ANALYTICA CHIMICA ACTA

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Internationale Monatsschrift für alle Gebiete der analytischen Chemie

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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.

For multi-author references, **all** authors must be named, and initials given, in the reference list, although the use of, for example, SMITH *et al.*, is desirable in the text.

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 35, No. 4, August 1966

THE DETERMINATION OF MAGNESIUM IN SILICATES BY ATOMIC ABSORPTION SPECTROSCOPY

The determination of magnesium in silicates by atomic absorption spectroscopy using a hot flame is discussed. Interference by aluminium observed in the air–acetylene flame is overcome by using the hotter nitrous oxide–acetylene flame. There is some evidence to suggest that the alkali metals interfere in this determination but this is not confirmed in the results obtained on standard rock samples. Values for magnesium are given for some new rock standards recently distributed by the U.S. Geological Survey.

R. W. Nesbitt,
Anal. Chim. Acta, 35 (1966) 413–420

NEUTRON ACTIVATION ANALYSIS OF MICROGRAM AMOUNTS OF THORIUM IN URANIUM ORES AND PROCESS LIQUORS BY MEANS OF THORIUM-233

A method is described for neutron activation analysis of thorium by employing thorium-233. Decontamination steps include anion exchange in 12.5 *N* HCl, precipitation of fluoride, extraction with mesityl oxide and thorium oxalate precipitation. The time spent is less than 1 h; spurious activities in counting samples amount only to 2% and can easily be corrected for. The sensitivity of the method is *ca.* 0.02 μg of thorium in a neutron flux of 10^{12} n/cm^2/sec with an irradiation time of 5 min.

A. Travesí, J. Palomares and G. Domínguez,
Anal. Chim. Acta, 35 (1966) 421–426

THE SIMULTANEOUS DETERMINATION OF SILVER, GOLD AND MERCURY IN HIGH-PURITY LEAD BY NEUTRON ACTIVATION ANALYSIS

A radiochemical method was developed to separate the group of the noble metals simultaneously from a lead matrix after irradiation with thermal neutrons. The resulting complex γ-spectrum was resolved by matrix calculus. Smoothing of the obtained data to determine the presence of small photopeaks among the background fluctuations, was done by convolution, based on a least squares approximation. The interference of antimony and bromine was studied. Amounts as low as 20–30 p.p.b. of Hg and less than 1 p.p.b. of Au were determined in the presence of up to 9 p.p.m. of Ag.

J. Op de Beeck and J. Hoste,
Anal. Chim. Acta, 35 (1966) 427–440

EMISSION INTENSITY OF STRONTIUM AND BARIUM IN FLAMES OF VARIOUS GAS COMPOSITIONS

The emission intensity of strontium at 460.7 mμ and barium at 553.6 mμ has been studied in hydrogen flames burning with varying mixtures of oxygen and nitrogen. With solutions of barium and strontium chloride in water and in various concentrations of EDTA, acetic and hydrochloric acids, it was found that the emission depended significantly on the oxygen: nitrogen ratio in the atomizing gas. Under some conditions, maximum emission intensity is found at compositions intermediate between air and pure oxygen. The emission of barium was found to be decreased significantly by EDTA at high pH under some flame conditions.

N. R. ANDERSEN AND D. N. HUME,
Anal. Chim. Acta, 35 (1966) 441–446

ALTERNATING CURRENT POLAROGRAPHY OF SOME COMPLEXES IN PRESENCE OF IONIC SURFACTANTS

Well defined a.c. polarographic waves are obtained in the presence of certain ionic surfactants. The current is brought about by an electron-transfer through the adsorbed layer, probably by the formation of a bridge which accelerates the electron-transfer between the electrode and the depolarizer. The resulting a.c. wave is accompanied by a d.c. polarographic step and the height of the wave increases proportionally to the bulk concentration of the depolarizer. In contrast to ordinary a.c. waves, the a.c. current of these waves increases linearly with increasing height of the mercury column above the capillary.

E. JACOBSEN,
Anal. Chim. Acta, 35 (1966) 447–452

THE EFFECT OF BASE ELECTROLYTES ON THE POLAROGRAPHIC REDUCTION OF METHYL BROMIDE

(in German)

The irreversible polarographic reduction of methyl bromide was studied in aqueous solution in the presence of various base electrolytes. $E_{\frac{1}{2}}$ values became more positive with increasing charge density and surface activity of the cations. Mixed electrolytes with alkali metal salts and tetraalkylammonium salts or cationic surfactants suppressed this increase in $E_{\frac{1}{2}}$ values. With such mixed electrolytes containing highly active surfactants of sufficient charge density, a normal polarographic determination of methyl bromide is possible. The final diffusion rate of the active component has also a considerable effect on $E_{\frac{1}{2}}$ values so that the $E_{\frac{1}{2}}$ values of such systems cannot be characterized by the solution composition alone.

H.-J. THAMM,
Anal. Chim. Acta, 35 (1966) 453–460

AN AUTOMATIC APPARATUS FOR SIMULTANEOUS THERMOGRAVIMETRIC AND MAGNETIC SUSCEPTIBILITY MEASUREMENTS

An apparatus is described which records automatically the continuous sample mass-change curve, the apparent mass-changes caused by the magnetic field, and the sample temperature, all simultaneously over the temperature range from room temperature to 500°. The use of the apparatus is illustrated by the thermal dissociation of $[Co(NH_3)_6]Cl_3$. Data obtained from the apparatus permit the plotting of mass-change, mass susceptibility, and molar percent reduction of cobalt(III) curves, all as a function of temperature. Such information is useful in elucidating the mechanism of the thermal dissociation reaction.

E. L. Simmons and W. W. Wendlandt,
Anal. Chim. Acta, 35 (1966) 461–466

THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

Studies of the extraction of thallium(I) from aqueous solution into an immiscible organic solvent have been made using 71 chelating reagent–solvent pairs involving 16 reagents and 17 solvents. The data have been analyzed to identify the predominant species involved, and association and partition constants have been estimated in many cases. The best extraction systems seem to be those involving 3-phenylpropylxanthate and chloroform, chlorobenzene or methylene chloride.

G. K. Schweitzer and J. E. Davidson,
Anal. Chim. Acta, 35 (1966) 467–478

THE SPECTROPHOTOMETRIC DETERMINATION AND SOLVENT EXTRACTION OF OSMIUM WITH *o*-(β-BENZOYLTHIOURIDO)BENZOIC ACID AS REAGENT

o-(β-Benzoylthiourido)benzoic acid is proposed as a spectrophotometric reagent for the determination of osmium. The brownish yellow complex formed is soluble in alcohol and in other organic solvents. The colour system obeys Beer's law from 3 to 18 p.p.m. of osmium at 410 mμ with an optimum range of 3–15 p.p.m., where the percent relative error per 1% absolute photometric error is 2.75%. A 1 : 1 complex is formed and the dissociation constant is of the order of 10^{-5}. With prior extraction of palladium as the azide complex with *n*-butanol, osmium can be separated from almost all ions, including those of platinum metals, by extraction with ethyl acetate.

