismuth (B-2: purity unknown; B-3: 99.999%; B-4: 99.9999%) and washed with dilute nitric acid to eliminate surface contamination. The sample was packed in aluminium foil. For the standard samples high purity zinc oxide was used, dissolved in 3 N hydrochloric acid and diluted to a 103.75 μg/ml solution; 100 μl were taken and sealed in a quartz ampoule. The sample and standard were packed together in the aluminium irradiation container. The irradiation was performed during 44 days in the BR-1 reactor at the neutron flux of $8 \cdot 10^{11}$ n/cm^2/sec.

After irradiation the sample was washed again with dilute nitric acid to remove surface contamination. Before unsealing the standard sample in the quartz ampoule, it was cooled in liquid air to reduce the vapour pressure which might have arisen inside during the irradiation, and 10 μl was taken for experiments.

For the preparation of synthetic samples from B-3 and B-4, approximately 1 g of metallic grains, machined from the metal block, was put into the quartz ampoules. To these, 1–5 μg of zinc, taken from prepared standard solution, were added, whereafter the ampoules were sealed and the contents mixed by shaking. The irradiation of these samples was performed under the same conditions as described above.

TABLE III

ANALYSIS OF SYNTHETIC SAMPLES

Sample	*Sample weight (g)*	*Chem. yield (%)*	*Zn added (p.p.m.)*	*Zn found (p.p.m.)*	*Activity*[a] *(counts/min)*
Standard sample	1.0 (μg)	98.75±0.85	—	—	1021±25
B-3	0.988	94.18	1.048	1.031	1053
B-3	1.012	93.97	2.046	2.086	2130
B-4	1.050	93.80	2.960	2.915	2976
B-4	1.010	85.61	4.102	4.180	4268
B-4	1.023	93.16	5.062	5.160	5268

[a] Activity for a 1-g sample and 100% chemical yield.

Radiochemical separation

After 5 days cooling, in order to reduce the activity of the matrix and of the short-lived nuclides, the sample was dissolved, with addition of 10.89 mg of zinc carrier, in 10 ml of 7 *N* nitric acid. The solution was evaporated almost to dryness and nitric acid was removed by evaporating in the presence of 3 ml of concentrated hydrochloric acid. Boiling was continued for another 10 min and the sample solution diluted with 50 ml of water. A white bismuth-oxychloride precipitate was formed, and filtered off through a glass filter.

The filtrate was evaporated to 20 ml. To this solution 10 ml of 10% ammonium thiocyanate were added and zinc was extracted twice with 20 ml of hexone. From the combined organic phase, zinc was stripped with 10 ml of 3 *N* ammonia solution.

The solution was boiled to reduce the ammonia concentration and after cooling, 10 ml of buffer solution (200 g of sodium acetate trihydrate dissolved in 300 ml of glacial acetic acid and diluted to 1 l) and 5 ml of quinaldic acid (3 g of quinaldic acid dissolved in 100 ml of water and neutralized with sodium hydroxide to pH 7) were added. A white precipitate was quantitatively formed within 10 min.

The precipitate was separated by centrifugation in a weighed counting vial. The precipitate was washed with water and alcohol. After evaporation of the last traces of alcohol under the infrared lamp the precipitate was dried for 1 h in the oven at a temperature of 100°. Then it was weighed to determine the yield.

The standard samples were also precipitated as zinc quinaldate.

For the synthetic samples, the unsealed quartz ampoules were transferred to a beaker and the samples dissolved in 5 ml of 7 *N* nitric acid. After complete dissolution, the quartz pieces were removed, washed with dilute nitric acid and discarded. The separation procedure was then followed as stated above.

Counting

The radiochemical purity of the separated zinc was checked by γ-spectrometry (400-channel analyzer coupled with the scintillation detector of 3″×3″ NaI(Tl) crystal). Only ^{65}Zn could be detected.

For quantitative measurements the photopeak at 1.11 MeV was selected and counted for 30 min, starting 6 days after the end of irradiation. A 1-μg portion of Zn standard gave rise to 1021±25 counts/min under the 1.11-MeV photopeak, whereas the background was 50±3 counts/min.

ACCURACY OF THE METHOD

The accuracy of the procedure was tested by an addition method. Seven samples were prepared by placing 1 g of bismuth grains (B-2) into a quartz ampoule. These were spiked with respectively 0.47, 0.89, 1.95, 4.15, 6.38, 8.89 and 13.51 p.p.m. of zinc, out of the standard solution. The quartz ampoules were sealed and their contents thoroughly mixed by shaking. After irradiation they were submitted to the chemical separation and counting described above. The results were calculated by the method of least squares for fitting a straight line to the experimental points[29]. The results are given in Fig. 3. X is the concentration of the component to be determined in the specimens, Y the measured activity, *a* the slope of the straight line (specific activity) and *b* the intercept with the ordinate. The original zinc content of the samples is of course given by b/a. The negative value of $b = -60$ counts/min indicates that no zinc is present. From the addition procedure the standard deviation was estimated as $\pm 1.2\%$. The specific activity of the addition method, compared with that of the standard method also allowed an appraisal of the accuracy. These two values were respectively 1026 ± 10 counts/min/p.p.m. and 1021 ± 25 counts/min/p.p.m. If a count rate equal to the background is taken as the limit, the method should allow determination of 0.05 p.p.m. of zinc in a 2-g bismuth sample.

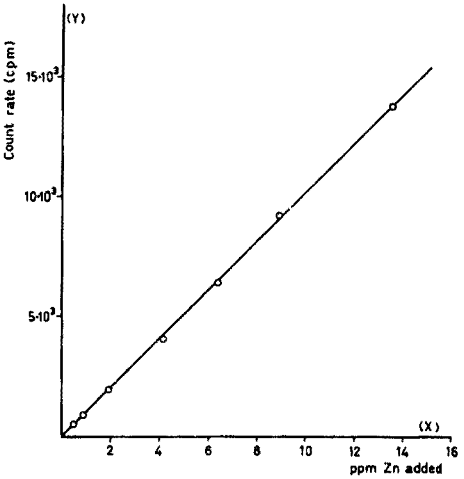


Fig. 3. Calibration graph for ^{65}Zn. $a = 1026 \pm 10$ counts/min/p.p.m.; $b = -60 \pm 64$ counts/min.

SUMMARY

A neutron activation analysis for the determination of zinc in bismuth was developed. After irradiating the samples for 44 days at $4 \cdot 10^{11}$ n/cm²/sec, zinc was separated quantitatively by hexone extraction and precipitation as quinaldate. The sensitivity of the method was estimated as 0.05 p.p.m. No zinc could be detected in the high purity bismuth samples. An addition method of analysis showed that the precision was 1.2%.

RÉSUMÉ

Une analyse par activation au moyen de neutrons est développée pour le dosage du zinc dans le bismuth. Après irradiation des échantillons pendant 44 jours à $4 \cdot 10^{11}$ n/cm²/sec, le zinc est séparé quantitativement par extraction avec l'hexone et précipitation sous forme de quinaldate. La sensibilité de la méthode est estimée à 0.05 p.p.m. Précision 1.2%.

ZUSAMMENFASSUNG

Mit der Neutronenaktivierungsanalyse wurde Zink in Wismut bestimmt. Die Proben wurden 44 Tage mit $4 \cdot 10^{11}$ n/cm²/sec bestrahlt und das Zink quantitativ durch Extraktion mit Hexon und Fällung als Chinaldat abgetrennt. In hochreinen Wismutproben konnte kein Zink nachgewiesen werden. Die Empfindlichkeit der Methode beträgt etwa 0.05 p.p.m., ihre Genauigkeit 1.2%.

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A RAPID RADIOCHEMICAL PROCEDURE FOR INDIUM

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A rapid radiochemical procedure for the separation of indium from mixed fission products was needed for the determination of cumulative and independent fission yields of indium nuclides. The procedure had to be rapid because the indium nuclides of mass numbers 121 and above have short half-lives. This precluded any repeated decontamination steps to achieve the required radiochemical purity. Also required was good decontamination from the descendants of indium, because the indium atoms were finally determined from the assay of the number of atoms of the longer-lived tin daughters or their descendants along a given mass chain. Different radiochemical procedures for rapid separation of indium that would satisfy the above requirements have been sought at this laboratory.

The procedure described here is based on precipitations from pyridine solutions. Another procedure based on sublimation of indium acetylacetonate has been developed by WEISS AND BALLOU[1].

Other radiochemical procedures reported[2-4] for the separation of indium employed combinations of hydroxide, sulfide, and 8-hydroxyquinoline precipitations and solvent extraction. The time required for separation varied from 30 min to about 4 h; chemical yields were greater than 50% and decontamination factors from interfering elements were generally larger than 10^2. These methods were unsatisfactory for studies of short-lived indium nuclides.

MOSER AND SEIGMANN[5] mentioned that pyridine precipitates indium completely, but that it was unsatisfactory for the separation of indium from other metals because they always coprecipitated to a certain extent. No data on this problem were presented. OSTROUMOV[6] described some methods for the separation and determination of a number of elements involving the use of organic bases, such as pyridine, α-picoline, and hexamethylenetetramine. In particular, he separated indium from manganese, zinc, cobalt, copper, and cadmium, using pyridine as the precipitant.

The present procedure differs from OSTROUMOV's procedure in the following manner. OSTROUMOV precipitates indium in an aqueous pyridine solution containing ammonium ion, whereas in the present procedure tin and other elements are precipitated, leaving the indium in solution by using an alcoholic pyridine solution containing no ammonia. We found that the presence of alkali ions is essential for the precipitation of indium.

The use of pyridine and its derivatives makes possible very accurate control of the pH of the solution in the precipitation of metal hydroxides, and this, together with the ability of pyridine to form readily soluble stable complexes, has been used to develop a new method for the separation of indium from tin and other fission-product elements.

In this radiochemical procedure, tin is initially precipitated by pyridine, leaving the indium in solution. This solution is then quickly filtered through a cellulose membrane filter under 75 psig pressure. Tin daughters of indium are allowed to grow into the indium filtrate and are separated as stannane with an alkaline borohydride solution. Tin is rapidly removed initially to ensure that there is no interference from tin formed independently in fission.

For fission-yield determinations, indium need not be separated with high radiochemical purity from most other fission products. It is necessary only that indium be initially well separated from tin and that, when the tin daughters grow into the indium fraction, the tin is finally separated from all other radionuclides.

EXPERIMENTAL

Apparatus

Apparatus for precipitation and pressure filtration. The apparatus for the precipitation and the pressure filtration of the tin precipitate is shown in Fig. 1. A precipitation chamber (A) is fitted with a 3-way stopcock; one leg provides vacuum for introducing the reactant solution into the chamber, the other provides nitrogen for forcing the solution rapidly into a pressure filtration chamber (B). The chamber is also fitted with a side-arm provided with a 10-ml container for introducing the alcoholic pyridine reagent into the chamber. A is connected to B through a glass stopcock (E) and a stainless steel valve (F). E and F are connected through a short piece of tygon tubing.

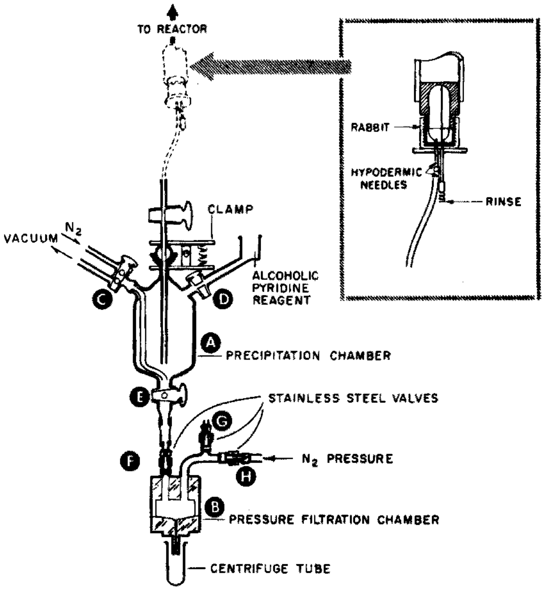
F is threaded into a tightly fitted opening in B. Another opening in B is fitted with 2 stainless steel valves (G, H). G serves as a pressure release vent. H is connected to a pressure gauge assembly and then to a high-pressure nitrogen tank by means of 0.25-in. diameter copper tubing. The gauge assembly must be capable of providing a nitrogen pressure of approximately 75 psig. A detailed drawing of the pressure filtration chamber is shown in Fig. 2.

The filtration chamber, machined from lucite, is supported on an aluminum frame with 3 screws. The apparatus is divided into 2 sections. The edges of the 2 sections are carefully machined to provide a leak-proof seal at high pressures. The top section is provided with 2 tapped holes; one hole leads to the precipitation chamber, the other to the high-pressure nitrogen supply.

The bottom section has a recess machined in its top surface, bevelled slightly toward the center hole to expedite the discharge of the filtrate. A woven-fiber glass-cloth disk is seated in the recess and a cellulose membrane filter is placed on this disk. The cellulose membrane filter is 70 mm (2.80 in.) in diameter and has an average pore diameter of 0.15 μ. The membrane filter is securely clamped into position when the bolts of the 2 brass plates are tightened to force the 2 sections together. Detailed discussion of a high-pressure ultra-filtration unit is given by CALLAHAN AND LAI[7].

Reagents

Tin and indium solution. 0.5 ml of a 1 *N* hydrochloric acid solution containing Sn and In is prepared by mixing 0.25 ml of 1 *N* hydrochloric acid containing 24 mg of tin (as $SnCl_2$), and 0.25 ml of standardized indium solution, containing 25 mg of indium. The indium solution is prepared by dissolving 5 g of pure indium metal in a minimum volume of 6 *N* hydrochloric acid and making up to 50 ml with 1 *N* hydrochloric acid. This solution is standardized with 8-hydroxyquinoline[4].



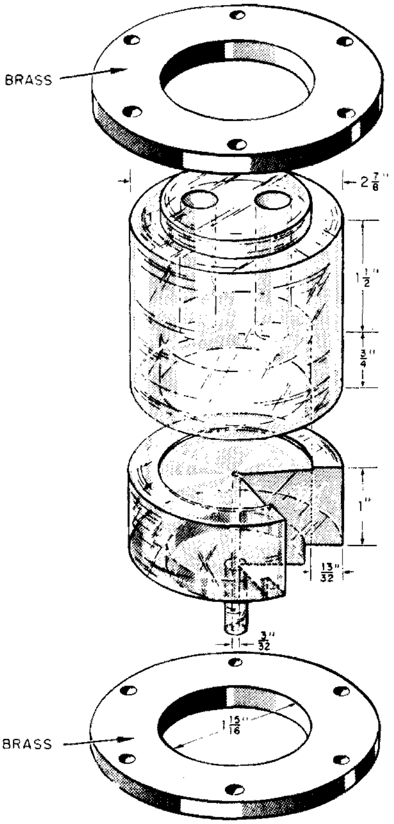


Fig. 1. Precipitation and pressure filtration apparatus.

Fig. 2. Pressure filtration chamber.

Alcoholic bromine reagent. Fresh reagent is prepared by dissolving 38 g of bromine in 100 ml of ethanol.

Uranium solution. For irradiation, 0.040 ml of 1 *N* hydrochloric acid containing 10 mg of enriched uranium-235 is prepared from the metal. For testing, 0.040 ml of 1 *N* hydrochloric acid containing 10 mg of natural uranium is prepared from $UO_2(NO_3)_2 \cdot 3H_2O$.

Alcoholic pyridine reagent. A 1:1 (v/v) pyridine–ethanol mixture is used. The volume of alcoholic pyridine reagent used in precipitation was 2.5 ml, unless otherwise specified.

Radioactive tracers. The specific activity (by volume) of each of the following radionuclides, ^{113}Sn–^{113}In, ^{124}Sb, ^{132}Te–^{132}I, ^{109}Cd, and ^{110}Ag in 1 *N* hydrochloric acid is approximately 10^6 counts per min per 0.1 ml. Each radioactive tracer solution contained 1 µg to 1 mg of isotopic carrier in 0.1 ml.

Reactant solution. The reactant solution is prepared by mixing 0.5 ml of the tin and indium solution, 0.3 ml of alcoholic bromine reagent, 0.040 ml of the uranium solution, and 0.5 ml of ethanol.

Borohydride solution. This solution contains 20 mg of potassium or sodium borohydride per ml of a 0.01 *N* sodium hydroxide solution.

Procedure

The reactant solution, containing about 10 mg of enriched ^{235}U, is introduced into a teflon rabbit for thermal-neutron irradiation. The irradiation and the delivery of the irradiated solution use the rabbit and pneumatic system described by GREENDALE AND LOVE[8]. After leaving the reactor, the rabbit containing the mixed fission-product solution impales itself upon 2 hypodermic needles. The solution is drawn through one hypodermic needle by vacuum into A (Fig. 1). The rabbit and needle assembly is quickly rinsed with 1 ml of ethanol, which is added through the other hypodermic needle. The fission-product indium isotopes are then separated by the procedure as described below.

Pyridine reagent (2.5 ml; placed in the container shown in Fig. 1) is quickly added to A. The tin precipitate is forced into filtration unit B by nitrogen at a pressure of 1 psig. Unit B is closed by shutting valves F and G. Valve H is opened, and about 75 psig nitrogen pressure is applied to filter the indium solution through the cellulose membrane filter. The filtrate is collected in a 50-ml centrifuge tube. Sufficient time is then allowed for the indium radionuclides in the filtrate to decay almost entirely to their descendents. Tin(IV) solution (5 mg Sn) is added to the organic filtrate and thoroughly mixed, and the tin precipitate is then centrifuged. The filtrate is decanted into a 50-ml centrifuge tube. This solution (designated M) and the one remaining from the stannane evolution (designated N) are combined and the indium content is determined, to establish the indium chemical yield, as described below.

The second tin precipitate is dissolved in 10 ml of 0.6 *N* hydrochloric acid, and the tin is separated by the method of GREENDALE AND LOVE[9]. The order of addition of the tin solution and the borohydride solution is in reverse to that of the published procedure. The alkaline borohydride solution (3 ml) is added slowly to the slightly acidic tin solution to form stannane. (The solution remaining after evolution of stannane is designated N.) The tin mirror resulting from the decomposition of stannane is assayed in a γ-spectrometer for identification of the tin descendants of their indium parents. The sample is finally dissolved with cold 50% sulfuric acid. LUKE's photometric method[10] for the determination of tin in microgram amounts may be used to find chemical yield.

The solutions, M and N, are each made 6 *N* in hydrochloric acid and then mixed. A known activity of ^{114}In tracer is added. Excess ammonia solution is added to precipitate $In(OH)_3$, which is digested in a hot water bath to coagulate the precipitate. The precipitate is centrifuged, and the filtrate is discarded. The precipitate is then dissolved in 10 ml of 4.5 *N* hydrochloric acid.

The indium is separated by a combination of bromide extraction into diethyl ether and anionic exchange with Dowex 2. The detailed procedure is described by SUNDERMAN, ACKERMANN AND MEINKE[4]. A known aliquot of the separated indium solution is counted in a γ-ray scintillation counter. The total amount of indium carrier in the entire solution is determined with 8-hydroxyquinoline by the method outlined for the standardization of the indium carrier[4]. The ^{114}In activity recovered is used to correct for the loss of indium carrier during the bromine extraction and the anionic exchange steps. The ratio of the total indium carrier (calculated to be present in solutions M and N) to the known indium carrier (initially added) is the indium chemical yield.

DETERMINATION OF OPTIMUM EXPERIMENTAL CONDITIONS

The procedure was tested with tracers to determine the chemical yield of indium and decontamination factors for tin and other radionuclides. The reactant solution contained unirradiated natural uranium and 0.1 ml of the appropriate radionuclide and its carrier. The pyridine reagent was added, the solution rapidly filtered, and the filtrate collected in a 50-ml centrifuge tube, as described above. The radioactivity was measured in a well-scintillation counter before and after the precipitation and filtration of tin. All parent–daughter pairs were allowed to come to equilibrium before counting, and decay corrections were made in the calculations of chemical yields and decontamination factors.

To test the chemical yield of tin in the stannane procedure, tin carrier and ^{113}Sn–^{113}In tracer were added to the organic filtrate which was collected in the 50-ml centrifuge tube. After the tin precipitate was centrifuged and dissolved in 0.6 *N* hydrochloric acid, the tin was separated as stannane and collected in a quartz tube. The radioactivity was measured in a scintillation well counter before and after the formation of stannane for determination of its chemical yield. Tin tracer was counted as an aqueous solution before precipitation, and was counted again as a tin mirror in the quartz tube after precipitation. No geometry correction was necessary.

DISCUSSION

The precipitation of tin by pyridine is sensitive to various components of the

TABLE I

CHEMICAL YIELD OF INDIUM AND DECONTAMINATION FACTOR OF TIN AS A FUNCTION OF URANIUM CONCENTRATION

Uranium added (mg)	*Radioactive tracer*	*Chemical yield of indium*[a] *(%)*	*Decontamination factor of tin*[a]
6.3	^{113}Sn–^{113}In	45[b]	$2 \cdot 10^3$ [b]
10	^{113}Sn–^{113}In	44	$2 \cdot 10^3$
12.6	^{113}Sn–^{113}In	51	$8 \cdot 10^2$
25	^{113}Sn–^{113}In	43	$2 \cdot 10^2$
121	^{113}Sn–^{113}In	39	60
6.3	^{114}In	37	

[a] Each value represents the average of duplicate experiments.

[b] The values obtained with the 6.3 mg of uranium that includes ^{113}Sn tracer represent the average of 8 experiments.

reactant solution and to the volume of pyridine solution. Tin precipitates readily when the initial acidity of the solution is 1 *N* hydrochloric acid or less and when a small amount of ethanol is present. Bromine is added to oxidize tin to its highest oxidation state in order to ensure exchange of the fission-product tin with its isotopic carrier.

Optimum conditions were determined by experiment. The volumes of the

TABLE II

DECONTAMINATION FACTORS FOR FIRST INDIUM SEPARATION

Radionuclides	*Isotopic carrier added (mg)*	*Decontamination factor*[a]
^{110}Ag	5	2
^{109}Cd	5	2
^{113}Sn	24	$2 \cdot 10^3$
^{124}Sb	5	$6 \cdot 10^2$
^{132}Te	0.01	$6 \cdot 10^2$
^{132}Te	5	$5 \cdot 10^2$
^{131}I	0.01	2
^{131}I	5	2

[a] Each value represents the average of duplicate experiments.

TABLE III

DECONTAMINATION FACTOR FOR TIN(IV) FROM INDIUM AS A FUNCTION OF VOLUME OF PYRIDINE REAGENT

Pyridine reagent added (ml)	*Decontamination factor*[a]
2	$2 \cdot 10^3$
4	$1 \cdot 10^3$
6	$5 \cdot 10^2$
10	$4 \cdot 10^2$
12	$2 \cdot 10^2$

[a] The amount of uranium added is 6.3 mg in all cases.

TABLE IV

CHEMICAL YIELD OF TIN SEPARATED AS STANNANE

Initial activity of ^{113}*Sn (counts/min)*	*Activity in tin precipitate (counts/min)*	*Activity in tin separated as stannane (counts/min)*	*Chemical yield of tin (%)*
$2.15 \cdot 10^5$	$2.15 \cdot 10^5$	$4.75 \cdot 10^4$	22
$1.69 \cdot 10^5$	$1.69 \cdot 10^5$	$7.75 \cdot 10^4$	46
$1.66 \cdot 10^5$	$1.66 \cdot 10^5$	$5.35 \cdot 10^4$	32
$1.69 \cdot 10^5$	$1.69 \cdot 10^5$	$7.91 \cdot 10^4$	47
		Average	37

reactant solution and the pyridine reagent, and the uranium content were chosen to give a good chemical yield of indium and a good decontamination for tin. Also, a suitable volume of filtrate was chosen to achieve rapid filtration. Table I shows the chemical yield of indium as 44% and the decontamination factor for tin as $2 \cdot 10^3$ when the uranium content in the reactant solution was 10 mg or less. Table II presents decontamination factors of various pertinent radionuclides. Table III shows the decontamination factor of tin as a function of the volume of pyridine reagent. Table IV shows that the average chemical yield of tin separated as stannane is 37%. Columns 1 and 2 show quantitative recovery of the tin by precipitation from the pyridine filtrate.

Under the experimental conditions the tin precipitate was quickly formed and readily filtered through a cellulose membrane filter under a pressure of 75 psig. These cellulose membrane filters are produced specially for filtration in the presence of organic solvents. Ordinary filter papers and millipore filters were found unsuitable for the filtration due to interferences by the alcoholic pyridine medium. The time required for precipitation of tin and filtration of indium is 10 sec.

SUMMARY

A rapid radiochemical procedure was developed for the separation of indium radionuclides from a mixed fission-product solution. An alcoholic pyridine solution is added to a uranium solution containing indium and tin carriers. The resulting tin precipitate is separated from the indium-containing solution by filtering through a cellulose membrane filter. The decontamination factor for tin is $2 \cdot 10^3$. Other fission products are only partially removed. The chemical yield of indium is about 44%, and the time required for the separation is about 10 sec. After the tin-separated indium has decayed, the tin daughters of indium are removed from all the other fission products at a specified time and measured, so that the amount of indium present at the time of the tin precipitation is determined.

RÉSUMÉ

Une méthode radiochimique rapide est décrite pour la séparation des radioisotopes de l'indium dans une solution de produits de fission. Une solution alcoolique de pyridine est ajoutée à une solution renfermant indium et étain comme entraîneurs. Le précipité d'étain est séparé de la solution renfermant l'indium par filtration à travers une membrane de cellulose. Rendement chimique de l'indium, environ 44%; le temps nécessaire pour le séparation est approximativement de 10 secondes.

ZUSAMMENFASSUNG

Es wurde ein schnelles radiochemisches Verfahren entwickelt zur Abtrennung von Indiumradionuklide aus einer Lösung mit mehreren Spaltprodukten. Dazu wird eine alkoholische Pyridinlösung zu einer Uranlösung hinzugegeben, die Indium und einen Zinnträger enthält. Der sich ergebende Zinnniederschlag wird von der Indium enthaltenden Lösung mit einem Cellulosemembranfilter abgetrennt. Der Dekontaminationsfaktor des Zinns beträgt $2 \cdot 10^3$. Andere Spaltprodukte werden nur teilweise

zurückgehalten. Die chemische Ausbeute des Indiums beträgt etwa 44%, die Zeit für die Trennung etwa 10 Sek. Nachdem das von Zinn abgetrennte Indium zerfallen ist, werden die Zinntöchter des Indiums von allen anderen Spaltprodukten befreit und nach einer bestimmten Zeit gemessen, so dass die Menge des anwesenden Indiums zu der Zeit der Zinnfällung bestimmt werden kann.

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RADIOMETRISCHE SCHNELLBESTIMMUNGEN MIT ÄDTE DURCH RÜCKMESSUNG

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Die Verwendung radioaktiver Indikatoren zur Endpunktsanzeige bei Titrationen oder anderen analytischen Arbeiten ist heute allgemein bekannt. Radiometrische Fällungsanalysen, radiometrische Titrationen mit punktweiser Bestimmung des Reaktionsablaufes, extraktive radiometrische Titrationen sowie automatisierte radiometrische Titrationen sind einige der bisher unter Heranziehung radioaktiver Indikatoren oder Masslösungen bearbeiteten Gebiete. Die vorliegende Arbeit zeigt die Anwendbarkeit der Radiometrie auch auf die in der komplexometrischen Titration mit ÄDTE häufig angewandte Rücktitration[1].

Die angegebene Bestimmungsmethode beruht auf der Eigenschaft der ÄDTE, mit Metallionen verschieden starke Komplexe zu bilden. Silberion ergibt hierbei einen der schwächsten Komplexe. Wird daher ^{110m}Silber-Jodat als fester, schwerlöslicher Indikator angewendet[2,3], so wird dieser erst dann von überschüssiger ÄDTE angegriffen, wenn alle Ionen der Lösung mit stärkerer Komplexbildungskonstante gebunden sind. Durch Auflösung einer entsprechenden Menge des radioaktiv markierten Niederschlages wird dabei die Impulsrate der Lösung ansteigen. Rückbleibender Silberjodatniederschlag wird abgetrennt. Unter Verwendung einer Eichkurve kann dann durch einmaliges Messen der Impulsrate eines aliquoten Anteiles der Bestimmungslösung der angewandte Überschuss bzw. der Verbrauch an ÄDTE für das zu bestimmende Ion errechnet werden.

GRUNDLAGEN ZUR METHODE

Bereitung eines mit ^{110m}Ag-markierten Silberjodatniederschlages

50 ml 0.1 N $AgNO_3$-lösung werden mit 50 μC (bzw. 500 μC) ^{110m}Ag (aus ^{110m}Silber-Nitratlösung, The Radiochemical Center, Amersham) markiert, mit einem Tropfen conc. Salpetersäure angesäuert und in der Hitze mit 1.6 g Kaliumjodat, gelöst in 15 ml Wasser, gleichfalls siedend, gefällt. 3 Stunden im Dunklen stehen lassen, durch einen Glasfiltertiegel Schott-G 4 absaugen und mehrmals mit kleinen Portionen Wasser waschen.

Der Niederschlag wird bei 105° getrocknet und in gepulvertem Zustand im Dunklen aufbewahrt. Der mit 50 μC markierte Niederschlag wird im Folgenden als Niederschlag I bezeichnet, der mit 500 μC markierte als Niederschlag II.

Geräte

*Kombiniertes Reaktions-, Filtrier- und Messgefäss**. Dieses Mehrzweckgefäss

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* P. Haack, Wien IX, Garnisong. 3.

besteht aus 3 Teilen (Fig. 1). Das Reaktionsgefäss (A) ist als Standgefäss ausgebildet, hat einen Fassungsraum von 15 ml und ist mit einem Innerschliff NS 24 versehen. Das dazu passende Mittelstück (B) hat eine eingeschmolzene Glasfritte G 4. Unter der Fritte befindet sich ein Aussenschliff NS 14.5, an dem das mit Absaugeansatz versehene, graduierte Messgefäss (C) anzuschliessen ist. Reaktionsgefäss und Messgefäss werden silikoniert.

Handhabung. Die Reaktion wird im Standgefäss A ausgeführt. Danach wird Teil B und Teil C aufgesetzt. Nach Drehung des Apparates um 180° wird mit schwachem Vakuum eine entsprechende Menge Flüssigkeit in das graduierte Messgefäss C abgesaugt. Dieses wird allein zur Messung gebraucht.

Zählgerät. FH 49 Frieseke & Hoepfner.

Messeinrichtung. Grundsonde FH 421, γ-Messkopf Z 11 (Bohrlochkristall).

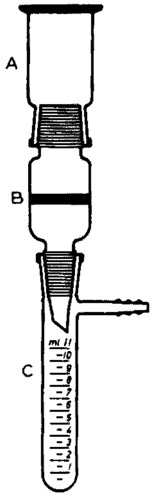

Fig. 1. Kombiniertes Reaktions-(A), Filtrier-(B) und Messgefäss (C).

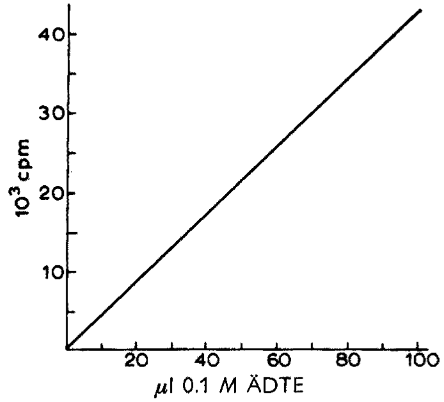

Fig. 2. Eichgerade.

Reagenzien

0.1 und 0.01 M ÄDTE-lösung. Titriplex III, Merck p.a.

0.2 M Boratpuffer, pH 10.2. Natriumborat 0.2 *M*: 12.404 g Borsäure + 100 ml *N* NaOH pro Liter; 0.1 *N* NaOH.

0.1 M Metallsalzlösungen. Diese werden in Polyäthylenflaschen aufbewahrt und vor Gebrauch entsprechend verdünnt.

Bidest. Wasser aus einer Quarzapparatur.

Bemerkungen

Der bei komplexometrischen Titrationen mit ÄDTE übliche Ammonchlorid–Ammoniak-Puffer kann nicht verwendet werden, da Silberjodat in Ammoniak leicht löslich ist. Für die Versuche benützte man daher den 0.2 *M* Borat-Puffer. Die Löslichkeit des Silberjodates in Wasser beträgt 4 mg/100 g bei 20°. Durch Zusatz von gesättigter Kaliumjodatlösung zum Reaktionsgemisch wird dieser Wert gesenkt und so die Höhe der auf reiner Löslichkeit beruhenden Impulsrate (Untergrundaktivität) gering gehalten.

Bestimmung der Dauer zur Einstellung des Lösungsgleichgewichtes einer Lösung mit Silberjodat und Festlegung der notwendigen Reaktionszeit für die Umsetzung von ÄDTE mit Silberjodat

Da bei dem zu beschreibenden Verfahren Eichkurven zur Ermittlung des ÄDTE-Verbrauches benützt werden, ist das Einhalten exakt gleicher Versuchsbedingungen notwendig. Es muss daher sowohl die Zeit bestimmt werden, die zur Einstellung des Lösungsgleichgewichtes nach Einbringen eines ^{110m}Silber-Jodatniederschlages in ein definiertes Reaktionsmilieu (Volumen, Elektrolytgehalt, Rührintensität) erforderlich ist, als auch jene Zeit, die zum Ablauf der Reaktion zwischen Silberjodatniederschlag (Silberion)–ÄDTE erforderlich ist.

Die Bestimmung der Dauer zur Einstellung des Lösungsgleichgewichtes erfolgt in folgendem Ansatz. 4 ml Wasser; 3 ml 0.2 *M* Boratpuffer; 1 ml gesättigte Kaliumjodatlösung. Diese Lösungen befinden sich im Standgefäss (A). Nach Zusatz einer Spatelspitze (ungefähr 20 mg) markierten Silberjodatniederschlages (I oder II) wird mit dem Magnetrührer (Magnetstäbe mit Plastik überzogen) kräftig gerührt. Die gewählte Rührintensität muss bei allen weiteren Versuchen gleich gehalten werden. Nach verschieden langer Rührdauer setzt man das Mehrzweckgefäss zusammen, saugt exakt 5 ml des Reaktionsgemisches ab und ermittelt die Impulsrate dieses aliquoten Anteiles. Nach einer Rührdauer von 3 Minuten herrscht über dem radioaktiv markierten Silberjodatniederschlag Sättigung, *d.h.* die Impulsraten eines Aliquoten bleiben auch bei längerer Rührdauer konstant.

Den *Reaktionsablauf zwischen Silber und ÄDTE* ermittelt man in gleichartigen Ansätzen wie bei der Bestimmung der Dauer zur Einstellung des Lösungsgleichgewichtes. Dem Reaktionsgemisch setzt man variierende (10–200 μl) Mengen 0.1 *M* oder 0.01 *M* ÄDTE-masslösung aus einer AGLA-mikrometerbürette zu, rührt verschieden lang und verfährt wie oben angegeben. Die Impulsraten eines Aliquoten des Überstandes erhöhen sich ab 5 Minuten Rührdauer für jede der gewählten ÄDTE-mengen nicht weiter.

Für die Methodik genügt daher eine Rührdauer von 5 Min. Der durch das Zufügen der Masslösung entstehende Verdünnungsfehler ist bis 100 μl Zusatz vernachlässigbar gering (1.25%). Zusätze über 100 μl werden durch entsprechend verminderte Wasserzugabe ausgeglichen.

Weder bei Bestimmung der notwendigen Zeit zur Einstellung des Lösungsgleichgewichtes noch bei der der Reaktionszeit bringt die Zugabe von mehr markiertem Silberjodatniederschlag eine schnellere Einstellung des Gleichgewichtes.

Einfluss der zugefügten ÄDTE-Menge auf den pH-Wert des Reaktionsgemisches

Durch Zugabe des Boratpuffergemisches wird der pH-Wert der angewendeten Reaktionslösung auf 10.0 eingestellt. Die ÄDTE-Masslösung selbst hat einen pH-Wert von 5.0–5.5. Die pH-Änderungen, welche bei Zufügen von verschiedenen Mengen Masslösung auftreten, sind in Tabelle I festgehalten.

Bei der Reaktion zwischen Metallion und ÄDTE werden unabhängig von der Wertigkeit des Metallions immer 2 Äquivalente Wasserstoffionen in Freiheit gesetzt[4]. Ihr Einfluss auf den pH-Wert der Lösung wurde in folgendem Ansatz untersucht.

Reaktionslösung wie in Tabelle I; zusätzlich 100 µl 0.1 *N* Kupfer(II)-Salzlösung. Nach der Reaktion mit 100 µl 0.1 *M* Titriplex-III-Masslösung wird ein pH-Wert von 9.78 gemessen. Die Pufferwirkung ist demnach stark genug, um die quantitative Reaktion aller jener Metallionen mit ÄDTE zu ermöglichen, deren Bestimmung mit einem Puffergemisch vom pH 10.0 durchführbar ist.

TABELLE I

(Reaktionslösung: 3.8 ml H_2O, 1 ml gesätt. KJO_3-Lösung, 3 ml Boratpuffer)

Zugefügte ÄDTE-Menge, µl 0.1 M	*pH der Lösung*
0	10.0
100	9.80
200	9.67
300	9.58

TABELLE II

Einwaage (mg)	*Silbergehalt (mg)*	*Gemessene Impulsrate (counts/min)*	*Berechnete Impulsrate für 100 µl 0.1 M ÄDTE-Masslösung in counts/min (Volumen korrigiert)*
2.805	1.070	118120	74550
2.391	0.912	100840	74430

TABELLE III

pH-Wert	*Impulsrate*	*Reaktionsrate (%)*	*pH-Wert*	*Impulsrate*	*Reaktionsrate (%)*
9.8	60000	80.5	11.2	71050	95.4
10.0	65740	88.3	11.5	69770	93.7
10.7	69100	92.8	11.7	69590	93.4
10.9	69910	93.8	12.1	67260	90.3

Abhängigkeit der Reaktionsrate Silberion–ÄDTE vom pH-Wert

Die niedere Komplexbildungskonstante (log $K = 7.2$) für das Silber liess erwarten, dass zwischen Silberion und ÄDTE keine quantitative Reaktion stattfindet. Zusätzlich sollte die Reaktionsrate sich als stark pH-abhängig erweisen. Um festzustellen, ob die für die zu beschreibende Methode ermittelten Bedingungen eine quantitative Reaktion oder eine für die Indikation ausreichende Umsetzung zwischen Silber und ÄDTE erlauben, wurde der Gang der Reaktionsrate wie folgt ermittelt. 2 Proben des radioaktiv markierten Silberjodatniederschlages I wurden eingewogen, in das Messgefäss (Teil C, Fig. 1) gebracht und mit konzentriertem Ammoniak auf 5 ml aufgefüllt. Nach Lösen und Durchmischen wurden die Impulsraten für jede Einwaage gemessen. Aus dem Silbergehalt der Einwaagen und dem Äquivalentgewicht des Silbers lässt sich die entsprechende Impulsrate für jede ÄDTE-Menge — quantitative Reaktion vorausgesetzt — berechnen (Tabelle II). Die gegebenen Werte zeigen gute Übereinstimmung. Als Vergleichswert (100%ige Reaktion zwischen Silberion und ÄDTE) wurde bei den folgenden Berechnungen stets 74490 eingesetzt.

Die tatsächlichen Impulsraten wurden nun in 8 Ansätzen bestimmt. 100 μl 0.1 *M* ÄDTE wurden mit dem Silberjodatniederschlag bei verschiedenen pH-Werten der Reaktion überlassen. In das Reaktionsgefäss brachte man jeweils 1 ml gesättigte Kaliumjodatlösung, 100 μl 0.1 *M* ÄDTE-Masslösung sowie variierende Mengen 1 *N* oder 0.1 *N* NaOH und füllte mit soviel Aquadest. auf, dass das Endvolumen jeweils 8 ml betrug. Nach einer Rührdauer von 5 Minuten wurden 5 ml in das Messgefäss abgesaugt, der eingestellte pH-Wert gemessen und die Impulsraten bestimmt. Aus der Relation mit den aus den Einwaagen gewonnenen theoretischen Impulsraten (für 100% Reaktion) kann die tatsächliche Reaktionsrate in % errechnet werden. Der Gang dieser Reaktionsrate mit dem pH-Endwert der Reaktionslösung ist in Tabelle III dargestellt. Der optimale pH-Wert für die Reaktion zwischen Silberion und ÄDTE liegt demnach bei 11.2.