A. K. Majumdar and S. K. Bhowal,
Anal. Chim. Acta, 35 (1966) 479–483

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH FERRON

Various metal complexes of 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) were found to be selectively extracted into immiscible alcohols. Vanadium(V) is almost completely extracted into *n*-butanol in a single extraction from solutions which are 0.05 *M* in sulphuric acid. A sensitive and selective spectrophotometric method can be based on this extraction. Beer's law is obeyed up to 15.3 μg of vanadium per ml; the sensitivity of the color reaction is 0.011 μg of vanadium per cm^2 at 430 mμ. The interference of iron(III) can be eliminated by adding excess pyrophosphate. The extracted species appears to contain vanadium, ferron and *n*-butanol in the ratio 1:2:4.

N. KURMAIAH, D. SATYANARAYANA AND V. PANDU RANGA RAO,
Anal. Chim. Acta, 35 (1966) 484–490

DETERMINATION OF ZIRCONIUM IN ZIRCONIUM METAL AND ZIRCONIUM POWDER BY USE OF MANDELIC ACID

An accurate gravimetric method is proposed for the determination of zirconium in zirconium metal and zirconium powder by use of mandelic acid. The sample is dissolved in a mixture of hydrofluoric, nitric, perchloric and sulfuric acids, the solution is evaporated to dryness, and the salts are dissolved in dilute hydrochloric acid. Zirconium mandelate is precipitated at 80°. The residual zirconium in the filtrate is recovered by heating at 80° overnight and the combined precipitates are ignited to zirconium dioxide. An investigation was made of the factors involved in the dissolution of the sample, precipitation with mandelic acid, ignition of the precipitate, and size of sample. The effect of hafnium is discussed.

G. NORWITZ,
Anal. Chim. Acta, 35 (1966) 491–498

A VOLUMETRIC DETERMINATION OF ARSENIC AND ANTIMONY IN MIXED MANGANESE ARSENIDE, ANTIMONIDE AND PHOSPHIDE COMPOUNDS

A procedure is described for the titrimetric determination of arsenic and antimony without separation. Total combined arsenic and antimony were determined by reduction with tin(II) chloride and titration with permanganate; antimony is found by selective reduction with mercury(I) chloride and titration with permanganate. A precision of 0.1–0.2% was obtained for total combined arsenic and antimony, and approximately 1% for antimony alone (small amounts in the presence of large amounts of arsenic). The procedure was developed for and applied to the analysis of synthesized compounds of the type $MnAs_{1-x}P_x$ and $MnAs_{1-y}Sb_y$.

E. R. WHIPPLE AND D. H. RIDGLEY,
Anal. Chim. Acta, 35 (1966) 499–507

DETERMINATION OF PLUTONIUM BY CONSTANT-CURRENT POTENTIOMETRY

(in French)

A new method is proposed for the determination of plutonium in the UO_2PuO_2 pellets for Rapsodie. The sample is dissolved in a mixture of 11 N nitric acid and 0.1 N hydrofluoric acid, and the plutonium is oxidized with silver(II) oxide. Plutonium(VI) is reduced in the presence of sulphamic acid with an excess of iron(II) which is back-titrated with cerium(IV) solution to a constant-current potentiometric end-point. Uranium and iron do not interfere and no separation is required. In routine work, the method gives a precision of 0.5%.

J. Corpel and F. Régnaud,
Anal. Chim. Acta, 35 (1966) 508–513

THE AUTOMATIC DETERMINATION OF SILICATE–SILICON IN NATURAL WATERS WITH SPECIAL REFERENCE TO SEA WATER

An automatic method using a Technicon AutoAnalyzer is described for the determination of silicate in natural waters in the range 0–4 mg Si/l. It is based on the conversion of silicate to β-silicomolybdic acid which is reduced by means of a metol–sulphite reagent to molybdenum blue. Interference of phosphate is prevented by oxalic acid. The relationship between silicate concentration and optical density is linear in both fresh waters and sea water. With sea water the salt error of the method is *ca.* 5% at a salinity of $35^0/_{00}$. A coefficient of variation of 0.8% was found at a silicate concentration of 1 mg Si/l with both fresh and sea waters.

P. G. Brewer and J. P. Riley,
Anal. Chim. Acta, 35 (1966) 514–519

HETEROMETRIC TITRATIONS OF GELATIN AND EGG ALBUMIN WITH HETEROPOLY ACIDS OR WITH SODIUM TETRAPHENYLBORATE

Heterometric titrations of gelatin and egg albumin with sodium tetraphenylborate, silicotungstic, phosphotungstic and phosphomolybdic acids were carried out at low pH values. The ratio of the nitrogen content reacting with the heteropoly acids to the total nitrogen was found to be 1:12 for gelatin and 1:20 for egg albumin. Both egg albumin and gelatin could be determined heterometrically with phosphomolybdic acid.

(the late) M. Bobtelsky and I. Barzily,
Anal. Chim. Acta, 35 (1966) 520–523

A NEW APPLICATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY: DETERMINATION OF PHTHALIC ACID BY SOLVENT EXTRACTION WITH NEOCUPROINE-COPPER(I) CHELATE

(Short Communication)

T. Kumamaru, Y. Hayashi, N. Okamoto, E. Tao and
Y. Yamamoto,
Anal. Chim. Acta, 35 (1966) 524–525

THE PRECIPITATION OF CALCIUM FLUORIDE FROM HOMOGENEOUS SOLUTION

(Short Communication)

R. Morales and P. W. West,
Anal. Chim. Acta, 35 (1966) 526–529

THE ROUTINE DETERMINATION OF URANIUM IN VEGETATION ASH

(Short Communication)

M. H. Dean, A. Stimson and D. E. Green,
Anal. Chim. Acta, 35 (1966) 530–533

DETERMINATION OF THALLIUM IN CESIUM IODIDE SCINTILLATORS

(Short Communication)

H. Kubota,
Anal. Chim. Acta, 35 (1966) 534–535

THE PREPARATION AND STABILITY OF URANIUM CARBIDE SAMPLES FOR THE DETERMINATION OF OXYGEN, HYDROGEN AND NITROGEN BY VACUUM FUSION

(Short Communication)

M. Pérez García,
Anal. Chim. Acta, 35 (1966) 536–539

AN ANALYTICAL METHOD FOR THE "SIMULTANEOUS" DETERMINATION OF DEUTERIUM AND TRITIUM

(Short Communication)

J. L. Garnett and W. A. Sollich–Baumgartner,
Anal. Chim. Acta, 35 (1966) 540–543

THE USE OF TETRACYCLINE AS A FLUORESCENT INDICATOR IN THE COMPLEXIMETRIC MICRODETERMINATION OF GROUP II CATIONS

(Short Communication)

A. A. Ashton,
Anal. Chim. Acta, 35 (1966) 543–545

SPOT TESTS IN ORGANIC ANALYSIS

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Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
Functional group tests	70	109
Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
Differentiation of isomers etc.	0	54
Applications in the testing of materials etc.	111	131

In total the book now gives in 561 sections information on more than 900 tests compared with 600 tests in 346 sections in the preceding edition.