Bei den für die Bestimmungsmethode festgelegten Bedingungen stellt sich ein pH-Wert von 9.7–9.8 ein, wobei die Reaktionsrate für das Silber noch 80% beträgt. Dies genügt, die für eine ausreichende Indikation notwendigen Impulsraten zu gewährleisten.

AUFSTELLUNG VON EICHKURVEN

Je nachdem ob 0.1 *M* oder 0.01 *M* ÄDTE-Masslösung zur Anwendung kommen soll, wird entweder der markierte Niederschlag I oder II verwendet. In das Reaktionsgefäss gibt man 1 ml gesättigte Kaliumjodatlösung, 3 ml Boratpuffer, 4 ml H_2O sowie eine Spatelspitze radioaktiv markierten Niederschlages. Nun wird 5 Minuten mit dem Magnetrührer gerührt, sodann 5 ml der Reaktionslösung in das Messgefäss abgesaugt. Die gemessene Impulsrate entspricht der Löslichkeit des Silberjodates im Reaktionsmilieu und stellt den Nullpunkt der Eichkurve dar. Weiteren Ansätzen gleicher Art werden steigende Mengen ÄDTE-Masslösung zugesetzt. Aus den gemessenen Impulsraten ergeben sich so für beide Masslösungen Eichgerade, denen bei den folgenden Bestimmungen nach einmaliger Messung der Impulsrate der vorhandene Überschuss an Masslösung entnommen werden kann (Fig. 2).

BESTIMMUNG VON KUPFER, NICKEL, BLEI UND ZINK

Bei der Bestimmung der Metalle ist die Reihenfolge des Zusammengebens der Reagenzien beim Ansatz der Reaktionslösung von Wichtigkeit. Kupfer, Nickel, Zink und Blei fallen bei pH 10.0 als Hydroxide aus; Blei ergibt zusätzlich eine Fällung mit den Jodationen. Diese Fällungen werden nur langsam von ÄDTE gelöst. Die Bildung dieser Niederschläge kann durch die Reihenfolge der Zugabe der Reagenzien — ÄDTE, Puffer, Jodatlösung — verhindert werden.

Arbeitsvorschrift

In das Reaktionsgefäss gibt man Probelösung sowie die berechnete Wassermenge. Nach Zufügen der ÄDTE-Masslösung im Überschuss wird unter ständigem Rühren 3 ml Boratpuffer sowie 1 ml gesättigter Kaliumjodatlösung zugesetzt. Das Endvolumen beträgt stets 8 ml. Mit einem der markierten Niederschläge I oder II wird 5 Minuten gerührt, sodann werden 5 ml abgesaugt und die Impulszahl dieses

Aliquoten bestimmt. Aus der zugehörigen Eichkurve ist dann der Überschuss an Masslösung zu entnehmen.

Tabelle IV zeigt eine Auswahl so bestimmter Werte für die Metallionen Cu(II), Ni(II), Pb(II) und Zn(II). Unter Verwendung von Niederschlag II und 0.01 *M* ÄDTE-Masslösung wurde Zn(II) nach der gegebenen Methode auch im Einermikrogrammbereich mit guter Genauigkeit bestimmt.

TABELLE IV

Metall-ion	*µg gegeben*	*µg gefunden*	*µg Abweichung*	*Relativer Fehler (%)*	*µl 0.1 M ÄDTE zugesetzt*
Cu^{2+}	63.2	66.1	+ 2.9	+ 4.6	30
		62.3	− 0.9	− 1.4	30
		64.2	+ 1.0	+ 1.6	30
		64.8	+ 1.5	+ 2.4	10
		64.8	+ 1.5	+ 2.4	30
Ni^{2+}	58.7	59.9	+ 1.2	+ 2.0	30
		54.0	− 4.7	− 8.1	50
		58.7	± 0.0	± 0	20
		61.6	+ 2.9	+ 4.9	30
Pb^{2+}	206.7	215.5	+ 8.8	+ 4.3	30
		198.9	− 7.8	− 3.8	30
		209.3	+ 2.6	+ 1.3	30
		207.2	+ 0.5	+ 0.2	30
		205.3	− 1.4	− 0.7	30
Zn^{2+}	65.5	70.6	+ 5.1	+ 7.8	30
		68.0	+ 2.5	+ 3.8	20
		65.4	− 0.1	− 0.2	30
					µl 0.01 M ÄDTE zugesetzt
Zn^{2+}	6.5	6.2	− 0.3	− 4.6	30
		6.9	+ 0.4	+ 6.1	30
		6.4	− 0.1	− 1.5	30
		6.2	− 0.3	− 4.6	60
		6.9	+ 0.4	+ 6.1	60
		6.0	− 0.5	− 7.7	40
		6.7	+ 0.2	+ 3.1	20

DISKUSSION

Die beschriebene Methode ist an Lösungen von Reinsubstanzen ausgearbeitet und erscheint für Reihenuntersuchungen besonders geeignet. Auch Lösungen, die mehrere Ionen enthalten, können gegebenenfalls analysiert werden. So wurde die Methode mit Erfolg auf die einfache Bestimmung der Wasserhärte mit ÄDTE angewendet. Bei Wässern mittlerer Härte (15 deutsche Härtegrade) findet man bei Verwendung von 0.1 *M* ÄDTE und Niederschlag I oder II mit 1 ml des zu untersuchenden Wassers als Probemenge das Auslangen. Die nach der gegebenen Methode erhaltenen Werte für die Härte eines Wassers stimmen mit den nach der üblichen ÄDTE-Methode ermittelten Werten überein. Einen Vorteil der Methode stellt dabei ihre Anwendbarkeit auf die Härtebestimmung in getrübten und gefärbten Wässern dar.

ZUSAMMENFASSUNG

Das Prinzip der Rücktitration mit ÄDTE wird für radiometrische Schnellbestimmungsmethoden herangezogen. Ein hierfür geeignetes, kombiniertes Reaktions-, Filtrier- und Messgefäss ist beschrieben. Die optimalen Versuchsbedingungen für die Verwendung von festem^{110m}Silber-Jodat als Indikator werden untersucht: Dauer der Einstellung des Lösungsgleichgewichtes einer überstehenden Lösung mit Silberjodat, Reaktionszeit für die Umsetzung von ÄDTE mit Silberjodat, pH-Abhängigkeit der Reaktionsrate Silber–ÄDTE. Eine Arbeitsvorschrift zur Aufstellung von Eichkurven und zur radiometrischen Schnellbestimmung von Kupfer(II), Nickel(II), Blei(II) und Zink(II) wird gegeben. Die Methode ist im Bereich der Einer-, Zehner- und Hundertermikrogramm verwendbar.

SUMMARY

The principle of back-titration with EDTA is applied to rapid radiometric methods. A suitable vessel for performing the reaction, filtration and count-rate measurement is described. The optimal conditions for the use of solid $^{110m}AgIO_3$ as indicator were studied: the time for solubility-equilibrium of solid silver iodate, the reaction time of EDTA with silver iodate, and the pH-dependence of the silver–EDTA reaction rate. Procedures are given for calibration curves and for rapid radiometric determinations of copper(II), nickel(II), lead(II) and zinc(II). The method is suitable for the range 1–100 μg.

RÉSUMÉ

L'auteur décrit une méthode de dosage radiométrique rapide, basée sur le titrage indirect de l'EDTA. On décrit un récipient approprié permettant réaction, filtration et mesure. Les conditions optimales pour l'utilisation de $^{110m}AgIO_3$ solide, comme indicateur sont examinées. On décrit des procédés pour le dosage radiométrique rapide du cuivre, du nickel, du plomb et du zinc. Cette méthode convient pour des teneurs de 1 à 100 μg.

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DOSAGE DE L'HYDROGENE, DE L'AZOTE ET DE L'OXYGENE DANS LE MONOCARBURE D'URANIUM

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L'emploi du monocarbure d'uranium comme combustible nucléaire est de plus en plus envisagé. Lors d'une fabrication importante de ce composé, il est nécessaire d'effectuer un nombre élevé de contrôles de manière à connaître avec le maximum de précision, la composition du produit obtenu. Ceci nous a conduit à développer une méthode rapide de dosage de l'azote, de l'oxygène et de l'hydrogène dans ce matérial, le dosage du carbone ayant été décrit précédemment[1].

Malgré l'existence de solutions solides U (C, N), très stables[2-4] et vraisemblablement U (C, N, O), les techniques basées sur l'extraction à chaud sous vide nous ont paru les plus adéquates au dosage simultané des 3 gaz.

Le dosage de l'oxygène dans l'UC par la méthode de "Vacuum fusion" avec bain de platine à la température d'environ 2000° a déjà été décrit[5-8]. Cette technique permet de doser en même temps l'hydrogène. Divers auteurs ont étudié le dosage de l'azote dans l'UC[9,10] par la méthode classique de Kjeldahl, mais il ne semble pas, d'après nos recherches bibliographiques, que l'on ait jusqu'ici proposé des méthodes se basant sur l'extraction sous vide à chaud.

Dans un but de clarté, nous décrirons rapidement les différentes techniques et les types d'échantillons utilisés dans notre étude:

(*a*) "Vacuum hot extraction": dégazage sous vide de l'échantillon tel quel, à une température inférieure à son point de fusion.

(*b*) "Vacuum fusion" avec bain de platine: dégazage de l'échantillon en le dissolvant sous vide dans un bain de platine préalablement dégazé.

(*c*) "Platinum flux": dégazage sous vide et à l'état liquide, de l'échantillon introduit dans le creuset avec un morceau de platine (flux), le rapport en poids échantillon-flux étant convenablement choisi.

(*d*) "Platinum flux modifié": dégazage de l'échantillon selon la technique (*c*), suivi d'une addition de quelques grammes de platine pour compléter l'extraction des gaz, dans des conditions qui seront décrites plus loin.

Les échantillons de monocarbure d'uranium analysés sont: UC en poudre, UC "préréagi" en morceaux*, UC fondu en morceaux. L'UC "préréagi" est poreux tandis que la densité de l'UC fondu est très voisine des valeurs théoriques.

Le point de fusion de l'UC est de l'ordre de 2500°.

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* UC provenant de la réaction sous vide et à la température de 1700-1800° de poudre d'UO_2 et de graphite et ayant une densité assez inférieure à la densité théorique. Il constitue le produit de départ pour préparer l'UC fondu.

APPAREILLAGE

L'appareil utilisé est le type St Re 0583 de la firme Feichtinger (Schaffhausen, Suisse)[11]. Les échantillons sont introduits dans un creuset de graphite porté à une température convenable et sont dégazés sous un vide de 10^{-5}–10^{-6} mm de mercure.

Les gaz extraits sont recueillis par une pompe Toepler automatique et injectés dans un chromatographe Perkin-Elmer mod. 116-E dont les conditions de fonctionnement sont:

gaz porteur: argon, débit 40 ml/min,
colonne : tamis moléculaire 5 Å, longueur 1 m, température 100°,
détecteur : cellule à conductibilité thermique.

Dans ces conditions, les hauteurs de pics sont proportionnelles aux quantités de gaz extraites. L'étalonnage du chromatographe est réalisé à l'aide de mélanges gazeux bien connus.

Quelques essais préliminaires ont également été effectués avec l'appareil VH6 de la firme Heraeus (Hanau sur Main, Allemagne)[12], basé sur le même principe. Les deux appareils diffèrent par le mode de chauffage du creuset; dans le premier il est effectué par un four à resistance, dans le second par haute fréquence.

DOSAGE DE L'HYDROGÈNE

Ce dosage ne présente aucune difficulté. Pour toutes les techniques décrites et pour tous les types d'UC, l'hydrogène est déjà totalement extrait à des températures inférieures à 2000°.

Le coefficient de variation calculé sur des échantillons en poudre est inférieur à 10% pour des teneurs en hydrogène comprises entre 15 et 60 p.p.m. La sensibilité du dosage est de l'ordre de 2 à 4 p.p.m. pour un prélèvement d'environ 200 mg.

DOSAGE DE L'AZOTE

Examen des différentes techniques — Résultats et discussion

"Vacuum hot extraction". Quelques essais effectués par cette technique à 2000° sur de l'UC en poudre (100 μ) ou en morceaux de 30–200 mg n'ont pas donné de résultats satisfaisants, l'extraction de l'azote étant incomplète et non reproductible[5]. Le faible coefficient de diffusion de cet élément, même à haute température[13], et la grande stabilité des nitrures[13,14] et des carbonitrures d'uranium[4] sont vraisemblablement responsables de cet état de chose.

"Vacuum fusion" avec bain de platine. En général, la carburation et la dissolution du métal à analyser dans un bain fondu convenablement choisi facilitent le dégagement de l'azote[13]. Cependant, dans notre cas, l'emploi de la "Vacuum fusion" dans un bain de platine à 2000°, bien que conduisant à des dégagements d'azote plus importants et plus rapides que dans le cas de la "Vacuum hot extraction", n'a donné que des extractions incomplètes.

"Platinum flux". La technique du "Platinum flux" utilisée par HANSEN *et al.* pour le dosage de l'oxygène dans le titane a retenu notre attention[15]. Elle consiste à introduire simultanément dans un creuset de graphite sous vide, l'échantillon et du platine dans des proportions déterminées. Le creuset a été, au préalable, porté à une

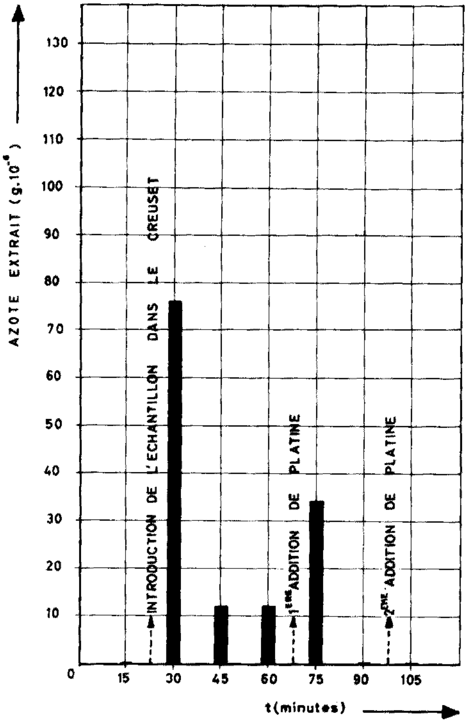
température convenable. Par suite de son aptitude à dissoudre à l'état fondu des quantités notables de graphite, le platine joue à la fois le rôle de fondant et d'agent carburant du métal à analyser. Cette méthode peut présenter certains avantages par rapport à la "Vacuum fusion" avec bain de platine. En effet, le "flux" n'étant pas initialement carburé comme le bain, est plus fluide et donc plus apte à dissoudre l'échantillon. De plus, en enveloppant l'échantillon à analyser dans le "flux", on peut favoriser le contact flux–échantillon. Malgré ces avantages, cette technique s'est revélée peu satisfaisante pour les échantillons d'UC examinés à 2000°.

(*1*) La moyenne des résultats obtenus (avec rapports en poids platine–échantillon variant de 2 à 8) est constamment inférieure à celle trouvée par voie chimique.

(*2*) Les résultats sont dispersés; le coefficient de variation est de l'ordre de 20–30% pour les poudres et encore plus élevé pour les morceaux.

(*3*) Dans de nombreux cas, les temps d'extraction sont anormalement élevés (de 60 à 90 min), sans pour cela conduire à une extraction quantitative de l'azote.

L'augmentation dans certaines limites de la proportion de platine n'améliore pas les résultats d'une manière significative. En fait, on observe qu'un échantillon d'UC en morceaux ou en poudre dégazé à fond au cours d'essais préliminaires où l'on



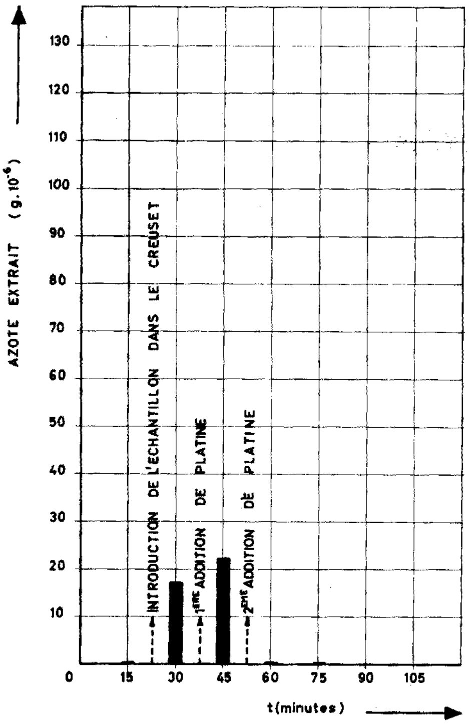


Fig. 1. Dégazage d'un échantillon de UC en poudre (~ 1200 p.p.m. N). Poids d'échantillon, 108.9 mg; rapport du Pt flux initial, 19.5/1; fond en N_2 de l'appareil, 0.25 μg N/15 min; contenu en N_2 du Pt ajouté, pas mesurable avec l'appareil utilisé.

Fig. 2. Dégazage d'un échantillon de UC en poudre (~ 400 p.p.m. N). Poids d'échantillon, 100 mg; rapport du Pt flux initial, 1.34/1; fond en N_2 de l'appareil, 0.20 μg N/15 min; contenu en N_2 du Pt ajouté, pas mesurable avec l'appareil utilisé.

TABLEAU I

DOSAGE DE L'AZOTE DANS UC ET UN

Echantillons	*Méthode du "Platinum flux modifié"*					*Méthode de Kjeldahl*				
	Nombre d'analyses	*Prise d'échantillons (mg)*	*Moyenne (p.p.m. N)*	*Ecart type*[a] *(p.p.m. N)*	*Coeff. var. méthode*[b] *(%)*	*Nombre d'analyses*	*Prise d'échantillons (mg)*	*Moyenne (p.p.m. N)*	*Ecart type (p.p.m. N)*	*Coeff. var. méthode (%)*
UC poudre No. 1	4	150–200	245	20	8.2	8	200–300	240	11	4.6
UC poudre No. 2	5	100–150	375	22	5.9	12	500	365	9	2.5
UC poudre No. 3	4	20–40	585	43	7.4	6	300–350	605	11	1.8
UC poudre No. 4	6	50–100	1075	120	11.1	6	200–250	1050	20	1.9
UC fondu morceaux No. 5	4	100–200	78	10	12.8	3	100–200	81	6	7.8
UC fondu morceaux No. 6	5	100–200	305	35	11.5	6	100–200	328	79	24.0
UC fondu morceaux No. 7	6	100–200	338	70	20.7	6	100–200	345	22	6.4
UC fondu morceaux No. 8	5	100–200	481	60	12.5	6	100–200	466	75	16.1
UN morceaux	3	5–10	5.35%	0.15%	2.8	4	50	5.60%	0.06%	1.1

[a] Ecart type $= \frac{(\Sigma(x - \overline{x})^2)^{\frac{1}{2}}}{n - 1}$ (x = valeur de chaque mesure, $\overline{x}$ = moyenne des n mesures).

[b] Coefficient de variation de la méthode $= \frac{\text{écart type} \cdot 100}{\overline{x}} \cdot \%$.

analyse seulement un échantillon par creuset avec un rapport platine/échantillon variable de 1 à 30, dégage à nouveau de l'azote quand on ajoute dans le creuset, sans modifier les conditions de vide, quelques grammes de platine à teneur en gaz connue.

Les quantités d'azote résiduelles extraites après l'addition de platine sont variables pour un même type de carbure et, semble-t-il, irrégulières et sans relation avec le rapport Pt/UC.

Après deux et quelquefois une seule addition de 2 g de platine, on n'observe plus de dégagement ultérieur d'azote soit par une élévation de température jusqu'à 2150°, soit par un nouvel ajout de métal (Figs. 1–3).

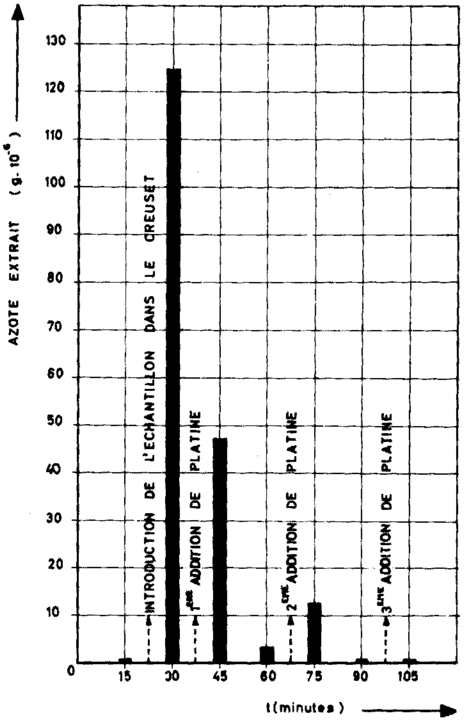


Fig. 3. Dégazage d'un échantillon de UC en poudre (~ 1200 p.p.m. N). Poids d'échantillon, 150.4 mg; rapport du Pt flux initial, 0.89/1; creuset contenant bain de platine, 12 g; fond en N_2 de l'appareil, ~ 1 µg N/15 min; contenu en N_2 du Pt ajouté, pas mesurable avec l'appareil utilisé.

L'addition de platine augmente donc la vitesse de dégazage de l'azote.

Il semble donc nécessaire, pour obtenir une extraction totale, d'employer la technique du "Platinum flux" suivie de 2 additions de platine. Nous désignerons cette nouvelle technique sous le nom de "Platinum flux modifié".

"Platinum flux modifié". Les résultats obtenus de cette manière sont résumés dans le Tableau I. Les échantillons examinés sont soit pulvérulents, soit fondus. Nous n'avons pas trouvé jusqu'ici d'échantillons d'UC "préréagi" ayant une teneur en azote supérieure à la limite de sensibilité de la méthode.

Les moyennes obtenues par la technique du "Platinum flux modifié" sont en bon accord avec celles trouvées par voie chimique (méthode classique de Kjeldahl). On remarque, de plus, une meilleure reproductibilité de la méthode pour les échantillons d'UC en poudre. Ceci semble pouvoir être attribué à l'hétérogénéité de la teneur en azote des échantillons d'UC fondu, en morceaux: en effet, alors que la méthode de Kjeldahl, appliquée aux poudres d'UC, donne un coefficient de variation inférieur à 5% même pour une prise d'échantillon de 200 mg, le coefficient de variation varie entre 6.5 et 24% pour les morceaux d'UC fondu (Tableau I).

La limite de sensibilité se situe entre 20 et 40 p.p.m. d'azote pour une prise d'échantillon de 200 mg; elle dépend essentiellement du blanc de l'instrument et de la teneur en azote du platine utilisé. Puisque le platine ajouté doit vraisemblablement recouvrir l'échantillon, le nombre de dosages et la quantité de platine nécessaire dépendent de la géométrie du creuset employé. Avec des creusets coniques du type KA 41 de l'appareil St Re 0783, nous avons analysé jusqu'à 10 échantillons par creuset et par jour, sans rencontrer de difficultés.

Cette nouvelle technique permet, comme nous le verrons dans la suite, le dosage simultané de l'oxygène. De plus, elle est avantageuse du point de vue de la sensibilité.

L'hétérogénéité probable et le peu d'échantillon d'UN en morceaux nécessaire à cette technique pourraient être responsables de la légère différence trouvée par rapport à la méthode chimique.

Dosage de l'azote par voie chimique

Ce dosage a été effectué par la méthode classique de Kjeldahl. On a montré[16] que dans le cas de l'UO_2 fondu, les résultats sont variables suivant le mode d'attaque. Ce fait nous a conduit à essayer divers modes de mise en solution de l'UC, par les mélanges suivants:

(*1*) Acides chlorhydrique et perchlorique[17,18],
(*2*) Acides chlorhydrique, fluosilicique et seleniate de cuivre[16,19],
(*3*) Acide sulfurique et eau oxygénée[9].

Les résultats obtenus sont identiques, quel que soit le mode de dissolution utilisé; toutefois dans le cas de la mise en solution par l'acide perchlorique, on doit éviter d'aller à sec ou de maintenir plus de 5 min à fumées blanches[17].

Pour le nitrure d'uranium, l'attaque est faite par le mélange (*2*)[16,19]. La prise d'essai de UC varie entre 0.20 et 1 g et la distillation (25–100 ml) est effectuée dans un appareil de micro Kjeldahl. Pour éviter d'éventuelles pertes d'ammoniac, 10 ml d'une solution d'acide borique à 1% sont introduits avant la distillation dans le récipient récepteur[9].

Deux méthodes sont utilisées pour le dosage colorimétrique ultérieur:

(*1*) la méthode au réactif de Nessler[20];
(*2*) la méthode au phénol–hypochlorite[21,22].

Les résultats obtenus par les deux méthodes sont en excellente concordance et les reproductibilités dans nos conditions opératoires, sont à peu près identiques.

La première méthode est la plus simple; mais la seconde présente l'avantage non négligeable d'être insensible à une contamination par l'ammoniac de l'air après développement de la couleur (bleu d'indophénol)[21].

Les résultats obtenus avec des échantillons homogènes, sont reproductibles à moins de 5% pour des teneurs en azote comprises entre 200 et 1000 p.p.m. La limite de sensibilité, compte-tenu de la valeur du blanc des réactifs, est de l'ordre de 10 p.p.m. d'azote par une prise d'échantillon de 1 g.

Tous les réactifs utilisés sont purifiés et protégés d'une contamination éventuelle par l'ammoniac ou les sels d'ammonium.

DOSAGE DE L'OXYGÈNE

A défaut d'étalons, nous avons comparé, pour les différents types de monocarbure d'uranium à notre disposition, les 3 techniques suivantes:
"Vacuum hot extraction"
"Platinum flux"
"Vacuum fusion" avec bain de platine
en prenant, comme méthode de référence, la dernière étant donné que différents auteurs[5-8] l'ont déjà utilisé, avec succès, à environ 2000°. Avec chacune des techniques, l'oxygène se dégage sous forme de CO et l'extraction est poussée jusqu'à l'obtention du blanc de l'appareil. La durée d'extraction, nécessaire à la température de 2000° et dans nos conditions opératoires, est de l'ordre de 20 min. Le Tableau II résume les résultats obtenus sur les différents échantillons d'UC. L'accord entre les résultats obtenus par les 3 techniques est satisfaisant, sauf pour l'UC fondu en morceaux. Dans ce cas, les résultats sont plus dispersés et le dégazage par la méthode de la "Vacuum hot extraction" est difficile et incomplet, comme d'autres auteurs[7] l'ont déjà fait remarquer.

Pour vérifier ce dernier point, nous avons effectué un dégazage en deux temps:

(*1*) "Vacuum hot extraction" à 2000° et mesure de l'oxygène dégagé.

(*2*) Ajout dans le creuset de 2 à 4 g de platine, suivi d'une nouvelle mesure de l'oxygène extrait (il y a lieu de déduire la teneur en oxygène du platine employé).

Ces essais ont montré que la "Vacuum hot extraction" seule ne donne pas une extraction quantitative de l'oxygène sur les fondus: en effet, pour des échantillons contenant de 200 à 1500 p.p.m. d'oxygène, l'ajout de platine amène un dégagement supplémentaire de 50 à 500 p.p.m. d'oxygène. De plus par la méthode simple de la "Vacuum hot extraction" il n'était jamais possible de retrouver la valeur initiale du blanc de l'appareil, même après un temps d'extraction d'une heure. Par contre les échantillons d'UC "préréagi", analysés dans les mêmes conditions, donnent, pour leur part, une extraction complète de l'oxygène avec la seule "Vacuum hot extraction"[5].

Il ne semble pas que la teneur en azote des échantillons soit de nature à influencer l'extraction de l'oxygène par cette technique comme le suppose TAYLOR[7]. En effet, on peut noter (Tableau II) que l'extraction de l'oxygène par la "Vacuum hot extraction" est incomplète et lente pour des échantillons d'UC fondu contenant 50 et 500 p.p.m. d'azote, alors qu'elle est, par contre, aisée pour une poudre (no. 9, Tableau II) à 600 p.p.m. d'azote, et pour les "préréagis" contenant moins de 40 p.p.m.

Cette différence de comportement pourrait être due à une différence de porosité et de dimension des cristaux de monocarbure qui conduit à une réactivité plus grande et une diffusion plus facile pour les poudres et les "préréagis".

Pour les 3 types d'UC préalablement dégazés par la technique du "Platinum flux", l'addition de platine n'a jamais donné de dégagement ultérieur d'oxygène. Même pour un rapport 1–1.5 de "flux", l'extraction de l'oxygène est complète et terminée généralement en 20 min. Il semble par ailleurs que la grande dispersion des

TABLEAU II

DOSAGE DE L'OXYGÈNE DANS LE MONOCARBURE D'URANIUM (COMPARAISON DES RÉSULTATS OBTENUS PAR LES DIFFÉRENTES TECHNIQUES)

Echantillons	*Platinum flux*			*Vacuum fusion avec bain de platine*[a]			*Vacuum hot extraction*		
	Nombre d'analyses	*Moyenne (p.p.m.O_2)*	*Ecart type (p.p.m.O_2)*	*Nombre d'analyses*	*Moyenne (p.p.m.O_2)*	*Ecart type (p.p.m.O_2)*	*Nombre d'analyses*	*Moyenne (p.p.m.O_2)*	*Ecart type (p.p.m.O_2)*
Poudres									
UC No. 3 (N ~ 600 p.p.m.)	7	2.350	95	3	2.365	165			
UC No. 4 (N ~ 1050 p.p.m.)	5	1.210	110	7	1.215	80			
UC No. 9 (N ~ 600 p.p.m.)	4	3.230	150				2	3.000[b]	
UC "préreagi" (en morceaux)									
UC No. 10 (N < 40 p.p.m.)				3	960	33	3	990	33
UC No. 11 (N < 40 p.p.m.)	2	570					2	585	
UC No. 12 (N < 40 p.p.m.)	3	1.820	137				3	1.815	31
UC fondu (en morceaux)									
UC No. 13 (N ~ 500 p.p.m.)	4	1.570	185	3	1.485	334		Dégazage	Incomplet
UC No. 14 (N ~ 50 p.p.m.)	4	150	49	3	75	26		Dégazage	Incomplet
UC No. 15 (N ~ 50 p.p.m.)	4	480	87	4	495	95		Dégazage	Incomplet

[a] Les poudres sont introduites dans le creuset, enveloppées dans la feuille de platine.

[b] La poudre, pastillée à froid et sous vide, a été introduite telle quelle dans le creuset. Vu la fragilité de la pastille, une légère perte s'est produite lors de l'introduction de l'échantillon dans le creuset.

résultats pour l'UC fondu soit due à l'hétérogénéité de la teneur en oxygène des morceaux d'un même échantillon plutôt qu'à un défaut de technique. Il est utile de se rappeler qu'une dispersion analogue a été trouvée dans le cas du dosage de l'azote dans les mêmes types d'UC.

En conclusion, il apparait que la "Vacuum hot extraction" n'est valable que pour des échantillons particuliers tandis que la technique du "Platinum flux" donne de résultats corrects pour toutes les formes d'UC, avec la même confiance que la méthode au bain de platine.

Le rapport platine/échantillon employé pour le "Platinum flux" varie généralement entre 1.5 et 3. Le poids d'échantillon est compris entre 30 et 200 mg. On peut effectuer jusque 20–25 analyses par creuset. La sensibilité de la méthode est de l'ordre de 20 à 40 p.p.m. d'oxygène pour une prise de 100 mg d'échantillon.

Il est évident que la technique du "Platinum flux modifié" peut également être utilisée avec succès au dosage de l'oxygène.

L'extraction de l'oxygène est pratiquement complète avant les additions de platine.

En utilisant le "Platinum flux modifié", il faut donc soustraire, pour le calcul du résultat final, seulement le blanc en CO de l'appareil et la teneur en oxygène de la feuille de platine et non la teneur en oxygène des morceaux de platine ajoutés.

MODES OPÉRATOIRES PROPOSÉS

Le Tableau III résume les conclusions obtenues pour les différentes techniques sur les 3 types d'échantillons d'UC.

TABLEAU III

APPLICABILITÉ DES DIFFÉRENTES TECHNIQUES D'EXTRACTION À CHAUD SOUS VIDE POUR LE DOSAGE DES GAZ DANS LES DIFFÉRENTS TYPES D'UC

Types d'échant.	*"Vacuum hot extraction"*			*"Vacuum fusion" avec bain de Pt*			*"Platinum flux"*			*"Platinum flux modifié"*		
	H_2	N_2	O_2	H_2	N_2	O_2	H_2	N_2	O_2	H_2	N_2	O_2
UC poudre	oui[a]	non[b]	oui	oui	non	oui	oui	non	oui	oui	oui	oui
UC "préréagi"	oui	—[c]	oui	oui	—	oui	oui	—	oui	oui	—	oui
UC fondu	oui	non	non	oui	non	oui	oui	non	oui	oui	oui	oui

[a] Oui: la méthode est applicable.

[b] Non: la méthode n'est pas applicable.

[c] — : pas essayé par manque d'échantillons avec une teneur en $N_2 >$ à la limite de sensibilité de la méthode.

Selon que l'on désire doser les 3 gaz simultanément ou uniquement l'hydrogène et l'oxygène nous proposons les modes opératoires suivants.

Dosage simultané de l'hydrogène, de l'oxygène et de l'azote

Les échantillons pesant de 30 à 200 mg, sont enveloppés dans une feuille de platine de 0.03 mm d'épaisseur ayant une teneur très basse en gaz (dans notre cas: environ 1 p.p.m. d'hydrogène, 15 p.p.m. d'oxygène et moins de 1 p.p.m. d'azote), dont le poids est compris entre 1.5 et 3 fois celui de l'échantillon.

Les échantillons enveloppés dans la feuille de platine et les morceaux de platine à ajouter sont introduits dans le porte échantillon de l'appareil; ce dernier mis sous vide.

On dégaze l'appareil et le creuset à une température de 2150–2200° sous un vide de 10^{-5} à 10^{-6} mm de Hg jusqu'à obtention d'un blanc constant. On abaisse ensuite la température à sa valeur de travail (2000° dans notre cas)* et on introduit le premier échantillon que l'on dégaze pendant 20 min.

L'hydrogène et l'oxygène sont totalement extraits, l'azote est partiellement extrait.

On ajoute alors dans le creuset deux fois 2 g de platine en morceaux, à basse teneur en gaz (dans notre cas $H_2 < 0.15$ p.p.m., O_2: 5 p.p.m. environ, $N_2 < 0.5$ p.p.m.), la seconde addition étant faite 10 min après la première et on poursuit l'extraction jusqu'à ce que le blanc en azote de l'appareil soit revenu à sa valeur initiale. Ce résultat est en général atteint en 10–15 min, après la seconde addition. On répète ces opérations pour chaque échantillon. On soustrait des résultats finaux les valeurs dues au blanc de l'appareil et à la teneur en gaz de la feuille de platine dans le cas de l'hydrogène et de l'oxygène, de la totalité du platine utilisé pour l'azote.

Dosage de l'hydrogène et de l'oxygène

Le mode opératoire est identique au précédent, à la différence que l'on n'effectue pas d'ajouts successifs de platine.

GÉNÉRALITÉS SUR LA CONSERVATION DES ÉCHANTILLONS DE MONOCARBURE D'URANIUM POUR L'ANALYSE DES GAZ

L'UC s'altère à l'humidité atmosphérique et cela conduit à une augmentation de la teneur en gaz. L'expérience nous a montré que les échantillons d'UC pouvaient se conserver dans un dessiccateur contenant de l'anhydride phosphorique, sous atmosphère d'argon. Après 2 semaines, nous n'avons pas constaté d'augmentation appréciable de la teneur en hydrogène et oxygène. Le contenu en azote ne varie pas de façon notable, même après quelques mois.

Les échantillons destinés à l'analyse sont préparés dans une boîte à gants en atmosphère inerte et sèche. Ensuite, ils sont enveloppés dans la feuille de platine et pesés à l'air.

Sur la base d'une série d'essais effectués sur des morceaux et sur des poudres, nous pouvons affirmer que la durée de l'opération à l'air est suffisamment brève pour ne pas apporter, au niveau des teneurs en gaz rencontrées**, des variations appréciables dans le contenu en gaz des échantillons.

CONCLUSION

Le dosage simultané de l'hydrogène, de l'oxygène et de l'azote dans l'UC est possible en employant la technique du "Platinum flux modifié".

Les résultats obtenus pour l'hydrogène et l'oxygène sont en bon accord avec

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* Température mesurée au pyromètre optique.

** 50–3000 p.p.m. pour les morceaux; 1000–20000 p.p.m. pour les poudres.

ceux trouvés par les autres techniques d'extraction à chaud sous vide. Quant à l'azote, la concordance avec la méthode classique de Kjeldahl est très satisfaisante.

Les coefficients de variation de la méthode sont généralement inférieurs à 10%. La quasi totalité du platine employé dans la méthode peut être récupérée.

Nous remercions, Monsieur H. LAURENT de son aide et pour avoir revu le texte, MM. BEYRICH et COLLIN de leurs conseils, Mlle BEVILACQUA et M. WEHKING de leur collaboration technique.

RÉSUMÉ

Méthodes de dosage de l'hydrogène, de l'oxygène et de l'azote dans le monocarbure d'uranium. L'hydrogène et l'oxygène sont dosés, avec un coefficient de variation inférieur à 10%, par la méthode classique ou modifiée du "Platinum flux" à 2000°.

L'azote est dosé à 2000° suivant une technique modifiée du "Platinum flux". Les résultats obtenus concordent avec ceux trouvés par voie chimique (Kjeldahl). Le coefficient de variation de la méthode est d'environ 10%.

Le mode opératoire du dosage simultané des 3 gaz est décrit.

SUMMARY

A method is described for the determination of hydrogen, oxygen and nitrogen in uranium monocarbide. Hydrogen and oxygen are determined by the classical or modified "Platinum flux" method at 2000° with a coefficient of variation of 10%. Nitrogen is determined at 2000° by the modification of the "Platinum flux" technique. The results obtained are in agreement with those found by Kjeldahl analysis. The coefficient of variation is about 10%. A procedure for the simultaneous determination of the 3 gases is given.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Wasserstoff, Sauerstoff und Stickstoff in Uranmonocarbid beschrieben. Wasserstoff und Sauerstoff lassen sich mit der klassischen oder modifizierten "Platinfluss"-Methode bei 2000° mit einem Variationskoeffizienten von 10% bestimmen. Die Ergebnisse stimmen gut mit denen, die nach der Kjeldahlmethode gefunden wurden, überein. Ein Verfahren für die gleichzeitige Bestimmung der 3 Gase wird angegeben.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH GLYOXIME AND CHLOROFORM EXTRACTION*

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Palladium has often been determined with dimethylglyoxime, not only gravimetrically[1] but also by an extraction procedure[2]. Several other dioximes have been used for the determination of palladium[3,4]. These facts suggested that it might be possible to determine palladium with the simplest of the dioximes, namely, glyoxime, $(HCNOH)_2$. Preliminary tests of solutions of the platinum-group elements indicated that palladium(II), ruthenium(III), and osmium(VI) reacted with glyoxime. Palladium(II) gave a yellow precipitate which was soluble in chloroform. Because of the intensity of color and the stability of the palladium(II) glyoximate chloroform solution, glyoxime was investigated as a reagent for the determination of palladium.

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Model DU spectrophotometer, using matched silica cells of 1.00-cm optical path. Measurements of pH were made with a Beckman Zeromatic pH meter, using glass and calomel electrodes. A Mettler microbalance, Type M-5, was used for making weighings requiring a high degree of accuracy.

Reagents

Standard palladium solution. Pure palladium(II) chloride was obtained from A. D. Mackay, Inc., New York. A sample was weighed out and dissolved in the stoichiometric amount of standard hydrochloric acid to form the tetrachloropalladate(II), and then diluted to known volume. The solution was also standardized gravimetrically by the procedure given by KOLTHOFF AND ELVING[1], and was found to be 0.2238 M.