An important feature is the inclusion of a large number of recently developed tests and comments which have not hitherto been published in any form.

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.

CONTENTS: 1. Development, present state and prospects of organic spot test analysis. 2. Preliminary (exploratory) tests. 3. Detection of characteristic functional groups in organic compounds. 4. Detection of structures and certain types of organic compounds. 5. Identification of individual organic compounds. 6. Application of spot tests in the differentiation of isomers and homologous compounds. Determination of constitutions. 7. Application of spot reactions in the testing of materials, examinations of purity, characterization of pharmaceutical products, etc... Appendix: Individual compounds and products examined. Author index. Subject index.

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Chimia

... Even in these days of physical instrumentation there is ample room for the techniques described in this book which were originated and largely developed by Prof. Feigl. They are mostly very quick and very economical on materials. They sometimes present solutions to problems so far insoluble by expensive physical methods...
Laboratory Practice

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47E

SUBMICRO METHODS OF ORGANIC ANALYSIS

by R. Belcher
Professor of Analytical Chemistry,
The University of Birmingham, Great Britain

6 × 9″, ix + 173 pages, 12 tables, 35 illus., 186 lit. refs., 1966, Dfl.27.50, 55s., $10.00

Contents: 1. Introduction. 2. The balance. 3. General apparatus. 4. The determination of nitrogen. 5. Carbon and hydrogen. 6. Chlorine. 7. Bromine and iodine. 8. Fluorine. 9. Sulphur. 10. Phosphorus and arsenic. 11. Carboxyl groups. 12. Organic bases in non-aqueous media. 13. Alkoxyl and N-methyl groups. 14. Acetyl groups. 15. The carbonyl group. 16. Olefinic unsaturation. 17. Oxidation with periodate. 18. The determination of nitro and nitroso groups. 19. Thiol groups. 20. The cryoscopic determination of molecular weight. Index.

TECHNIQUES OF OSCILLOGRAPHIC POLAROGRAPHY

Second Edition, completely revised and enlarged
by R. Kalvoda
Institute of Polarography, Czechoslovak Academy of
Sciences, Prague, Czechoslovakia
with a preface by Professor J. Heyrovský

6 × 9″, 213 pages, 3 tables, 90 illus., 263 lit. refs., 1965, Dfl. 30.00, 60s., $11.00

Contents: Preface (J. Heyrovský); Author's Preface; 1. Introduction. 2. Examples of application of the oscillopolarographic method. 3. Practical oscillopolarographic exercises. 4. Maintenance of apparatus and construction of auxiliary electrical circuits. Index.

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. Beynon, R. A. Saunders and A. E. Williams
Research Department, Imperial Chemical Industries Ltd.,
Manchester, Great Britain

9½ × 6½″, xix + 392 pages, 1965, Dfl. 45.00, 90s., $16.50

These tables are intended to make it easy to determine the ionic reaction which gives rise to any meta-stable peak in a mass spectrometer, and will prove indispensable to any laboratory possessing this equipment. The introduction is given in English, German, French and Russian, to make the tables more generally useful.

STATIONARY PHASE IN PAPER AND THIN-LAYER CHROMATOGRAPHY

Second International Symposium organized by the Chromatography
Group of the Czechoslovak Chemical Society, at Liblice
by K. Macek and I.M.Hais

7 × 10″, 358 pages, 69 tables, 135 illus., 494 lit. refs., 3 coloured plates, 1965, Dfl. 42.50, 85s., $16.00

Contents: List of participants in the discussion. Introduction. Opening speech. I. Chromatography papers. II. Thin-layer materials. III. Stationary liquids and adsorbents in paper chromatography. IV. Stationary liquids and impregnations for thin layers. V. General problems of the stationary phase. Discussion. Closing remarks. Author index. Subject index.

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NEUERSCHEINUNG

Gerhard Spiteller

Massenspektrometrische Strukturanalyse organischer Verbindungen

Eine Einführung

mmer wieder steht der Chemiker vor dem Problem, Molekulargewicht, Zusammensetzung und Struktur einer Sub-
tanz bestimmen zu müssen, die nur in äußerst geringer Menge vorhanden ist. Hier helfen ihm vor allem die in den
tzten Jahrzehnten außerordentlich verfeinerten spektroskopischen Methoden. Eine von diesen ist die Massenspek-
ometrie, die besonders bei der Untersuchung der Struktur organischer Verbindungen ständig an Bedeutung
ewonnen hat. Der geringe Substanzbedarf und die bescheidenen Reinheitsanforderungen machen die Methode
or allem für den Naturstoffchemiker zu einem unentbehrlichen Hilfsmittel. Ein ebenso großes Anwendungsfeld
eginnt sich der Massenspektrometrie bei der Schnellanalyse roher Syntheseprodukte zu erschließen: Das Ziel des
nthetisch arbeitenden Chemikers ist die Darstellung des Endproduktes in möglichst hoher Ausbeute. Eine Er-
öhung der Ausbeute gelingt nur, wenn die Bildung von Nebenprodukten durch Änderung der Reaktionsbedin-
ngen so weit wie möglich eingeschränkt wird. Dies setzt die Kenntnis der Struktur der Nebenprodukte voraus.
ur Auffindung dieser Nebenprodukte und zur Aufklärung ihrer Struktur direkt aus dem Reaktionsansatz ohne
rhergehende Reinigungsoperationen kann die Massenspektrometrie viel beitragen.

ber Einzelheiten und Variationen dieses Verfahrens sowie vor allem über die Spektren verschiedener Substanz-
assen, über die im Massenspektrometer ablaufenden Vorgänge, über ihre Beeinflussung durch Substituenten und
er die Deutung der Spektren unterrichtet das Buch von Professor G. Spiteller. Zahlreiche Spektren und Formel-
lder erleichtern das Verständnis des Textes. Die erworbenen Kenntnisse können an Hand von Übungsaufgaben
n Ende des Buches, zu denen ausführliche Lösungen angegeben sind, überprüft und gefestigt werden.

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■ **General prospectus on request!**

THE DETERMINATION OF MAGNESIUM IN SILICATES BY ATOMIC ABSORPTION SPECTROSCOPY

R. W. NESBITT

Department of Geology and Mineralogy, The University of Adelaide, Adelaide (South Australia)

(Received January 20th, 1966)

Magnesium is one of the most difficult major elements to determine quantitatively in silicate rocks, either by conventional wet chemical methods or by X-ray fluorescence spectroscopy. The present paper draws attention to the method of atomic absorption spectroscopy using the nitrous oxide–acetylene flame as a technique for the routine analysis of magnesium in silicates.

The principles and instrumentation of the atomic absorption method have been fully described[1–3], and the advantages of this technique over flame emission spectroscopy have been outlined in many review articles (*e.g.* David[4]). However, the flame absorption method has the same limitations as the flame emission method with respect to chemical interference. For example, Allan[5] has demonstrated the interfering effect of aluminium in the determination of magnesium in agricultural materials. In a review of the technique, David[4] discusses this and other interferences found in the atomic absorption method.

Interference by aluminium in the air–acetylene flame

Most silicates contain significant concentrations of aluminium (a granite for example contains about 7%) and hence aluminium interference is a major problem in the determination of magnesium. The methods of overcoming this chemical interference generally involve a prior separation of aluminium or its suppression[6–9] by the addition of swamping concentrations of calcium, strontium, lanthanum or 8-hydroxyquinoline. The additive method is generally used because of its simplicity and apparent effectiveness. The mechanism of suppression is probably a chemical one, in that the additive forms a more stable compound with aluminium than does magnesium, so that magnesium can appear as a free ground atom in the flame. The writer has found the addition of 100 μg of strontium/ml an effective method for the suppression of interference caused by 15 μg of aluminium/ml on the absorption of 4 μg of magnesium/ml. This necessitates addition of similar amounts of strontium to the standards since this element produces an appreciable enhancement of absorption by magnesium.

Another method of overcoming aluminium interference is to raise the temperature of the flame so that the aluminium–magnesium compound is no longer stable and dissociates. This method is discussed in the next section.

No other serious interferences have been described in the determination of magnesium in the air–acetylene flame. The interferences described by Firman[10] using an air–propane flame have not been observed in the hotter air–acetylene flame. The depressing effect of sulphate or phosphate noted in the determination of calcium does not occur in the determination of magnesium unless these anions are present in high concentrations[5].

The nitrous oxide–acetylene flame and its application

Recent work in Australia by AMOS AND THOMAS[11] and WILLIS[12] has resulted in the development of a high-temperature burner using a nitrous oxide–acetylene mixture. The original description by AMOS AND THOMAS[11] covered the use of the burner with a pre-mixed flame of acetylene burning in a 50% oxygen–50% nitrogen mixture. WILLIS[12] suggested the use of nitrous oxide as the oxidising agent on the basis that a comparable temperature is achieved and that the lower burning velocity of nitrous oxide–acetylene (Table I) enables a longer burner to be used and also decreases the risk of an explosion.

TABLE I

CHARACTERISTICS OF FLAMES SUITABLE FOR ATOMIC ABSORPTION SPECTROSCOPY (AFTER WILLIS, 1965)

Gas mixture	*Maximum flame speed (cm/sec)*	*Maximum temperature (°)*
Air–acetylene	160	2300
Oxygen–acetylene	1130	3060
Nitrous oxide–acetylene	180	2955

TABLE II

RECOVERY OF MAGNESIUM IN THE PRESENCE OF ALUMINIUM USING DIFFERENT FLAME TYPES

Amount of magnesium originally present (μg/ml)	*Amount of aluminium present (μg/ml)*	*Amount of magnesium found (μg/ml)*	
		A[a]	*B*[b]
1	0	1	1
1	5	0.925	1
1	10	0.86	1
1	15	0.83	1
1	20	0.820	1
1	25	0.810	1

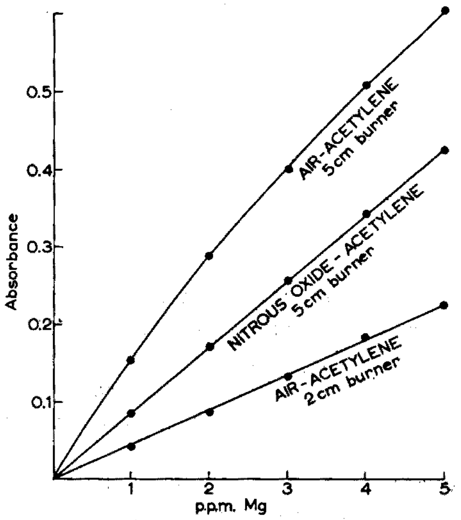
[a] A = Air–acetylene flame.
[b] B = Nitrous oxide–acetylene flame.

Table II shows results of experiments using air–acetylene and nitrous oxide–acetylene flames. The same burner (5 cm) was used in both sets of measurements. The results show that the addition of moderate quantities of aluminium produces significant suppression of magnesium absorption when the cooler flame is used.

In the case of the granite G1, which has an aluminium: magnesium ratio of about 30:1, an analysis using the air–acetylene flame would produce results about 20% low. Since this ratio is much lower in the diabase W1, the relative error would be about 7%.

Table II demonstrates also the complete elimination of aluminium interference in the nitrous oxide–acetylene flame. The use of a hotter flame results in a lower sensitivity because the magnesium absorption is actually much less than in the air–acetylene flame. This loss in sensitivity (about one half) is of no consequence in the analysis of silicates, because magnesium is normally present in quantities over 1,000 p.p.m. and the sensitivity for magnesium is still extremely high in the hot flame. With a nitrous oxide–acetylene flame and a burner with a 50 mm × 0.46 mm slot, a solution containing 0.05 μg of magnesium/ml produces 1% absorption (this value could certainly be improved by using organic solvents, and multiple pass devices). If 50 mg of rock is finally taken up in 50 ml of solution, this 1% absorption represents 50 p.p.m. or 0.005% magnesium in the rock.

The problem, however, is commonly one of too great a sensitivity and this can be overcome in several ways. For the air–acetylene flame, a burner with a 2-cm slot length was constructed. This decreased the sensitivity substantially as can be seen from Fig. 1, and, in most cases, excessive dilution was unnecessary. Another method, which can be applied to both flame types, is to turn the burner at right-angles to the light path. This has proved very successful in dealing with silicates containing moderate to high magnesium concentrations. The calibration curve for the nitrous oxide–acetylene flame with the burner at right-angles, shown in Fig. 2 is linear over the range 0–25 μg of magnesium/ml (0–40% absorption). This linearity is also displayed by the calibration curve for 0–5 μg of magnesium/ml (0–60% absorption) when the burner is parallel to the light beam and a nitrous oxide–acetylene flame is used. This contrasts with the non-linear curve obtained using the air–acetylene flame (Fig. 1).



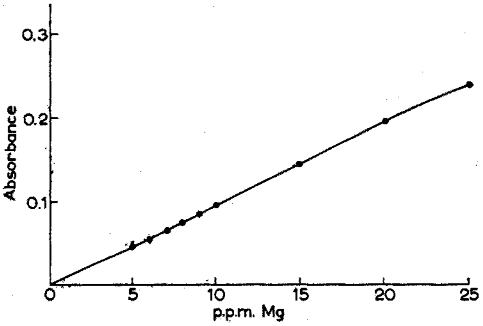


Fig. 1. Comparison of calibration curves for a 5-cm burner using air–acetylene and nitrous oxide–acetylene and a 2-cm burner using air–acetylene.