Glyoxime. This reagent was purchased from Frinton Laboratories, South Vineland, New Jersey. The following solutions were prepared:

(*1*) 0.1 M glyoxime in 25% aqueous alcohol (reagent).
(*2*) $1.000 \cdot 10^{-3}$ M aqueous glyoxime solution.
(*3*) Saturated solution of glyoxime in chloroform.
(*4*) $9.94 \cdot 10^{-4}$ M solution of glyoxime in chloroform.
(*5*) 0.1022 M solution of glyoxime in 1:1 dioxane–water.

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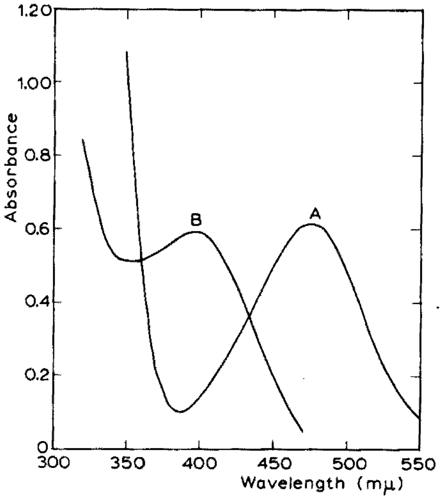
Chloroform. A.C.S. grade chloroform was used.

Buffers. Buffer solutions were prepared by the formulations of Clark and Lubs[5] and MacIlvaine[5].

Preparation and analysis of palladium(II) glyoximate

A small amount of palladium chloride solution was mixed with the glyoxime reagent solution. The yellow precipitate which formed was washed several times with water, then with alcohol, and dried to constant weight at 110°.

The standard palladium(II) solution was diluted with hydrochloric acid to give a series of standard solutions in 5% hydrochloric acid. The absorption spectrum of one of these solutions is shown in Fig. 1, curve A. The absorption maximum occurs at 475 mμ. The absorbance of each of the other standard solutions was measured at 475 mμ. A plot of absorbance against concentration was a straight line; the specific absorptivity was 1.54 ml/mg/cm. Spectrophotometric measurement, at 475 mμ, in 5% hydrochloric acid solution is a reliable method for the determination of palladium[6].



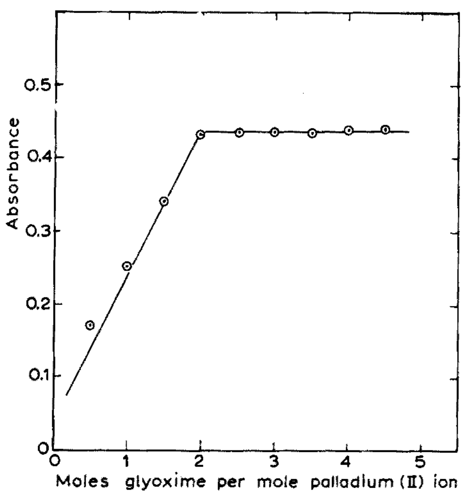


Fig. 1. Spectral curves. (A) 0.400 mg of palladium(II) chloride per ml in 5% hydrochloric acid. (B) $2.49 \cdot 10^{-4}$ *M* palladium(II) glyoximate in chloroform.

Fig. 2. Mole ratio determination of formula of palladium(II) glyoximate.

A sample of palladium(II) glyoximate weighing 0.077308 g was taken. Organic matter was destroyed by heating with aqua regia; the residue was dissolved, transferred to a 10-ml volumetric flask, and made up to volume. Aliquots (1 ml) were transferred to 10-ml volumetric flasks. The solution in each flask was taken to dryness, treated with 1 ml of 1:1 nitric acid and 1 ml of perchloric acid and again taken to dryness. It was then taken to dryness three times with hydrochloric acid, and finally diluted to volume with hydrochloric acid and water to give a solution of palladium(II) in 5% hydrochloric acid. The absorbance of each solution was measured at 475 mμ, and the amount of palladium in the glyoximate was calculated from the calibration data.

TABLE I

ANALYSIS FOR PALLADIUM IN PALLADIUM(II) GLYOXIMATE

(Spectrophotometric measurement of Pd(II) in 5% HCl)

Sample	*Absorbance at 475 mμ*	*Pd found (%)*	*Deviation (%)*
1	0.444	37.45	0.6
2	0.440	37.20	0.1
3	0.442	37.33	0.3
4	0.439	36.93	0.6
Average		37.23	0.5

The results are shown in Table I. Palladium found in the precipitate, 37.23%; palladium calculated for $Pd(C_2H_3O_2N_2)_2$, 37.67%.

Preparation and standardization of palladium glyoximate chloroform solution

A saturated solution of palladium glyoximate in chloroform was prepared and filtered. Ten ml of the clear solution was transferred to a volumetric flask and evaporated to dryness. The precipitate was decomposed with perchloric acid and the palladium present was determined spectrophotometrically in 5% hydrochloric acid as before. The original palladium glyoximate solution in chloroform was found to be $7.07 \cdot 10^{-4}$ *M*. Other standard solutions were prepared by volumetric dilution.

The absorption spectrum of $2.49 \cdot 10^{-4}$ *M* palladium(II) glyoximate in chloroform is shown in Fig. 1, curve B; absorption maximum occurs at 397 mμ. Absorbance of more dilute standard solutions was measured at 397 mμ. A plot of absorbance against concentration is a straight line; the specific absorbance in terms of palladium is 0.237 ml/mg/cm. This method can be used for determining directly the amount of palladium glyoximate in chloroform solution.

Extraction procedure

An aqueous solution (5 ml) containing a known amount of palladium(II) at a known pH was transferred to a small glass-stoppered Erlenmeyer flask. Chloroform (5 ml) containing a known concentration of glyoxime was added, and the flask was stoppered and swirled by hand for 5 min. The system was allowed to stand for a few minutes for the separation of phases. The chloroform phase was removed with a small capillary pipet and transferred to a small flask, or directly to the absorption cell. If multiple extraction was made, another 5 ml of chloroform solution was added, and the extraction procedure was repeated, using, however, only 1 min for each extraction. The chloroform extracts were combined and the absorbance was measured at 397 mμ. The amount of palladium present was calculated from the previous calibration.

Extraction of palladium glyoximate at different pH values

An aliquot (1 ml) of $5.00 \cdot 10^{-3}$ *M* palladium solution was transferred to a 25-ml volumetric flask and diluted with buffer solution to the mark. A 5-ml aliquot of this solution was extracted with 5 ml of $9.94 \cdot 10^{-4}$ *M* glyoxime in chloroform. The absorbance of the extract was measured at 397 mμ, and the palladium content was

TABLE II

EFFECT OF pH ON EXTRACTION

(Palladium taken, $2.00 \cdot 10^{-4}$ *M*, except as noted. Results are averages of 2 to 4 samples at each pH)

pH	*Buffer system*	*Absorbance at 397 mμ*	*Pd found ($M \cdot 10^4$)*	*Pd extracted (%)*
0.0	HCl	0.049	0.20	10
0.2	HCl	0.103	0.42	21
0.6	HCl	0.328	1.38	69
1.0	HCl–KCl	0.384	1.62	81
1.0	HCl–KCl	0.223	0.94[a]	94
1.4	HCl–KCl	0.362	1.54	77
2.0	HCl–KCl	0.353	1.49	74
3.0	Na_2HPO_4–citric acid	0.330	1.40	70
4.2	Na_2HPO_4–citric acid	0.152	0.64	32
5.0	Na_2HPO_4–citric acid	0.096	0.40	20
6.0	Na_2HPO_4–citric acid	0.047	0.20	10
7.0	Na_2HPO_4–citric acid	0.017	0.08	4
1.0	HCl–KCl	0.428	1.80[b]	90

[a] Palladium taken, $1.00 \cdot 10^{-4}$ *M*; average extraction at pH 1.0, 85%.
[b] In this experiment a small additional amount of solid glyoxime was used.

TABLE III

EXTRACTION OF PALLADIUM GLYOXIMATE IN THE PRESENCE OF FOREIGN IONS

(Foreign ion and palladium(II) each at $1.00 \cdot 10^{-3}$ *M* (= 0.532 mg palladium), and 4 extractions except as noted. Results are averages of 2 to 4 samples for each test)

Foreign ion	*Absorbance at 397 mμ*	*Pd found (mg)*	*Pd extracted (%)*	*Relative error (%)*
Pt(II)	0.601	0.541	101.7	+1.7
Rh(III)	0.590	0.531	99.7	−0.3
Ru(III)	0.585	0.526	98.9	−1.1
Ir(III)[a]	0.202	0.136	102.2	+2.2
Os(VI)	0.588	0.529	99.4	−0.6
Au(III)	0.616	0.554	104.1	+4.1
Ni(II)	0.593	0.531	100.1	+0.1
Co(II)	0.600	0.540	101.4	+1.4
Cu(II)	0.590	0.530	99.6	−0.4
Fe(III)	0.486	0.436	82.1	−17.9
Fe(II)	0.500	0.458	86.1	−13.9
$H_2PO_4^-$	0.605	0.544	102.3	+2.3
H_2O_2[b]	0.595	0.535	100.6	+0.6
ClO^-[b]	0.563	0.506	95.1	−4.9
CN^-[b]	0	0		

[a] Concentration of iridium(III) and palladium(II) each $2.5 \cdot 10^{-4}$ *M* (= 0.133 mg palladium); three extractions,
[b] Very large excess of foreign ion used in these tests.

determined from the calibration. The data for these extractions are shown in Table II. The maximum amount of palladium was extracted at pH 1.0.

Extraction of palladium glyoximate in the presence of diverse ions

Standard palladium(II) solution containing a known amount of foreign ion at a pH of 1 was prepared; aliquots of the solution were extracted 4 times with a standard solution of glyoxime in chloroform. The absorbance of the combined extract was measured at 397 mμ and the amount of palladium extracted was calculated. The data for these extractions are shown in Table III.

In the next series, palladium was extracted from several foreign ions in the same solution, at pH 1. A solution was prepared which was $2.000 \cdot 10^{-4}$ *M* in palladium(II) and $2 \cdot 10^{-4}$ *M* each in platinum(II), rhodium(III), ruthenium(III), iridium(III), and osmium(VI). Three 1-min extractions were made, and the combined extracts were measured at 397 mμ. Data for these extractions are given in Table IV, part A. Another series of extractions was made from solution which was $1.000 \cdot 10^{-3}$ *M* in palladium(II), $5.0 \cdot 10^{-4}$ *M* each in platinum(II), rhodium(III), ruthenium(III), osmium(VI), and $1.25 \cdot 10^{-4}$ *M* in iridium(III). The pH of the aqueous phase was slightly higher than 1, because the amount of hydrochloric acid was decreased; potassium chloride was not used. Four extractions were made and the absorbance of

TABLE IV

EXTRACTION OF PALLADIUM GLYOXIMATE FROM MIXTURES OF FOREIGN IONS

Run no.	*Absorbance at 397 mμ*	*Pd found (mg)*	*Pd extracted (%)*	*Error (%)*
Foreign ions: platinum metals				
Part A: 0.1064 mg palladium taken				
1	0.173	0.1154	108.5	+8.5
2	0.172	0.1147	107.8	+7.8
3	0.169	0.1124	105.6	+5.6
4	0.169	0.1124	105.6	+5.6
			Average:	+7
Part B: 0.532 mg palladium taken				
5	0.597	0.537	100.8	+0.8
6	0.595	0.535	100.5	+0.5
7	0.592	0.532	100.0	0.0
8	0.590	0.537	100.9	+0.9
9	0.600	0.540	101.4	+1.4
10	0.597	0.537	100.9	+0.9
11	0.588	0.529	99.3	−0.7
12	0.588	0.529	99.3	−0.7
13	0.592	0.532	100.0	0.0
14	0.594	0.535	100.5	+0.5
			Average:	+0.4
Foreign ions: non-platinum metals				
Part C: 0.532 mg palladium taken				
15	0.504	0.456	85.7	−14.3
16	0.506	0.455	85.5	−14.5
17	0.503	0.452	85.0	−15.0
18	0.500	0.450	84.5	−15.5
			Average:	−15

the combined extracts was measured. The results are shown in Table IV, part B. Another series of extractions was made from solution of pH 1 containing a known amount of $1.000 \cdot 10^{-3}$ *M* palladium(II) and the same amount of each of several transitional metal cations: zinc, nickel(II), vanadium(IV, V), copper(II), bismuth(III), manganese(II), cadmium, mercury(II), iron(III), gold(III); also potassium dihydrogen phosphate. The results are shown in Table IV, part C.

Extraction of palladium glyoximate in the presence of diverse ions and EDTA

A $1.000 \cdot 10^{-3}$ *M* solution of palladium(II) was also made 0.001 *M* in each of the ions mentioned above, enough hydrochloric acid and potassium chloride to give a pH of 1, and 0.050 *M* in EDTA. Aliquots of this solution were extracted 4 times with saturated solution of glyoxime in chloroform. The results are shown in Table V, part A.

TABLE V

EXTRACTION OF PALLADIUM GLYOXIMATE IN THE PRESENCE OF FOREIGN IONS AND EDTA

(Palladium taken: 0.532 mg)

Run no.	*Absorbance at 397 mμ*	*Pd found (mg)*	*Pd extracted (%)*	*Error (%)*
Part A. Foreign ions, non-platinum metals				
1	0.597	0.534	100.9	+0.9
2	0.596	0.536	100.7	+0.7
3	0.620	0.557	104.8	+4.8[a]
4	0.593	0.533	100.2	+0.2
5	0.599	0.539	101.2	+1.2
6	0.596	0.536	100.7	+0.7
7	0.593	0.533	100.2	+0.2
8	0.591	0.531	99.9	−0.1
			Average:	+0.5
Part B. Foreign ions, platinum metals				
9	0.597	0.537	100.9	+0.9
10	0.597	0.537	100.9	+0.9
11	0.587	0.528	99.2	−0.8
12	0.583	0.524	98.5	−1.5
			Average:	−0.1

[a] Not included in the average.

A $1.000 \cdot 10^{-3}$ *M* solution of palladium(II) was also made $2.5 \cdot 10^{-4}$ *M* each in ruthenium(III), platinum(II), rhodium(III), iridium(III) and osmium(VI), 0.1 *M* in hydrochloric acid, and excess EDTA added. Aliquots of the solution were extracted and measured as before. The results are shown in Table V, part B.

Composition of reaction product

The mole ratio method of YOE AND JONES[7] was used to determine the moles of glyoxime reacting with one mole of palladium(II). One ml of $2.000 \cdot 10^{-3}$ *M* palladium(II) solution was added to a series of 10-ml volumetric flasks. A different known amount of $1.000 \cdot 10^{-3}$ *M* glyoxime in 1:1 dioxane–water was added to each flask and the solution diluted to volume with 1:1 dioxane–water. The absorbance of each solution was measured at 375 mμ (the absorption maximum in this solvent mixture); the data are shown in Table VI. The corrected absorbance is the observed absorbance less the absorbance due to unreacted palladium(II) chloride in 1:1 dioxane–water, assuming palladium and glyoxime react in a 1:2 mole ratio. A plot of absorbance against moles of glyoxime per mole of palladium is shown in Fig. 2; a sharp break occurs at a ratio of 2 moles of glyoxime per mole of palladium(II).

TABLE VI

DATA FOR DETERMINING MOLE RATIO

(1 ml of $2.00 \cdot 10^{-3}$ *M* palladium(II) and increasing amounts of $1.00 \cdot 10^{-3}$ *M* glyoxime. Solvent, dioxane–water)

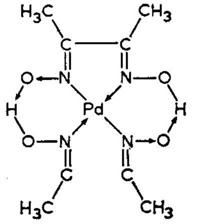
Glyoxime (ml)	*Absorbance at 375 mμ*	*Absorbance corrected for unreacted Pd*
1	0.187	0.172
2	0.262	0.252
3	0.347	0.342
4	0.432	0.432
5	0.437	0.437
6	0.439	0.439
7	0.439	0.439
8	0.440	0.440
9	0.442	0.442

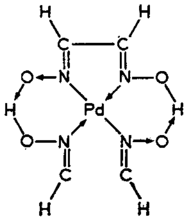
The same solute species was present in all the chloroform solutions—whether formed by direct dissolution of solid palladium glyoximate, or by extraction from palladium alone or in the presence of many other cations and EDTA—as shown by the superimposability of spectral curves plotted as log absorbance against wavelength.

Analysis of the palladium glyoximate sample which was soluble in chloroform gave 37.23% palladium; this corresponds to the product formed by reaction of palladium(II) and glyoxime in a 1:2 mole ratio. Another sample of palladium(II) glyoximate, made by precipitation in 1 *M* hydrochloric acid, turned from orange to yellow upon digestion. This product, which was not soluble in chloroform, also contained 37.49% palladium, which is consistent with a product containing palladium and glyoxime in a 1:2 ratio. The yellow precipitate and the orange precipitate gave different X-ray diffraction patterns; it appears that palladium glyoximate exists in two different crystal forms.

DISCUSSION

GODYCKI AND RUNDLE[8] determined the structure of palladium dimethylglyoximate, using the single crystal X-ray diffraction method; they report that the structure may be represented by formula (I). Palladium dimethylglyoximate is soluble in chloroform. Since palladium glyoximate in one of its forms is soluble in chloroform, since palladium(II) and glyoxime react in a 1:2 mole ratio, and since the solid contains palladium corresponding to the composition $Pd(C_2H_3O_2N_2)_2$, it seems reasonable that formula (II) might represent the palladium(II) glyoximate. DWYER AND MELLOR[9] studied the reaction of palladium(II) with benzildioxime. They report that benzildioxime is a mixture of three isomers, known as α-, β-, and γ-benzildioxime; only the α-form reacts with palladium in a 2:1 mole ratio, while the β- and γ-forms react in a 1:1 mole ratio. Similarly, dimethylglyoxime exists in three forms, only the α-form of which gives the characteristic pink precipitate with nickel(II). In view of these facts, it is reasonable to assume that palladium(II) reacts with the α-form of glyoxime.


(I)


(II)

KOLTHOFF AND SANDELL[10] developed an equation for the extractability of organo-metallic complexes:

$$\frac{[MR_2]_o}{[M^{2+}]_w} = K \frac{[HR]_o^2}{[H^+]_w^2}$$

where $[MR_2]_o$ is the concentration of the metal complex in the organic phase, $[HR]_o$ is the concentration of organic reagent in the organic solvent (*e.g.*, chloroform) phase, $[M^{2+}]_w$ is the concentration of divalent cation in the aqueous phase, $[H^+]_w$ is the concentration of hydronium ion in the aqueous phase, and K is a constant.

In studying the influence of pH on the extraction of palladium glyoximate into chloroform, it was found that maximum extraction occurred at pH 1.0, but only about 85% of the palladium taken was recovered by a single extraction. It is evident that multiple extractions are required in order to obtain quantitative extraction.

After an initial rapid increase in the amount of palladium extracted as the pH increased from 0 to 1, there was a decrease in the percent extracted as the pH increased, the extractability becoming insignificant at a pH above 6. This behavior, which is the reverse of the effect of pH predicted by the above equation, may be explained by the following considerations. The palladium solutions used contained additional chloride ion; the palladium was therefore present largely as tetrachloropalladate(II) ion and not as the simple divalent aquo cation[11]. The solubility product constant of palladium(II) hydroxide is quite small[12] and indicates that palladium(II) should begin to precipitate as hydroxide at a pH of about 0.7. Because of the various reactions competing for palladium(II), it might be expected that the system would not follow the relations expressed by the above equation. However, by the use of multiple extractions, quantitative extraction of palladium glyoximate was attained.

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SUMMARY

Palladium(II) reacts with glyoxime in a 1:2 mole ratio to form a yellow water-insoluble chelate, which is soluble in chloroform; the solution has an absorption maximum at 397 mμ. Absorbance measurements at 397 mμ allow determination of the palladium glyoximate in solution. The maximum amount of palladium is extracted at pH 1.0. Platinum(II), iridium(III), gold(III), and phosphate cause some positive interference, and iron(II, III) causes negative interference; the interferences can be eliminated by masking with EDTA. The species extracted has been shown to be identical with that used to prepare the original palladium glyoximate chloroform solution. With EDTA and multiple extractions, the method is satisfactory for the determination of palladium in the presence of other platinum-group elements and many other cations.

RÉSUMÉ

Le palladium réagit avec les glyoximes (rapport moléculaire 1:2), pour former un chélate jaune, insoluble dans l'eau, soluble dans le chloroforme; absorption maximum à 397 mμ. La quantité maximum de palladium est extraite au pH 1.0. Platine(II), iridium(III), or(III), phosphate et fer(II, III) gênent. Il est possible de doser le palladium en présence des autres éléments du groupe du platine et de nombreux autres cations avec masquage à l'EDTA et extractions.

ZUSAMMENFASSUNG

Palladium(II) reagiert mit Glyoxim im Molverhältnis 1:2 zu einem gelben wasserunlöslichen, jedoch in Chloroform löslichen Chelat. Das Palladium wird beim pH 1 extrahiert und die Absorption bei 397 mμ gemessen. Platin(II), Iridium(III), Gold(III) und Phosphat verursachen positive, Eisen(II, III) dagegen negative Störungen. Die Störungen können durch Maskierung mit AEDTE eliminiert werden. Bei mehrfacher Extraktion eignet sich die Methode befriedigend zur Bestimmung von Palladium in Gegenwart anderer Platingruppenelemente und vieler anderer Kationen.

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THIOBENZOYLPHENYLHYDROXYLAMINE: POTENTIAL ANALYTICAL REAGENT

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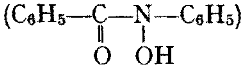
N-Benzoyl-N-phenylhydroxylamine (BPHA), introduced as a gravimetric reagent by SHOME[1] in 1950, has been one of the most useful reagents to appear in recent years; it has been used extensively for the determination of many metals[2] and its analytical possibilities are still being vigorously pursued. This paper records the results of a preliminary investigation of the thio-analogue of BPHA, thiobenzoylphenylhydroxylamine (TBPHA), in which the carbonyl oxygen of BPHA  $(C_6H_5\text{—}\underset{\underset{O}{\|}}{C}\text{—}\underset{\underset{OH}{|}}{N}\text{—}C_6H_5)$ has been replaced by a sulphur atom.

A change in donor atoms can provide new possibilities for analytical reagents by taking advantage of metal preference for particular donors and by changing ligand basicity; the 2 oxygen donors in BPHA favor reaction with d° type ions. Substitution of a sulphur donor for an oxygen donor atom would be expected, through decreased electronegativity and the availability of orbitals for π bonding, to result in changes in reagent behaviour. The reactivities of BPHA and TBPHA with metal ions have, therefore, been compared; acid dissociation constants and a few formation constants in aqueous 50% dioxane are also reported in this preliminary paper.

EXPERIMENTAL

Preparation of thiobenzoylphenylhydroxylamine

TBPHA was made by reacting thiobenzoyl chloride with phenylhydroxylamine. The thiobenzoyl chloride was obtained from the reaction between thionyl chloride and dithiobenzoic acid.

Phenylmagnesium bromide, prepared in the usual way by the mixing of a solution of bromobenzene (204 g) in dry ether (600 ml) with magnesium metal (33 g), was added, under nitrogen, to a solution of carbon disulphide (154 g) in dry ether (300 ml); after standing overnight the mixture was acidified with 25% hydrochloric acid and the dithiobenzoic acid extracted with ether[3]. Thionyl chloride (83 g) was added to the ether extracts and, after warming over a steam bath for 7 h, the purple thiobenzoyl chloride was distilled off[4] under reduced pressure between 150–220°. The yield was 19.2 g (0.12 moles).

The crude thiobenzoyl chloride was added as quickly as its purple color disappeared on reaction, to 19.6 g (0.18 moles) of phenylhydroxylamine in a minimum amount of ether. The yellow solution was evaporated under reduced pressure until crystallization began; it was then stored under refrigeration and crystallization of TBPHA allowed to take place slowly. The crude yellow solid was recrystallized from alcohol–water mixtures to a melting point of 102–103° (reported melting point[5] is 100–101°); the yield was 3–4 g. The analytical results found were (%): C 68.1, H 4.8, N 6.1, S 14.0; calculated for $C_{13}H_{11}NOS$: C 67.7, H 4.7, N 6.1, S 14.2.

The TBPHA is stable indefinitely as a solid and an alcoholic 1% solution of the reagent showed no decomposition after several weeks.

Reactions with metal ions

Qualitative comparative reactions of BPHA and TBPHA with metal ions were done by adding two drops of a 10 mg/ml metal solution and three drops of alcoholic 1% solutions of the reagents to 1 ml of water in a test tube. Reagent blanks and metal ion blanks were run concurrently. If a noticeable reaction occurred, the test was repeated and the product extracted with chloroform. Tests were also done in which 1 ml of 1:10 hydrochloric acid was substituted for the 1 ml of water. The results are summarized in Table I.

The qualitative tests are limited, of course, in that only reactions giving a visible product are noted; only metals which showed visible signs of reaction under the conditions employed are listed in Table I. Thus, cadmium, cobalt, manganese and zinc gave no evidence of reaction with BPHA in these qualitative tests but it is well known that they do react[2] and potentiometric titrations showed that protons are

TABLE I

REACTIONS OF METALS WITH BPHA AND TBPHA

Metal	*Color of precipitate*		*Color of chloroform extract*		*Reaction in 1:10 HCl*	
	BPHA	*TBPHA*	*BPHA*	*TBPHA*	*BPHA*	*TBPHA*
Ag(I)		White		Pale yellow		Yes
Al(III)	White	White	Colorless	Colorless	No	No
Au(III)		Brown		Yellow		No
Bi(III)		Yellow		Pale yellow		Yes
Cd(II)		White		Colorless		No
Ce(IV)	Brown	Cream	Yellow	Colorless	No	No
Co(II)		Brown		Golden		No
Cu(II)	Yellow	Brown	Yellow-green	Yellow	No	Yes
Fe(III)	Violet	Dark-brown	Violet	Dark-brown	Yes	Yes
Hg(I)	Yellow	Cream	Yellow	Colorless	No	Yes
Hg(II)	Yellow	White	Colorless	Unextractable	No	Yes
Mn(II)		Yellow-green		Yellow-green		No
Mo(VI)		Yellow		Yellow		Yes
Nb(V)	White	Cream	Colorless	Pale yellow	Yes	Yes
Ni(II)	White	Brown	Colorless	Yellow	No	No
Pb(II)	White	Cream	Colorless	Pale yellow	No	No
Pd(II)	Gray-green	Buff	Gray-green	Yellow	No	Yes
Pt(IV)		Yellow		Yellow		Slow
Sn(IV)	White	White	Colorless	Colorless	Yes	Yes
Ta(V)	White	Cream	Unextractable	Colorless	Yes	Yes
Th(IV)		White		Unextractable		No
Ti(IV)	Yellow	Pale yellow	Yellow	Pale yellow	Yes	Yes
U(VI)	Copper	Brown	Copper	Unextractable	No	No
V(V)	Purple	Green	Purple	Green	Yes	Yes
W(VI)	Cream	Cream	Pale yellow	Pale yellow	Yes	Yes
Zn(II)		White		Colorless		No
Zr(IV)	White	Yellow	Colorless	Pale yellow	Yes	Yes

released on titration of mixtures of these metals and BPHA. The tests do show, however, that the effect of the sulphur atom is to allow reaction with a wider range of metal ions and that TBPHA is less sensitive than BPHA to acid. In the classification scheme of atoms as electron acceptors by AHRLAND *et al.*[6], the additional metals reacting with TBPHA are mainly class (b) acceptors which do have a preference for sulphur over oxygen donors.

Potentiometric titrations

The chelates of some divalent metal ions (Mn, Co, Ni, Cu and Zn) were studied by performing a series of titrations using standard 0.1 N sodium hydroxide as titrant. The limited solubility of the chelates in water necessitated the use of 1:1 dioxane–water in which the chelates were more soluble. The titration apparatus was essentially the same as that described by HAINES *et al*[7].

The acid dissociation constants of BPHA and TBPHA were determined by titrating a mixture of the ligand and perchloric acid with standard base. Protonation of the ligands is negligible; titration curves of perchloric acid and perchloric acid–reagent solutions of the same acid concentration were superimposable up to the strong acid end-point. Figure 1 shows the sharp break in the titration curve for the TBPHA end-point and the relatively poor one obtained for BPHA. The constants calculated from titration curve values in the buffer region between the perchloric acid and reagent end-points, were 10.45 and 8.00 for BPHA and TBPHA respectively and were reproducible within ±0.02 pK units.

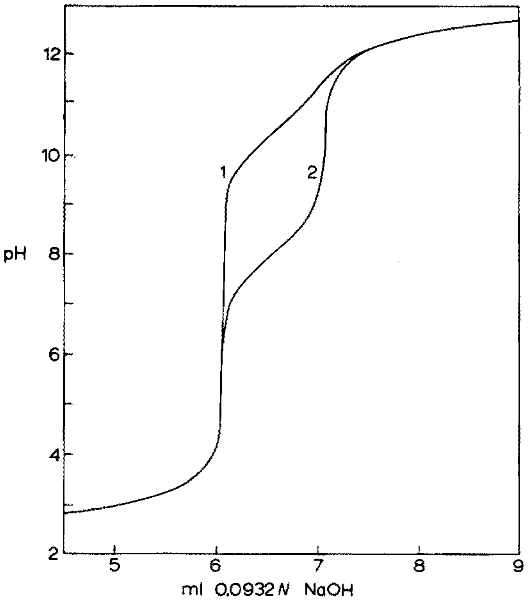


Fig. 1. Reagent titrations. (1) 50.0 ml of $1.141 \cdot 10^{-2}$ N perchloric acid and $9.39 \cdot 10^{-5}$ moles BPHA; (2) perchloric acid and $9.39 \cdot 10^{-5}$ moles TBPHA.

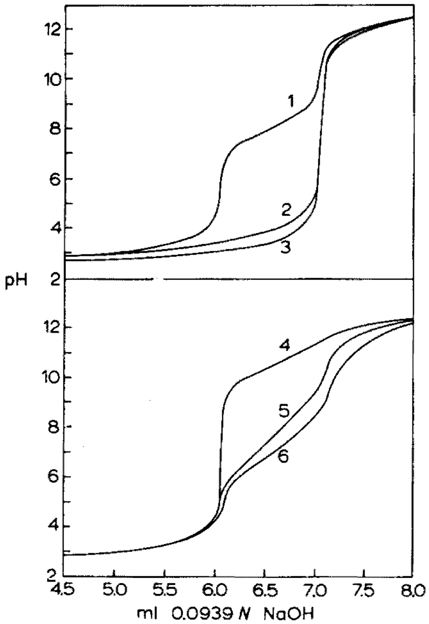


Fig. 2. Chelate titrations. (1) perchloric acid and TBPHA; (2) as 1 with $4.69 \cdot 10^{-5}$ moles zinc; (3) as 1 with $4.67 \cdot 10^{-5}$ moles nickel; (4) perchloric acid and BPHA; (5) as 4 with $4.67 \cdot 10^{-5}$ moles nickel; (6) as 4 with $4.69 \cdot 10^{-5}$ moles zinc.

Formation constants were determined by titrating mixtures of perchloric acid, ligand and metal ion with standard base. Typical titration curves are shown in Fig. 2. The formation constants were determined by plotting $\bar{n}/(1-\bar{n})R$ against $(2-\bar{n})R/(1-\bar{n})$ where $\bar{n}$ is the formation function and R is the reagent anion concentration; the slope and intercept of the straight line are equal to k_1k_2 and k_1 respectively. The results, calculated from titration curves of 2:1 mole ratios of reagent to metal, are shown in Table II.

TABLE II

FORMATION CONSTANTS IN 1:1 DIOXANE–WATER AT 25°

Metal	*Ligand*	*log k_1*	*log k_1k_2*
Mn(II)	BPHA	5.9	10.8
	TBPHA	5.2	9.7
Ni(II)	BPHA	7.0	12.5
	TBPHA	8.0	15.5
Cu(II)	BPHA	10.3	18.7
Zn(II)	BPHA	7.2	13.8
	TBPHA	8.2	15.4

No formation constants are reported for cobalt. Titration curves for 6:1 and 2:1 mole ratios of TBPHA and cobalt(II) suggest oxidation to cobalt(III). In the 6:1 titration there are two sharp breaks in the titration curve; the first break corresponds to the titration of perchloric acid plus 2 moles of proton per mole of cobalt and the second break corresponds to the titration of an additional 3 moles of proton. Since a total of 6 moles of proton should be ultimately titrated, 1 mole of proton has disappeared during reaction; previous experience[8] suggests that cobalt(II) is oxidized to cobalt(III) with 1 mole of hydrogen ion being lost in the oxidation process. The 2:1 mole ratio titration curves are explainable on this basis but magnetic measurements must be made to check this postulate. There was no evidence of oxidation from the BPHA–cobalt(II) titration curves but log k_1k_2 values calculated from the curves were higher (by more than one pK unit) than those for nickel–BPHA; this result is not in agreement with the normal stability order of oxygen–oxygen bidentate ligands[9] and a more thorough investigation of the reactions with cobalt is necessary.

The chelates of nickel and copper with TBPHA were so insoluble that they precipitated immediately on mixing; the 2:1 mole ratio solutions contained $5 \cdot 10^{-5}$ moles of metal ion, 10^{-4} moles of reagent, and $5 \cdot 10^{-4}$ moles of perchloric acid in 100 ml of 1:1 dioxane–water. It was possible to prevent precipitation by decreasing the concentrations and the formation constants for nickel with TBPHA could be calculated from the titration curves obtained at concentrations 1/20 the above. This was not possible for copper and no formation constants are reported for TBPHA–copper chelates; there is no doubt, however, that the values are higher than for the BPHA–copper chelates.

DISCUSSION

The substitution of sulphur for the carbonyl oxygen in BPHA considerably increases the reagent acidity even though sulphur is less electronegative than oxygen; the strong hydrogen bonding in BPHA[10] is probably responsible for its lesser acidity.

Despite the greater acidity, the metal chelates of TBPHA are generally more stable than those of BPHA; the exception of the manganese chelates may be attributed to its class (a) acceptor properties[6]. With both an oxygen and a sulphur donor atom, TBPHA combines some donor characteristics of each and reacts with a wider range of metal ions than BPHA.

The results suggest that TBPHA has definite potential as an analytical reagent. Formation constants of its metal chelates are generally higher than those of BPHA, precipitates are formed in more acid solutions, and the complexes, like BPHA, are readily extractable with chloroform. The greater acidity of TBPHA should permit the preparation of a stable ammonium salt so that aqueous reagent solutions are possible; this can be advantageous for gravimetric determinations. These characteristics, and its similarity to the proven BPHA, would recommend a more detailed investigation of the reactions and analytical potentialities of TBPHA; such a study is now in progress.

SUMMARY

Thiobenzoylphenylhydroxylamine has been prepared and its reactions with metal ions compared to those of its oxygen analogue, benzoylphenylhydroxylamine. Acid dissociation constants and a few formation constants in 1:1 dioxane–water are reported. The thio compound is more reactive, more acidic, and forms chelates of generally greater stability.

RÉSUMÉ

On a préparé la thiobenzoylphénylhydroxylamine; ses réactions avec des ions métalliques ont été comparées à celles de la benzoylphénylhydroxylamine. On donne les constantes de dissociation acides et quelques constantes de formation dans le mélange eau–dioxane 1:1. Le thiocomposé est plus réactif, plus acide et forme des chélates généralement de plus grande stabilité.

ZUSAMMENFASSUNG

Es wurde Thiobenzoylphenylhydroxylamin hergestellt und seine Reaktionen mit Metallionen mit denen von Benzoylphenylhydroxylamin verglichen. Es werden die Säuredissoziationskonstanten und einige Bildungskonstanten in Dioxan–Wasser (1:1) angegeben. Die Thioverbindung ist reaktionsfähiger, saurer und bildet Chelate mit allgemein grösserer Stabilität.

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DETERMINATION OF ZIRCONIUM, THORIUM AND SCANDIUM WITH 2,5-DIHYDROXY-1,4-BENZOQUINONE

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The rare earths, with their high neutron cross-section are inadmissible as impurities in nuclear fuels, such as thorium, and in materials for construction of nuclear reactors, such as zirconium; the separation of thorium is also an important step in purification procedures for the rare earths. 2,5-Dihydroxy-1,4-benzoquinone has been used for the gravimetric determination of thorium in the presence of lanthanons and uranium[1], of zirconium in the presence of a large number of cations including titanium, lanthanons and uranium[1,2], and of lanthanons, uranium and titanium from pure solutions[3]; it has also been proposed as a reagent for the qualitative detection of scandium[4]. The present work has shown that, with 2,5-dihydroxy-1,4-benzoquinone, zirconium can be separated from 10 times its amount of scandium in 1 *N* hydrochloric acid and thorium can be separated from uranium, yttrium, lanthanum, cerium(IV) and scandium at pH 0.5. Scandium can be determined in the pH range 1.4–2.0 and is separated from equivalent amounts of lanthanum at pH 1.5; small amounts of yttrium (>0.5 mg Y_2O_3) interfere.

EXPERIMENTAL

Reagents

Standard solutions of scandium, thorium and zirconium were prepared from spectrographically pure materials obtained from Johnson, Matthey & Co., England.

2,5-Dihydroxy-1,4-benzoquinone was prepared by the method of JONES AND SHONLE[5]. A saturated (room temperature) solution of this reagent in water was used for the precipitation of metal ions.

Determination of zirconium

The zirconium solution was acidified with hydrochloric acid and 150 ml of reagent solution added; the final volume of the solution was never more than 200 ml. The solution was boiled for 5 min, cooled to room temperature and one drop of anticreep solution (Schleicher & Schüll) added. The precipitate was filtered through S & S 589 blue ribbon filter paper and washed with 150 ml of reagent solution of the same acidity as the final experimental solution, containing one drop of S & S ashless anticreep. The filter paper with the precipitate was dried and ignited at 800° to constant weight.

The results in Table I show that precipitation is quantitative in 1.5 *N* hydrochloric acid and that large amounts of scandium do not interfere.

Determination of thorium

The thorium solution was adjusted to pH 0.5 and 150 ml of reagent solution (pH adjusted to 0.5) added; the final volume of the solution was never more than 200 ml. The remainder of the procedure was as for zirconium, the precipitate being washed with 150 ml of reagent solution (pH 0.5).

TABLE I

DETERMINATION OF ZIRCONIUM

ZrO_2 taken (mg)	ZrO_2 found (mg)	Normality in HCl	Foreign ion added
11.03	11.00	1	
11.03	11.00	1.5	
11.03	10.50	2	
11.03	10.07	3	
11.03	2.95	4	
11.03	No ppt.	5	
11.03	11.00	1	55 mg Sc_2O_3
11.03	11.10	1	110 mg Sc_2O_3

TABLE II

DETERMINATION OF THORIUM

ThO_2 taken (mg)	ThO_2 found (mg)	Foreign ion added
9.90	9.90	
9.90	9.95	102 mg U_3O_8 (added as U(VI))
9.90	9.90	52 mg CeO_2 (added as Ce(IV))
9.90	10.30	101 mg CeO_2 (added as Ce(IV))
9.90	9.90	51 mg La_2O_3
9.90	9.90	101 mg La_2O_3
9.90	9.90	51 mg Y_2O_3
9.90	10.00	101 mg Y_2O_3
9.90	9.95	51 mg Sc_2O_3
9.90	9.20	101 mg Sc_2O_3

The results in Table II show that 2,5-dihydroxy-1,4-benzoquinone quantitatively separates thorium from uranium(VI), cerium(IV), lanthanum, yttrium and scandium at pH 0.5. Precipitation of thorium was incomplete at higher acidities; for example 9.50 mg, 8.38 mg and 3.05 mg of thorium oxide were recovered when 9.90 mg was taken for analysis in 0.5, 0.7 and 1.0 *N* hydrochloric acid. The low result in the presence of 100 mg of scandium oxide was due to the formation of a water-soluble reddish-purple complex of scandium which ties up reagent so that there is insufficient excess for complete precipitation of thorium.

Determination of scandium

The pH of the scandium solution was adjusted between 1.4 and 2.0, and 85 ml of reagent solution (suitable pH) added; the final volume of the solution was approximately 100 ml. The remainder of the procedure was as for zirconium, the precipitate being washed with 100 ml of reagent solution adjusted to the same pH as the experimental solution.

The results are shown in Table III.

The scandium solutions were standardised by both the oxine method[6] (scandium oxide taken, 10.94 mg; found, 10.90 mg) and the mandelic acid method[7] (scandium oxide taken, 10.94 mg; found, 10.70 mg). It is well known that traces of scandium often remain unprecipitated due to the presence of hydrolysed species[8] and that best results have been obtained, in pure scandium solutions, with oxine. Table III shows that similar results are obtained with 2,5-dihydroxy-1,4-benzoquinone; the results are usually a little lower than those obtained with oxine but higher than those obtained by the mandelic acid procedure. At least 3.5 moles of reagent per g-atom of scandium are required for quantitative precipitation. Increases in the volume of experimental solution or of wash solution beyond 100 ml result in solubility losses. Lanthanum does not interfere in the determination of small quantities of scandium when present in equal amounts but yttrium with an ionic radius closer to that of scandium is significantly co-precipitated. Tartrate interferes in the determination of scandium.

TABLE III

DETERMINATION OF SCANDIUM

Sc_2O_3 *taken (mg)*	Sc_2O_3 *found (mg)*	*pH*	*Foreign ion added*
10.94	9.60	1.00	
10.94	10.32	1.35	
10.94	10.75	1.40	
10.94	10.85	1.45	
10.94	10.80	1.55	
10.94	10.70	1.65	
10.94	10.80	1.75	
10.94	10.90	1.85	
10.94	10.85	1.90	
10.94	10.90	2.00	
10.94	10.60	2.10	
10.94	8.00	2.50	
5.23	5.10	1.50	
5.23	5.10	1.50	1.1 mg La_2O_3
5.23	5.20	1.50	2.3 mg La_2O_3
5.23	5.15	1.50	5.7 mg La_2O_3
5.23	5.85	1.50	11.4 mg La_2O_3
5.23	5.30	1.50	0.6 mg Y_2O_3
5.23	5.80	1.50	2.3 mg Y_2O_3
5.23	4.35	1.60	1.0 g tartaric acid

The composition of the scandium complex with 2,5-dihydroxy-1,4-benzoquinone was found to be variable; three typical results for scandium: carbon ratios were 1:9.4, 1:8.5 and 1:11.5. A thermogravimetric study of the complex showed that decomposition occurs rapidly above 200° to give rise to oxide at 500°; the complex can therefore be heated to any suitable temperature above 500° to give Sc_2O_3.

Effect of using solid reagent

Zirconium can be quantitatively precipitated in 1–5 *N* hydrochloric acid using 0.5 g of solid reagent for precipitation[1,9]; in the present work, with a saturated aqueous solution of reagent, precipitation was incomplete at acidities greater than 1.5 *N*. For thorium, quantitative precipitation is reported from 1–2 *N* hydrochloric acid using 0.5 g of solid reagent[1], but with aqueous reagent solution, precipitation has now been found not to be quantitative below pH 0.5. Similar results were found with scandium in the present work; scandium is quantitatively precipitated at pH 0.7 using 0.5 g of solid reagent, but with aqueous reagent solution, precipitation was not quantitative below pH 1.4. This difference in behaviour is at least partly due to the large increase in the solubility of reagent with temperature; a saturated solution of 2,5-dihydroxy-1,4-benzoquinone contains 0.13 g per 100 ml at room temperature (22°) and 1.01 g at 100°. Similar results have been reported by KLINGENBERG *et al.*[10] when benzilic acid was used as a reagent for zirconium; increase in concentration of the reagent was found to counteract the effect of increased acidity on the precipitation of the metal.

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SUMMARY

Zirconium is quantitatively precipitated by 2,5-dihydroxy-1,4-benzoquinone and is separated from scandium in 1 *N* hydrochloric acid solution. Thorium is separated at pH 0.5 from uranium(VI), cerium(IV), lanthanum, yttrium and scandium. Scandium is quantitatively precipitated by this reagent in the pH range 1.4–2.0 and at pH 1.5 equivalent amounts of lanthanum do not interfere; small amounts of yttrium cause interference.

RÉSUMÉ

Le zirconium est précipité quantitativement par la 2,5-dihydroxy-1,4-benzoquinone et séparé du scandium en milieu acide chlorhydrique 1 *N*. Le thorium est séparé au pH 0.5 d'avec uranium(VI), cérium(IV), lanthane, yttrium et scandium. Le scandium est précipité quantitativement au pH 1.4 à 2.0. Au pH 1.5 des quantités équivalentes de lanthane ne gênent pas. De faibles quantités d'yttrium gênent.

ZUSAMMENFASSUNG

Zirkonium wird quantitativ durch 2,5-Dihydroxy-1,4-benzochinon gefällt und in 1 *N* salzsaurer Lösung vom Scandium abgetrennt. Thorium wird beim pH 0.5 von Uran(VI), Cer(IV), Lanthan, Yttrium und Scandium getrennt. Scandium wird im pH-Bereich von 1.4 bis 2.0 quantitativ gefällt. Beim pH 1.5 stören äquivalente Mengen von Lanthan nicht; kleine Mengen Yttrium verursachen Störungen.

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SIMULTANEOUS DETERMINATION OF PHOSPHORUS, ARSENIC AND GERMANIUM AND THE SEPARATION OF SILICON AND ARSENIC BY SOLVENT EXTRACTION

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Methods have been reported for the simultaneous determination of silicon and phosphorus[1], phosphorus and arsenic[2] and arsenic, phosphorus and silicon[3] in the presence of each other. It was decided to extend these studies to include germanium since, like silicon, phosphorus and arsenic, germanium reacts with ammonium molybdate in acid solutions to form the yellow germanomolybdic acid which is reduced to the heteropoly blue by benzidine[4] or iron(II) ammonium sulphate[5,6]. In the present investigation it was found that accurate and reproducible results for germanium determination were obtained when the germanomolybdic acid was reduced with 1-amino-2-naphthol-4-sulphonic acid in the presence of perchloric acid, and this method of determination of germanium has been used throughout the present studies.

Previous studies[2,7] on the separation of phosphorus, silicon, arsenic and germanium showed that phosphorus can be separated from mixtures of the 4 elements as the phosphomolybdic acid by selective solvent extraction with isobutyl acetate at pH 1.0–0.8. It can then be determined directly in the solvent phase after reduction of the phosphomolybdic acid with 1-amino-2-naphthol-4-sulphonic acid in the presence of perchloric acid[2]. Preliminary investigations on the separation of arsenic, germanium and silicon in the remaining aqueous phase after phosphomolybdic acid was removed, showed that if the pH of the remaining mixed heteropoly acids in the aqueous phase was lowered to about 0.4, then germanomolybdic acid could be completely extracted by 2-ethylhexanol (isooctyl alcohol); the silicomolybdic acid was only partially extracted while the arsenomolybdic acid remained unextracted under these conditions. Furthermore, if the pH of the mixed heteropoly acids of silicon, arsenic and germanium was lowered still further to about pH 0.2, then both silico- and germanomolybdic acid were completely extracted by 2-ethylhexanol, but arsenomolybdic acid again remained unextracted in the aqueous phase. These preliminary tests also showed that the extracted silico- and germanomolybdic acid in the solvent phase were readily re-extracted by water so that the determination of both silicon and germanium in an aqueous medium as their heteropoly blue became possible once they had been separated from arsenic.

This paper describes a method for the simultaneous determination of arsenic, phosphorus and germanium by selective solvent extraction of, firstly, phosphomolybdic acid with isobutyl acetate at pH 1.0–0.8 and its direct reduction in the solvent

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phase, then the selective solvent extraction of germanomolybdic acid in the remaining aqueous phase by 2-ethylhexanol at pH 0.4 and its re-extraction into water followed by reduction with 1-amino-2-naphthol-4-sulphonic acid in the presence of perchloric acid, and the determination of arsenic in the remaining aqueous phase after reduction of the unextracted arsenomolybdic acid with hydrazine sulphate. A method is also described for the simultaneous determination of arsenic and silicon by selective solvent extraction of silicomolybdic acid by 2-ethylhexanol at pH 0.2 in the presence of arsenomolybdic acid, subsequent re-extraction of the silicomolybdic acid into water and its reduction with 1-amino-2-naphthol-4-sulphonic acid. Arsenic in the remaining aqueous phase was determined as the heteropoly blue after reduction with hydrazine sulphate.

EXPERIMENTAL

Reagents and apparatus

All reagents were of AnalaR grade. Distilled water was used throughout. All reactions were carried out at room temperature.

Phosphate and arsenate solutions. Prepare stock solutions of phosphorus or arsenic by dissolving 0.100 g of disodium hydrogen phosphate (anhydrous) or disodium hydrogen arsenate (heptahydrate) in water and diluting to 100 ml. Prepare further solutions from these by dilution.

Silicate solutions. Prepare solutions of soluble silica by fusing 0.100 g of pure precipitated silica with about 1.5 g of anhydrous sodium carbonate in a platinum crucible, and dissolving the melt in 100 ml of water in a polythene beaker. Prepare further solutions of soluble silica from it by dilution.

Germanate solutions. Prepare stock solutions of germanium by fusing 0.100 g of germanium dioxide with about 0.5 g of anhydrous sodium carbonate in a platinum crucible and dissolving the melt in 100 ml of water in a polythene beaker. Prepare further solutions from it by dilution.

1-Amino-2-naphthol-4-sulphonic acid reagent. Dissolve 1-amino-2-naphthol-4-sulphonic acid (0.20 g), sodium sulphite heptahydrate (2.4 g) and sodium metabisulphite (12.0 g) in water and dilute to 100 ml. Store in a dark bottle and prepare freshly weekly.

An EEL Spectra colorimeter was used.

Procedures

Determination of phosphorus, arsenic and germanium in the presence of each other. Pipette 2.00-ml portions of the test solution into a 50-ml separating funnel, add 2.0 ml of 2 *N* hydrochloric acid and mix. Add 2.0 ml of 5% (w/v) ammonium molybdate solution, mix the contents of the funnel again and allow to stand for 15 min for the complete formation of the phospho-, arseno- and germanomolybdic acid complexes. Then extract with 10 ml of isobutyl acetate by shaking for 1 min. Withdraw the aqueous layer containing the unextracted arseno- and germanomolybdic acid complexes into another separating funnel. Reduce the phosphomolybdic acid in the solvent phase by the procedure already reported[2] in order to determine phosphorus.

Treat the remaining aqueous phase containing the arseno- and germanomolybdic acid with 1.0 ml of 60% perchloric acid (s.g. 1.54) to adjust the pH to 0.4. Then extract with 10.0 ml of 2-ethylhexanol (isooctyl alcohol) by shaking for 30 sec. After the layers have separated, withdraw the aqueous phase containing the unextracted arsenomolybdic acid and reduce with 1.0 ml of 1% (w/v) hydrazine sulphate in the presence of 1.0 ml of the 60% perchloric acid. Leave for 1 h for maximum colour development, and measure the arsenoheteropoly blue at 690 mμ (deep red filter) against a similarly extracted blank.

Treat the iosoctyl alcohol layer containing the germanomolybdic acid with 6.0 ml of water and re-extract the germanomolybdic acid into the aqueous phase by shaking for 30 sec. After the layers have separated, withdraw the aqueous phase, treat with 1.0 ml of the 60% perchloric acid and 1.0 ml of the aminonaphtholsulfonic acid reagent. After mixing, leave for 1 h for maximum colour development, and then measure the germanium heteropoly blue at 690 mμ against a similarly treated blank.

Determination of arsenic and silicon by solvent extraction. Pipette a 2.0-ml portion of the test solution into a separating funnel followed by 2.0 ml of 2 *N* hydrochloric acid, and mix the contents of the funnel. Add 2.0 ml of 5% (w/v) ammonium molybdate solution, mix again and stand for 15 min for complete formation of the arseno- and silicomolybdic acid. At the end of this period add 2.0 ml of the 60% perchloric acid and mix again. The pH of this solution should be 0.2. Add 10.0 ml of isooctyl alcohol and extract the silicomolybdic acid by shaking vigorously for 30 sec. After the layers have separated withdraw the aqueous phase containing the arsenomolybdic acid and reduce with 1.0 ml of 1% (w/v) hydrazine sulphate without the addition of more perchloric acid. Mix, leave for 1 h for maximum colour development and measure the arsenoheteropoly blue at 690 mμ.

Treat the solvent phase containing the silicomolybdic acid with 6.0 ml of water and re-extract into this aqueous phase by vigorous shaking for 30 sec. Allow the layers to separate, withdraw the aqueous phase now containing the silicomolybdic acid and treat with 0.5 ml of the aminonaphtholsulphonic acid. After mixing, leave the solution for 40 min for maximum colour development and measure the silicoheteropoly blue at 690 mμ.

RESULTS AND DISCUSSION

The results of Table I show that over a wide range of concentration arsenomolybdic acid is not extracted by isooctyl alcohol when 1 ml of perchloric acid is added to the arsenomolybdic acid before extraction (pH 0.4) whereas the germanomolybdic acid is virtually completely extracted under these conditions. Silicomolybdic acid

TABLE I

EXTRACTION OF ARSENO- AND GERMANOMOLYBDATE ACIDS AT pH 0.4 BY 2-ETHYLHEXANOL

As in aq. phase before extn. (μg)	*As in aq. phase after extn. (μg)*	*Ge in aq. phase before extn. (μg)*	*Ge in aq. phase after extn. (μg)*
25	25	20	0
50	50	40	0
100	100	60	1
200	198	80	1
300	300	100	2

is only partially extracted under the same conditions but is completely extracted along with germanomolybdic acid when 2.0 ml of perchloric acid are added to the heteropoly acids (pH 0.2) before extraction with isooctyl alcohol. Arsenomolybdic acid is not extracted under these conditions (Table II). Further tests showed that both germano- and silicomolybdic acid complexes are completely extracted by isooctyl alcohol in the presence of arsenomolybdic acid when the mixed heteropoly acids are treated with 2.0 ml of concentrated hydrochloric acid, indicating that the extraction of germano- and silicomolybdic acid and the non-extraction of arsenomolybdic acid by isooctyl alcohol is pH dependent and not the effect of the perchlorate ion.

TABLE II

EXTRACTION OF ARSENO-, GERMANO- AND SILICOMOLYBDIC ACIDS BY 2-ETHYLHEXANOL AT pH 0.2

As in aq. phase before extn. (μg)	*As found in aq. phase after extn. (μg)*	*Ge in aq. phase before extn. (μg)*	*Ge found in aq. phase after extn. (μg)*	*Si in aq. phase before extn. (μg)*	*Si found in aq. phase after extn. (μg)*
25	25	20	0	10	0
50	50	40	0	20	0
100	98	60	0	40	0
200	200	80	1	60	2
300	300	100	1	80	2

TABLE III

RECOVERY OF ADDED ARSENIC AND GERMANIUM IN MIXTURES OF EACH OTHER

Mixtures	*As added (μg)*	*As found (μg)*	*Ge added (μg)*	*Ge found (μg)*
A	300	295	10	10
B	200	200	40	40
C	300	300	70	71
D	25	28	90	88
E	100	98	20	19
F	50	55	50	49

TABLE IV

SIMULTANEOUS DETERMINATION OF ARSENIC AND SILICON IN THE PRESENCE OF EACH OTHER

Mixtures	*As present (μg)*	*As found (μg)*	*Si present (μg)*	*Si found (μg)*
A	300	300	80	81
B	200	202	50	49
C	100	100	70	71
D	50	52	10	10
E	25	25	20	20
F	300	298	10	10

Table III records the recovery of added arsenic and germanium in mixtures. These results show that the proposed method of separation of germanium in the presence of arsenic by the selective solvent extraction of germanomolybdic acid at pH 0.4 by isooctyl alcohol, and the subsequent re-extraction of the germanomolybdic acid from the solvent phase into an aqueous phase is efficient. The results in Table IV

TABLE V

SIMULTANEOUS DETERMINATION OF PHOSPHORUS, ARSENIC AND GERMANIUM IN THE PRESENCE OF EACH OTHER

Mixtures	*P present (µg)*	*P found (µg)*	*As present (µg)*	*As found (µg)*	*Ge present (µg)*	*Ge found (µg)*
A	25	25	200	195	20	20
B	250	250	50	50	40	38
C	100	100	300	295	80	79
D	100	100	100	98	10	13
E	200	198	25	30	70	68
F	50	55	300	300	100	100

demonstrate that silicon is effectively separated from arsenic by solvent extraction of the silicomolybdic acid when the pH of the heteropoly mixture is less than 0.4; the silicomolybdic acid in the solvent phase is efficiently re-extracted by water, thus allowing a simple, accurate and reliable method for the simultaneous determination of arsenic and silicon.

To complete this study, phosphorus, arsenic and germanium were determined in the presence of each other in recovery experiments using isobutyl acetate to separate the phosphomolybdic acid at pH 1.0–0.8 and isooctyl alcohol to separate the germanomolybdic acid at about pH 0.4 from arsenomolybdic acid. The results recorded in Table V demonstrate that this procedure allows excellent recoveries of phosphorus, arsenic and germanium over a wide range of concentrations.

In a previous communication[3], a method was reported for the simultaneous determination of arsenic, phosphorus and silicon based on the solvent extraction of phosphomolybdic acid by isobutyl acetate at pH 1.0–0.8, differential formation of phospho- and arsenomolybdic acid when perchloric acid was added before the addition of ammonium molybdate, and selective destruction of phospho- and arsenomolybdic acid complexes by citric acid in the presence of silicomolybdic acid. By means of the procedure described in this paper for the simultaneous determination of arsenic and silicon by selective solvent extraction of silicomolybdic acid at pH 0.2, together with the prior extraction of phosphomolybdic acid with isobutyl acetate at pH 1.0–0.8, a method is obtained for the simultaneous determination of arsenic, phosphorus and silicon. The method is identical to that reported here for the simultaneous determination of phosphorus, arsenic and germanium, except that silicomolybdic acid is extracted by isooctyl alcohol at pH 0.2.

Since both silico- and germanomolybdic acid are extracted by isooctyl alcohol below pH 0.8, the former only partially at pH 0.4 but completely at pH 0.2, then before a method can be found for the simultaneous determination of arsenic, phosphorus, germanium and silicon in mixtures of each other, silico- and germanomolybdic acid must firstly be separated from each other. Work is presently being undertaken to effect this separation at both the heteropoly acid stage and the heteropoly blue stage by solvent extraction.

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SUMMARY

A simple, rapid, accurate and reliable method for the simultaneous determination of phosphorus, arsenic and germanium as their heteropoly blue complexes is reported. The method involves selective extraction of phosphomolybdic acid at pH 1.0–0.8, and selective extraction of germanomolybdic acid by isooctyl alcohol at pH 0.4, followed by back-extraction of the germanomolybdic acid with water, and reduction of arsenomolybdic acid in the remaining aqueous phase. A rapid and reliable method is also reported for the simultaneous determination of arsenic and silicon by selective extraction of silicomolybdic acid with isooctyl alcohol at pH < 0.4 and the back-extraction of the silicomolybdic acid with water; arsenic is determined in the remaining aqueous phase. The procedure can be applied to the simultaneous determination of phosphorus, arsenic and silicon.

RÉSUMÉ

Une méthode simple, rapide, précise est décrite pour le dosage simultané du phosphore, de l'arsenic et du germanium, sous forme de leurs hétérocomplexes bleus. On procède à une extraction sélective de l'acide phosphomolybdique, au pH 1.0–0.8, et à une extraction sélective de l'acide germanomolybdique par l'alcool iso-octylique, au pH 0.4, enfin à une extraction en retour de l'acide germanomolybdique avec l'eau et réduction de l'acide arsénomolybdique dans la phase aqueuse résultante. Une méthode rapide est également décrite pour le dosage simultané de l'arsenic et du silicium par extraction sélective de l'acide silicomolybdique avec l'alcool iso-octylique à un pH < 0.4 et extraction en retour de l'acide silicomolybdique, dans l'eau.

ZUSAMMENFASSUNG

Über eine einfache, schnelle, genaue und zuverlässige Methode zur gleichzeitigen Bestimmung von Phosphor, Arsen und Germanium als Heteropolysäuren des Molybdäns wird berichtet. Die Methode umfasst die selektive Extraktion der Molybdatophosphorsäure beim pH 1.0–0.8 und die selektive Extraktion der Molybdatogermaniumsäure mit Isooctylalkohol beim pH 0.4 und nachfolgender Rückextraktion der Molybdatogermaniumsäure mit Wasser. Die in der wässrigen Phase zurückbleibende Molybdatoarsensäure wird reduziert. Ferner wird eine schnelle und zuverlässige Methode zur gleichzeitigen Bestimmung von Arsen und Silicium durch selektive Extraktion der Molybdatokieselsäure mit Wasser beschrieben. Arsen wird in der zurückbleibenden wässrigen Phase bestimmt. Das Verfahren kann zur gleichzeitigen Bestimmung von Phosphor, Arsen und Silicium verwendet werden.

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INTERNAL ELECTROLYSIS FOR THE SEPARATION OF IONS

PART I. SEPARATION AND DETERMINATION OF SILVER, BISMUTH, COPPER AND CADMIUM

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ULLGREN's demonstration[1] in 1868 that copper could be determined electrogravimetrically by displacement reactions led to the development of electroanalytical determination of metals by depositing them in a galvanic cell utilising the electromotive force of the cell itself[2-4]. To decrease the internal resistance to a minimum for the effective and complete deposition of metals, with a very small potential difference, LURIE AND GINSBERG[5] suggested the use of a simple short-circuited cell consisting of an ordinary platinum gauze cathode and a bent plate of a base metal connected securely with a copper wire. This simple technique has been in use for quite a number of years.

To prevent cementation and to obtain a good adherent deposit on the cathode the anode must be so chosen that the potential difference between it and the metal to be deposited is not large. Thus for the complete deposition of silver, lead or copper is preferred to a zinc anode, but if the silver solution contains lead ion also, neither zinc nor cadmium can be used because the potentials of both these anodes are sufficiently negative to reduce lead ion to the metal. In such a case, an anode of copper or bismuth having a potential between that of silver and lead can be used. Because of these limitations, anodes used are of the same metal as the metal salt of the anolyte[6-10].

Recently we have studied the effectiveness of this simple assembly for the separation and determination of ions and found that by the proper control of conditions, that is, by the adjustment of pH and with the use of proper complexing agents, it is possible to separate electro-depositable ions from each other and from many other ions with only one anode. In this paper the use of zinc as anode is reported for the determination and separation of copper, silver, bismuth and cadmium from each other and from other ions.

Thus, with EDTA as the masking agent, copper was determined after its separation from beryllium, zinc, manganese, cobalt, nickel, tin(IV), iron, aluminium, lanthanum, chromium, gallium, indium, thallium(I), zirconium, thorium, tellurium(IV), tantalum(V), vanadium, alkali and alkaline earth metals at pH 2.5–3, and from cadmium, lead, arsenate, titanium, uranyl and tungstate ions at pH 8.5–9.0. Typical results are shown in Table I. For the separation of copper from silver or bismuth, the latter was first deposited at pH about 9.0, in presence of EDTA and cyanide, and from the resultant solution copper was deposited after demasking its cyanide complex with formaldehyde or after decomposing the complex by fuming with sulphuric acid.

TABLE I

DETERMINATION AND SEPARATION OF COPPER FROM ALL OTHER IONS

pH	*Time (h)*	*Cu taken (mg)*	*Cu found (mg)*
3.0	6	2.75	2.72
3.0	6	1.37	1.36
3.0	6	2.85	2.84
8.5	24	2.85	2.83
8.5	24	1.37	1.35
8.5	24	2.75	2.73

TABLE II

DETERMINATION AND SEPARATION OF SILVER FROM ALL OTHER IONS

pH	*Time (h)*	*Ag taken (mg)*	*Ag found (mg)*
9.0	12	2.0	1.98
9.0	12	1.0	1.0
9.0	12	3.0	2.98
9.0	12	2.0	1.96

TABLE III

DETERMINATION AND SEPARATION OF BISMUTH FROM ALL OTHER IONS

pH	*Time (h)*	*Bi taken (mg)*	*Bi found (mg)*
3.0	6	1.93	1.92
3.0	6	1.93	1.90
3.0	6	3.86	3.86
8.5	6	3.86	3.85
8.5	6	2.89	2.88
8.5	6	2.89	2.89

TABLE IV

DETERMINATION AND SEPARATION OF CADMIUM FROM ALL OTHER IONS

pH	*Time (h)*	*Cd taken (mg)*	*Cd found (mg)*
4.0	6	2.66	2.63
4.0	6	1.33	1.32
5.0	6	2.66	2.65
5.0	6	1.33	1.33

Silver was determined by deposition at pH 8.5–9.0, in presence of a mixture of EDTA and cyanide, which kept all the ions mentioned above including copper and molybdate in solution. Results are shown in Table II. Bismuth behaved exactly like copper in presence of EDTA at pH 2.5–3.0. However, at pH 8.5–9.0 in presence of

EDTA and cyanide, bismuth behaved like silver and so could be determined in presence of all the ions including copper and molybdate, except silver. Representative results are shown in Table III.

Cadmium was deposited at pH 4.0–5.0 in presence of tartrate and cyanide, and could be separated from all those ions in presence of which copper could be determined, including titanium and tungstate, but excluding tin(IV) and tellurium(IV). Results are shown in Table IV. For separation from copper, the latter was deposited at pH 9.0 in presence of EDTA, and then cadmium was deposited by lowering the pH to 4.0. Similarly for the separation from silver or bismuth, the latter was deposited from the solution containing both EDTA and cyanide at pH 9.0; cadmium was then separated at pH 4, after removing the cyanide by fuming with sulphuric acid, or by masking with formaldehyde. Thus from a mixture of copper and cadmium or of cadmium and silver or bismuth, the metals could be easily deposited separately and determined. From a mixture of lead and cadmium, with simple adjustment of pH, lead was first deposited and determined at pH 2.5; subsequently cadmium was determined at pH 4.

For the determination of silver in presence of bismuth, the zinc anode was of no use, because both metals were reduced, but with a copper anode and EDTA as the complexing agent, silver was separated first at pH 9.0. From the resulting solution and at the same pH, bismuth was deposited after copper had been masked with an excess of cyanide.

Although many complexing agents under different pH conditions were examined for the separation of ions, only those conditions which helped towards a single separation from a large number of ions are described in this paper.

EXPERIMENTAL

Apparatus

pH measurements were made with a Cambridge pH meter. For internal electrolysis, the assembly consisted of a platinum gauze cathode and a zinc plate anode, similar to that suggested by LURIE AND GINSBERG[5].

Solutions

In all studies, chemicals of highest purity were used. A standard solution of copper as sulphate was prepared from a weighed amount of electrolytic copper. This was dissolved in nitric acid, fumed with concentrated sulphuric acid and made up to a volume of 250 ml with water. The solution was standardized by internal[5] and external[11] electrolysis.

Standard solutions of silver, bismuth and cadmium ions were prepared by dissolving their nitrates separately in water with a few drops of nitric acid to prevent hydrolysis. Each of these solutions was then diluted with water to 500 ml. The respective solutions were standardized as follows: cadmium by compleximetric titration[12], bismuth as oxide[13], and silver as chloride[13].

Solutions of other ions were prepared from their chlorides, nitrates or sulphates, and standardized by the standard procedures.

Solutions (10%) of sodium potassium tartrate, EDTA (di-sodium salt) and potassium cyanide were prepared and used as complexing agents.

General procedure

The solution of the ion to be determined was mixed with the solutions of all the other ions mentioned above (each 8.0–12.0 mg) in a tall beaker. Solutions of EDTA and/or other complexing agents, each at least 10 times the total quantity of the ions present, were then added. When only one or two of the interfering ions was present the weight of interfering ion taken was 50–100 times the weight of the ion to be deposited. The pH of the solution was adjusted to the proper value after dilution to 250–300 ml.

The electrode assembly with the previously weighed platinum gauze cathode was then placed into the solution. When the deposition was complete, the electrodes were removed from the beaker, washed over the beaker with a jet of water from a washing bottle and disconnected. The cathode was removed and again washed with alcohol, dried at 80–90° and weighed. The difference in weight of the cathode gave the weight of the ion deposited.

Separation of cadmium and lead from each other

To the solution containing cadmium and lead was added, as usual, an excess of EDTA. The pH of the solution after dilution to 250 ml was adjusted to 2.5. On electrolysis for 6 h, lead was completely deposited and removed from the solution as described under the General procedure. From the solution cadmium was next deposited quantitatively on electrolysis for about 12 h at pH 4.0. Results are shown in Table V.

TABLE V

SEPARATION OF CADMIUM AND LEAD FROM EACH OTHER

Pb taken (mg)	*Pb found (mg)*	*Cd taken (mg)*	*Cd found (mg)*
2.64	2.64	1.33	1.34
1.32	1.32	2.66	2.64
1.32	1.32	1.33	1.31

Separation of silver and bismuth from each other

A solution of bismuth and silver was treated with EDTA (at least 10 times the weight of the combined ions was added) and made distinctly ammoniacal; the pH was adjusted to 9.0 after dilution to 250 ml. From this solution, silver was deposited, washed, dried and weighed by following the General procedure, but with the use of a copper anode in place of zinc. During this operation it was observed that the addition of a few crystals of copper nitrate beforehand hastened the rate of silver deposition.

To the residual solution was then added an excess of cyanide to mask completely the effect of copper and with the help of the Pt–Zn assembly, bismuth was deposited at pH 9.0. Results are given in Table VI.

Separation of silver, copper, cadmium and bismuth from each other

Ten-fold excesses of the EDTA and cyanide solutions were added to the solution containing silver, copper, cadmium and bismuth, which was then diluted to 250 ml. After the adjustment of the pH to 9.0, the electrode assembly with the zinc anode was placed in the solution. Both silver and bismuth were thus removed by deposition on the cathode. The well-washed deposit of silver and bismuth was then dissolved in nitric acid and diluted; from this solution silver and bismuth were separately deposited and determined as described above.

The residual solution, which contained both copper and cadmium was boiled with sulphuric acid and fumed to remove the cyanide, or the cyanide was masked by addition of an excess of formaldehyde. From this solution, diluted to 250 ml, copper was deposited at pH 9.0 with the zinc anode; cadmium was then deposited from the same solution with the same anode at pH 4.0. Thus copper and cadmium were separated and determined. Results for the entire sequence are shown in Table VII.

TABLE VI

SEPARATION OF SILVER AND BISMUTH FROM EACH OTHER

pH	*Time (h)*	*Ag taken (mg)*	*Ag found (mg)*	*Bi taken (mg)*	*Bi found (mg)*
9.0	6	1.0	1.0	1.93	1.93
9.0	6	2.0	1.99	1.93	1.92
9.0	6	3.0	2.98	0.96	0.97

TABLE VII

SEPARATION OF SILVER, BISMUTH, COPPER AND CADMIUM FROM EACH OTHER

Taken (mg)				*Total deposit*	*Found (mg)*			
Ag	*Bi*	*Cu*	*Cd*	*Ag + Bi (mg)*	*Ag*	*Bi*	*Cu*	*Cd*
2.0	1.93	2.14	2.66	3.92	1.99	1.91	2.14	2.64
1.0	0.96	2.14	2.66	1.96	1.00	0.97	2.12	2.65
1.0	1.93	1.07	1.33	2.93	1.00	1.92	1.05	1.33

SUMMARY

The technique of internal electrolysis is recommended for the separation of ions. By proper control of the conditions, *i.e.* by adjustment of pH and by addition of complexing agents, it is possible to separate silver, bismuth, copper and cadmium from each other and from many other ions.

RÉSUMÉ

L'électrolyse interne est recommandée pour la séparation d'ions. On a pu séparer ainsi, par contrôle du pH et addition de complexants, argent, bismuth, cuivre, cadmium, les uns des autres et d'avec de nombreux autres ions.

ZUSAMMENFASSUNG

Die Technik der inneren Elektrolyse wird für die Trennung von Ionen empfohlen. Durch genaue Kontrolle der Bedingungen, wie z.B. des pH-Werts, und durch

Zugabe von komplexbildenden Reagenzien ist es möglich, Silber, Wismut, Kupfer und Cadmium voneinander und von vielen anderen Ionen zu trennen.

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COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN SELENIUM(IV) AND 1,1'-DIANTHRIMIDE

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In a previous paper[1] the spectrophotometric determination of selenium as selenium(IV) with 1,1'-dianthrimide was described. This paper also contained the results of preliminary studies of the complex formation, which indicated the presence of a 1:1 complex. The present paper describes a closer study of the complex formation.

EXPERIMENTAL

Instruments and equipment

The extinction measurements were made with a Beckman DB recording spectrophotometer, a Zeiss spectrophotometer PMQ II and 1- and 4-cm cells of glass and silica.

All solutions were prepared in 50-ml bottles (Jena Geräteglas) with ground-glass stoppers; these were heated where necessary in a thermostatically controlled drying oven.

Reagents

The 1,1'-dianthrimide (Fluka AG, Switzerland), the selenium dioxide (Light & Co., Ltd., Great Britain) and the other chemicals were of reagent-grade quality. The 1,2,7,8-diphthaloylcarbazole* was synthesized as described by LECHER, SCALERA AND FORSTER[2].

Standard solutions

Standard solutions of selenium, 1,1'-dianthrimide and 1,2,7,8-diphthaloylcarbazole were prepared by dissolving the proper amounts in concentrated sulfuric acid and diluting to a known volume with acid of the same concentration.

Sulfuric acids of varying strength were prepared by adding either distilled water or fuming acid to 95–97% acid, the exact concentration being determined titrimetrically.

Heating time, heating temperature and concentration of sulfuric acid

On the basis of previous studies[1], a heating time of 16 h at 70° was used. Within the range 90–97% sulfuric acid the absorption curves for the 1,1'-dianthrimide–

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* 1,2,7,8-Diphthaloylcarbazole may be derived from 1,1'-dianthrimide by replacing the two hydrogen atoms in the 2- and 2'-positions by a bond.

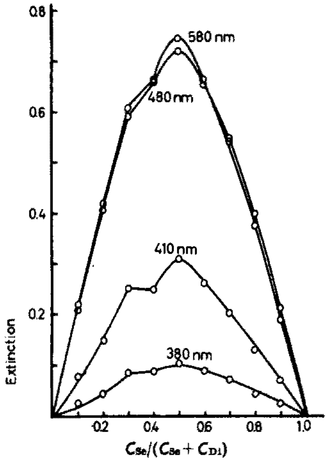
selenium complex were practically identical. An acid concentration of 96.0% was used in most experiments.

Absorption curves

Two solutions were prepared with mole ratios of selenium to 1,1'-dianthrimide corresponding to 9:1 and 1:9; these were measured against blanks containing the same amount of ligand. The two curves exhibited the same form, but the maxima on the curve for the solution containing an excess of selenium were found at 600 and 495 nm, while on the other curve the maxima appeared at 590 and 480 nm. The former curve had its highest extinction at 495 nm, while on the latter curve the highest value was found at 590 nm. It was assumed that the two curves originated from different complexes.

The method of continuous variation

A series of solutions were prepared in 96.0% sulfuric acid. The curves recorded at different wavelengths are shown in Fig. 1. All the curves exhibit a maximum at the mole fraction 0.5, indicating the presence of only one complex with the mole ratio 1:1. The curves also exhibit an irregular form in the mole fraction range 0.3–0.4. Some of the left curve branches have a parabolic form, while the right branches are all with-



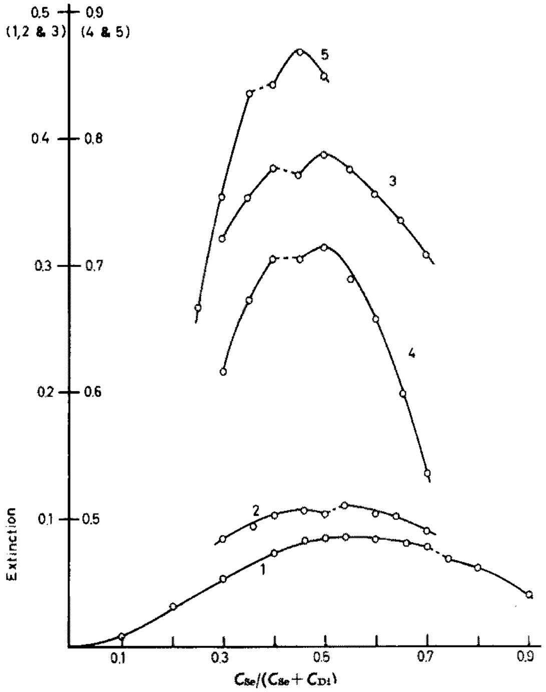


Fig. 1. Curves of continuous variation plotted at different wavelengths for a series of solutions with the constant total concentration of $1.62 \cdot 10^{-4}$ *M*.

Fig. 2. Curves of continuous variation recorded at 590 nm for series of solutions with different total concentration. Concentration of sulfuric acid 96.0%. Total concentrations: curve 1, $0.25 \cdot 10^{-4}$ *M*; curve 2, $0.50 \cdot 10^{-4}$ *M*; curve 3, $1.00 \cdot 10^{-4}$ *M*; curve 4, $1.50 \cdot 10^{-4}$ *M*; curve 5, $1.70 \cdot 10^{-4}$ *M*.

out inversions and show a final gradient different from zero. Other curves, recorded with other mixtures, showed the same irregularity. Detailed curves were then plotted for series of solutions with different total concentrations and with mole fractions near zero and one. The curves recorded for mole fractions near zero again approached the axis parabolically, while the curves for mole fractions near one, as before, gave curves without inversions and with a final finite gradient.

It was concluded that in the low mole fraction range of selenium the predominant complex contained more than one atom of selenium. Correspondingly, in the high mole fraction range of selenium the predominant species contained one molecule of 1,1′-dianthrimide. These results again pointed to the presence of at least two complexes.

Curves of continuous variation were also plotted at 480 and 590 nm for series of solutions with different total concentrations, the series being prepared in both 96.0 and in 92.0% sulfuric acid. In Fig. 2 some of the curves recorded in 96.0% acid are reproduced. These curves, as well as other more detailed curves, showed that the irregularity could more correctly be described as a discontinuity of the type previously found in the system selenium(IV)–2,2′-dianthrimide[3].

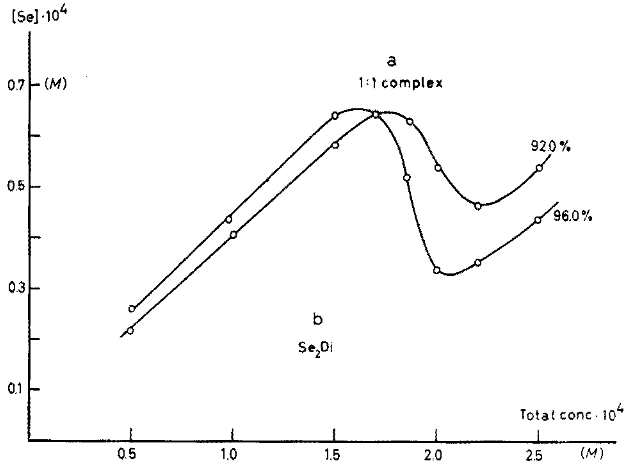


Fig. 3. Curves showing the complex transformation in 96.0 and 92.0% sulfuric acid as a function of the total concentration of the reactants and of the concentration of selenium.

It can be seen from Fig. 2 that the discontinuity is present in all the curves and that, in accordance with previous observations[3], an increase in the total concentration of the reactants results in a shift of the discontinuity towards lower mole fractions of selenium. The curves recorded in 92.0% acid confirmed these results. The data on the discontinuity were used to construct Fig. 3, which gives the discontinuity in 96.0 and 92.0% acid as a function of the total concentration of the reactants and of the concentration of selenium. Other experiments showed that the Se_2Di complex could be transformed into the 1:1 compound by changing the experimental conditions from those existing in region b (see Fig. 3) to those prevailing in region a, but that the reverse transformation was not possible.

The straight-line method

This method was used to determine the composition of the complexes predominating in the regions a and b of Fig. 3. The composition of the complex predominating in region a may be found by preparing and measuring two series of solutions, one series with a constant concentration of 1,1′-dianthrimide and varying amounts of selenium, the former reactant being maintained in excess; and the other series containing, in excess, a constant concentration of selenium and varying amounts of 1,1′-dianthrimide. In region b series with an excess of selenium cannot be prepared and for this reason the following two series were prepared. In one of the series a constant concentration of 1,1′-dianthrimide was maintained, while the content of selenium was varied. In this series the former reactant was maintained in excess. The other series contained a constant concentration of selenium and varying amounts of 1,1′-dianthrimide, the latter reagent being kept in excess*. The two series were prepared in both 96.0 and 92.0% sulfuric acid. Data relating to the use of the straight-line method are given in Table 1, from which it can be seen that the composition of the complexes predominating in the regions a and b is SeDi and Se_2Di, respectively.