Fig. 2. Calibration curve for burner turned at right-angles to light path (nitrous oxide–acetylene flame).

Operation of the nitrous oxide–acetylene flame

The use of the nitrous oxide–acetylene mixture greatly increases the chances of an explosion when lighting or extinguishing a flame. This fact is rather surprising considering that the flame speed quoted by WILLIS[12] is fairly close to that for air–acetylene (Table I). However, there is certainly a much greater tendency for the flame to burn back and explode the gases in the spray chamber when nitrous oxide is used instead of air. This danger can be minimised by replacing the nitrous oxide with air before turning off the acetylene supply. This is achieved by inserting a Y junction on the low-pressure outlet side of the nitrous oxide cylinder, one pipe going to the gas control unit and the other to a compressed air supply. This system has proved satisfactory over an extended period and no explosion has occurred since its installation. The gradual introduction of air into the Y junction at a greater pressure than the nitrous oxide results in the blocking off of this gas. At this instant the flame changes abruptly from a nitrous oxide–acetylene to an air–acetylene type as can be observed by the sudden increase of luminosity. This mixture can be safely extinguished by shutting off the acetylene supply. The nitrous oxide supply is then turned off and finally the air.

The operation of lighting and extinguishing the burner when using nitrous oxide is as follows:

(1) With all gas and air valves to the burner closed, preset the nitrous oxide to 20 p.s.i. and acetylene to 10 p.s.i. The air cylinder should be ready for use*.

(2) Open the control valve to allow acetylene to flow to the burner. When a strong smell of acetylene is detected, ignite.

N.B. No nitrous oxide must be present and an extractor system must be operating above the burner.

(3) Turn the acetylene up to a flow rate of 3.0 l/min (a value of 6 on the "Techtron" flow gauge) and quickly allow the nitrous oxide to enter, gradually building up the pressure to 15 p.s.i. The flame should have a characteristic crimson "feather" just above the cone at all times, the height of which is an indication of the fuel to nitrous oxide ratio. With decreasing acetylene the "feather" will become smaller.

(4) When ready to extinguish, slowly turn on the air supply from either a bottle source or compressor. When this pressure exceeds the nitrous oxide pressure (20 p.s.i.) a luminous air–acetylene flame will result.

(5) Turn off the acetylene, nitrous oxide, and air in that order.

Interferences in the nitrous oxide–acetylene flame

With the nitrous oxide–acetylene flame, there are few serious interferences. Of these, the presence of alkali metals in high concentrations is the most troublesome. The interference is always an enhancement and can be explained by the abnormally high ionisation of these metals in the hotter flame. The presence of a high concentration of electrons liberated in this ionisation tends to suppress the natural ionisation of magnesium, and consequently to increase the absorption (AMOS AND WILLIS[19]).

Table III shows the results of recovery experiments on solutions containing 1 μg of magnesium/ml in the presence of sodium.

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* Note that if a compressed air supply from a large storage tank is used, then a non-return valve must be inserted along the air line.

In the case of G1 granite, in which the ratio of magnesium to sodium is about 1 to 10, this interference would cause a relative error of 7%. Greater errors could be expected in some acidic rocks where the magnesium content is extremely low (less than 0.1%), but would be negligible in rocks containing significant quantities of magnesium.

TABLE III

RECOVERY OF MAGNESIUM IN THE PRESENCE OF SODIUM (NITROUS OXIDE–ACETYLENE FLAME)

Amount of magnesium originally present (µg/ml)	*Amount of sodium present (µg/ml)*	*Amount of magnesium found (µg/ml)*
1	—	1
1	10	1.07
1	20	1.11
1	30	1.15

TABLE IV

PER CENT MgO VALUES OBTAINED ON STANDARD ROCK SAMPLES

Rock standard	*Atomic absorption value*	*Recommended values*	*Rock type*	*Interlaboratory comparison*	*Source and reference*[d]
G1	0.39	0.41[a]	Granite	0.27–0.53[b]	13
W1	6.67	6.62	Diabase	6.23–6.93[b]	13
S1	4.08	4.07	Syenite	3.25–4.81[c]	14
T1	1.86	1.89	Tonalite	1.75–1.95[b]	15
GH	0.03	0.03	Granite		16
GA	0.92	0.95	Granite		16
GR	2.38	2.41	Adamellite	2.16–2.68[b]	16
BR	13.30	12.60	Basalt		16
T13	3.31	3.40	Tonalite		17

[a] Since Ba is thought to precipitate with magnesium (STEVENS[18], p. 10) in gravimetric methods, the value for G1 would be lowered to about 0.32% MgO.
[b] Limits of acceptability.
[c] Reported range from 19 analysts.
[d] 13 United States Geological Survey (FLEISCHER AND STEVENS [13], STEVENS[18]).
14 Canadian Association for Applied Spectroscopy (WEBBER[14]).
15 Mineral Resources Division, Tanzania (THOMAS[15]).
16 Centre Nationale de la Recherche Scientifique, Nancy, France (ROUBAULT *et al.*[16]).
17 MERCY[17].

However, it appears that the effect is not straightforward and the present results (Table IV) suggest that enhancement of magnesium absorption does not occur in solutions of natural material. The most probable reason for this is that, as well as alkali metals, there are several other cations which will ionise to a considerable extent in the hot flame, and this will complicate the simple picture of ionisation suppression just given. The results presented in Table IV tend to support such an empirical conclusion since there is no evidence of consistently high values in the standard silicate rocks used.

EXPERIMENTAL

Apparatus

The atomic absorption spectrophotometer used was a single-beam Techtron unit (model AA3). The following settings were used: lamp current 6 mA, slit width 0.05 mm, 2852 Å resonance line; nitrous oxide–acetylene premixed flame. The burner was of stainless steel construction 14.5 cm long, 1.5 cm thick, and 5 cm wide, with a 50 mm × 0.46 mm slit, manufactured by Techtron Pty. Limited, Melbourne. One cylinder of nitrous oxide of 1800 gal. capacity has an initial pressure of 600 p.s.i. and gave a total burning time of about 22 h. Since the gas is used for medical purposes, it is freely available.

Procedure

Sample powders were all dried at 105°. Digest 50–100 mg of sample in 4 ml of 40% hydrofluoric acid and 1 ml of 1:1 sulphuric acid. Best digestion results are obtained if the samples are left covered for 12 h in platinum crucibles and then taken almost to dryness. Add hydrofluoric acid and sulphuric acid again and then evaporate off, taking care to avoid spluttering. Dissolve the residue in 1:1 hydrochloric acid and then make up to volume. The series of operations from the initial evaporation to making up to volume requires 3 h. Prepare standards from analytical-grade magnesium oxide and take a blank through the digestion procedure.

Spray the samples directly against standards, the pH of which is close to that of the unknowns. Take rough absorption measurements to indicate the approximate magnesium concentrations in the solution. In samples with high magnesium contents, rotate the burner to a right-angle position to the light path. Before final measurements are taken, allow the burner to warm up for 10–15 min and the lamp and electronic equipment for 30 min. Spray the samples at least 6 times, rotating between the unknown, the standards and the blank. Choose the standards to bracket the unknown as closely as possible. Convert the average readings to absorbance and subtract the blank absorbance value to give the final value. Since the sensitivity of the method is so high, it is essential to correct for a blank solution.

RESULTS

Results of analyses for magnesium (as MgO) are presented in Tables IV and V. The range of MgO varies from 0.03 to 13.0% and covers the common rock stan-

TABLE V

PER CENT MgO VALUES OBTAINED ON U.S.G.S. STANDARD ROCK SAMPLES (DISTRIBUTED, 1965)

Rock standard	*Atomic absorption value (% MgO)*	*Recommended value*[a] *(% MgO)*	*Rock type*
G2	0.74	0.75	Granite
GSP1	0.94	0.98	Granodiorite
AGV1	1.44	1.50	Andesite
BCR1	3.31	3.48	Basalt

[a] Average of 2 determinations from U.S. Geological Survey (MUNSEN AND SMITH).

TABLE VI

ANALYSIS OF VARIANCE ON SEVERAL DETERMINATIONS OF MAGNESIUM IN TWO SILICATE ROCKS

	Mean	*Estimated standard error of the mean*	S_1[a]	S_2[b]
G1	0.387	0.0056	0.01	0.087
GSP1	0.939	0.0160	0.05	0.01

[a] S_1 = estimated standard deviation of sampling (between samples).
[b] S_2 = estimated standard deviation of analysis (within sample).

dards. The standards distributed by the United States Geological Survey in 1965 are listed in Table V.

An analysis of variance on the results of repeated digestion and replicate determinations on G1 and GSP1 was carried out. Four and five separate samples of G1 and GSP1 respectively were digested and duplicate analysis carried out on each; the results are shown in Table VI.

The results presented suggest that magnesium can be measured in silicates quickly and precisely using atomic absorption spectroscopy. The necessity to overcome aluminium interference by addition of lanthanum or strontium is avoided by using the hotter nitrous oxide–acetylene.

The author is indebted to Dr. J. B. WILLIS for discussion of the paper by AMOS AND WILLIS before publication, to Professor JAMES for advice on the statistical treatment of the data and to Mr. D. GRAY for assistance in the laboratory.

SUMMARY

The determination of magnesium in silicates by atomic absorption spectroscopy using a hot flame is discussed. Interference by aluminium observed in the air–acetylene flame is overcome by using the hotter nitrous oxide–acetylene flame. There is some evidence to suggest that the alkali metals interfere in this determination but this is not confirmed in the results obtained on standard rock samples. Values for magnesium are given for some new rock standards recently distributed by the U.S. Geological Survey.

RÉSUMÉ

L'auteur examine le dosage du magnésium dans les silicates par spectroscopie par absorption atomique, utilisant une flamme très chaude. On peut éliminer l'interférence de l'aluminium, observée dans la flamme air–acétylène, en employant la flamme plus chaude oxyde nitreux–acétylène. Il semblerait que les métaux alcalins gênent, mais cela n'est pas confirmé par les résultats obtenus avec des échantillons standards de roches.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Magnesium in Silikaten mit der Flammenabsorptionsspektroskopie unter Verwendung einer heissen Flamme diskutiert. Störungen durch Aluminium, wie sie bei der Luft–Acetylenflamme auftreten, werden durch Anwendung einer heisseren Stickstoffoxid–Acetylenflamme vermieden. Einige Hinweise lassen die Vermutung zu, dass die Alkalimetalle bei dieser Bestimmung stören. Das wird jedoch mit Standardgesteinsproben nicht bestätigt. Es werden Werte für Magnesium in einigen neuen Standards angegeben.

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NEUTRON ACTIVATION ANALYSIS OF MICROGRAM AMOUNTS OF THORIUM IN URANIUM ORES AND PROCESS LIQUORS BY MEANS OF THORIUM-233

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Several analytical procedures have been developed for the assay of thorium traces in ores and minerals[1-3]. Activation methods have also been worked out because of the favorable features of natural isotope thorium-232 (100% isotopic abundance; neutron activation cross-section, 7.3 barns); the following reactions occur under neutron irradiation:

$$^{232}\mathrm{Th} \xrightarrow{(n,\gamma)} {}^{233}\mathrm{Th} \xrightarrow[T_{\frac{1}{2}}=23\ \mathrm{min}]{\beta} {}^{233}\mathrm{Pa}\ (T_{\frac{1}{2}} = 27.4\ \mathrm{d})$$

The most widely used activation methods utilize ^{233}Pa, a β,γ-emitter which is easy to handle and measure[4,5]. The use of ^{233}Th has been regarded as less attractive because of its short half-life (23 min) and its nature as a pure β-emitter. However, JENKINS[6] has utilized this isotope to assay thorium in ores by means of a radiochemical procedure involving oxalate precipitation and chromatographic separation on an alumina column. The main drawbacks of JENKINS' method are that it is time-consuming (2–3 h per sample are required with the consequent sensitivity losses) and that there is some contamination from neptunium-239 when the method is applied to uranium-bearing ores; to overcome the latter difficulty, weaker β-particles of neptunium-239 can be filtered out with an aluminium absorber, but the thorium-233 activity (and hence the sensitivity) also decreases.

From the point of view of reactor utilization, it is advantageous to use the thorium-233 isotope because the theoretical sensitivity achieved in an irradiation of 22 min is as high as that obtained after 27 days of irradiation under the same neutron flux with ^{233}Pa; when the available reactor does not run continuously, this feature is even more important. Another factor in favour of thorium-233 is the ready availability of a carrier to correct for radiochemical yield, thus obviating the need for a strictly quantitative separation procedure.

These well-known advantages of thorium-233 led us to develop a method suitable for handling many samples of uranium ores and of uranium mill products and by-products. By making use of ion exchange, liquid–liquid extraction and precipitation steps it is possible quickly to recover satisfactorily pure thorium-233 with a quite good ultimate sensitivity.

EXPERIMENTAL

Irradiation

Weighed ore samples of about 100 mg or 2-ml aliquots of sample solutions were placed in plastic containers and irradiated in the pneumatic facility of the JEN-1 reactor for 5 min at a neutron flux[7] of 10^{12} n/cm^2/sec. Aliquots of solutions containing known amounts of thorium (about 100 μg/ml) were irradiated in similar containers together with the unknown samples. Small strips of pure nickel sheet were attached to both ends of each container to monitor for flux differences from sample to sample during irradiation.

Sample dissolution

Irradiated ore samples were mixed with about 10 g of sodium peroxide and fused in a Parr bomb[8]. The melt was leached with water containing 20 mg of thorium carrier. The hydroxide precipitate was centrifuged, the supernate discarded and the precipitate then washed with water, before its dissolution in 10 ml of 12.5 *N* hydrochloric acid at room temperature.