TABLE 1

DATA RELATING TO THE STRAIGHT-LINE METHOD

Concn. (in %) of H_2SO_4	*Reactant varied*	*Concn. varied*		*Concn. of the other reactant 10^4 M*	*Region in Fig. 3*	*Coefficients (Se_mDi_n)*
		from (10^4M)	*to (10^4M)*			
	Se	0.40	1.08	1.60	a	$m = 1$
96.0	1,1′-di	0.04	0.50	1.00	a	$n = 1$
	Se	0.04	0.08	1.00	b	$m = 2$
	1,1′-di	1.50	3.00	0.20	b	$n/m = \frac{1}{2}$
	Se	0.50	1.08	1.60	a	$m = 1$
92.0	1,1′-di	0.04	0.50	1.00	a	$n = 1$
	Se	0.04	0.08	1.00	b	$m = 2$
	1,1′-di	1.50	4.00	1.20	b	$n/m = \frac{1}{2}$

This result explained the differing absorption curves, as well as the curves of continuous variation. The part of the curves of continuous variation lying between the discontinuity and the left end of the curve corresponds to experimental conditions under which Se_2Di predominates, while the other part of the curves corresponds to conditions favoring the formation of the 1:1 complex. The discontinuity results, as reported previously[3], from a sudden transformation of one of the complexes into the other. The factors regulating the transformation are the total concentration of reactants, and/or the concentration of selenium and the concentration of the sulfuric acid.

Synthesis of the solid 1:1 compound

In about 200 ml of 96.0% sulfuric acid 5.55 g of selenium dioxide and 2.14 g of 1,1′-dianthrimide (mole ratio of selenium to 1,1′-dianthrimide 10:1) were dissolved. Under these experimental conditions the 1:1 compound predominates. After heating for 70 h at 70°, the solution was cooled to room temperature and then transferred

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* The theoretical basis for this modification of the straight-line method has been discussed by HOLME AND LANGMYHR[4].

slowly into a 2-l beaker containing a vigorously stirred mixture of water and ice. On standing the dark precipitate settled. The preparation was filtered on a paper filter, washed with hot and cold water until the filtrate reacted neutrally and dried in contact with air. The product was a dark crystalline powder.

Investigations of the solid 1:1 compound

A 0.05% (w/v) solution of the solid was prepared in 96.0% sulfuric acid. A 1.00-ml aliquot was mixed with 20 ml of 96.0% sulfuric acid and an absorption curve was recorded against a blank of 96.0% acid. Similarly, 0.0647 g of selenium dioxide and 0.0252 g of 1,1'-dianthrimide (the mole ratio of selenium to 1,1'-dianthrimide again being 10:1) were dissolved in 96.0% sulfuric acid, and the solution was diluted to 50 ml with the same solvent. After heating for 16 h at 70°, 1.00 ml was mixed with 20 ml of 96.0% acid and an absorption curve was recorded as above. The two absorption curves were identical in form.

It was considered of interest to compare the absorption curve of a solution containing selenium(IV) and 1,1'-dianthrimide in proportions ensuring the predominance of the 1:1 complex, with the curve of a mixture prepared from selenium(IV) and 1,2,7,8-diphthaloylcarbazole. As apparent from Fig. 4, the two curves exhibit the same form.

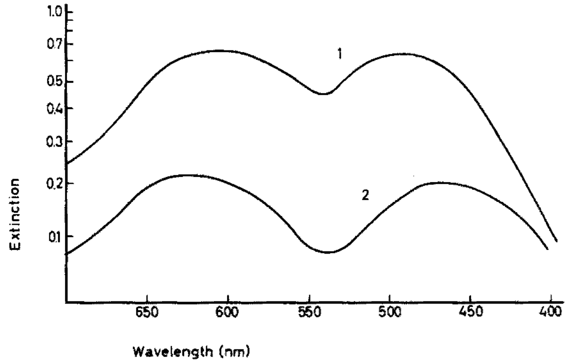

Fig. 4. Absorption curves of two solutions, one containing selenium(IV) and 1,1'-dianthrimide (curve 1) and the other containing selenium(IV) and 1,2,7,8-diphthaloylcarbazole (curve 2).

Qualitative analysis of the preparation showed the presence of selenium and nitrogen, while tests for sulphur and halogen were negative. Quantitative elemental analysis gave the following results: C 58.60, H 2.53, N 2.81, Se 15.60 (Calc. for $C_{28}H_{13}NO_6Se \cdot 2\,H_2O$(574.4): C 58.60, H 2.86, N 2.44, Se 13.8).

Infrared spectra (nujol mull) were recorded of 1,1'-dianthrimide, the 1:1 compound and 1,2,7,8-diphthaloylcarbazole. The spectra of 1,1'-dianthrimide and the solid complex were different. A comparison indicated that the complex was pure, and that one or more of the carbonyl groups of 1,1'-dianthrimide were engaged in complex formation. A further study, which included comparison with the spectra of different derivatives, indicated that in the complex the 2- and 2'-positions were not occupied by hydrogen. The spectra of the solid complex and of 1,2,7,8-diphthaloylcarbazole showed many similarities and indicated that the complex contained a carbazole bond.

Paper chromatography was attempted, but it was difficult to find suitable solvents for the solid complex. In the upper layer of a mixture of butanol, ethanol and water (volume ratios 5:1:4, respectively) the complex gave only one spot, which indicated that the preparation was pure.

Attempts at a determination of the molecular weight of the complex by an ebullioscopic method failed, as no suitable solvent could be found.

It was considered of interest to record the NMR spectrum of a solution of the 1:1 complex in concentrated sulfuric acid; 0.3115 g of the complex were dissolved in 5 ml of 97.1% acid, but no satisfactory spectrum was obtained.

RESULTS AND DISCUSSION

The present system was found to contain two species, a 1:1 compound and the Se_2Di complex.

On the basis of the investigations by FLOWERS, GILLESPIE AND ROBINSON[5], it was assumed that selenium(IV) participated in the reactions as the ion $HSeO_2^+$. In solutions of 1,1′-dianthrimide (Di) in concentrated sulfuric acid the following equilibrium exists:

$$Di + xH_2SO_4 \rightleftharpoons DiH_x^{x+} + xHSO_4^-$$

In 100% sulfuric acid the value of x has been found[6] to be 3. Under the present experimental conditions the value of x may be below 3. In any case, the first proton can be assumed to be attached to the most basic group. *viz.* the imino group. The two hydrogen atoms of this group are believed to form intramolecular hydrogen bonds with the two adjacent oxygen atoms, as indicated in the structural formulae.

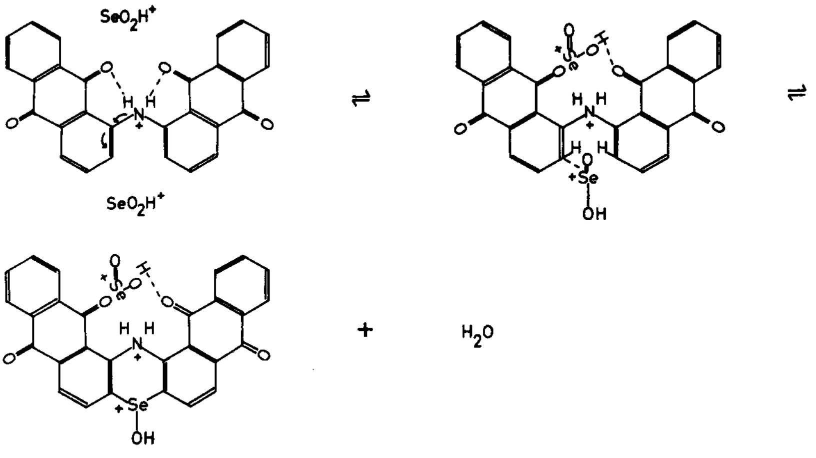

Fig. 5. Scheme suggested for the primary reaction of selenium(IV) with 1,1′-dianthrimide.

The scheme in Fig. 5 is suggested for the primary reaction of selenium(IV) with 1,1′-dianthrimide, which results in the formation of the Se_2Di complex. Under certain experimental conditions, the secondary reaction proposed in Fig. 6 takes place. In this reaction one selenium atom is split off, resulting in the formation of a carbazole bond* and the 1:1 complex. The presence of the carbazole bond is strongly supported by the infrared investigations and by the absorption curves shown in Fig. 4. The formation of the carbazole bond makes the secondary reaction irreversible. The 1:1 compound should therefore more correctly be designated as the selenium–1,2,7,8-diphthaloylcarbazole complex. A probable structural formula of the solid selenium–1,2,7,8-diphthaloylcarbazole complex is given in Fig. 7.

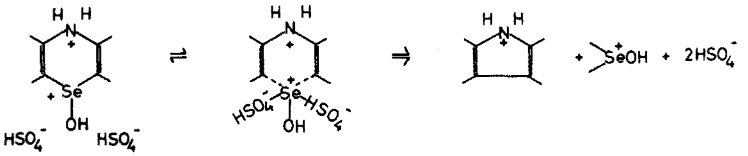

Fig. 6. Proposed scheme for the secondary reaction resulting in the formation of the selenium(IV)–1,2,7,8-diphthaloylcarbazole complex.

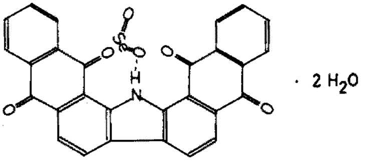

Fig. 7. Probable structural formula of the solid selenium(IV)–1,2,7,8-diphthaloylcarbazole complex.

TABLE II

DATA RELATING TO THE STABILITY CONSTANT OF THE Se_2Di COMPLEX

Total concn. of reactants $C \cdot 10^4$ *M*	*Mole fraction of selenium*	*Concentrations of*			$k_{2,1}$ 10^{-8}
		Se $a \cdot 10^4$ *M*	*1,1′-di* $b \cdot 10^4$ *M*	*complex* $y \cdot 10^4$ *M*	
2.0	0.034	0.068	1.932	0.0137	4.3
2.2	0.030	0.066	2.134		
2.0	0.120	0.240	1.760	0.0788	6.9
2.2	0.107	0.235	1.965		

In a previous paper[1] describing the spectrophotometric determination of selenium(IV) with 1,1′-dianthrimide, a positive deviation from the Lambert–Beer law was registered. The solutions prepared for these calibration data contained an excess of 1,1′-dianthrimide. The present work showed that under these conditions the Se_2Di complex predominates and that a positive deviation should be obtained, as demonstrated *e.g.* by the left curve branches in Fig. 1.

Stability constants

From two detailed curves of continuous variation and by following the directions of Foley and Anderson[7], the values in Table II were calculated for the stability constant of the Se_2Di complex. Two determinations gave an average value of

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* The present procedure does not seem to have been used before for the preparation of carbazoles.

$k_{2,1} = 5.6 \cdot 10^8$. Using the modified straight-line method of HOLME AND LANGMYHR[4], a stability constant of $k_{2,1} = 6.1 \cdot 10^8$ was calculated.

SUMMARY

The complex formation in concentrated sulfuric acid between selenium(IV) and 1,1′-dianthrimide (Di) was studied by spectrophotometry, infrared spectroscopy and chemical analysis. The system was found to contain two species, a Se_2Di complex and a selenium–1,2,7,8-diphthaloylcarbazole complex. The primary complex reaction was assumed to be the formation of the Se_2Di compound; unter certain experimental conditions one selenium atom is split off, resulting in the irreversible formation of a carbazole bond. The selenium–1,2,7,8-diphthaloylcarbazole was prepared in the solid state.

RÉSUMÉ

Les auteurs ont examiné la formation de complexe entre sélénium(IV) et 1,1′-dianthrimide (Di), en milieu acide sulfurique concentré, par spectrophotométrie, spectroscopie infrarouge et analyse chimique. Le système peut renfermer 2 espèces: un complexe Se_2Di et un complexe Se–1,2,7,8-diphtaloylcarbazole. On a pu préparer le sélénium–1,2,7,8-diphtaloylcarbazole à l'état solide.

ZUSAMMENFASSUNG

Die Komplexbildung zwischen Selen(IV) und 1,1′-Dianthrimid (Di) in konzentrierter Schwefelsäure wurde spektralphotometrisch, infrarotspektroskopisch und durch chemische Analyse untersucht. Es wurden zwei Spezies gefunden, Se_2Di und ein Selen–1,2,7,8-Diphthaloylcarbazol-Komplex. Vermutlich wird primär Se_2Di gebildet. Unter gewissen experimentellen Bedingungen spaltet ein Selenatom ab und bildet irreversibel eine Carbazolbindung. Das Selen–1,2,7,8-Diphthaloylcarbazol wurde im festen Zustand hergestellt.

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COMPLEX FORMATION IN CONCENTRATED SULFURIC ACID BETWEEN BORIC ACID AND QUINALIZARIN OR ALIZARIN

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Several hydroxyanthraquinones react in concentrated sulfuric acid with boric acid or boron oxide; some of these, *e.g.* quinalizarin, alizarin and purpurin, have long been employed for the photometric determination of small amounts of boron. A literature survey on the use of these reagents showed that the composition and stability of the boron complexes had not been determined.

FEIGL AND KRUMHOLZ[1] studied the reactions of various hydroxyanthraquinones with boric acid and concluded that complex formation required a hydroxyl group situated next to a carbonyl group, *i.e.* in the positions 1, 4, 5 or 8. FEIGL AND KRUMHOLZ suggested a structural formula in which the boron atom participated in bond formation with the oxygen atoms of 1 hydroxyl and 1 carbonyl group. In accordance with these results, BERGER AND TRUOG[2] assumed that the complex of boric acid with quinalizarin contained 2 boron atoms.

The present investigation was designed to elucidate the complex formation of boric acid with some analytically important hydroxyanthraquinones. The reagents selected were quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) and alizarin (1,2-dihydroxyanthraquinone). The structural formula of these reagents is evident from Fig. 1 (*vide infra*). It was further considered of interest to establish whether or not these complexes were of the same type as that formed between boric acid and 1,1'-dianthrimide. This complex has recently been found[3] to consist of a 6-membered ring (containing 1 sulfur, 2 boron and 3 oxygen atoms) to which two 1,1'-dianthrimide molecules are attached.

EXPERIMENTAL

Instruments and equipment

Extinction measurements were made with a Beckman DB recording spectrophotometer, a Zeiss PMQ II spectrophotometer and 1-cm cells.

The different solutions were prepared and heated in 50-ml bottles (Jena Geräteglas) with ground-glass stoppers.

Reagents

The quinalizarin (Riedel-DeHaën, Germany), boric acid and alizarin (both reagents from Merck, Germany), sulfuric and fuming sulfuric acid were of reagent-grade quality.

Standard solutions

Standard solutions of boric acid and the 2 reagents were prepared by weighing out and dissolving the proper amounts in acid of known concentration and diluting to a known volume.

The boric acid–quinalizarin system

The absorption curve of a solution of quinalizarin in 96.0% sulfuric acid showed a maximum at 570 mμ and a shoulder in the range 530–550 mμ. Preliminary studies of the complex reaction demonstrated that in 93.0% acid, equilibrium conditions were reached after 15 min at room temperature. In accordance with the results of SMITH[4], the highest sensitivity was found in about 93% acid; this acid concentration was therefore used for the preparation of the standard solutions and for dilution.

Standard solutions, $1.60 \cdot 10^{-4}$ *M*, were prepared of boric acid (B) and quinalizarin (Q). Absorption curves of mixtures containing the reactants in the mole ratios 10:1 and *vice versa* were recorded. The 2 curves exhibited the same form and it was therefore assumed that the same complex predominated in both mixtures. Both absorption curves showed maxima at 348 and 610 mμ.

A curve of continuous variation was recorded at 610 mμ of a series of solutions having a constant, total concentration of $0.80 \cdot 10^{-4}$ *M*. The curve showed a rounded maximum at the mole fraction 0.5; it had no inversions and the gradients at the endpoints were different from zero. This pointed to the presence of a mononuclear complex with the composition BQ.

If one complex (of composition B_mQ_n) predominates in all solutions irrespective of the mole ratio between the reactants, the straight-line method can be employed to ascertain the coefficients *m* and *n*. Two series of solutions were prepared, one with a constant excess of quinalizarin and varying contents of boric acid, and the other with a constant excess of boric acid and varying amounts of quinalizarin. The former series resulted in a straight line for $m=1$, while the latter series gave a straight line for $n=1$. Thus, the straight-line method confirmed the composition BQ. A modification of the straight-line method was also used to establish the value of the coefficients *m* and *n*. In this modification the concentration of the reactant maintained in excess is varied. The applicability of this modification has been discussed by HOLME[5]. Using this method a straight line was obtained for $n/m=1$.

It was concluded that the present system contained a single complex of composition BQ.

The stability constant of the BQ complex was calculated by the method of SCHAEPPI AND TREADWELL[6] and the experimental data from the method of continuous variation; a value of $k_{1,1}=0.87 \cdot 10^5$ was calculated. With the experimental data for the modified straight-line method and the directions of HOLME[5], the constant was calculated to be $k_{1,1}=0.87 \cdot 10^5$.

The boric acid–alizarin system

The absorption curve of alizarin in 96.0% acid exhibited a maximum at 495 mμ.

In this system the highest sensitivities were again found at acid concentrations of about 93%. The standard solutions ($1.60 \cdot 10^{-4}$ *M*) were prepared in 93.2% acid, and acid of this concentration was used for dilution. The complex reaction reached equilibrium conditions after 15 min at room temperature.

The absorption curve of the complex exhibited maxima at 348 and 585 mμ. The form of the curve and the position of the maxima were uninfluenced by changing the mole ratio between the reactants, which pointed to the presence of only one species.

To establish the composition of the complex B_mA_n the molar ratio, the straight-line and the modified straight-line methods were employed. All extinction measurements were made at 585 mμ. The first method showed that the mole ratio between the reactants was 1:1. The other two methods gave the coefficients $m = 1$ and $n = 1$.

The system boric acid–alizarin thus contained a single complex of composition BA.

RESULTS AND DISCUSSION

The 2 hydroxyanthraquinones examined both reacted with boric acid to form 1:1 complexes. The structure suggested by BERGER AND TRUOG[2] is therefore not correct. In agreement with the conclusions of FEIGL AND KRUMHOLZ regarding the reactions of boron with certain hydroxyanthraquinones, the results of the present investigation indicated that this group of reagents all form 1:1 complexes. In Fig. 1, a scheme is proposed for the reaction of boric acid with quinalizarin. This scheme also applies to the reaction with alizarin.

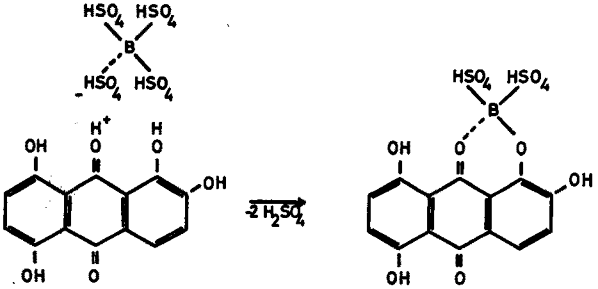

Fig. 1. Proposed scheme for the reactions of boric acid with quinalizarin and alizarin.

In the reactions of boric acid with hydroxyanthraquinones it can be assumed that boron participates as the tetra(hydrogensulfato)boric acid. In the reaction of boric acid with 1,1′-dianthrimide, however, the final complex consists of a 6-membered ring containing 2 boron atoms, to each of which a 1,1′-dianthrimide molecule is attached. This reaction may also be explained by assuming the initial presence of the tetra(hydrogensulfato)boric acid. At some intermediate stage a ring formation takes place and the 2:2 compound is formed.

The hydroxyanthraquinones react with boric acid without heating, whereas mixtures of boric acid with 1,1′-dianthrimide have to be heated to obtain complex formation. The latter reaction is not influenced by preheating separately solutions of the reactants. The ring formation may therefore be the heat-requiring reaction.

SUMMARY

The complex formation in concentrated sulfuric acid between boric acid and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) or alizarin (1,2-dihydroxyanthraquinone) was studied by spectrophotometry. Both systems contained only one species, *viz.* a complex between one boric acid and one hydroxyanthraquinone molecules. The reactions of boric acid with hydroxyanthraquinones are discussed and compared with the reaction of boric acid with 1,1′-dianthrimide.

RÉSUMÉ

On a examiné spectrophotométriquement la formation des complexes acide borique–quinalizarine et acide borique–alizarine, en milieu acide sulfurique concentré. Chacun de ces complexes renferme un acide borique et une molécule hydroxyanthraquinone. Les réactions de l'acide borique avec les hydroxyanthraquinones sont discutées et comparées avec la réaction acide borique–1,1′-dianthrimide.

ZUSAMMENFASSUNG

Es wurde in konzentrierter Schwefelsäure die Komplexbildung zwischen Borsäure und Chinalizarin (1,2,5,8-Tetrahydroxiantrachinon) oder Alizarin (1,2-Dihydroxiantrachinon) spektralphotometrisch untersucht. Beide Systeme enthielten nur eine Spezies, nämlich einen Komplex zwischen einem Borsäure- und einem Hydroxiantrachinon-Molekül. Die Reaktionen von Borsäure mit Hydroxiantrachinonen werden diskutiert und mit der Reaktion von Borsäure mit 1,1′-Dianthrimid verglichen.

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COMPLEX FORMATION AND FLUORESCENCE

PART IV. 8-QUINOLINOL-5-SULFONIC ACID AS A TITRANT FOR BIVALENT CATIONS

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During the course of work previously reported[1,2], it was observed that oxidation of the reagent (as indicated by darkening of solutions on standing) did not take place in solutions in which 8-quinolinol-5-sulfonic acid ($OxSO_3$) was complexed by cations. EATON[3] has commented on this in the case of other phenols. Repeated standardizations during the present investigation showed a change in one $Mg(OxSO_3)_2$ standard solution from $1.87 \cdot 10^{-3}\,M$ to $1.90 \cdot 10^{-3}\,M$ with respect to $OxSO_3$.

The formation constants shown in Table I indicate that it should be possible to use a solution of $Mg(OxSO_3)_2$ as a titrant in a replacement titration, the appearance of fluorescence from the excess of reagent being taken as the end-point. Preliminary tests showed that this could be followed best by an instrumental method, using a procedure similar to that used in photometric titrations[4].

TABLE I

FORMATION CONSTANTS OF $OxSO_3$ COMPLEXES[a]

Cation	*Log K_1*	*Log K_2*	*ML_2 fluorescence*
Mg	4.8	3.7	Yes
Mn(II)	6.6	4.9	No
Cd	7.6	5.9	Yes
Fe(II)	8.4	6.7	No
Zn	8.4	6.7	Yes
Pb(II)	8.5	7.6	No
Co(II)	9.2	7.6	No
Ni	10	8.1	No
Cu	12.5	10.6	No

[a] Values of the formation constants taken from ref. 5.

It has been reported[1,6] that the fluorescence of $Mg(OxSO_3)_2$ is at a maximum about pH 7 and decreases above pH 8. Since the other cations are more strongly complexed than magnesium, it is to be expected that the end-point of the overall reaction

$$M(II) + Mg(OxSO_3)_2 \rightleftharpoons M(OxSO_3)_2 + Mg(II) \qquad (1)$$

should be observed best over this range of pH (7 to 8).

EXPERIMENTAL

Reagents

Magnesium 8-quinolinol-5-sulfonate. This was prepared by weighing out enough 8-quinolinol-5-sulfonic acid (obtained from the Eastman Kodak Co. and used without further purification) to make the final concentration about $2 \cdot 10^{-3}$ *M*, and dissolving in water containing enough magnesium sulfate to give a 10^{-3} *M* solution. To this solution was added 1 g phosphate buffer per liter to give pH 7. It is not necessary for the ratio of $OxSO_3$ to Mg to be exactly 2:1 but it should not be less than 1:1 and oxidation of uncomplexed $OxSO_3$ may take place if it is greater than 2:1. The titrant solution was dispensed from a McClosky buret, with divisions of 0.02 ml. This arrangement gave a closed system, air being admitted only during a titration.

The other chemicals used were reagent-grade nitrates, with the exception of copper sulfate, and in the cases of Hg(II), Pd(II) and Pt(II). Both $HgCl_2$ and $Hg(NO_3)_2$ were used with equally good results. $PdCl_2$ and K_2PtCl_4 were obtained from A.D. Mackay, Inc., New York, N.Y. Solutions of approximately 10^{-3} *M* were prepared from more concentrated solutions, and the diluted solutions used in the titrations.

The concentrations on which the fluorescence was actually measured were about 10^{-5} *M*. A small crystal of sodium sulfite was added to the iron(II) and the manganese(II) solutions to prevent air oxidation of these solutions.

Standardization

The $OxSO_3$ solutions were standardized against copper sulfate heptahydrate. The ratio of the formation constants of the copper and magnesium complexes is such that there is no doubt of the completeness of the reaction.

Fluorescence measurements

These were made using the Farrand Spectrofluorimeter which has been described previously[1]. The incident beam for excitation of fluorescence was set at 365 mμ and a filter to cut off stray light was used after the sample. The peak wavelength for the magnesium complex was at 495 mμ and for the zinc and cadmium complexes at 515 mμ. When both magnesium and zinc complexes fluoresced (as in the last portion of the experiments of Figs. 5 and 6) the peak "broadened" to extend from 515 to 495 mμ. Fluorescent measurements were also made on some of the solutions using a Turner Model 110 Fluorimeter with results similar to those shown.

Titration procedure

Titrations were carried out by pipetting a fixed volume of the cation solution into a 100-ml volumetric flask, and adding varying volumes of the titrant. The solution was made up to 100 ml and the fluorescence measured about 1 h after mixing. The fluorescence was measured again after the solutions had been standing overnight. There was no significant change, indicating that the replacement reaction was a rapid one.

DISCUSSION

End-point phenomena in compleximetric titrations have been discussed by other investigators[4,7-9], but they have restricted themselves experimentally to systems involving 1:1 complexes. In the present series of experiments, two possible complexes of each cation had to be considered. Calculations on the effect of pH on the extent of complexation showed that all of the cations studied were essentially complexed to form $M(OxSO_3)_2$ at pH 7. Some $MOxSO_3$ complex will be formed, however, when the ratio of *total* cation to complexing agent is 1:1, which is the case at the end-point of all the titrations discussed in this paper. For two cations, M and M′, the following equilibria must be taken into account (L = ligand)

$$ML_2 + M' = ML + M'L \tag{2}$$

$$K' = \frac{(ML)(M'L)}{(ML_2)(M')} = \frac{K_{1(M'L)}}{K_{2(ML_2)}} \tag{3}$$

$$ML + M'L = M'L_2 + M \tag{4}$$

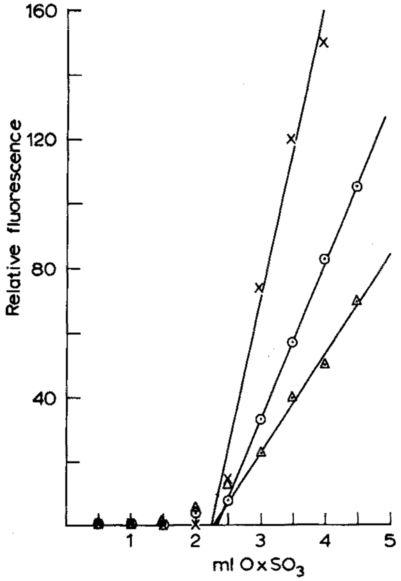
$$K'' = \frac{(M'L_2)(M)}{(ML)(M'L)} = \frac{K_{2(M'L_2)}}{K_{1(ML)}} \tag{5}$$

where K_1 and K_2 are formation constants.

At the equivalence point, it may be assumed that

$$(M') = (ML_2) \tag{6}$$

$$(ML) = (M'L) \tag{7}$$



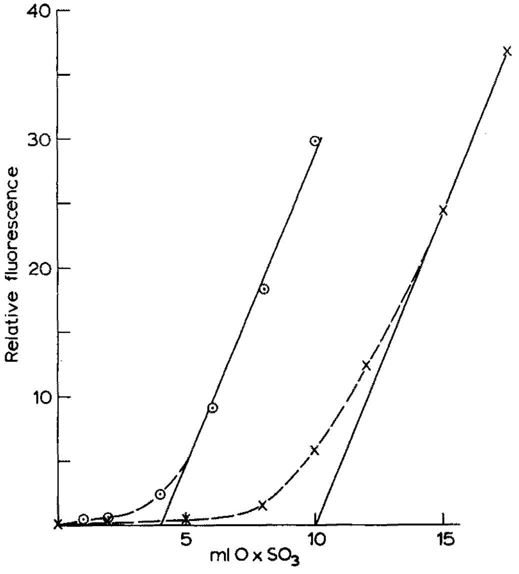


Fig. 1. Titration of Cu, Ni and Co with $Mg(OxSO_3)_2$ *vs.* $8.89 \cdot 10^{-3}$ *M* $OxSO_3$. (×), 1 ml 0.0100 *M* Cu(II); (○), 1 ml 0.0100 *M* Ni(II); (△), 1 ml 0.0103 *M* Co(II).

Fig. 2. Titration of Fe(II) with $Mg(OxSO_3)_2$. (×), 5 ml Fe(II) *vs.* $1.87 \cdot 10^{-3}$ *M* $OxSO_3$; $M_{(Fe)} = 1.87 \cdot 10^{-3}$. (○), 2 ml Fe(II) *vs.* $1.87 \cdot 10^{-3}$ *M* $OxSO_3$; $M_{(Fe)} = 1.92 \cdot 10^{-3}$. These results give an indication of reproducibility.

$$(M'L_2) = (M) \tag{8}$$

The ligand will be distributed as follows

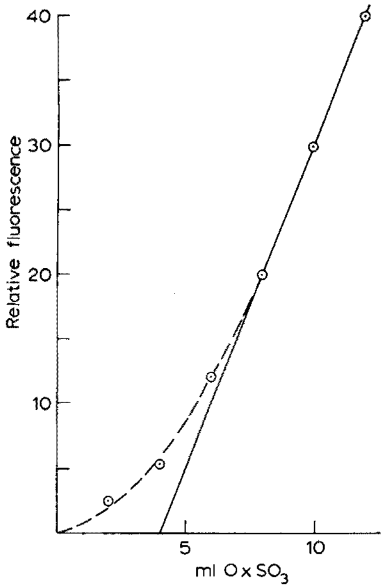
$$\Sigma L = ML_2 + ML + M'L + M'L_2 \tag{9}$$

Substituting from eqns. (3), (5), (6), (7) and (8)

$$\Sigma L = ML\,[(1/(K')^{\frac{1}{2}}) + 2 + (K'')^{\frac{1}{2}}] \tag{10}$$

With $Mg(OxSO_3)_2$ as titrant (ML_2), and substituting values for the constants calculated from Table I, it was found that for the bivalent cations forming non-fluorescing complexes the percentages of titrated cation in the form of $M'L_2$ were as follows: Cu 99.4; Ni 96; Co 93; Fe 82; Mn 35.

The experimental results justify the assumptions made, as shown in Figs. 1–3. Figure 4 shows the titration of mercury(II) by $Mg(OxSO_3)_2$. No constant for the formation of mercury(II) complexes with $OxSO_3$ has been reported, but a comparison of its titration curve with Figs. 2 and 3 would indicate values in the neighborhood of those for the manganese(II) complexes.



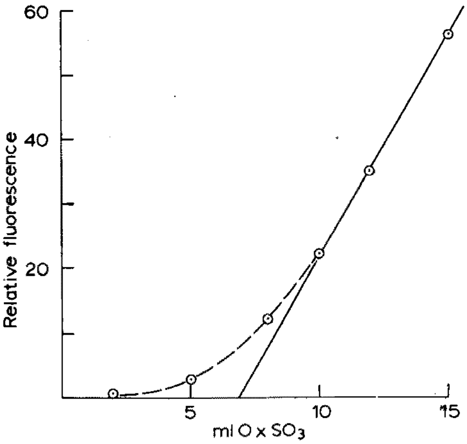


Fig. 3. Titration of Mn(II) with $Mg(OxSO_3)_2$. 5 ml Mn(II) *vs.* $1.87 \cdot 10^{-3}$ *M* $OxSO_3$; $M_{(Mn)} = 0.74 \cdot 10^{-3}$.

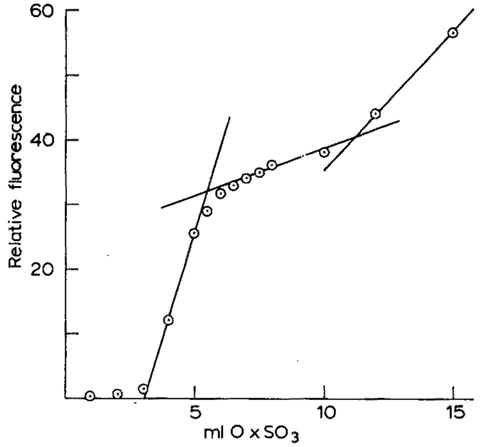
Fig. 4. Titration of Hg(II) with $Mg(OxSO_3)_2$. 5 ml $Hg(NO_3)_2$ *vs.* $1.87 \cdot 10^{-3}$ *M* $OxSO_3$; $M_{(Hg)} = 1.26 \cdot 10^{-3}$.

In Fig. 1, the difference in the slopes of the $Mg(OxSO_3)_2$ after the end-point is probably due to differences in light absorption of the copper, nickel and cobalt complexes. The copper and nickel complexes are different shades of green, while the cobalt complex has a pink tinge. The light absorbed is thus probably due to the emitted fluorescence, but it might be due to variation in the absorption of the exciting light.

In the cases of the manganese(II), iron(II) and mercury(II) curves, the rise of the curves above the base line as the end-point is approached, is a measure of the incompleteness of the reaction involved. As in the case of photometric titrations, this does not prevent the determination of the equivalence point by extrapolation, which explains why this method is more universal as an instrumental method. Copper(II), which is very strongly complexed compared to magnesium, can be titrated very accurately visually, using a "blacklite" in a dark room.

When eqns. (3) and (5) were applied to the Cu–Zn, Zn–Mn, and Mn–Mg pairs, and the same assumptions were made as before, it was possible to construct Table II to show the possibility of titrating a solution containing Cu, Zn and Mn(II) with $Mg(OxSO_3)_2$. Experimental results for this titration are shown in Fig. 5.

Figure 6 shows the results obtained when solutions containing Cu, Zn and Hg(II) were titrated with $Mg(OxSO_3)_2$.



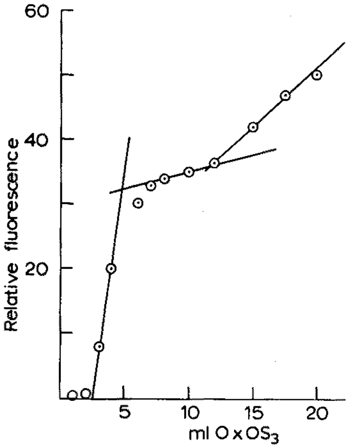


Fig. 5. Titration of Cu, Zn and Mn(II) in one solution. 3 ml Cu + 3 ml Zn + 3 ml Mn(II) *vs.* $1.33 \cdot 10^{-3}$ *M* $OxSO_3$. Same Zn solution as in Fig. 6, different Cu solution. Cu = $0.55 \cdot 10^{-3}$ *M*; Zn = $0.55 \cdot 10^{-3}$ *M*; Mn = $1.49 \cdot 10^{-3}$ *M*.

Fig. 6. Titration of Cu, Zn and Hg(II) in one solution. 3 ml Cu + 3 ml Zn + 3 ml Hg(II) *vs.* $1.33 \cdot 10^{-3}$ *M* $OxSO_3$. Same Zn solution as in Fig. 5. Cu = $0.67 \cdot 10^{-3}$ *M*; Zn = $0.55 \cdot 10^{-3}$ *M*; Hg = $1.16 \cdot 10^{-3}$ *M*.

TABLE II

EXCHANGE CONSTANTS OF $OxSO_3$ COMPLEXES

M	*M'*	*Log K'*	*Log K''*	*% ML_2 at equivalence point*
Cu	Zn	−2.2	−5.8	87
Zn	Mn	−0.1	−3.5	35
Mn	Mg	−0.1	−2.9	35

Inspection of Figs. 5 and 6 indicates that the titration of Cu and Zn (or Cu and Cd) in the same solution can be carried out easily, but that the titration of 3 cations using $Mg(OxSO_3)_2$ was feasible only when the cation with its formation constants closest to those of the magnesium complexes was present in relatively large amount.

It is also apparent that it should be possible to titrate a mixture of copper and zinc using a solution containing $Hg(OxSO_3)_2$.

Figure 7 shows the result of such a titration, along with the titration of a copper–cadmium mixture using the same titrating solution. In these titrations the same volumes of copper solution were used, along with the same volumes of zinc and cadmium solutions which had slightly different concentrations. The copper solution was used as an internal standard.

Of the bivalent cations, barium and calcium are less strongly complexed than magnesium and therefore cannot be titrated. Attempts to titrate palladium(II) and platinum(II) were unsuccessful, possibly due to strong complexing of these ions with chloride. The constants given for lead in Table I indicate that this complex should form and that lead should be titratable. However, the titration of this ion was not successful, nor was the titration of tin(II). Since both of these ions form strong hydroxy complexes, it is possible that mixed complexes were formed. Beryllium also could not be titrated.

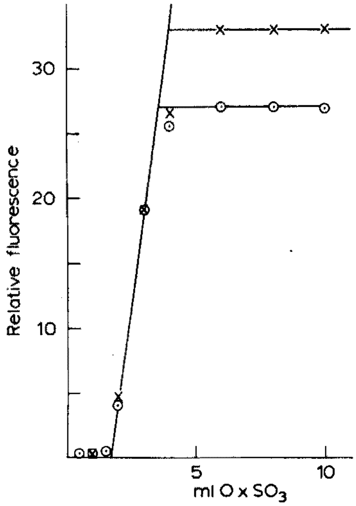


Fig. 7. Titrations of mixtures using $Hg(OxSO_3)_2$ (not fluorescent) $M_{Cu} = 0.67 \cdot 10^{-3}$ M (used as standard) to give $M_{OxSO_3} = 1.53 \cdot 10^{-3}$. × = Cu + Cd solution; $M_{Cd} = 0.82 \cdot 10^{-3}$. ○ = Cu + Zn solution; $M_{Zn} = 0.67 \cdot 10^{-3}$.

SUMMARY

8-Quinolinol-5-sulfonic acid can be used in compleximetric titrations by means of a displacement type of titration; a fluorescent weak complex is used to titrate an ion which forms a non-fluorescing stronger complex, the end-point being the appearance of fluorescence. The titration is best performed by an instrumental method. A non-fluorescing weak complex can similarily be used for the titration of a cation which is strongly complexed and fluoresces. By making use of suitable combinations, it is possible to titrate a non-fluorescing complex former and a fluorescing complex former in the same solution.

RÉSUMÉ

L'acide hydroxy-8-quinoléine sulfonique-5 peut être utilisé pour des titrages compleximétriques par déplacement: un complexe fluorescent, faible, est utilisé pour titrer un ion formant un complexe non-fluorescent plus fort. L'apparition de la fluorescence indique le point final du titrage. L'inverse est également possible. On peut ainsi combiner le titrage d'un complexe non fluorescent avec celui d'un complexe fluorescent, dans une même solution.

ZUSAMMENFASSUNG

8-Hydroxychinolin-5-sulfonsäure kann bei komplexometrischen Titrationen in Form einer Verdrängungstitration verwendet werden. Es wird ein fluoreszierender schwacher Komplex verwendet um ein Ion, welches einen nichtfluoreszierenden stärkeren Komplex bildet, zu titrieren; der Endpunkt zeigt sich durch das Auftreten von Fluoreszenz an. Die Titration lässt sich sehr gut mit einer instrumentellen Methode durchführen. Ein nichtfluoreszierender schwacher Komplex kann in ähnlicher Weise für die Titration eines Kations verwendet werden, welches durch einen starken Komplex gebunden wird und fluoresziert. Durch günstige Kombination ist es möglich, einen nichtfluoreszierenden Komplexbildner und einen fluoreszierenden Komplexbildner in derselben Lösung zu titrieren.

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DOSAGE ELECTROCHIMIQUE RAPIDE, EN UNE SEULE OPERATION ET SANS SEPARATION, DU CALCIUM ET DU MAGNESIUM EN PRESENCE L'UN DE L'AUTRE

APPLICATION AUX DOSAGES DE CES ELEMENTS DANS LE SERUM SANGUIN ET DANS L'URINE

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Le dosage du calcium et du magnésium en présence l'un de l'autre, et plus spécialement dans les milieux biologiques, a fait l'objet, ces dernières années, de nombreuses publications. La majorité des méthodes proposées est basée sur l'estimation, à l'oeil ou photométriquement, du changement de teinte d'un indicateur coloré; quelques-unes font appel à l'électroanalyse; très rares sont celles qui permettent de doser en une seule opération ces 2 cations. Nous proposons ici une méthode titrimétrique de dosage de petites quantités et de traces de calcium puis de magnésium, sur une même prise, les points équivalents étant mis en évidence soit par potentiométrie, soit par ampérométrie. Dans ce dernier cas nous proposons un appareil simplifié.

KINGSLEY[1] a donné une liste des travaux de dosages Ca+Mg dans les milieux biologiques publiés en 1963–1964, signalant l'introduction de la spectrométrie d'absorption atomique (DECKER *et coll.*[2]) et de la photométrie de flamme (MUNDAY ET MAHY[3]). MONNIER ET ROUÈCHE[4,5] ont donné une revue des méthodes utilisant les indicateurs colorés. HÖFER[6] dose le calcium par photométrie, après séparation sur résine, en présence de naphtohydroxamate de sodium et le magnésium en présence de Noir Eriochrome T. BACZYK ET BARANOWSKA[7] précipitent le calcium comme oxalate puis le titrent en présence de "Cal. red", le magnésium étant titré dans le filtrat en présence de Noir Eriochrome T. PODDAR *et coll.*[8] séparent le calcium du magnésium par précipitation au moyen de l'acide salicylohydroxamique. JONES ET MCGUCKIN[9] proposent un dosage complexométrique semi-automatique en présence du bleu Eriochrome SA (EBSE) et FERGUSON ET BANKS[10] un dosage simultané de traces de calcium et de magnésium par spectrophotométrie en présence de chlorphosphonazo-III mais signalent l'interférence de la plupart des métaux, hormis les métaux alcalins. DELWICHE ET VOSTERS[11] proposent le dosage de microquantités de calcium et de magnésium par spectrométrie de masse. On trouve, enfin, deux méthodes d'électroanalyse, celle de MONNIER ET ROUÈCHE[4,5] permettant un dosage ampérométrique rapide du calcium par l'acide éthylène-glycol-bis-(amino-2-éthyl-éther)-N,N'-tétracétique (EGTA), puis du magnésium par l'acide éthylène-diamine-tétracétique (EDTA), et celle de SETHU RAO *et coll.*[12], dosage ampérométrique du calcium par l'EDTA, au pH 11.75 puis du magnésium au pH 9.60.

ÉTUDE DE LA MÉTHODE

Principe

On titre successivement par potentiométrie ou par ampérométrie, au pH = 10.5, en présence d'éthanolamine qui sert de tampon, le calcium par l'EGTA (Z^{4-}), le magnésium par l'EDTA (Y^{4-}):

$$(1)\ Ca^{2+} + Z^{4-} \rightarrow CaZ^{2-};\ (2)\ Mg^{2+} + Y^{4-} \rightarrow MgY^{2-}$$

Dans la suite de cet exposé nous négligerons, pour simplifier, la charge des particules.

Les constantes conditionnelles (dites aussi constantes apparentes) K'_{CaZ}, et K'_{MgZ} sont suffisamment grandes pour que les réactions (1) et (2) soient pratiquement quantitatives même pour des quantités inférieures au µg/ml de chacun de ces métaux. D'autre part, K'_{CaZ} et K'_{MgY} sont suffisamment différentes et K'_{MgY} suffisamment petite pour qu'à la fin de la titration du Ca^{2+}, on aperçoive un courant dû à l'excès de Z. Enfin les constantes K'_{MgY} et K'_{CaZ} sont telles que la réaction

$$CaZ + Y \rightarrow CaY + Z$$

ne se produit pas au cours de la titration du magnésium.

Constantes conditionnelles des complexes utilisés

Nous admettrons que l'éthanolamine ne forme pas de composés suffisamment stables avec le calcium et le magnésium pour avoir un effet notable sur la réaction de titration. Nous tiendrons compte des particules susceptibles d'exister dans nos conditions de travail, soit: Ca^{2+}, Ca(OH), CaZ, $CaHZ^{-}$, Ca_2Y, CaHY, CaY et les mêmes avec le magnésium (sauf Mg_2Y qui n'existe pas). On a donc:

$$\log {}^{Y}_{CaY} = 10.7 \quad \log {}^{H}_{CaYH} = 3.1 \quad \log {}^{Ca}_{Ca_2Y} = 2.0 \quad \log {}^{OH}_{CaOH} = 1.3$$

$$\log {}^{Z}_{CaZ} = 11.0 \quad \log {}^{H}_{CaZH} = 3.8$$

$$\log {}^{Y}_{MgY} = 8.7 \quad \log {}^{H}_{MgYH} = 3.9 \quad \log K^{OH}_{MgOH} = 2.6$$

$$\log {}^{Z}_{MgZ} = 5.2 \quad \log {}^{H}_{MgZH} = 7.7$$

Dans la plupart des cas on a $\alpha = 1$. Nous ne tiendrons compte que de $\alpha_{HY} = 10^{0.3}$ ce qui donne comme constantes conditionnelles

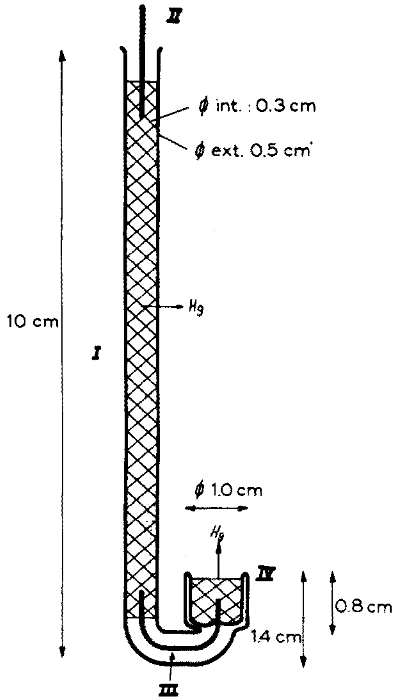
$$K'_{CaY} = \frac{K_{CaY}\alpha_{CaY}}{\alpha_{CaOH}\alpha_{YH}} = 10^{10.4} \quad K'_{MgY} = 10^{8.4} \quad K'_{CaZ} = 10^{11.0} \quad K'_{MgZ} = 10^{5.2}$$

Nous avons effectué les mêmes calculs avec les solutions de citrate, utilisées pour nos dosages lorsqu'ils se font en présence de fer, en tenant compte des particules CaHcit, CaH_2cit, CaH_3cit, MgHcit, MgH_2cit, et des diverses constantes acide–base de ce complexant et nous avons montré qu'il est pratiquement sans effet sur les réactions du dosage.

Les considérations théoriques sur le choix et le comportement des complexes ont été données par REILLEY[13–15] et RINGBOM[16]. Reprenant le travail de l'un de nous[4] nous avons constaté qu'en remplaçant l'électrode de calomel saturé par un fil de platine dans les conditions de notre dosage, il était possible d'effectuer l'analyse du calcium et du magnésium, sans imposer au système un potentiel, ce qui permet de simplifier le dispositif ampérométrique. Les fins de titration se manifestent par un brusque saut de courant ou de potentiel dû à un très léger excès d'EGTA pour le calcium et d'EDTA pour le magnésium.

Appareillage et électrodes

Le circuit est constitué de 2 électrodes: un fil de platine et une électrode inspirée de celle de REILLEY formée de (*a*) un tube de verre rempli de mercure (I), (*b*) un fil de cuivre (II) plongeant dans le mercure et reliant l'électrode à l'appareil de mesure, (*c*) un tube de verre plein (III) à l'intérieur duquel se trouve noyé un fil de platine. Ce fil de platine met en contact le mercure du tube I avec le mercure de la petite cupule (IV), qui est en contact direct avec la solution* et constitue la seconde électrode (Fig. 1). Les deux électrodes sont reliées à l'appareil de mesure au moyen d'un tube coaxial.



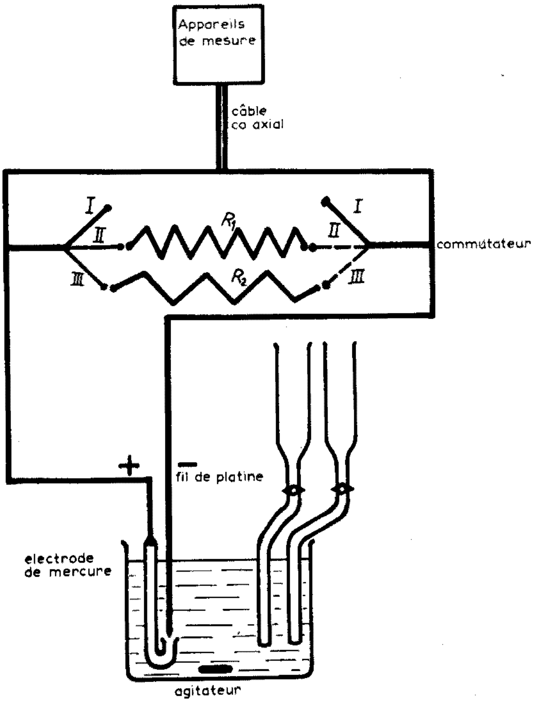


Fig. 1. Electrode indicatrice: II, fil de cuivre; III, fil de platine.

Fig. 2. Dispositif de titration. R_1, R_2: résistances dont les valeurs sont données dans le texte.

Appareils de mesure. Nous avons utilisé soit un appareil enregistreur (Potentiograph Metrohm E-336) soit un appareil à cadran permettant la lecture directe des variations de courant (Titriskop Metrohm E-366). On notera (Fig. 2) l'introduction d'un commutateur dans le circuit électrique reliant les électrodes. L'appareil de mesure est branché aux bornes de ce commutateur qui permet, sur la position I, de travailler en potentiométrie et, sur les positions II et III, d'introduire diverses résistances dans le circuit qui ont pour effet, lorsqu'elles sont judicieusement choisies, d'augmenter la sensibilité de la méthode, c'est-à-dire les brusques changements de courant aux points équivalents dus à l'oxydation du mercure en présence d'un excès d'EGTA, puis d'EDTA. Le choix des résistances résulte d'essais préliminaires effectués sur chacun

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* En effet, des traces de cuivre dissoutes dans le mercure modifient les potentiels ox/réd de telle sorte que le dosage n'est plus possible.

des milieux étudiés. Nous recommandons d'utiliser du mercure très pur et de le changer dès que l'on enregistre des résultats aberrants. Ce mercure doit être du reste soigneusement rincé à l'eau distillée entre chaque dosage. Moyennant ces précautions, il est possible de réaliser plusieurs dizaines de dosages sans enregistrer de perturbations.

Enregistrement (*résistances en circuit*). Les graphiques obtenus sont pratiquement des droites sur lesquelles la détermination du point équivalent est aisée. Il suffit, en effet, d'arrêter l'addition de réactif dès qu'on observe un brusque changement de direction de la plume enregistreuse. On dose le calcium par addition d'EGTA, on observe un saut au point équivalent (Fig. 3). Après quelques instants, on change la position du commutateur pour introduire une autre résistance dans le circuit et après stabilisation, on titre le magnésium avec l'EDTA (Fig. 3).

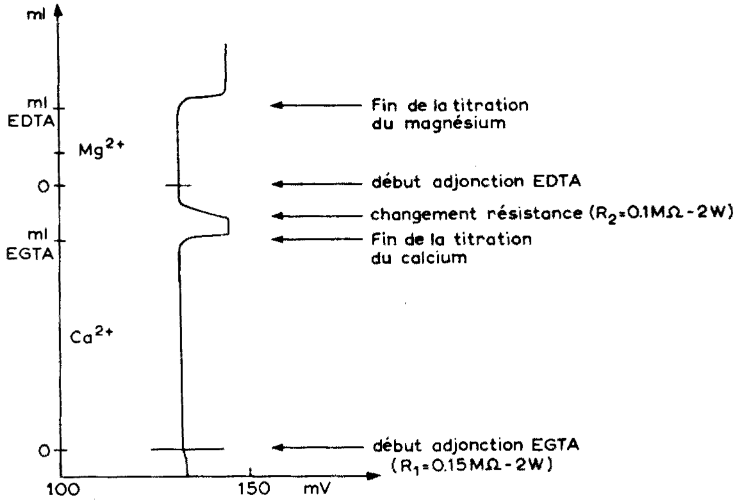

Fig. 3. Enregistrement d'un dosage calcium–magnésium dans un sérum labtrol fourni par la Maison Merz et Dade (ampérométrie). Dans la solution, au moment de la titration, il y a $[Ca^{2+}] = 3.5 \cdot 10^{-4}$ *M* soit $[Ca^{2+}] = 1.41$ µg/ml et $[Mg^{2+}] = 1.5 \cdot 10^{-5}$ *M* soit $[Mg^{2+}] = 0.35$ µg/ml.

Remarque! Le changement de résistance n'est pas toujours indispensable mais il améliore les conditions de dosage.

Burettes. Nous avons travaillé avec des microburettes en verre, de type courant dans le commerce, graduées au 0.01 ml. L'extrémité des burettes a été étirée en capillaire et, lors des titrations, leur orifice est immergé dans la solution et placé au-dessous de la surface de l'électrode de mercure.

Agitateur. Il doit être du type à aimant permanent. En effet, un agitateur du type électromagnétique perturbe la titration. Le bâtonnet métallique (enrobé de matière plastique) doit tourner avec grande régularité et ne heurter ni les parois du récipient, ni les électrodes, ni les extrémités des burettes.

Réactifs utilisés. (*1*) *Solution tampon* (*pH=10.5*). On introduit 6.1 g d'éthanolamine dans un ballon jaugé de 1 l, ajoute de l'eau presque au litre et porte la solution au pH 10.5 par addition d'acide nitrique concentré. On complète au trait de jauge avec de l'eau bidistillée.

(2) *Solutions de calcium et de magnésium destinées à l'étalonnage des réactifs.* Elles sont préparées à partir de $CaCO_3$ et $MgCO_3$.

(3) *Solution d'EGTA 10^{-2} M.* On dissout 3.8036 g d'EGTA (forme acide) dans 10 ml de NaOH 1 *M* en chauffant légèrement. On complète au litre avec de l'eau bidistillée.

(4) *Solution d'EDTA 10^{-2} M.* Préparée par dissolution du sel disodique dihydraté de l'acide éthylène-diamine-tétracétique.

(5) *Solution tampon complexante de citrate et de tartrate.* 1.00 g de citrate de sodium $C_6H_5O_7Na_3 \cdot 5\frac{1}{2}H_2O$ et 1 g de tartrate sodicopotassique sont dissous dans 100 ml d'eau bidistillée. Cette solution sert à masquer le fer(III), lors du dosage du Ca et Mg dans l'urine.

Tous les réactifs utilisés sont des produits "pro anal" Merck, Fluka ou Siegfried; les solutions sont conservées dans des flacons en polyéthylène.

Les solutions d'EGTA et d'EDTA sont renouvelées chaque mois car leur titre diminue légèrement au cours du temps.

DOSAGES DE SOLUTIONS PURES: MÉLANGES CALCIUM + MAGNÉSIUM

Mode opératoire

On introduit dans un bécher, 2 ml de la solution à doser ($0.3 \cdot 10^{-3}$ *M* en calcium et $0.125 \cdot 10^{-3}$ *M* en magnésium), on ajoute 5 ml d'une solution d'éthanolamine 10^{-1} *M* (pH = 10.5) et 10 ml d'eau bidistillée. On introduit les électrodes et branche l'agitateur, qui assure un brassage effectif et sans à coups de la solution. Les réactifs (EGTA 10^{-2}–10^{-3} *M* pour le calcium et EDTA 10^{-2}–10^{-3} *M* pour le magnésium) sont introduits au moyen de microburettes graduées au 0.01 ml. La titration est arrêtée dès que l'on observe un brusque saut de courant. Il faut éviter tout excès d'EGTA qui nuit à la précision du dosage ultérieur du magnésium. On lit alors le volume de solution titrée utilisée sur la microburette. Les résultats de quelques dosages sont donnés dans le Tableau I. L'essai I est fait par potentiométrie directe (l'appareil de mesure étant plus difficile à stabiliser). Les essais II sont faits par ampérométrie (courant

TABLEAU I

TITRATION Ca ET Mg DANS DES SOLUTIONS PURES

(Solutions titrées: EDTA 10^{-3} *M*, EGTA 10^{-3} *M*; $[Ca^{2+}] = 3.5 \cdot 10^{-4}$ *M* soit $[Ca^{2+}] = 1.41\ \mu g/ml$; $[Mg^{2+}] = 1.5 \cdot 10^{-5}$ *M* soit $[Mg^{2+}] = 0.35\ \mu g/ml$.)

Quantités trouvées en mg/l:

I série: potentiométrie

$[Ca^{2+}]$ 1.41, 1.41, 1.42, 1.42, 1.41, 1.42, 1.42, 1.41, 1.41, 1.41, 1.42
$[Mg^{2+}]$ 0.34, 0.34, 0.35, 0.36, 0.35, 0.35, 0.35, 0.35, 0.35, 0.35, 0.36
Moyenne: $[Ca^{2+}] = 1.413$; $[Mg^{2+}] = 0.35$

II série: ampérométrie

$[Ca^{2+}]$ 1.40, 1.41, 1.41, 1.41, 1.41, 1.41, 1.41, 1.41, 1.42, 1.41, 1.41
$[Mg^{2+}]$ 0.33, 0.35, 0.35, 0.36, 0.35, 0.35, 0.35, 0.35, 0.35, 0.35, 0.36
Moyenne: $[Ca^{2+}]=1.410$; $[Mg^{2+}]=0.346$

plus stable et sauts plus nets). La résistance R_1 (Fig. 2) est de 4.7 MΩ (2 W) pour le calcium et $R_2 = 1$ MΩ pour le magnésium.

Mesures

Nous donnons ci-dessus (Tableau I) les résultats obtenus pour les dosages des mélanges pures du calcium + magnésium, par potentiométrie et par ampérométrie. Pour les 2 séries d'essais on introduit 2 ml d'une solution de calcium 12 μg/ml ($3 \cdot 10^{-4}$ *M*) et 3 μg/ml ($1.75 \cdot 10^{-4}$ *M*) et y ajoute 10 ml d'eau bidistillée et 5 ml de tampon éthanolamine (pH = 10.5); volume final de la solution: 17 ml.

Remarque. La précision des résultats, dans nos conditions de travail, dépend de la lecture des burettes et non de la méthode elle-même. Une étude est en cours pour établir la fidélité et l'exactitude de cette méthode.

On constate (Fig. 3) que le courant enregistré est constant et que la courbe n'est pas en dents de scie comme c'est le cas lorsqu'on impose un potentiel[4]. Précisons que le graphique donne le courant en fonction du temps (c'est-à-dire en fonction de la vitesse de déroulement du papier, qui peut être synchronisée avec la vitesse d'écoulement de la solution titrée renfermée dans la microburette, ce qui n'est pas le cas ici, la lecture de la burette se faisant au moment du saut).

APPLICATIONS

Nous avons appliqué notre méthode au dosage du calcium et du magnésium dans divers milieux. Nous donnerons ici les résultats obtenus dans le sérum sanguin et dans l'urine.

Dosage du calcium et du magnésium dans le sérum sanguin

Les résistances utilisées sont de $R_1 = 0.15$ MΩ pour le dosage du calcium et $R_2 = 0.1$ MΩ pour celui du magnésium (Fig. 2).

Mode opératoire. 0.2 ml de sérum sont additionnés de 5 ml de tampon éthanolamine 10^{-1} *M* (pH = 10.5) puis de 10 ml d'eau bidistillée. On procède aux mesures selon la manière décrite pour les solutions pures, en changeant la résistance du circuit après le saut de courant indiquant la fin de titration du calcium.

TABLEAU II

TITRATION DU CALCIUM ET DU MAGNÉSIUM DANS LE SÉRUM SANGUIN

Valeurs trouvées en mg/l:

[Ca^{2+}] 84, 84, 83, 84, 85, 85, 84, 85, 85, 84
[Mg^{2+}] 21.1, 21.8, 21.1, 20.4, 21.1, 21.1, 21.1, 21.1, 21.1, 21.1
Moyenne: [Ca^{2+}] = 84.3; [Mg^{2+}] = 21.1
Valeurs trouvées par volumétrie compleximétrique: [Ca^{2+}] = 85; [Mg^{2+}] non dosé.

Dosages. Nous donnons ci-dessus (Tableau II) les résultats obtenus sur 1 sérum provenant de la Policlinique Universitaire de Médecine à Genève (Professeur E. MARTIN). Avant de procéder aux dosages, nous avons, à chaque essai, étalonné nos solutions par rapport au sérum standard Labtrol. Les réactifs utilisés étaient: EGTA 10^{-3} *M* et EDTA 10^{-3} *M*.

Nous avons effectué l'analyse de 3 autres sérums. Pour chacun d'eux il a été fait

10 dosages. Nous donnons ci-dessous les moyennes des valeurs avec les écarts extrêmes et entre parenthèses la valeur trouvée (en mg/l) par compleximétrie:

Calcium: 95 ± 1 (100), 59.1 ± 1 (63), 89.2 ± 1 (90)

Magnésium: 25.4 ± 1, 22.9 ± 1, 29.1 ± 1

Même remarque que ci-dessus; les erreurs proviennent essentiellement de la lecture des graduations des burettes. On peut donc augmenter la précision de la méthode ce qui n'est pas nécessaire ici.

Dosage du calcium et du magnésium dans l'urine

Ainsi que l'ont signalé MONNIER ET ROUÈCHE[5], un certain nombre de matières organiques sont électroactives et masquent les sauts. Le dosage direct dans l'urine n'est pas possible, un traitement préalable est nécessaire. Les diverses méthodes proposées dans la littérature pour la défécation de l'urine ne sont pas applicables à notre méthode de dosage. Elles font appel, en effet, à des sels de métaux qui sont complexés par l'EGTA et l'EDTA et faussent le dosage du calcium et du magnésium. Quant à la défécation par l'acide trichloracétique elle nécessite une neutralisation incompatible avec notre méthode. Le traitement au permanganate de potassium[5] ne convient pas non plus. D'autre part la minéralisation est trop longue, notre but étant d'établir une méthode rapide et directe.

Nous avons, par contre, remarqué que l'addition d'une trace de nitrate d'argent (0.1 à 0.3 ml $AgNO_3$ $N/100$) donne d'excellents résultats, rendant les sauts de fin de titration parfaitement décelables. En outre, l'utilisation de nitrate d'argent (en plus de la solution tampon complexante de citrate et de tartrate décrite ci-dessus, v. p. 235) permet d'augmenter le volume de la prise à doser et, de ce fait, d'augmenter la concentration des réactifs à 10^{-2} M.

Mode opératoire. Une prise de 1 ml d'urine fraîche est additionnée de 10 ml de solution tampon d'éthanolamine 10^{-1} M (pH = 10.5) puis de 0.2 ml de solution tampon complexante de citrate et de tartrate et enfin de 5 ml d'eau bidistillée. Après mélange, on additionne à la solution 0.3 ml d'une solution de nitrate d'argent 0.01 N. Un précipité blanc de chlorure d'argent apparaît quelques instants puis se dissipe, vraisemblablement par formation d'un complexe. On procède alors au dosage comme il est indiqué à la p. 235 avec une solution 10^{-2} M d'EGTA puis 10^{-2} M d'EDTA. Les résultats obtenus sont consignés dans le Tableau III.

TABLEAU III

DOSAGE DU CALCIUM ET DU MAGNÉSIUM DANS L'URINE AVEC EGTA 10^{-2} M ET EDTA 10^{-2} M

Valeurs trouvées en mg/l:			*Moyenne (mg/l)*
I[a]	$[Ca^{2+}]$	107, 106, 106, 104	105.6
	$[Mg^{2+}]$	49.2, 50.4, 49.2, 50.4	49.8
II[a]	$[Ca^{2+}]$	114, 112, 116, 116, 114, 112	114
	$[Mg^{2+}]$	39.6, 40.8, 40.1, 40.1, 38.9, 39.6	39.7
III[b]	$[Ca^{2+}]$	142, 144, 142, 142, 142, 138	142
	$[Mg^{2+}]$	72.6, 73.2, 72.0, 70.8, 73.2, 72.0	72.3

[a] Les essais I et II ont été effectués avec l'enregistreur. (p. 233)

[b] L'essai III au moyen d'un millivoltmètre à cadran.

Les points équivalents ont été détectés par ampérométrie en mettant en circuit une résistance R_1 de 0.15 MΩ pour le dosage du calcium puis en la remplaçant par une résistance R_2 de 47 kΩ pour le dosage du magnésium (Fig. 2).

Remarques

(*1*) Le rôle du nitrate d'argent fait l'objet d'une étude qui sera publiée ultérieurement. Nous avons toutefois montré qu'il ne gênait pas la titration.

(*2*) Ainsi que déjà signalé[5] la détermination du point final du titrage du calcium demande une certaine attention. On observe en effet un brusque saut de courant avant le point équivalent, saut dû probablement au fait qu'une partie du calcium est complexé aux protéines. Le courant du circuit ampérométrique reprend sa valeur initiale après quelques secondes. Une nouvelle addition d'EGTA cause le même phénomène. On poursuit le titrage du calcium jusqu'à ce que l'addition d'une trace de réactif ne provoque plus de variation de courant.

(*3*) La précipitation des protéines au cours du temps entraîne des quantités de calcium de plus en plus importantes. Notre méthode permet de suivre facilement ce phénomène.

(*4*) Le fait signalé au paragraphe précédent nous a conduit à travailler avec des urines fraîches. Nous nous réservons d'étudier le problème de la remise en solution des protéines précipitées lorsqu'on fait le dosage d'urines prélevées depuis un certain temps.

Nous remercions le Fonds National Suisse grâce auquel nous avons pu entreprendre ce travail.

RÉSUMÉ

Une simplification importante est proposée pour le dosage électrochimique du calcium et du magnésium en une seule opération dans le sérum sanguin et dans l'urine. En utilisant une électrode à fil de platine et une électrode à surface de mercure on peut doser le calcium par l'ion éthylèneglycol-bis-(amino-2-éthyl-éther)-N,N'-tétracétate, puis le magnésium par l'ion éthylène-diamine-tétracétate en présence d'un tampon (pH = 10.5) et éventuellement, d'un complexant (citrate–tartrate). Le courant qui se manifeste lors de l'oxydation du mercure en présence d'EGTA ou d'EDTA marque la fin de la titration. Ce courant peut être enregistré, ou lu sur un appareil à cadran. Dans le cas du sérum sanguin aucune opération préliminaire n'est nécessaire, dans le cas de l'urine le dosage est rendu possible par la simple adjonction de faibles quantités de nitrate d'argent.

SUMMARY

An important simplification is proposed for the simultaneous electrochemical titration of calcium and magnesium in blood serum and urine. By using platinum wire and mercury electrodes, calcium can be titrated with EGTA and then magnesium with EDTA in the presence of a buffer (pH 10.5) and possibly a citrate–tartrate masking agent. A current due to oxidation of mercury in presence of EGTA or EDTA marks the end-point, and can be read directly or recorded. For blood serum, no preliminary operation is needed; for urine, prior addition of a little silver nitrate makes the method satisfactory.

ZUSAMMENFASSUNG

Es wird eine Vereinfachung für die gleichzeitige elektrochemische Titration von Calcium und Magnesium in Blutserum und Urin vorgeschlagen. Verwendet man einen Platindraht und Quecksilberelektroden, so kann Calcium mit AeGTE und anschliessend Magnesium mit AeDTE titriert werden in Gegenwart eines Puffers (pH 10.5) und von Zitrat und Tartrat. Ein Strom, der in Gegenwart von AeGTE oder AeDTE zur Oxydation des Quecksilbers gehört, kennzeichnet den Endpunkt und kann direkt abgelesen oder aufgezeichnet werden. Für Blutserum sind keine vorhergehenden Arbeiten erforderlich; beim Urin erwies sich eine anfängliche Zugabe von Silbernitrat als günstig.

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THE SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM IN SEA WATER

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Most of the published data on the occurrence of chromium in the sea relates to near-shore waters, and there appears to be a complete dearth of information about its concentration in oceanic waters, particularly at depth. Such figures as there are, range from 0.04 to 2.5 μg Cr/l (Table I), and were obtained either spectrographically or spectrophotometrically following a preliminary concentration of the element by coprecipitation[1-5]. With the exception of that used by LOVERIDGE *et al.*[5], very few of the analytical processes have been thoroughly studied.

TABLE I

PREVIOUS DETERMINATIONS OF CHROMIUM IN SEA WATER

Chromium found (μg/l)	*Sampling locality*	*Method of concentration*	*Method of determination*	*Reference*
0.2	Gullmar fjord	Coprecipitation	Spectrographic	1
1.0–2.5	British coastal waters	Coprecipitation with tannin + thionalide + oxine in presence of Fe^{3+} and Al^{3+}	Spectrographic	2
0.04–0.07	Japanese coastal waters	Coprecipitation with aluminium hydroxide	Spectrophotometric with diphenylcarbazide	3,4
0.13–0.25	Unspecified	Coprecipitation with aluminium hydroxide	Spectrophotometric with diphenylcarbazide	5

An investigation of the marine geochemistry of trace elements including chromium is in progress in these laboratories. This paper describes the development and evaluation of a method for the determination of chromium at the level of *ca.* 0.4 μg/l in natural waters.

Concentration of chromium from sea water

Since the chromium content of sea water is low it must be concentrated from a large volume of sample before spectrophotometric analysis can be performed. Coprecipitation or cocrystallization appeared to be the most effective methods for the concentration of the element and experiments were therefore carried out using radioisotopic tracer techniques to select the most suitable carrier.

Aliquots (2 l) of sea water which had been filtered through a 0.5 μ filter were acidified, and enriched with *ca.* 0.1 μc of chromium-51 as chromium(III) (0.075 μg chromium carrier). Solutions of iron(III) chloride or aluminium ammonium sulphate equivalent to 4 mg Fe or 10 mg Al respectively were then added; the solutions were heated to 50–60° and adjusted to a range of pH values by addition of appropriate amounts of a borate buffer of pH 11 with vigorous stirring. The solution was allowed to stand overnight and the clear supernatant liquid was siphoned off through a Whatman GF/B glass-fibre filter. The remaining liquid carrying the bulk of the precipitated hydrous oxide was quantitatively transferred to the filter which was then washed with a 1.5% (w/v) ammonium chloride solution. The precipitate was dissolved in concentrated hydrochloric acid and the solution was evaporated to small volume and diluted to 10 ml. The chromium-51 activity of a suitable aliquot of this solution was then determined using a scintillation counter. This activity was compared with that of a suitable aliquot of the original chromium-51 solution. The results of these experiments (Table II) indicate that both aluminium and iron(III) hydroxide will coprecipitate chromium efficiently, but that the pH range for *ca.* 99% coprecipitation with the latter (7.0–9.0) is considerably greater than with aluminium (pH 7.5–8.0). In the analysis of sea water using coprecipitation with aluminium hydroxide, difficulties were encountered owing to coprecipitation of silicic acid, which made the hydroxide precipitate difficult to filter. This difficulty did not occur with iron(III) hydroxide which was therefore adopted for concentration of chromium from sea water.

TABLE II

RECOVERY OF CHROMIUM FROM SEA WATER AT VARIOUS pH VALUES USING HYDROUS IRON(III) OXIDE AND HYDROUS ALUMINIUM OXIDE

Volume of sea water (l)	*Amount of chromium added (µg)*	*Hydrous iron(III) oxide*		*Hydrous aluminium oxide*	
		pH	*% recovered*	*pH*	*% recovered*
2	0.075	3.0	15.5	6.0	16.7
2	0.075	6.5	47.1	7.0	91.7
2	0.075	7.0	98.7	7.5	98.6
2	0.075	8.0	98.5	8.0	98.4
2	0.075	8.5	98.8	8.5	94.3
2	0.075	9.0	98.4	9.0	93.5

Hydrous manganese dioxide (prepared by the reaction between manganese(II) and permanganate ion at pH 4–5[6]) was also investigated as a possible selective coprecipitant for chromium; it was found that the precipitate (equivalent to 100 mg of manganese) carried down only *ca.* 23±2% of the chromium present in sea water.

Experiments were carried out to test the efficiency of the coprecipitation technique employed by BLACK AND MITCHELL[2] for concentration of a number of trace elements, including chromium, from sea water. In this method the trace elements are coprecipitated at pH 5.1 by means of a mixture of tannin, thionalide and 8-hydroxyquinoline; aluminium and iron(III) are apparently added as carrier although this is not explicitly stated in their paper. Repetition of their work using 2 l of sea water and 10 mg each of Fe^{3+} and Al^{3+}, gave a chromium recovery of 78% (determined radio-chemically); in the absence of iron and aluminium only 45% was recovered.

Chromium could be cocrystallised in >99% yield by treating a 3-l aliquot of sea water buffered to pH 9.0 with 15 ml of a solution of 5,7-dibromo-8-hydroxyquinoline in acetone. Difficulties involved in the subsequent destruction of the reagent prevented the adoption of this reagent for the concentration of chromium from sea water.

Separation of chromium from iron

Iron(III) hydroxide was found to be the most satisfactory coprecipitant for chromium. Since milligram amounts of iron interfere in the photometric determination of microgram amounts of chromium with diphenylcarbazide, it is necessary to separate the two elements. ISHIBASHI and his co-workers[3,4] used alkaline fusion for the separation of chromium from aluminium; under these conditions chromium is oxidized to the 6+ oxidation state and can be leached from the hydrous aluminium oxide residue with water. Experiments carried out by fusing iron(III) hydroxide precipitates (equivalent to 6 mg Fe), bearing *ca.* 1 μg of chromium enriched with ^{51}Cr, with 0.5 g of sodium carbonate as described by ISHIBASHI *et al.*[3,4], showed that only *ca.* 88% of the chromium present could be leached from the fused cake with water. The remainder of the chromium was retained by the iron(III) oxide residue (*ca.* 3%) and by the platinum crucible in which the fusion was performed (*ca.* 9%).

In view of the strong uptake of iron(III) from concentrated hydrochloric acid medium by anion exchangers, it can be readily separated from metals such as chromium which do not form chloro-anions[7]. The separation of chromium from iron was therefore studied using a 5 cm × 0.8 cm diameter column of Permutit De-Acidite FF (SRA 71) anion-exchange resin in its chloride form. This ion exchanger is a strongly basic (quaternary ammonium) polystyrene resin 7–9% cross-linked with divinylbenzene; the mesh size is 100–200 B.S.S. mesh grading. It was found that if a solution of *ca.* 1 μg of chromium containing *ca.* 0.1 μc of chromium-51 in 5 ml of concentrated hydrochloric acid was allowed to flow through the column, and if the latter was then washed with 3 successive 5-ml aliquots of concentrated hydrochloric acid, >99% of the chromium was present in the combined percolate and washings. If a solution of iron(III) chloride (equivalent to 6 mg of iron) in 5 ml of concentrated hydrochloric acid was treated in the same manner it was quantitatively retained on the column. Anion exchange thus provides a simple and convenient method of separating *ca.* 1 μg of chromium from the 6 mg of iron used for its coprecipitation from 3 l of sea water.

The combined hydrochloric acid washings from the ion-exchange columns when evaporated to dryness leave a faintly yellow coloured organic residue. This must be destroyed by evaporation with hydrogen peroxide before spectrophotometry, since it interferes in the photometric determination.

Photometric determination of chromium

The *sym*-diphenylcarbazide photometric method was selected for the determination of chromium on account of its high sensitivity (0.0025 μg/cm^2). In this procedure, chromium is oxidized to the 6+ state; after destruction of excess oxidizing agent the chromate ion is allowed to react with diphenylcarbazide yielding a red-violet colour, the intensity of which is measured. A number of oxidizing agents has been described for oxidizing the chromic ion to chromate. Preliminary tests showed that neither alkaline fusion (see also above) nor persulphate oxidation were satisfactory with 1-μg amounts of chromium. Oxidation with cerium(IV) in dilute sulphuric acid medium was effective and gave a *ca.* 99.5% yield of chromate even at the 0.5 μg Cr level. The modification of this procedure described by BLUNDY[8] was adopted, and it was found that it gave a coefficient of variation of 2.2% at a level of 1 μg of chromium/25 ml final volume.

Comparatively few elements interfere in the determination of chromium with diphenylcarbazide. The interference of iron from the coprecipitation is avoided by its anion-exchange removal before determination. Vanadium in moderate amounts interferes by giving a yellow coloration, but since its concentration in sea water (1.9 μg/l) is only about 4 times that of chromium[9], its interference is negligible. Molybdenum and mercury would only cause interference at concentration levels many times those at which they occur in sea water.

Oxidation state of chromium in sea water

Chromium occurs in nature in both the 3+ and 6+ oxidation states. Although thermodynamic considerations suggest that chromium occurs in sea water almost entirely in the 3+ state, it was thought desirable to prove that this is in fact so. Experiments made using radio-isotope techniques showed that using the method developed above for coprecipitation of chromium(III), only *ca.* 1.2% of chromium in the 6+ oxidation state was coprecipitated. However, when sea water containing *ca.* 0.07 μg/l of chromium(VI) spiked with ^{51}Cr(VI) was treated with a small volume of a saturated solution of sulphur dioxide to reduce the chromate, *ca.* 99% of the added chromium was coprecipitated with iron(III) hydroxide. Aliquots (2 l) of a number of samples of sea water were analysed by the methods described below both with and without treatment with sulphur dioxide before the coprecipitation stage. In each instance the amounts of chromium found both with and without reduction were the same within the experimental error of the method. This suggests that chromium occurs mainly in the 3+ oxidation state in the sea. The chromic ion probably occurs in a partially hydrolysed form.

EXPERIMENTAL

Determination of chromium in sea water

A Unicam SP500 spectrophotometer was used for all photometric measurements. Measurements were made in a 4-cm glass cell against a compensator cell containing distilled water. An EKCO scintillation counter Type N664A with a NaI(Tl) well crystal coupled to an EKCO scaler Type N530F was used for counting γ-activity of chromium-51 solutions.

Reagents

Borate buffer. Dissolve 19.07 g of sodium tetraborate decahydrate and 4.0 g of sodium hydroxide in water and dilute to 1 l.

Iron(III) chloride solution. Prepare from reagent-grade iron(III) chloride solution a solution containing 1 mg of iron/ml.

Ammonium ceric nitrate solution, 0.02 N. Dissolve 10.96 g of ammonium ceric nitrate in 1 *N* sulphuric acid and dilute to 1 l with 1 *N* sulphuric acid.

Sodium azide solution, 4% (w/v). Prepare 5 ml of this reagent immediately before use.

Diphenylcarbazide. Dissolve 0.25 g of *sym*-diphenylcarbazide in 100 ml of acetone. The reagent is stable for at least 1 month if kept in a refrigerator.

Standard chromium solution. Dissolve 0.282 g of potassium dichromate (dried at 120°) in *ca.* 900 ml of 1 *N* sulphuric acid. Reduce the dichromate to the chromic state by passing a stream of sulphur dioxide through the solution. Boil until the excess sulphur dioxide has been removed and after cooling dilute to 1 l. This stock solution, which contains 100 μg Cr/ml is used for the preparation of a working standard solution containing 1 μg Cr/ml; this solution should be renewed weekly.

Ion-exchange columns

Wash De-Acidite FF ion-exchange resin (7–9% cross-linked, 100–200 mesh) by decantation with 1 *N* hydrochloric acid. Pour sufficient of the resin into an 8-mm bore ion-exchange tube to give a packed length of 5 cm. Wash the resin with 50 ml of 1 *N* hydrochloric acid and then with four 10-ml aliquots of concentrated hydrochloric acid. After use, regenerate the resin by washing it with 50 ml of 1 *N* hydrochloric acid and then with four 10-ml aliquots of concentrated hydrochloric acid. The resin deteriorates with repeated use and should be rejected after it has been used 3 times.