When solutions were irradiated, 2-ml aliquots were measured and added directly to 10 ml of 12.5 *N* hydrochloric acid containing 20 mg of thorium carrier.

Decontamination

Removal of impurities by anion exchange. The solutions obtained as above were percolated at a flow rate of 2 ml/min through a Dowex 1-X8, 50–100 mesh, anion-exchange column previously equilibrated with 12.5 *N* hydrochloric acid. The column was 10 cm high and 1 cm in diameter. The column was washed with 15 ml of 12.5 *N* hydrochloric acid at the same flow rate and all effluents were collected in a 50-ml lusteroid centrifuge tube.

Precipitation of fluoride. Thorium fluoride was precipitated in the collected effluents by adding 2–3 ml of concentrated hydrofluoric acid. The precipitate was centrifuged, washed with water and dissolved in 10 ml of 1.2 *N* nitric acid saturated with aluminium nitrate. Dissolution was very fast at room temperature.

Mesityl oxide extraction. The solution thus obtained was extracted with 20 ml of mesityl oxide in a 50-ml separatory funnel for 20 sec; after phase separation, the aqueous layer was discarded and the organic layer scrubbed three times, for 20-sec periods, with 20 ml of 1.2 *N* nitric acid saturated with aluminium nitrate to remove traces of rare earths. Thorium was back-extracted from mesityl oxide with 20 ml of distilled water.

Final thorium precipitation. Ethanol (15–20 ml) was added to the aqueous solution and thorium was precipitated with 4–5 ml of a saturated solution of oxalic acid. The precipitate was centrifuged, slurried in a few ml of water, heated to boiling and filtered in a Hirsh funnel on a tared filter paper (S.S. blue band). The oxalate precipitate was washed 3 times with acetone and ether, weighed and mounted for counting.

Activity measurements

Counting was done with an end-window, halogen-filled Geiger counter and a JEN-made scaler. Several 1-min counts were taken of samples and standards during four or five thorium-233 half-lives and times were controlled to check decay. Four hours after the last count, the residual activities of samples and standards were measured for 5–10 min.

Calculations

The residual activity of each sample, as measured after 10 thorium-233 half-lives, represented about 1–2% of the initial activity and was subtracted from all 1-min counts mentioned above. Then all activities thus obtained were corrected for decay at a common initial time origin, usually 60 min after the end of irradiation. Excellent agreement was generally found among the activities corrected in this way, from the counts of the same sample—five at least—taken at different time intervals.

The mean value from these activities was used to calculate the thorium contents of irradiated samples by comparison with the activities of the standards treated in the same way; all activities were previously corrected for chemical yield and neutron flux differences.

RESULTS

This method has been so far applied to the assay of thorium traces in a uranium ore standard prepared by JEN for IAEA, the composition of which[9] is shown in Table I, and in solutions resulting from their leaching with sulphuric acid under uranium mill conditions[10].

TABLE I

COMPOSITION OF URANIUM ORE STANDARD

Semiquantitative spectrographic analysis of impurities				*Quantitative analysis by direct reading spectrography*	
Oxides	%	*Oxides*	%	*Oxides*	%
B_2O_3	0.02	MnO	0.02	Al_2O_3	4.5
BaO	0.03	NiO	0.001	GaO	0.078
BeO	0.003	PbO	0.008	CuO	0.024
Cr_2O_3	0.001	SnO	0.003	Fe_2O_3	10.0
Ga_2O_3	0.002	TiO_2	0.04	MgO	0.15
Li_2O		V_2O_5		Na_2O	0.07
				SiO_5	76

U_3O_8: 0.31% (average of 30 determinations by different methods)

TABLE II

RESULTS OF THORIUM NEUTRON ACTIVATION ANALYSIS

Standard ore		*Sulphuric liquor*	
Assay	*Th (μg/g of ore)*	*Assay*	*Th (μg/ml)*
1	9.3	1	0.43
2	8.9	2	0.42
3	9.0	3	0.44
4	8.3	4	0.40
5	8.6	5	0.40
6	7.8	6	0.42
	Av. 8.65 ± 0.5 (±6%)		Av. 0.42 ± 0.02 (±5%)

The results obtained in 6 individual determinations of each sample are tabulated in Table II. Standard deviation values are also shown, which are much better than 10%, a figure generally accepted for good quality activation analysis of trace amounts.

Sensitivity is good. Under the conditions used (irradiation for 5 min at 10^{12} n/cm^2/sec and 1 h for sample processing), 1 μg of thorium gives an initial activity of about 20,000 counts/min with the counting equipment employed. This sets a thorium detection limit as low as 0.02 μg, an amount that produces an activity several times higher than the background and the residual long half-life activities.

DISCUSSION

The goals to be achieved in this work were: fast separation steps so that the final sensitivity would not be diminished, and high decontamination factors from activated matrix components and from uranium fission products because no cooling could be allowed.

The Parr bomb method used as a first step for solid samples requires only a few minutes and gives excellent results for 100–150-mg samples of many types of ores and minerals[8]. Leaching with pure water containing thorium carrier prevents silica from becoming insoluble and thus allows this matrix bulk component to be removed easily.

According to KRAUS AND NELSON[11–13], thorium is not absorbed on anionic resin at any hydrochloric acid concentration, and this allows its separation from many other elements such as uranium(IV and VI), several fission products and neptunium-239. By means of radioactive tracers it was found that under the conditions stated above, the decontamination factors for neptunium-239 and zirconium-95 (2 main active components of irradiated ores and solutions) were as high as 10^6, whereas the thorium recovery was quantitative. The time needed for this step was only 10–12 min, several samples could be processed simultaneously and difficulties from radiation were easily overcome; the radiation dose rate was drastically reduced after this step, a very important fact for speeding the subsequent handling. Other possible methods have been described for thorium purification from rare earths and some other contaminants: retention of thorium in cation-exchange resins[14,15] or in anionic resins in nitric acid[16]. However, the cation-exchange procedure is not specific whereas DANON's method[16] requires a lot of nitric acid and—more important—time to elute rare earths completely (this was checked with lanthanum-140 and dysprosium-165 tracers).

One radioactive contaminant that must be removed with a very high efficiency is uranium-239, a 1.21-MeV β-emitter with a 23.5-min half-life which is virtually indistinguishable from the 23-min, 1.23-MeV thorium-233 β-activity. However, uranium can be completely removed with anionic exchanger, both U(IV) and U(VI) being strongly retained in 12.5 N hydrochloric acid[12,13]. Experiments carried out by irradiating uranyl nitrate solutions which had been freshly purified from thorium-234 (UX_1) and the uranium contents of which were 40 times higher than that present when ore samples are assayed, showed that no 23-min activity existed in processed samples counted one hour after the end of irradiation.