Preparation of fibre-glass filters and cleaning of apparatus

The 3-cm diameter Whatman glass-fibre filters used for the filtration of the iron(III) hydroxide contain appreciable amounts (0.1–0.2 μg) of acid-soluble chromium. Before they are used for filtration, they must be washed with 50 ml of a mixture of 50 ml of concentrated nitric acid, 150 ml of concentrated hydrochloric acid and 200 ml of water[10]. Apparatus used in the determination should be cleaned, when necessary, with this acid mixture and not with chromic acid which tends to be adsorbed on glass surfaces.

Determination of chromium in sea water

Filter the sample through a 0.5 μ filter as soon as possible after collection and add 4 ml of 2 *N* hydrochloric acid per 2 l of water. The sample may now be stored in the dark in bottles made of high density polyethylene for up to at least 3 weeks without risk of loss of chromium. Place 2 l of the sample in a 4-l conical flask and add to it 4 ml of iron(III) chloride solution (equivalent to 4 mg Fe). Heat the flask to 50–60° on a hot plate and then add with stirring 60 ml of borate buffer; this will bring the pH of the solution to *ca.* 7.5. Allow the solution to stand overnight. Siphon the clear supernatant liquid through an acid-washed 3-cm diameter Whatman glass-fibre filter. Transfer the precipitate to the filter using a jet of 1.5% (w/v) ammonium chloride solution, and wash it thoroughly with the same solution. Suck the precipitate almost dry and then insert the stem of the filter column holding the filter into the top of the ion-exchange column. Dissolve the precipitate by the dropwise addition of 5 ml of concentrated hydrochloric acid, and wash the filter with a further three 5-ml portions of concentrated hydrochloric acid. Collect the percolate and washings in a 50-ml silica beaker and evaporate to dryness on the water bath. Add 0.5 ml of 100-vol. hydrogen peroxide and 5 ml of distilled water. Heat the covered beaker on the water bath to destroy organic decomposition products from the ion exchanger. Evaporate the solution to dryness, and add 2 ml of ammonium ceric nitrate solution, 2 ml of 2.5 *N* sulphuric acid and 4–5 ml of water. Heat the covered beaker on a hot plate for *ca.* 45

min. Add to the cool solution sufficient sodium azide solution to destroy the yellow colour of the excess cerium(IV) plus one drop in excess. Transfer the solution to a 25-ml graduated flask, using not more than 15 ml of water to complete the transfer. Add 2 ml of diphenylcarbazide solution and dilute to volume. After 15 min measure the optical density of the solution at 540 mμ in a 4-cm cell against a compensating cell containing distilled water.

Determine the reagent blank as described above using sea water which has been stripped of chromium by precipitation of iron(III) hydroxide in it. Calibrate the method either by carrying out spectrophotometric diphenylcarbazide determinations on 1-μg amounts of chromium, or preferably by analysing 2-l aliquots of stripped sea water which have been spiked with 1 μg of chromium.

RESULTS

In order to check the reproducibility of the proposed method, replicate analyses (5) were carried out on 2-l aliquots of a membrane-filtered sample of surface water from the Irish Sea. These showed the presence of 0.46 ± 0.016 μg Cr/l. Quadruplicate analyses were also carried out on 2-l aliquots of another sea water (found to contain 0.48 μg Cr/l) which had each been spiked with 1.00 μg of chromium and with ^{51}Cr. Amounts of chromium of 1.49, 1.49, 1.46 and 1.48 μg were found, showing that the efficiency of the analytical process was satisfactory. This was in agreement with the radiochemically determined overall yield of the process which was $98.5 \pm 0.3\%$.

Storage of samples

Since several weeks may elapse between the collection of samples on oceanographic expeditions and their analysis, the effect of storage on the chromium content of filtered sea water was investigated. Aliquots (2 l) of filtered (0.5 μ membrane filter) sea water were brought to *ca.* pH 2.0 by addition of 4 ml of 2 *N* hydrochloric acid and spiked with ^{51}Cr containing 0.075 μg of inert chromium carrier. The spiked solutions were transferred to 2-l bottles of soda glass, pyrex glass and high-density polyethylene and allowed to stand at 20° in the dark for 10 days. At the end of this time, iron(III) hydroxide precipitations were carried out in the solutions and the ^{51}Cr activities of the precipitates were determined by scintillation counting. It was found that 13.9 and 11.7% of chromium had been lost from the water samples stored in soda and pyrex glass bottles respectively, presumably by adsorption onto their surfaces. However, no loss occurred in bottles made of polyethylene, and it is recommended that samples should be acidified and stored in containers constructed of this material.

SUMMARY

The coprecipitation of chromium from sea water by several precipitates was examined. With hydrous iron(III) oxide a recovery of chromium of >99% was obtained within the pH range 7.0–9.0 at a chromium level of *ca.* 0.4 μg/l. Chromium was separated from iron by anion exchange and determined spectrophotometrically using diphenylcarbazide. The method showed a precision of ± 0.02 μg Cr/l. Chromium occurs in sea water in the 3+ oxidation state.

RÉSUMÉ

Les auteurs ont examiné la coprécipitation du chrome dans l'eau de mer, au moyen de plusieurs précipités. Avec l'hydroxyde ferrique, on a pu obtenir un rendement de >99% de chrome entre les pH 7 et 9, pour des teneurs en chrome de 0.4 μg/l. Le chrome est ensuite séparé d'avec le fer par échangeur d'anions et dosé spectrophotométriquement au moyen de diphénylcarbazide. Précision: ±0.02 μg Cr/l. Dans l'eau de mer le chrome se trouve au degré d'oxydation +3.

ZUSAMMENFASSUNG

Es wurde die Mitfällung von Chrom aus Seewasser durch verschiedene Fällungen untersucht. Mit wässrigem Eisen(III)-oxid wurde eine Rückgewinnung des Chroms von mehr als 99% erhalten bei einem pH-Bereich von 7.0 bis 9.0 und einem Chromgehalt von *ca.* 0.4 μg/l. Chrom wurde vom Eisen mit Hilfe eines Anionaustauschers abgetrennt und spektralphotometrisch mit Diphenylcarbazid bestimmt. Die Methode besitzt eine Genauigkeit von ±0.02 μg Cr/l. Chrom tritt im Seewasser in der dreiwertigen Oxydationsstufe auf.

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A MODIFIED APPARATUS FOR DETERMINATION OF CARBON IN METALS BY THE LOW PRESSURE METHOD

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Since carbon in metals and alloys has a considerable effect on their physical properties, a simple and precise method for its determination is often required. Of the many available methods for determination of carbon at low levels[1-8] the low pressure method has the highest precision and is usually preferred. In this paper the low pressure method has been improved with important modifications to give a simple and precise procedure, whereby some of the difficulties encountered in previous methods are eliminated. Liquid oxygen is usually employed in the low pressure method for the separation of carbon dioxide from the stream, but because of its hazardous nature, RAMAKRISHNA[9] replaced it with liquid air with a modified trap. However, a large amount of oxygen then condensed during a determination and a long time was required to pump off all the condensed oxygen[10]. In an attempt to overcome these difficulties, a slush bath of isopentane cooled in liquid air to yield a temperature of −160° was used so that no oxygen was condensed whereas carbon dioxide was completely condensed. A differential oil manometer used in the place of the McLeod gauge enhanced the sensitivity of the method. A sample tree was introduced to minimise the blank and the experimental time. This method was standardised and employed for the determination of carbon in metals and alloys such as uranium, iron, zirconium, stainless steel and cupronickel.

EXPERIMENTAL

Apparatus

The general set-up is shown in Fig. 1 and consists of purification, combustion, freezing and measuring assemblies. The oxygen is purified by passing over hot copper oxide at 900° (C) and then over Ascarite and Anhydrone (D). A flow meter (E) controls the rate of flow of oxygen.

The compact combustion assembly consists of a pyrex sample tree (H) joined by a B40 ground glass joint, with its male part joined permanently to a 1.2″ I.D. recrystallised alumina tube (I) by means of elastomer. The sample tree has 4 sample spoons (see Fig. 2) at the top, from which the samples can be dropped one at a time into the hot zone by rotation of the ground glass joint. The lower part of the oxygen inlet tube is of quartz joined by a graded joint. The samples are received in an alumina crucible (10 ml) kept over alumina powder at the bottom of the combustion tube; the crucible is renewed every 10 determinations. A vertical furnace (B_2) wound with

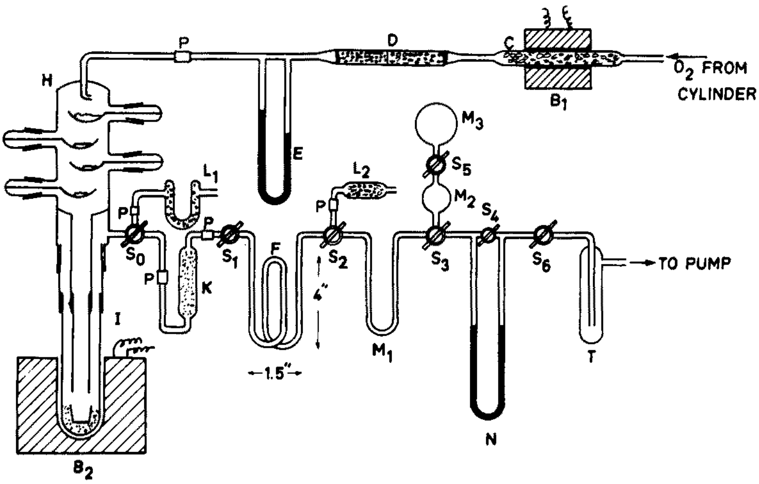

Fig. 1. Apparatus for the determination of carbon. B_1, B_2, Furnace; C, CuO packed tube; D, anhydrone + soda-lime tube; E, Flow meter; F, Five coil freezing trap; H, Sample tree; I, Combustion tube; K, Ag-vanadate trap; L_1, L_2, Soda-lime guard tubes; M_1, Calibrated U tube (I.D. = 3.5 mm); M_2, M_3, Calibrated bulbs; N, Oil manometer; P, Small tygon tube connection; S_0, S_2, S_3, Three-way vacuum stop cocks; S_1, S_4, S_5, S_6, Two-way vacuum stop cocks; T, Liquid air trap.

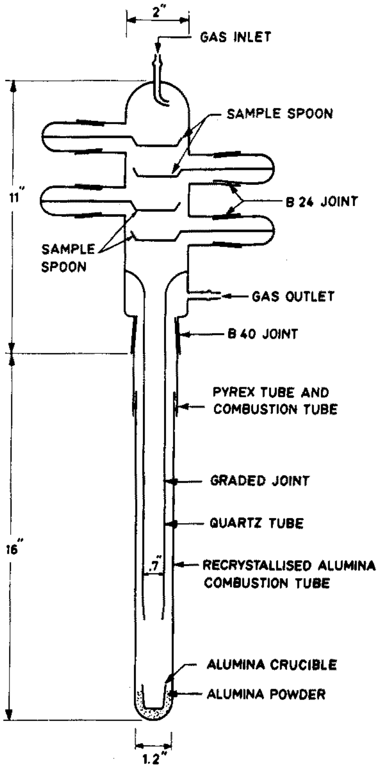

Fig. 2. Sample tree and the combustion system.

"Kanthal A" wire is used to ignite the sample at 800° but for higher temperatures a furnace with Pt–20% Rh wire as the heating element is necessary. A silver vanadate trap (K) removes any traces of sulphur oxides.

The freezing coil (F) (consisting of 5 coils of glass tube, I.D. 2 mm and 4″ high) separates carbon dioxide from the stream. The coil is cooled by a bath of isopentane immersed in a bath of liquid air (−160°). A trap of dry ice–acetone slurry retains traces of moisture in the coil while the carbon dioxide is transferred and recondensed in tube M_1. The carbon dioxide is then expanded in a suitable calibrated volume (M_1, M_2 or M_3) and the pressure exerted is measured by means of the differential oil manometer (N) filled with Apiezon A oil.

Guard tubes of Ascarite and Anhydrone (L_1 and L_2) at the outlets prevent any possible contamination from the atmosphere.

Procedure

Furnaces B_1 and B_2 are brought to appropriate temperatures and the oxygen flow is adjusted to 400 ml/min. The freezing and measuring assembly is connected to a vacuum pump. Prepared metal samples (to contain 5–100 μg of carbon) are accurately weighed and transferred to the spoons in the sample tree. Freezing trap (F) is immersed in isopentane cooled by liquid air. After the combustion system has been flushed for a few minutes the oxygen flow is diverted to the atmosphere through the freezing trap and guard tube (L_2). The sample is dropped into the combustion tube by turning the lowest sample spoon. After 6 min, the oxygen flow is diverted to the atmosphere through S_0, S_1 is closed and S_2 is opened to vacuum. S_2 is then closed, and the isopentane bath is removed and replaced by an acetone–dry ice slurry. The calibrated U-tube M_1 is isolated from the rest of the system and kept immersed in liquid air. S_2 is opened to tube M_1 and S_3 is connected to vacuum. S_2 and S_3 are closed and tube M_1 is brought to room temperature. S_4 is closed and S_3 is carefully opened to the oil manometer and the corresponding differential pressure is noted along with room temperature. The amount of carbon (in μg) is calculated from the following formula.

$$C = K \cdot \frac{Z}{(273+t)} \left(\frac{Z}{2} \cdot 0.181 + V\right)$$

where

$$K = \frac{12 \cdot 10^3}{22.4} \cdot \frac{273}{76} \cdot \frac{d_{\text{oil}}}{d_{\text{Hg}}} = 122.9$$

d_{oil} = density of Apiezon A oil = 0.8539
d_{Hg} = density of mercury = 13.546

0.181 is the area of cross-section of the manometer tube (in cm^2).

Z = difference in oil levels (in cm).

V = volume (in ml) in which carbon dioxide is expanded at t°.

The blank is determined by following the above procedure without the sample.

RESULTS AND DISCUSSIONS

In the present apparatus three calibrated volumes 12.17, 26.40 and 73.66 ml were provided to facilitate the use of the apparatus for different ranges of carbon content. These calibrated volumes, of course, did not include the correction volumes due to the lowering of the oil level in the manometer. Appropriate correction for this was included in the final calculation. With the smallest calibrated volume (M_1) 1 mm of difference in the oil level corresponded to 0.5 μg or 0.00005% of carbon on the basis of a 1-g sample.

It was found that the use of the differential oil manometer was not at all cumbersome and that there was no difficulty in reading up to 1 mm difference in the oil levels. The oil levels attained steady positions fairly quickly. It may be pertinent to point out here that the disadvantages of using an oil manometer are not as serious as has been generally thought, at least for the pressures measured here (0.06 mm Hg).

The overall blank of the apparatus and the methods after a series of experiments was found to be 4 mm of oil for the lowest volume, which corresponds to 2 μg of carbon for a combustion period of 6 min.

A standard was prepared by diluting A.R. grade calcium carbonate with fine pre-ignited quartz powder so that 1 mg corresponded to 1 μg C. The procedure as detailed above was followed taking various quantities of the standards in the range of 5–100 μg of carbon. For the combustion of the standards in the form of powders, the vertical combustion system was replaced by a horizontal tube. A series of standards at the level of 5, 15, 25, 60 and 100 μg of C were ignited. The standard deviations and coefficient of variation found for this series are given in Table I; it can be seen that as little as 5 μg of carbon could be determined with a coefficient of variation of 16%; the coefficient decreased to 3.3% at the 100-μg level. The results of a series of determinations on the carbon content of uranium, zirconium, pure iron, stainless steel and cupronickel alloy are given in Table II. The results on the uranium metal samples obtained by our present conductometric method are given in the Table for comparison.

TABLE I

RECOVERY OF CARBON FROM $CaCO_3$–QUARTZ STANDARDS

Sr. no.	*Amount of C taken (μg)*	*Amount of C recovered (μg)*	*Mean (μg)*	*Standard deviation (σ)*	*Coefficient of variation (%)*
1	5	4.8, 3.6, 5.0, 5.7, 5.2, 5.9	5.0	0.8	16.0
2	15	13.9, 16.3, 17.7, 15.6, 13.0, 17.0, 16.5	15.7	1.7	11.3
3	25	27.6, 26.1, 25.1, 27.7, 26.2, 24.8, 24.5, 26.1, 28.1	26.3	1.4	5.6
4	60	63.5, 57.5, 59.4, 53.5, 61.5	59.1	3.9	6.5
5	100	98.6, 98.0, 102.0, 92.9, 102.1, 97.7, 95.7	98.1	3.3	3.3

Good agreement and precision were observed in all cases, except in the case of the cupronickel alloy where the value obtained by the present method (0.006% ± 0.0004% s.d.) was much lower than the B.C.S. certified value of 0.02%. This B.C.S. value of 0.02% is an average of 9 results varying from 0.03 to 0.008%; for 4 of these results, *viz.* 0.01, 0.014, 0.009 and 0.03%, details of the methods are not described. In 2 cases when a flux was used the values were 0.03 and 0.029%, the temperature being

TABLE II

DETERMINATION OF CARBON IN METALS AND ALLOYS

Sr. no.	*Sample*	*Combustion temp. (°)*	*Carbon obtained*	*Mean value*	*Standard deviation (σ)*	*Reference value*
1	Uranium metal A	800°	76.5, 85.1, 76.8, 81.8, 87.2, 81.2 (p.p.m.)	81.4 (p.p.m.)	4.3 µg	87 p.p.m.[a] (σ = 4.3)
2	Uranium metal B	800°	82.2, 80.8, 76.3, 83.4, 87.1, 86.5, 82.2 (p.p.m.)	82.5 (p.p.m.)	3.5 µg	81 p.p.m.[a] (σ = 5.3)
3	Uranium metal C	800°	95.3, 98.2, 95.6, 100.0, 94.3, 97.5, 97.7 (p.p.m.)	96.9 (p.p.m.)	2.0 µg	93 p.p.m.[a] (σ = 7.1)
4	Zirconium metal	1300°	0.0312, 0.0310, 0.0306, 0.0290 (%)	0.0305 (%)	0.0009%	—
5	Pure iron B.C.S. No. 260	1300°	0.0192, 0.0191, 0.0173, 0.0185, 0.0176, 0.0167 (%)	0.0181 (%)	0.001 (%)	0.018%
6	Stainless steel B.C.S. No. 246	1300°	0.0581, 0.0605, 0.0639, 0.0583, 0.0600, 0.0630, 0.0645 (%)	0.0612 (%)	0.0026 (%)	0.062%
7a	Cupronickel alloy B.C.S. No. 180	1300°	0.0062, 0.0063, 0.0058, 0.0062, 0.0056, 0.0063 (%)	0.0061 (%)	0.0003 (%)	0.02%
7b	Cupronickel alloy B.C.S. No. 180 with flux	1000°	0.0067, 0.0059, 0.0061, 0.0065, 0.0068 (%)	0.0064 (%)	0.0004 (%)	0.02%
7c	Cupronickel alloy B.C.S. No. 180 with flux	1300°	0.0059, 0.0058, 0.0059, 0.0065 (%)	0.0060 (%)	0.0003 (%)	0.02%

[a] Average of 5 determinations by conductometric method[11].

specified (1000°) in only one case. Values obtained in experiments where carbon was determined on the residue after treatment with ammonium copper(II) chloride were 0.015 and 0.007%; this value also agreed with the results of direct combustion (0.009%) obtained by the same laboratory. In experiments involving treatment with ammonium copper(II) chloride, the question of release of carbon should be secondary. The values in the two cases were lower than those obtained by use of fluxes.

The determination of carbon is generally done at 1000° and fluxes are added to accelerate combustion. However, when the percentage of carbon lies in the region of about 0.02%, blanks from the fluxes are of the same order or greater and are likely to introduce considerable errors in analysis. In order to avoid this likely source of error it was decided to carry out the combustions at considerably higher temperatures, as in the case of cupronickel alloy, at 1300°.

A further series of determinations was made on this alloy by using red lead as a flux, the temperatures being 1000° and 1300° respectively. The blank value for 0.2 g of the flux was 11 μg which was comparable with about 12 μg of carbon in 0.2 g of the sample. The results (Table II) obtained by use of the flux after correcting for the blank indicate no deviation from the results obtained without the flux but at a temperature of 1300°.

SUMMARY

The low pressure method of determination of carbon in metals and alloys was modified to include certain new techniques. An isopentane slush bath dispensed with the use of liquid oxygen and the usual McLeod gauge was replaced by a differential oil manometer, which increased the sensitivity. As little as 5 μg of carbon in $CaCO_3$–quartz standards could be determined with a coefficient of variation of 16.0% which improved to 3.3% at the 100-μg level. The apparatus was used for the determination of carbon in metals such as uranium, zirconium and iron and in steels and cupronickel alloy.

RÉSUMÉ

Les auteurs décrivent une modification d'appareil pour le dosage du carbone dans les métaux, par la méthode à basse pression, avec utilisation d'un manomètre à huile, différentiel, afin d'améliorer la sensibilité. 5 μg C dans des étalons $CaCO_3$–quartz peuvent être dosés avec un coefficient de variation de 16%, atteignant 3.3% pour des teneurs de 100 μg. Application au dosage du carbone dans les métaux, tels que uranium, zirconium, fer, ainsi que dans les aciers et cupronickel.

ZUSAMMENFASSUNG

Die Niedrigdruck-Methode zur Bestimmung von Kohlenstoff in Metallen und Legierungen wurde modifiziert. Neu eingeführt wurde ein Differentialölmanometer, welches die Empfindlichkeit steigerte. 5 μg Kohlenstoff in einem Calciumcarbonat–Quartz-Standard konnte mit einem Variationskoeffizienten von 16.0% bestimmt werden, der sich bis auf 3.3% bei 100 μg verbesserte. Die Apparatur wurde für die Bestimmung von Kohlenstoff in Metallen wie Uran, Zirkonium und Eisen und in Stählen und Kupfernickellegierung verwendet.

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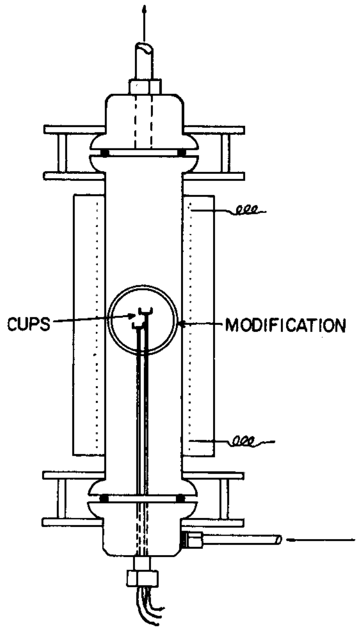
SHORT COMMUNICATIONS

A simultaneous DTA–GEA–MSA apparatus

We have recently described an apparatus[1] in which gas evolution analysis (GEA) and mass spectrometric analysis (MSA) can be performed simultaneously on the same sample under identical conditions of pyrolysis. We wish to report here a slight modification of this apparatus which will enable the simultaneous determination of the differential thermal analysis (DTA), gas evolution analysis, and mass spectrometric analysis of a sample. This simple adaptation thus increases the utility of this apparatus and extends the list of simultaneous techniques by one other thermoanalytical technique[2].

Experimental

The apparatus and pyrolysis procedure employed remained essentially the same as previously described[1] except for the pyrolysis chamber. This modification is shown in Fig. 1. The single ceramic insulator tube was replaced by 2 double-bore ceramic insulator tubes through which the thermocouple wires were led. Small stainless-steel cups, 6 mm in diameter by 2 mm in depth, obtained from the Technical



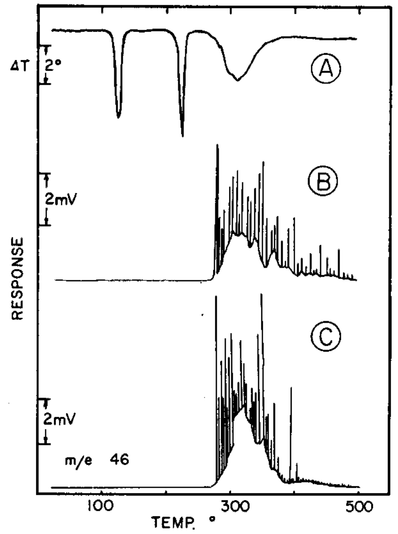


Fig. 1. Modification of pyrolysis chamber.

Fig. 2. The pyrolysis of potassium methylsulfate. (A) DTA curve; (B) GEA curve; (C) MSA curve; helium atmosphere.

Equipment Corporation, Denver, Colorado, were welded to the ends of the thermocouple wires. Two cups were employed, one for the sample, the other for the reference material (generally α-Al_2O_3). The emf output from the differential thermojunctions was amplified by a Leeds and Northrup Model 9835-B d.c. microvolt amplifier and displayed on the Y-axis of a Houston Instruments Corporation X-Y recorder. The sample temperature, as detected by the sample cup thermojunction, was displayed on the X-axis of the recorder.

Sample sizes employed ranged in weight from 20 to 25 mg and were heated at a furnace heating rate of 15°/min.

The potassium methylsulfate used was the same as previously described[3].

Results and discussion

The use of the apparatus is illustrated by the simultaneous DTA–GEA–MSA curves of potassium methylsulfate, as shown in Fig. 2.

This compound undergoes the following thermal transitions[3]:

$$\alpha\text{-}KCH_3SO_4(s) \xrightarrow{\sim 110^\circ} \beta\text{-}KCH_3SO_4(s)$$

$$\beta\text{-}KCH_3SO_4(s) \xrightarrow{\sim 233^\circ} KCH_3SO_4(l)$$

$$KCH_3SO_4(l) \xrightarrow{>250^\circ} K_2S_2O_7(s) + (CH_3)_2O(g)$$

These transitions are evident in the 3 endothermic peaks seen in the DTA curve in Fig. 2A. The GEA curve (curve B) shows that dimethyl ether is evolved during the last peak and that it is given off in small bursts such as bubbles of gas being evolved from a liquid. On setting the mass spectrometer to monitor a m/e of 46 entity, the curve in Fig. 2C was obtained. This curve followed the general shape of the GEA curve and again indicated the sporadic nature of the dimethyl ether evolution.

The addition of DTA to the GEA–MSA apparatus thus increases its utility and application to the solution of certain chemical problems. Three types of thermoanalytical data can easily be obtained from a single sample under identical conditions of pyrolysis.

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Titration of iron(III) and copper with EDTA using N-benzoyl-N-phenylhydroxylamine as indicator

Iron(III) and copper have been determined by EDTA titrations with many different indicator systems. In the present investigation, iron or copper was titrated with EDTA in the presence of a N-benzoyl-N-phenylhydroxylamine (BPHA) solution in chloroform as indicator. Iron and copper form reddish violet and greenish yellow complexes respectively with BPHA which can be extracted with chloroform[1]. The advantage of BPHA as the metal indicator in the determination of copper is that the end-point is sharp (the chloroform layer changes to colourless from greenish yellow) and copper can be titrated in the presence of many foreign ions, *e.g.* Zn^{2+}, Cr^{3+}, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Ti^{4+}, Th^{4+}, and small amounts of Mn^{2+}. In the titration of iron(III), the end-point is also sharp and even small amounts (50 μg) of iron(III) can be determined; again few ions interfere.

Determination of iron or copper

Procedure (a). Dilute a measured amount of iron(III) chloride or copper sulphate solution to 50 ml. For the iron titration adjust the pH to 1.0–1.3 with dilute hydrochloric acid solution, and for the copper solution adjust to pH 4.2–5.4 by adding 10% sodium acetate solution and dilute hydrochloric acid. Add 8–10 ml of 0.001 *M* BPHA in chloroform for iron, or 10–15 ml of 0.005 *M* BPHA in chloroform for copper. Titrate with standard EDTA solution, shaking the solution so that the chloroform layer becomes coloured (red for iron or greenish yellow for copper). Shake vigorously as the end-point is approached. At the end-point, the chloroform layer becomes colourless. Typical results are shown in Table I.

TABLE I

DETERMINATION OF IRON OR COPPER USING BPHA IN CHLOROFORM AS INDICATOR

Iron present (mg)	*Iron found (mg)*	*Error (mg)*	*Copper present (mg)*	*Copper found (mg)*	*Error (mg)*
0.341[a]	0.340	−0.001			
			4.65	4.63	−0.02
3.41	3.47	+0.06			
6.82	6.86	+0.04	9.3	9.3	0.00
10.23	10.25	+0.02	18.6	18.68	+0.08
10.23	10.28	+0.05	27.9	27.92	+0.02
13.64	13.7	+0.06			
			37.2	37.3	+0.1
0.1705[a]	0.1700	−0.0005	55.8	56.0	+0.2
0.0852[a]	0.0856	+0.0004			

[a] The initial volume of solution was only 10 ml.

Standard 0.001186 *M* and 0.0001186 *M* EDTA solutions were used for the titration of semimicro and micro amounts of iron; a 0.01234 *M* solution was used for the titration of copper.

Procedure (b). Dilute the iron(III) solution to 100 ml and adjust the pH to 1.5–2.0. Add an alcoholic 1% solution of BPHA (10–12 drops) as indicator and titrate the iron with standard EDTA solution. The end-point is indicated by a change from red-violet to colourless or light yellow. Results are shown in Table II.

TABLE II

DETERMINATION OF IRON EMPLOYING 1% BPHA IN ALCOHOL AS INDICATOR

Iron present (mg)	*Iron found (mg)*	*Error (mg)*	*Iron present (mg)*	*Iron found (mg)*	*Error (mg)*
0.1705[a]	0.1709	+0.0004	6.82	6.76	−0.06
0.0852[a]	0.0860	+0.0008	10.23	10.2	−0.03
3.41	3.38	−0.03	0.341	0.330	−0.011

[a] The initial volume of the solution was 10 ml.

Effect of pH

When the pH value was adjusted by adding dilute hydrochloric acid and/or 10% sodium acetate solution, the titrations of iron and copper could be performed in the pH ranges 0.8–1.4 and 3.9–5.4 respectively. Outside these ranges EDTA does not form 1 : 1 stoichiometric complexes with the metals.

It should be noted that iron(III) and copper could not be titrated in the same solution because the colourless chloroform layer obtained after the titration of the iron again became reddish when the pH was raised above 3.

Effect of concentration of organic reagent

Iron(III) could be titrated using a very dilute chloroform solution of BPHA as indicator, just sufficient to develop the colour in the chloroform layer. It was, however, best to use 6–8 ml of 0.0008 to 0.002 *M* BPHA in chloroform. The results tended to be erratic with reagent concentrations above 0.003 *M*. In the titration of iron(III) in presence of the ethanolic reagent solution the reagent concentration did not play any important role, but the sharpness of the end-point was less satisfactory than in the extraction method.

Copper was best titrated with EDTA using 10–15 ml of 0.005 *M* reagent in chloroform as indicator. A slight variation in the concentration of BPHA did not affect the titration of copper but a large excess of the reagent caused appreciable error.

The accuracy of the visual titrimetric methods was checked by a type of spectrophotometric titration in which the absorbances of the chloroform layer were measured after addition of varying amounts of EDTA solution.

Effect of foreign ions in the titrations of iron and copper

Measured amounts of iron solutions were titrated in the presence of different amounts of foreign ions at pH 1.2 by Procedure (a), and at pH 1.5 by Procedure (b). Results are shown in Table III. Traces of Mo^{6+}, Th^{4+}, VO_3^- interfered in both cases. In Procedure (a), even small amounts of Ni^{2+} and Cu^{2+} interfered; in the presence of

TABLE III

EFFECT OF FOREIGN IONS IN THE TITRATION OF IRON AND COPPER

Foreign ion added (mg)	*Metal ion found (mg)*	*Error (mg)*	*Foreign ion added (mg)*	*Metal ion found (mg)*	*Error (mg)*
Titration of iron (0.341 mg)[a]			*Titration of copper (4.65 mg)*[c]		
Cd^{2+} (10)	0.341	0.00	Zn^{2+} (6)	4.59	−0.06
Ti^{4+} (1)	0.345	+0.004	Zn^{2+} (8)	Interferes	
Ni^{2+} (5)	0.345	+0.004	Mn^{2+} (5)	4.55	−0.1
Hg^{2+} (80)	0.339	−0.002	Cr^{3+} (26)	4.64	−0.01
UO_2^{2+} (15)	0.341	0.00	Fe^{3+} (17)[d]	4.63	−0.02
Ce^{3+} (3)	0.343	+0.002	Al^{3+} (30)[d]	4.57	−0.08
Mn^{2+} (32)	0.341	0.00	Th^{4+} (10)[d]	4.62	−0.03
Cu^{2+} (15)[b]	0.347	+0.006	Mo^{6+} (50)	4.66	+0.01
Ni^{2+} (20)[b]	0.347	+0.006	Hg^{2+} (50)	4.63	−0.02
Al^{3+} (15)	0.341	0.00	UO_2^{2+} (36)	4.65	0.00
Ca^{2+} (40)	0.341	0.00	Ce^{3+} (5)	4.67	+0.02
Mg^{2+} (60)	0.341	0.00	Ti^{4+} (20)[d]	4.62	−0.03
Titration of iron (0.341 mg)[e]					
Al^{3+} (160)	0.343	+0.002	Mo^{6+} (23)[f]	0.345	+0.004
Cu^{2+} (0.2)	0.346	+0.005	Mo^{6+} (115)[f]	0.345	+0.004
Zn^{2+} (44)	0.341	0.00	Ce^{3+} (12)	0.35	+0.009
UO_2^{2+} (15)	0.341	0.00	Mg^{2+} (60)	0.341	0.00
Ni^{2+} (8)	0.352	+0.011	Ca^{2+} (20)	0.341	0.00
Cr^{3+} (50)	0.341	0.00	Ti^{4+} (6)[f]	0.341	0.00
Mn^{2+} (64)	0.349	+0.008	Cd^{2+} (15)	0.345	+0.004
			Hg^{2+} (10)	0.342	+0.001

[a] With 10–15 ml of 0.001 *M* BPHA in $CHCl_3$.
[b] Tartrate added.
[c] With 10–15 ml of 0.005 *M* BPHA in $CHCl_3$.
[d] Fluoride added.
[e] With 1% BPHA in alcohol as indicator.
[f] In 50% alcohol.

tartaric acid or tartrate appreciable amounts of these ions could be tolerated. Iron(III) could be titrated in the presence of large amounts of Mo^{6+} and Ti^{4+} (6–7 mg) in 50% alcoholic solution, using an alcoholic 1% BPHA solution as indicator.

Copper was titrated between pH 4.4 and 4.6 with EDTA in the presence of foreign ions using the extraction end-point (Table III). Large amounts of Mo^{6+} could be tolerated when sufficient indicator solution was added to make the organic layer distinctly greenish yellow in colour. Ordinarily trace amounts of Fe^{3+}, Ti^{4+}, Th^{4+}, Al^{3+} interfered, but the addition of fluoride prevented these interferences.

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Chemical separation and determination of small quantities of calcium and magnesium

Chemical separation of small quantities of calcium from magnesium by the well-known oxalate method has various defects: magnesium oxalate invariably post-precipitates[1,2], and handling difficulties impose a serious restriction on the quantity of separable calcium. To overcome these difficulties, a new method of separation based on the coprecipitation of calcium with strontium sulphate from an alcoholic aqueous solution was investigated. Direct compleximetric titrations of an aliquot of the mixture, and of an aliquot of the filtrate containing the separated magnesium fraction allows a complete analysis of both the components of the mixture (magnesium directly and calcium by difference).

The efficiency of the separation procedure was checked by testing for calcium in the separated magnesium fraction, and testing for magnesium in the calcium-bearing strontium sulphate precipitate; for calcium, the radioactive isotope, calcium-45 was used as indicator[3], and for magnesium, a dilute acid extract of the precipitate was tested with Magneson II.

The optimum experimental conditions, ensuring quantitative uptake of calcium by the strontium sulphate precipitate and complete absence of magnesium in the solid phase, were worked out by a systematic study of the influence, under otherwise identical conditions, of the significant factors.

The results showed that for quantitative separation, the optimum conditions were: (*a*) alcohol concentration, between 38 and 46.5%; (*b*) pH of the precipitation medium, between 3.2 and 4.0; (*c*) strontium sulphate carrier, $\geqslant 325$ mg; (*d*) the mole ratio $[SO_4^{2-}]/[Sr^{2+}]$, between 1.5 and 1.75; and (*e*) quantity of calcium $\leqslant 1$ mg; magnesium contents varying between 2 and 20 mg had no influence.

Reagents

All reagents used were of AnalaR grade. A 0.01 *M* EDTA solution was used for the final determination with a microburette graduated to 0.01 ml.

Procedures

Separation method. A typical separation is described. Add gradually a solution containing 375 mg of strontium nitrate in aqueous ethanol (21.5 ml of ethanol diluted to 30 ml with water) to 20 ml of a hot (*ca.* 60°) solution of calcium (0.8 mg) and magnesium (5.0 mg) containing 430 mg of potassium sulphate. Adjust the pH to *ca.* 3.5 with sodium acetate solution and allow to stand, with occasional stirring, for 30–45 min. Filter the precipitate through Whatman no. 42 filter paper, and wash 4 times with 5-ml portions of wash solution (containing 260 mg of potassium sulphate per 100 ml of 43% ethanol).

Radiochemical test for calcium in the magnesium fraction. Appropriate amounts of potassium sulphate, strontium nitrate and ethanol were added to the filtrate. The pH was adjusted to 3.2–5.0 and the suspension was centrifuged. The residue was made to a slurry with acetone and transferred to a clean dry planchet with a dropper, after which it was dried by infrared heating. The activity was measured with an end-window G.M. counter in conjunction with a decatron scaler. Corrections for the background count-rate were made; decay and dead time were insignificant.

Determination of calcium and magnesium

The separated magnesium was determined in an aliquot of the filtrate by titration with EDTA using eriochrome black T indicator[4]. The total amount of calcium and magnesium was determined in an aliquot of the original solution by a similar titration; from the two observations, the quantity of calcium in the mixture was obtained by difference. The possible interference in the compleximetric determination of magnesium by passage of traces of strontium into the filtrate was examined carefully. Blank experiments showed that under the specified conditions of separation, no strontium ions appeared in the filtrate; to check for strontium, the filtrate was evaporated to dryness and the residue was examined for strontium by the flame colour.

Results and discussion

The results of analysis of a few typical mixtures (Table I) indicate the suitability of the procedure for mixtures involving small quantities. Separation of calcium by coprecipitation is limited by factors such as pH, alcohol and sulphate ion concentrations. The method is also limited by the quantity of calcium (< 1 mg); larger quantities could probably be separated by increasing the amount of strontium sulphate carrier. The quantity of magnesium in the mixtures poses no problem in the separation, although the determination of small quantities of magnesium in the filtrate is subject to the normal limitations of EDTA titrations. However, by adding a known amount of magnesium to a trace amount in the filtrate, down to 0.05 mg of magnesium can be determined. An advantage of the procedure is that an analysis can be completed within 2–3 hours.

TABLE I

DETERMINATION OF CALCIUM AND MAGNESIUM IN MIXTURES

(Amount of carrier ($SrSO_4$) = 325 mg; pH = 3.5; $[Sr^{2+}]/[SO_4^{2-}]$ ratio = 2:3; ethanol in the aqueous medium = 43%)

Composition of mixture before sepn.		*Amounts determined in filtrate after coprecipitation*		*Calcd. amount of Ca coprecipitated with $SrSO_4$ (mg)*	*Calcd. amount of Mg coprecipitated with $SrSO_4$ (mg)*
Ca (mg)	*Mg (mg)*	*Ca (mg)*	*Mg (mg)*		
0.2	5.0	Nil[a]	5.002	0.196	Nil[b]
0.4	5.0	Nil[a]	4.995	0.408	Nil[b]
0.6	5.0	Nil[a]	4.991	0.615	Nil[b]
0.8	5.0	Nil[a]	5.002	0.796	Nil[b]
0.8	2	Nil[a]	2.000	0.800	Nil[b]
0.8	4	Nil[a]	3.993	0.811	Nil[b]
0.8	5	Nil[a]	4.995	0.808	Nil[b]
0.8	20	Nil[a]	19.991	0.815	Nil[b]

[a] Checked radiochemically.

[b] Checked with Magneson II.

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The homogeneous precipitation of lead molybdate

The determination of molybdenum as a lead salt was proposed as early as 1871 by CHATARD[1]; subsequent work has been reviewed by BUSEV[2]. Although accurate, the present gravimetric methods are time-consuming. Taking advantage of the slowness of reaction between chromium(III) and EDTA[3-5] we have developed a method of homogeneous precipitation based on the reactions

$$H_2Y^{2-} + Pb^{2+} \rightarrow PbY^{2-} + 2\ H^+$$

$$PbY^{2-} + Cr^{3+} + MoO_4^{2-} \rightarrow CrY^- + PbMoO_4$$

where H_2Y^{2-} represents the ionized form of the disodium salt of ethylenediaminetetraacetic acid. Precipitates obtained in this fashion were more granular and more readily filtered and washed than those obtained by heterogeneous precipitation. In addition, the precipitate showed no tendency to cling to the walls of containers as did precipitates formed in the traditional manner.

Procedure

The order of addition of reagents was critical; for samples containing *ca.* $5.6 \cdot 10^{-4}$ moles of molybdenum the following method of operation gave good results.

Place the sample in a 150-ml beaker, together with a magnetic stirring rod. Add 21 ml of 0.1 *M* Na_2H_2Y, adjust the pH to 4 (acetic acid or sodium hydroxide) and adjust the total volume to about 50 ml. Place the beaker on a combination magnetic stirrer–hot plate. Cover with a special watch glass containing a small hole in the center. Adjust the stirrer to stir gently and heat the solution to near boiling. Add 15 ml of 0.1 *M* lead nitrate. If the solution becomes cloudy, add more Na_2H_2Y dropwise until the cloudiness just disappears. Increase the temperature to obtain gentle boiling. When boiling has been maintained for *ca.* 60 sec, place a buret containing 0.2 *M* chromium(III) nitrate through the hole in the cover glass so that the tip is about 1.5 cm below the level of the glass. Add the chromium(III) solution very slowly until sufficient is present for complete precipitation of the molybdate. For the concentrations of molybdate and other reactants used here, 6.5–7.0 ml of chromium(III) solution is recommended. Remove the buret and continue heating at the boiling point for an additional 10 min. Cool to *ca.* 40°. Decant the purple liquid through a filtering crucible containing a glass fiber filter pad. Wash the precipitate with water to remove all traces of purple material. Transfer the precipitate to the filter, thoroughly cleaning the magnetic stirring bar with a rubber policeman. Heat the crucible and contents at 200° to constant weight, and weigh as $PbMoO_4$.

Results

Synthetic samples of molybdate were prepared from samples of $Na_2MoO_4 \cdot 2H_2O$. The results of the analysis of these samples are shown in the Table.

Qualitative experiments indicated that the best results were obtained when the amount of chromium(III) added did not surpass the amount of EDTA present. Since a 1:1 chromium–EDTA complex is formed, judgement could be made as to how much chromium(III) was needed.

TABLE I

RESULTS FOR SYNTHETIC SAMPLES

$Na_2MoO_4 \cdot 2H_2O$ *taken (mg) (96.7% purity)*	*$PbMoO_4$ (mg)*	
	Theoretical	*Found*
136.6	200.4	201.1
137.0	201.1	201.3
138.7	203.6	204.6
139.0	204.0	204.0
139.1	204.1	205.4
Average	202.6	203.3

The same treatment was applied to sulfate samples as that used for molybdate. However, there was no noticeable Cr–EDTA complex formed. Instead of the characteristic reddish purple color of the complex, a green colored solution was produced, and no precipitate of lead sulfate appeared. It may be postulated that the sulfate inhibits Cr–EDTA complex formation, although more investigation is necessary to ascertain the exact role of the sulfate.

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Séparation du sodium par précipitation

La chromatographie par échange d'ions est fréquemment utilisée pour le dosage des traces (en analyse par activation). Une élimination rapide de la matrice est toujours recherchée, ce qui permet d'opérer sur des petites colonnes avec des solutions très peu concentrées en cations.

En général, le poids de matrice traitée est de l'ordre de quelques centaines de milligrammes. Mais lorsque la mise en solution nécessite une attaque par fusion, au peroxyde de sodium par exemple, le poids de fondant requis peut atteindre 10 fois celui de la matrice. Il en résulte une solution initiale très concentrée en ions sodium qu'il faut éliminer si on veut éviter l'emploi de grosses colonnes et des perturbations lors de la fixation et de l'élution des autres cations.

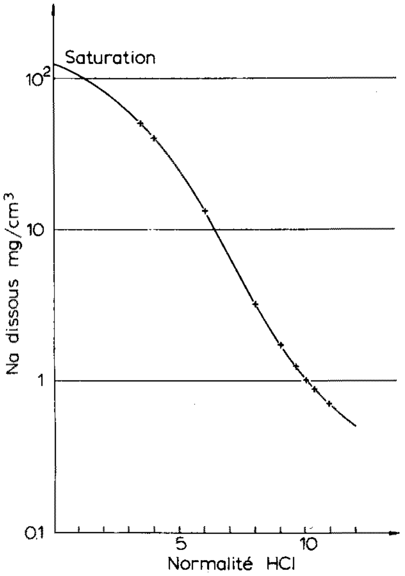

Fig. 1. La concentration en sodium en fonction de la normalité en HCl.

L'élimination du sodium peut se faire par précipitation de NaCl en milieu butanol–HCl[1,2]. Mais la présence de butanol dans le milieu final modifie considérablement les chromatographies. Nous avons donc cherché à éviter l'emploi de butanol en précipitant le NaCl en milieu chlorhydrique concentré. Le graphique représente la variation de la concentration en sodium en fonction de la normalité en HCl de la solution. NaCl a été précipité en ajoutant à 10 ml de solution saturée à 316 g par litre à 20° une solution chlorhydrique préparée à partir de HCl concentré 12 *N* servant par ailleurs à la préparation d'éluants pour chromatographie. La concentration de la solution surnageante, après précipitation, est mesurée par le rapport de son activité en ^{24}Na à celle de la solution initiale.

L'élimination de la majeure partie du sodium est donc possible à condition d'effectuer la reprise après fusion dans le plus petit volume possible et de saturer ensuite par HCl gazeux.

Il fallait aussi vérifier que les éléments à l'état de traces se retrouvaient bien dans la solution. En précipitant NaCl en milieu HCl 10 N, ^{89}Sr, ^{134}Cs, ^{60}Co, ^{51}Cr(III), ^{46}Sc, ^{153}Gd, ^{124}Sb, ^{233}Pa se retrouvent à plus de 96% dans la solution surnageante. Une double précipitation de NaCl permet de récupérer quantitativement ces éléments. ^{110m}Ag se partage entre la solution et le précipité. Dans certains cas, la fixation des cations pourra se faire directement à partir du milieu final.

Cette méthode donc est à utiliser lorsqu'on désire se débarrasser d'une grande quantité de sodium. Une autre application de cette méthode est le dosage du sodium à l'état de traces, après activation neutronique et addition d'entraîneur.

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The behaviour of crystal violet and methyl violet in anhydrous acetic acid medium

In titrations of basic substances with perchloric acid titrants in anhydrous acetic acid medium, crystal violet or methyl violet are frequently employed as end-point indicators; both are used indiscriminately, even in determinations of one specific substance[1,2]. To elucidate whether such an arbitrary choice is justified, the behaviour of both indicators was investigated in anhydrous acetic acid medium. The experiments were performed in antipyrine (phenazone) buffer solution, and the indicators were evaluated by means of complementary tristimulus colorimetry[3,4].

Apparatus

Extinction curves were measured by means of a Spekol spectrophotometer (VEB Zeiss, Jena) with cells of 1.000 cm inner diameter. Millivolt values in the antipyrine buffer solution were measured with a Multoskop V electron tube potentiometer (Laboratorní potřeby, National Enterprise) using a SEV 2 glass indicator electrode (Labora National Enterprise) and a KALC 4 saturated calomel reference electrode (Labora). Before use the device was calibrated in the millivolt range with the aid of a QTK technical compensator (Metra National Enterprise).

Reagents

Antipyrine buffer solution was prepared by mixing appropriate volumes of 0.1 M antipyrine solution in anhydrous acetic acid and 0.1 N perchloric acid in the same solvent.

A 0.1 *N* solution of perchloric acid in anhydrous acetic acid was prepared as proposed[5] for the PhBs III (Czechoslovak Pharmacopeia, 3rd Revision, in preparation). Both the anhydrous acetic acid and the concentrated perchloric acid complied with the requirements proposed for the PhBs III[5]. Antipyrine (99.92%) complied with official requirements of purity[6], and was recrystallized from ethanol before use. The indicators complied with official requirements: crystal violet (Bayer) with those proposed for the PhBs III[5], and methyl violet (LPC London) with those of PhBs II[6]. Each was dissolved in anhydrous acetic acid to give a 0.02% indicator solution.

Methods

Antipyrine buffer solutions were prepared graded in steps of 20 mV within the range of mV values usual in titrations in anhydrous acetic acid medium. To these solutions appropriate volumes of the respective indicator solutions were added, and colour changes were observed. In samples exhibiting selected colour tints, at the appropriate mV value, extinction curves were measured. From these curves, complementary chromaticity values were obtained by the 10 selected ordinates method[3,4] using the illuminant C (simulating average daylight). The x and y values were then plotted, yielding a complementary chromaticity diagram[3,4]. In measurements of extinction curves, anhydrous acetic acid was used as blank solution. The measurements were made immediately after the addition of the indicator solution to the buffer solution.

Results and discussion

Both crystal violet and methyl violet are serviceable end-point indicators in assays of numerous substances in anhydrous acetic acid medium[1]. Both indicators appear to exhibit equal colour changes at the end-point. The present detailed examination showed that the colour changes of both indicators in antipyrine buffer solution were identical within given mV intervals (Table I).

TABLE I

COLOUR CHANGES* OF CRYSTAL VIOLET AND METHYL VIOLET IN ANTIPYRINE BUFFER SOLUTION

mV	360–440	460	480	500	520	540	560	580–600	620	640–660
Colour	v	v-b	b	l-b	g-b	b-g	g	l-g	g-y	y

* v = violet, b = blue, l = light, g = green, y = yellow.

The absorbance curves were also virtually identical: at low mV values both had a maximum at 590 nm, at higher mV values another maximum at 630 nm, and both indicators exhibited a transition at 520 mV (Fig. 1).

Complementary tristimulus colorimetry showed that the respective positions of complementary colour points for the two indicators in the chromaticity diagram (Fig. 2) coincided; all points for both indicators always lay on the same curve and within the same colour sectors.

The respective colour specifications expressed in the terms of brightness, dominant wavelength, and purity[3] were practically identical for both indicators, as shown in Table II.

This investigation proves that crystal violet and methyl violet exhibit identical colour changes, which is clearly due to their closely related chemical structures[7].

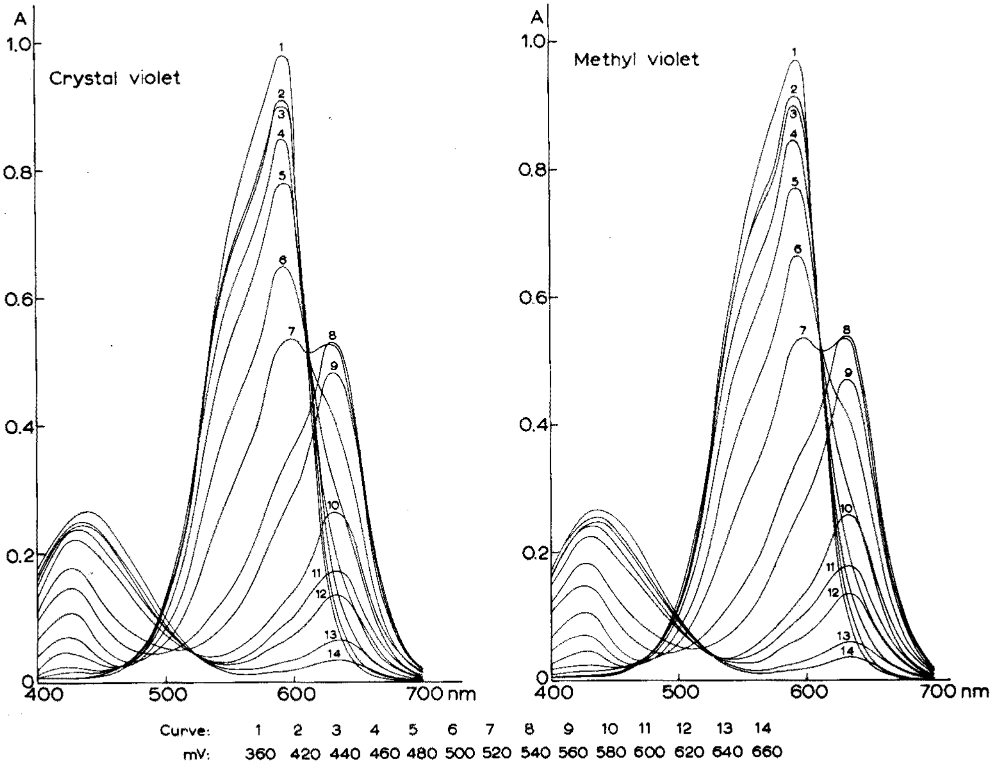

Fig. 1. Absorbance curves of crystal violet and methyl violet in antipyrine buffer solution at various mV values. Each 10 ml of buffer solution contained 0.20 ml of indicator solution.

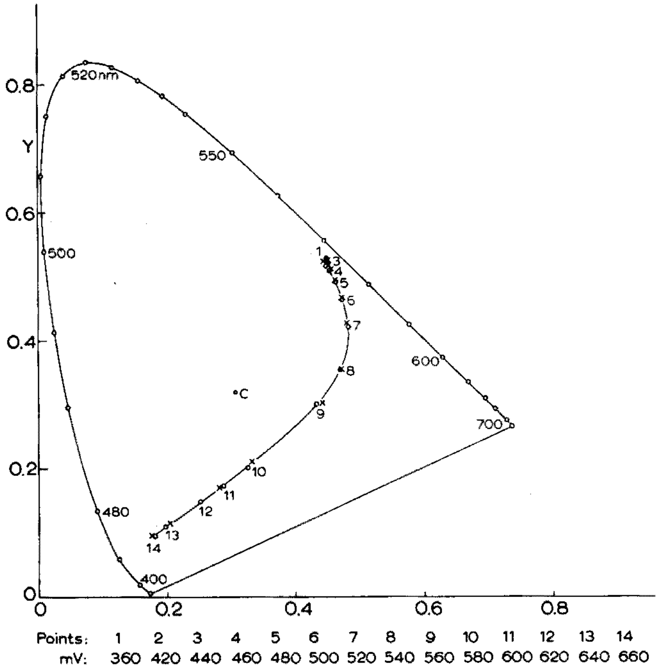

Fig. 2. Chromaticity diagram showing positions of complementary colour points of the indicators. (—x—x—), crystal violet; (—o—o—), methyl violet.

TABLE II

COLOUR SPECIFICATION OF CRYSTAL VIOLET AND METHYL VIOLET

mV	*Brightness*		*Dominant wavelength*		*Purity*	
	Crystal violet	*Methyl violet*	*Crystal violet*	*Methyl violet*	*Crystal violet*	*Methyl violet*
360	56.8	56.8	572.2	572.1	93.5	93.3
420	54.1	54.4	571.8	572.2	91.5	92.2
440	53.9	54.3	572.8	572.7	91.0	90.7
460	49.9	50.5	573.3	573.5	90.0	90.0
480	47.1	46.2	575.3	575.5	87.5	87.7
500	39.4	39.5	578.5	578.7	83.0	83.0
520	32.1	32.0	584.0	584.3	74.5	74.2
540	20.9	21.4	597.3	597.2	52.2	51.8
560	16.9	16.2	660.0	650.0	30.5	29.5
580	9.3	9.0	538.7	544.3	47.4	49.0
600	7.0	7.3	559.6	558.4	53.8	53.5
620	5.9	5.9	564.7	564.9	56.2	56.5
640	4.1	3.9	453.2	455.6	68.8	70.7
660	3.5	3.5	462.5	461.5	78.4	77.9

Consequently an arbitrary choice of one or the other indicator in titrations of any specific substance in an anhydrous acetic acid medium is justified.

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Chromatography of halide ions on thin layers of cellulose

In the paper-chromatographic separation of the halides, the R_F values increase with increasing atomic weight[1] and this trend is general for separations on paper and silica gel thin layers[2] but with conventional ion-exchanger materials, the order for chloride, bromide and iodide is usually reversed[3]. Since paper is only a poor cation exchanger, owing to relatively few exchange sites being available, the use of thin layers of cellulose, with a greater surface area/weight ratio should increase the resolution.

Reagents

All water used was freshly distilled and deionised. All salts used were aqueous 0.5%(w/v) solutions of the respective halides prepared from analytical-grade substances. Acetone (freshly distilled, b.p. 56°–56.5°)–water mixtures were used as eluants.

Chromatographic procedure

The layers were 0.30 mm thick and were prepared by spreading a slurry of 15 g of cellulose MN300HR (Macherey, Nagel and Co., Duren) in 65 ml of acetone. The plates were air-dried and stored in a desiccator until required.

Samples (1 µl) of the halide solutions were spotted on the plate using the template method previously described[4]. Each plate held 12 spots. The chromatograms were developed by an ascending technique in a double saturation chamber[4]. A glass-fibre wick previously cleaned by boiling with water, rinsing with acetone, and air-drying, was used to transport the eluant to the plate.

For visualization of the halides the plates were sprayed with an ethanolic solution of dichlorofluorescein (0.1%, w/v), and then oversprayed with silver nitrate. Under U.V. light the fluoride appeared as a yellow spot and the other halides as dark spots on a light background. The positions of the cations relative to the anions were determined in the system 4:1 acetone–water on separate plates from those used for the halide detection. For potassium the plates were sprayed with an ethanolic 1.0% (w/v) solution of morin; the cation appeared as light brown spots. For sodium and ammonium, the plates were sprayed with zinc uranyl acetate in acetic acid and viewed under U.V. light. Both cations appeared as diffuse yellow spots on a darker background.

Results and discussion

Table I shows the R_F values obtained for the halides with eluants of varying water/acetone ratios. Figure 1 shows the separation of the anions and cations.

The solvent front under U.V. light was a band approximately 0.25 cm wide (the leading edge was taken as the solvent front). The width of the double front increased if no attempt was made to saturate the tank atmosphere; with the system indicated, the width did not vary at any composition of the eluant.

The R_F values increased with increasing atomic number of the halide, and to a first approximation the R_F value of a particular halide ion was independent of the cation. However, more compact spots and greater resolution of the halide ions were obtained than have been hitherto reported.

TABLE I

R_F VALUES[a] OF HALIDE IONS

% (w/v) Acetone	Fluoride			Chloride			Bromide			Iodide		
	NH_4^+	Na^+	K^+	NH_4^+	Na^+	K^+	NH_4^+	Na^+	K^+	NH_4^+	Na^+	K^+
0	Spots moved with solvent front											
70	0.11	0.13	0.11	0.55	0.51	0.43	0.67	0.70	0.66	0.85	0.86	0.82
75	0.09	0.11	0.09	0.50	0.45	0.36	0.61	0.60	0.62	0.81	0.81	0.81
80	0.06	0.05	0.05	0.33	0.33	0.25	0.50	0.49	0.49	0.80	0.80	0.78
85	0.02	0.02	0.02	0.16	0.13	0.10	0.28	0.24	0.19	0.59[b]	0.58[b]	0.55[b]
90	0.00	0.00	0.00	0.06	0.05	0.04	0.16	0.13	0.11	0.54[b]	0.55[b]	0.53[b]
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04

[a] All values except [b] are the average of at least 2 results and were reproducible to ±0.01. Internal standardization of the system was achieved by randomly choosing one plate from each batch and using it in the 80% (v/v)acetone–water eluant, Any batch of plates that gave results varying by more than ±0.01 R_F unit from the mean reported for this eluant, were discared. Each plate was allowed to run for 14±0.5 cm. The time taken for a run was 30–40 min.

[b] These spots were not discrete, but were streaked over an R_F range of approximately 0.2.

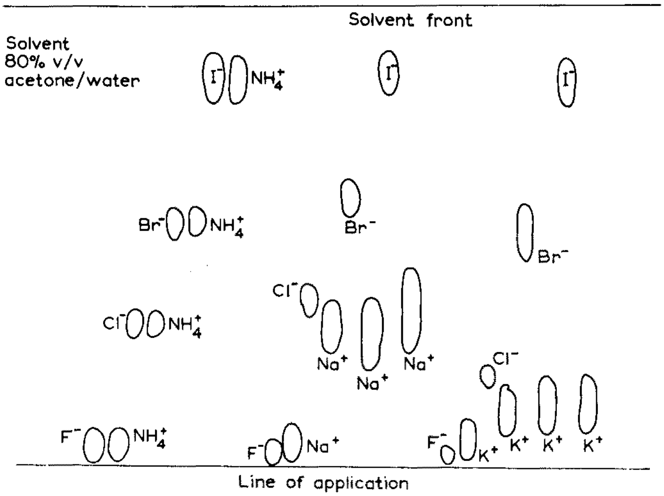

Fig. 1

As the spot was dried before the development, the initial mechanism would be dissolution and hence the R_F values should be related to the order of solubilities of the salts. This was shown to be true for the potassium salts in acetone–water (80:20) where solubilities of 0.005, 0.10, 0.19, and 0.89 mole/100 ml were calculated for the 4 halides.

It is suggested that the separation of the halides from the cations is due to cation exchange on the cellulose. Whilst the elution order is not that found on cation exchangers using aqueous solutions, it is not anomalous for cation exchange using acetone–water mixtures[5]. NAKANO[6] in paper chromatography observed only partial separation of the anions from the cations and did not attribute the separation to ion exchange. However, since a thin-layer chromatoplate of cellulose powder has a much greater contact area for ions than has a corresponding superficial area of paper, the number of exchange sites per unit length of eluant flow would be much greater for powder than for paper. Thus complete separation of the anions and cations should be achieved for cations with a relatively large affinity for the exchanger if the anions associated with them are in a relatively highly soluble salt.

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An improved method for the detection and estimation of micron-sized sulfate particles: Correction

LODGE AND PARBHAKAR[1] reported a method for specifically identifying individual particles containing sulfate, and for estimating the particle size. Almost immediately, private communications were received reporting difficulty with the method, and the present authors found that some field samples gave reaction spots too faint to analyze.

In the original procedure the chemical reaction was brought about by floating the filter bearing the sample on distilled water. Apparently some substances dissolved and diffused away from the site of impaction before the chemical reaction could occur. The following modification has been found to give consistently good results.

The washing step is omitted. Instead, the filters are placed for 24 h in an environment of 100% relative humidity (a desiccator with water in the bottom, or other closed vessel). At the end of this time the filters are transferred to a desiccator containing a suitable drying agent. Under these conditions none of the reaction spots fades for at least a month. For extended field trips it has been found convenient to prepare small plastic moist jars and dry jars. Their construction will be described in detail elsewhere. In essence, they are small cylindrical containers having a removable lid at each end and a porous plastic divider press-fitted into the center. Either desiccant or moist blotting paper can be placed in one end and the membrane filters in the other.

Samples from a variety of environments have been analyzed by this method and have given clear and consistent results. The visibility of the final reaction spots can be improved by illuminating them with a yellowish-green filter in the microscope light source.

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BOOK REVIEWS

J. KING, *Practical Clinical Enzymology*, D. Van Nostrand, London, 1965, viii + 363 pp., price 75 s.

This book is made up of 8 chapters. The first 3 deal with the nature, kinetics and measurement of enzyme activity whilst in the following 4 chapters, the oxidoreductases, transferases, hydrolases, lyases and isomerases are discussed in detail. In the final chapter, a useful survey of enzyme heterogeneity is given.

In discussing the assay of the clinically important enzymes a detailed procedure (including reagents and in many instances a calculation of the results) is given for each enzyme, though alternative methods of assay are mentioned as well. The descriptions of enzyme assay are followed by short sections on the clinical interpretation of the observed enzyme activities.

It is obvious that the author took great care in writing this book. He is also aware of the fact that there are already well established reference books on enzyme methodology as well as on clinical enzymology. It should, therefore, be pointed out that, according to the preface and the dust cover, this book aims primarily at medical laboratory technicians and students preparing for the Institute for Medical Laboratory Technology and similar examinations.

G. HUBSCHER (Birmingham)

Anal. Chim. Acta, 35 (1966) 272

W. NEUDERT AND H. RÖPKE, *Steroid-Spektrenatlas/Atlas of Steroid Spectra* (in German and English), Springer-Verlag, Berlin–Heidelberg–New York, 1965, viii + 471 pp., price DM 144.—.

The ability to identify milligram quantities of substances has allowed spectroscopic methods to achieve an importance in studies of steroids greater than in other branches of chemistry. This atlas brings together a large number of steroid spectra obtained under standard conditions and covering a wide range of structures. Half of the book is devoted to the infrared spectra of 900 steroids; in this respect the book represents a supplement to the atlases compiled by R. N. JONES *et al.* There follow shorter sections dealing with ultraviolet spectra (41 types are indicated) and NMR spectra (95). Sections dealing with the theoretical framework of the spectroscopic methods, structure assignment charts, experimental methods and other physical measurements follow. A comprehensive index and data retrieval system is included.

The spectra are clearly presented although it is unfortunate that no wavenumber scale is included on the infrared spectra. It is disappointing that the NMR measurements were restricted to 40 Mc/s in view of the widespread use of 60 Mc/s spectrometers. The restriction of the infrared spectra to measurements on KBr discs greatly reduces the value of the spectra as does the use of a NaCl prism instrument. The increasing availability of grating spectrometers and the desirability of making measurements on solutions suggest that any supplement to this volume should include such data. Nevertheless, the scope of this book makes it a useful, if expensive, addition to the literature.

K. J. MORGAN (Lancaster)

Anal. Chim. Acta, 35 (1966) 272

B. TRÉMILLON, *Les Séparations par les Résines Echangeuses d'Ions,* Collection: Monographies de Chimie Minérale, Gauthier-Villars, Paris, 1965, viii+400 pp., Cartonné 90 F.

Cette monographie comble très heureusement une lacune qui existait dans la littérature scientifique française dans le domaine moderne des échangeurs d'ions.

L'auteur nous présente un livre particulièrement bien documenté et clairement présenté avec une bibliographie très abondante comportant les informations de base nécessaires aux utilisateurs des échangeurs d'ions, comme le précise l'auteur dans l'avertissement figurant en tête de l'ouvrage.

La première partie est consacrée aux propriétés fondamentales des résines échangeuses d'ions: équilibres d'échanges ioniques en phases aqueuses ou non aqueuses, gonflement, équilibre de Donnan. Le problème de la cinétique d'échange ionique est traité de façon plus sommaire malgré l'importance de la question dans le cas des séparations difficiles ou industrielles.

Par contre, l'auteur consacre, à juste titre, une partie importante de la première partie à l'étude de l'influence des réactions chimiques sur les coefficients de distribution; celle-ci joue un rôle fondamental non seulement dans les applications analytiques, mais encore dans l'étude des réactions en solution. La méthode de présentation basée sur l'introduction des constantes d'échanges conditionnelles nous paraît particulièrement heureuse.

La seconde partie (pages 153 à 400) est consacrée au fonctionnement et aux applications des colonnes d'échangeurs d'ions et 3 chapitres traitent respectivement de l'analyse frontale, de la séparation par élution et de celle par déplacement particulièrement intéressante en chimie préparative.

Il est tout indiqué de signaler ici l'intérêt du chapitre VIII qui expose les principes des colonnes d'échangeurs d'ions à contre-courant, susceptibles de développements industriels importants.

Enfin, les 2 derniers chapitres traitent d'une part des applications électrochimiques des résines (électromigration et membranes échangeuses) et d'autre part des bases de la technique expérimentale des échangeurs d'ions.

Signalons pour terminer que les 50 dernières pages de cette monographie contiennent une documentation extrêmement riche, souvent présentée sous forme graphique et d'une grande utilité pour les chimistes, sur les coefficients de partage d'un grand nombre d'ions en fonction de la composition de la phase aqueuse.

Cette analyse très brève permettra, je l'espère, au lecteur de se rendre compte que l'ouvrage du Professeur TRÉMILLON représente, à l'heure actuelle, pour tout chimiste qu'il soit ingénieur ou docteur, une source de documentation indispensable et un outil de travail du plus haut intérêt.

G. DUYCKAERTS (Liège)

Anal. Chim. Acta, 35 (1966) 273

HAROLD F. WALTON, *Principles and Methods of Chemical Analysis*, 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., 1964, xvi+484 pp.

The first edition of this book appeared in 1952 and was well-received because it dealt with the principles of chemical analysis, applied to methods which are widely-practised, in a concise and palatable way. The new edition has been extensively revised; because of the rapid progress of analytical chemistry since the first edition appeared, a considerable amount of entirely new material is now included.

The book contains new chapters on precipitation from homogeneous solution, solvent extraction, acid–base titrations in non-aqueous solutions and "linear-titration" methods. The sections on compleximetric titrations and ion-exchange separations have been rewritten and expanded; some of the sections on older methods of classical analysis have been omitted or curtailed in order to save space. The preface contains some interesting philosophical observations.

This second edition maintains the same high standard set by the first edition. It should serve both as a student text and as a reference book for all analytical chemists.

R. BELCHER (Birmingham)

Anal. Chim. Acta, 35 (1966) 274

N. D. CHERONIS AND T. S. MA, *Organic Functional Group Analysis by Micro and Semimicro Methods*, Interscience Publishers–John Wiley and Sons, Inc., New York, 1964, xxvi+696 pp., price 188 s ($ 25.00).

This book is divided into 3 main parts: (I) Principles and Techniques; (II) A Critical Survey of the Analytical Methods for Functional Group Determination; (III) Experimental Procedures. Through its treatment of micro and semimicro methods, it fills a gap in the literature which has existed since the appearance of SIGGIA's text on macro methods. Moreover, CHERONIS AND MA have produced a very conscientious survey of methods and literature; this is a welcome guide to all who practice organic analysis.

Many workers will appreciate the full descriptions of experimental procedures in two sections, one dealing with determinations using ordinary equipment and the second with determinations requiring special apparatus. In the writer's opinion, however, more stress should be laid in future editions on the use of small volumes of strong titrants instead of rather large volumes of weak titrants. It is rather surprising that the authors have devoted 100 pages to principles and techniques instead of referring to specific textbooks and supposing that the users of the book are already familiar with normal analytical operations and equipment. It would be preferable to have an introduction dealing with special requirements for carrying out organic reactions and handling samples on the micro scale. This would also avoid unnecessary detail on reaction mechanisms which are tricky or not well established. The text is not free from error (*e.g.* the K_a value of formic acid in Table 3.3, and equation (28) on p. 39) but, nevertheless it can be recommended as a standard work on organic analysis.

E. A. M. F. DAHMEN (Amsterdam)

Anal. Chim. Acta, 35 (1966) 274

Methods of Forensic Science, Vol. 3, Edited by A. S. CURRY, Interscience Publishers–John Wiley and Sons, New York, 1964, xiii+342 pp., price 95 s.

Reviews are given on: Lead poisoning (S. L. TOMPSETT); Non-biological applications of neutron activation analysis in forensic studies (V. P. GUINN); Biological applications of activation analysis (H. SMITH AND J. M. A. LENIHAN); Forensic chemical analysis of urine for drugs (E. B. HENSEL); The administration of a forensic science laboratory (R. F. BORKENSTEIN); Examination of fiduciary counterfeits and forgeries (P. FAUCONNIER, J. COGNIARD AND P. F. CECCALDI); The toxicology of cyanides (M. A. GUATELLI); The acid phosphatase test (S. S. KIND); Erasures (W. R. HARRISON).

Methods of Forensic Science, Vol. 4, Edited by A. S. CURRY, Interscience Publishers–John Wiley and Sons, New York, 1965, xii+369 pp., price 105 s.

Reviews are given on: Methods for determining alcohol (H. W. SMITH); The examination of glass fragments (D. F. NELSON); Coloured fibres in criminal investigation with special reference to natural fibres (M. FREI-SULZER); Searching for drug metabolites in viscera (L. K. TURNER); Thin-layer chromatography in forensic science (G. MACHATA); The detection of soap abortions (W. SCHWERD); Infra-red absorption spectroscopy in forensic toxicological practice (A. ALBA AND V. TAMMINEN); Recent advances in the grouping of dried blood and secretion stains (R. A. OUTTERIDGE).

Organic Reagents for Metals and for Certain Radicals, Vol. 2, Edited by W. C. JOHNSON, Hopkin and Williams, Ltd., Chadwell Heath, Essex, 1964, ix+275 pp., price 30 s.

Reagents considered are: alizarin fluorine blue, N-benzoyl-N-phenylhydroxylamine, bis-(3-methyl-1-phenylpyrazol-5-one), *p*-bromomandelic acid, carmine, N-cinnamoyl-N-phenylhydroxylamine, curcumin, di-(*o*-hydroxyphenylimino)ethane, bathocuproine, neocuproine, bathophenanthroline, dibenzoylmethane, cuproine, stable dithiol derivatives, dithizone, eriochrome cyanine R, furil α-dioxime, haematoxylin, 3-methoxynitrosophenol, α-methoxyphenylacetic acid, nitroso-R salt, *syn*-phenyl-2-pyridyl ketoxime, sodium tetraphenylboron, thioacetamide, thorin, tiron, 2,4-xylenol, zincon.

Compleximetric indicators considered are: acid alizarin black SN, calcein, calcichrome, calcon, calmagite, catechol violet, *o*-dianisidine-N,N,N′,N′-tetraacetic acid, di-(*o*-hydroxyphenylimino)ethane, eriochrome black T, HSN indicator, metalphthalein, methylthymol blue, murexide, xylenol orange, zincon.

R. H. STOKES AND R. MILLS, *Viscosity of Electrolytes and Related Properties*, International Encyclopedia of Physical Chemistry and Chemical Physics, Vol. 3, Pergamon Press, Oxford, 1965, ix+151 pp., price 50 s.

Chapter headings: Hydrodynamics of viscous liquids; Experimental techniques; Long-range electrostatic interaction; β-Coefficient; Shape and size effects; Mobilities of ions in relation to viscosity; Concentrated solutions and molten salts; Appendices.

LEV IOSIFIVICH MIRKIN, *Handbook of X-ray Structure Analysis of Polycrystalline Materials*, authorised translation from the Russian by J. E. S. BRADLEY, Fizmatgiz, Moscow, 1961– Consultants Bureau, New York, 1964, xx + 731 pp., $ 35.00.

This book provides a comprehensive collection of tables, diagrams and charts for aiding in the selection of conditions for obtaining X-ray diffraction patterns and for the interpretation of these patterns. There is no other comparable collection of data in a single volume.

The first 4 chapters give basic data including wavelengths, absorption coefficients (Table 1-6e is incorrectly headed "mass absorption coefficients" instead of "linear absorption coefficients"), methods for indexing patterns and calculating line intensities. The chapter on indexing contains numerous diagrams and charts, although some of the charts are too crowded to be of use.

The remaining 8 chapters deal with applications. Qualitative analysis is dealt with at length, but the ASTM Powder Data File which was included in the Russian edition has been omitted from the English translation. Brief mention is also made of quantitative analysis by X-ray diffraction. The other topics dealt with are precision lattice parameter measurements, stress determination, line broadening, preferred orientation (mainly referring to the now obsolete film method), small-angle scattering and short sections on electron and neutron diffraction.

The author does not aim to present material found in ordinary text books on the subject, and explanatory notes for the use of tables and diagrams have been kept very brief.

A very successful translation has been accomplished and the book will be of great value in any laboratory concerned with X-ray analysis of polycrystalline materials.

W. T. ROBERTS (Birmingham)

ANNOUNCEMENT

The Istituto Superiore di Sanità is organizing a one-day Symposium on GEL FILTRATION, to be held on September 24th 1966 (Viale Regina Elena 299, Roma, Italy).

The morning session will consist of three main lectures:

TH. WIELAND: Some recent developments in gel chromatography, with special reference to thin layers;

H. BENNICH: Gel filtration and its application to biochemical separation problems;

J. C. JANSON: Adsorption phenomena on Sephadex.

Original papers are invited for the afternoon session. Registration is free. The lectures and papers will be published together after the Symposium. For registration and information, please write to Prof. F. DENTICE, Istituto Superiore di Sanità, Viale Regina Elena 299, Roma, Italy.

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1966. XXVIII, 356 pages. Plastic DM 30.00 = $ 7.50 = FF 37.00.
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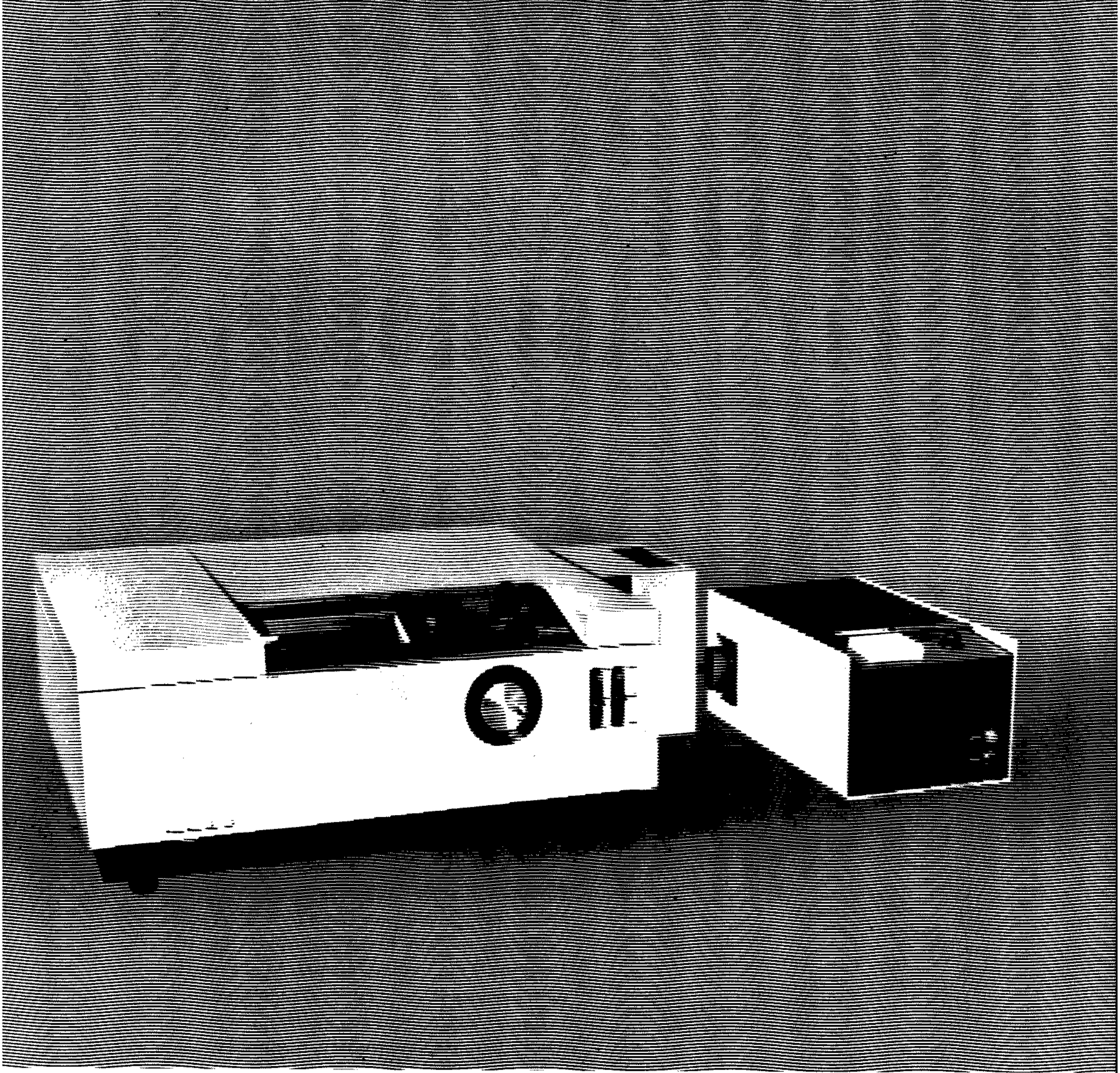

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This 7th edition has involved complete revision and reorganisation of the subject in order to present a still clearer picture of the multitudinous applications open to organic spot test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot test techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis*) and by limiting the number of tables and structural formulae.
Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
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Applications in the testing of materials etc.	111	131

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It is the author's hope that this work will help to correct the widespread impression that physical instrumentation is always superior to chemical methods for solving analytical problems. Each of the chapters presents instances of problems for which no solutions by physical means have yet been developed, or for which the rapid spot tests are equal or superior to the expensive instrumental procedure.

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