The use of mesityl oxide to extract milligram amounts of thorium has been repeatedly reported[17,18]. In the present work, tests were made with neptunium-239, lanthanum-140 and dysprosium-165 to check the purification of thorium from these contaminants; the complete recovery of thorium was also checked with thorium-234 tracer. The method described here is shorter than previously published procedures.

Precipitation of thorium fluoride between the anion exchange and extraction steps is an easy and fast way of changing from the hydrochloric acid medium coming from the column to the nitric acid medium needed for extraction. Moreover, it introduces an additional purification from U(VI), Np(VI) and many fission products; this is also true for the oxalate precipitation.

The total time spent by an expert operator in the radiochemical procedure is less than one hour for simultaneous processing of 4 ore samples and 2 standards. This is why a time of 60 min after the end of irradiation was chosen as a common time basis to correct for radioactive decay.

SUMMARY

A method is described for neutron activation analysis of thorium by employing thorium-233. Decontamination steps include anion exchange in 12.5 *N* HCl, precipitation of fluoride, extraction with mesityl oxide and thorium oxalate precipitation. The time spent is less than 1 h; spurious activities in counting samples amount only to 2% and can easily be corrected for. The sensitivity of the method is *ca.* 0.02 μg of thorium in a neutron flux of 10^{12} n/cm^2/sec with an irradiation time of 5 min.

RÉSUMÉ

On décrit une méthode d'analyse du thorium par activation au moyen de neutrons, en utilisant du thorium-233. Ce procédé comprend: échange d'anions dans HCl 12.5 *N*, précipitation du fluorure, extraction au moyen d'oxyde de mésityle et précipitation de l'oxalate de thorium. La sensibilité de la méthode est de 0.02 μg de thorium, dans un flux de neutrons de 10^{12} n/cm^2/sec, avec une irradiation de 5 minutes.

ZUSAMMENFASSUNG

Es wird eine Methode zur neutronenaktivierungsanalytischen Bestimmung von Thorium beschrieben unter Verwendung von Thorium-233. Im einzelnen werden folgende Schritte durchgeführt: Anionenaustausch in 12.5 *N* HCl, Fällung als Fluorid, Extraktion mit Mesithyloxid und Fällung des Thoriums als Oxalat. Für die Analyse benötigt man weniger als 1 Std. Spurenaktivitäten betragen nur 2% und können leicht korrigiert werden. Die Empfindlichkeit der Methode beträgt *ca.* 0.02 μg Th bei einem Neutronenfluss von 10^{12} n/cm^2/sec und einer Bestrahlungszeit von 5 Min.

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THE SIMULTANEOUS DETERMINATION OF SILVER, GOLD AND MERCURY IN HIGH-PURITY LEAD BY NEUTRON ACTIVATION ANALYSIS

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Neutron activation analysis has been mainly restricted to the determination of a limited number of elements at one time. This means that a separate sample and irradiation are needed for the determination of each element or group of elements. Fast non-destructive methods and more specific counting techniques such as γ,γ-coincidence, sometimes eliminate the need for separate samples for every element and have proved to be highly specific and sensitive; nevertheless they remain of a restricted applicability. In order to analyse simultaneously a larger number of elements in a given matrix and to avoid the use of complicated and tedious precipitation or ion-exchange procedures, large computer-programmed, automatic, non-destructive, multi-element analysis systems have been developed.

It is the aim of this work to show that it is possible to apply multi-element analysis by an adequate combination of simple destructive chemical separation techniques without large computer programs or special counting techniques.

The elements Au, Ag, Hg, Cu, Bi, Cd, Sb and Tl for instance can be determined, in the given order, in high-purity lead after a single irradiation. The impurities are then separated into three groups:

(*1*) Au, Ag, Hg,
(*2*) Cu, Bi,
(*3*) Cd, Sb, Tl.

This work describes the determination of the first group. Detailed information about the two other groups will be published in due course.

For the purpose the following criteria had to be met:

(*a*) a radiochemical laboratory with standard counting equipment: G.M.-counters, γ-spectrometer, preferably of the multichannel type;

(*b*) no reactor in the immediate vicinity of the laboratory;

(*c*) a desk-type calculator.

NUCLEAR DATA

Irradiation of natural lead, silver, mercury and gold with thermal neutrons gives rise to several radioisotopes, the characteristics of which are shown in Table I[1-3]. From Table I it is obvious that lead is a favourable matrix for thermal neutron activation analysis, since only one isotope with a medium half-life is formed by a (n, γ) reaction. This isotope is a pure β-emitter and does not interfere with the γ-spectrometric analysis. Only ^{203}Pb formed by a (n,2n) reaction can be a source of interference. However, due to the small abundance of ^{204}Pb and the low cross-section for this reaction, this interference is only important for extremely pure lead samples. Moreover, the small average absorption cross-section for natural lead (0.17 barn) avoids neutron shadowing effects in the samples.

TABLE I

NUCLEAR DATA[a]

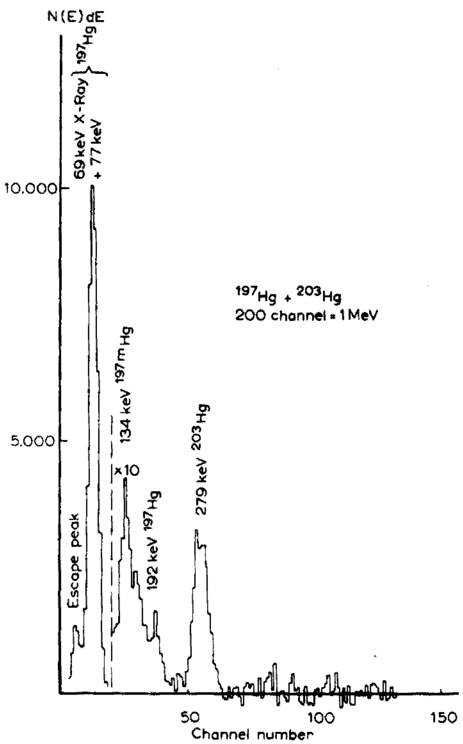
Element	*Isotope*	*% Abundance*	*Reaction*	*Product isotope*	*Cross-section*[b] *(barn)*	*Half-life*	*Decay mode*	*γ-Energy*
Pb	^{204}Pb	1.48	(n, γ)	^{205}Pb	0.7	$3 \cdot 10^7$ y	—	—
			(n, 2n)	^{203}Pb	0.0029	2.17 d	EC, γ	279, 404
	^{208}Pb	52.3	(n, γ)	^{209}Pb	0.0006	3.2 h	β^-	—
Hg	^{196}Hg	0.146	(n, γ)	^{197}Hg	880	65 h	EC, γ	78, 192
				^{197m}Hg	420	24 h	EC, I.T. γ	—
	^{198}Hg	10.02	(n, γ)	^{199m}Hg	0.018	42 m	IT	—
	^{202}Hg	29.80	(n, γ)	^{203}Hg	3.8	46.9 d	β^-, γ	279
	^{204}Hg	6.85	(n, γ)	^{205}Hg	0.43	5.6 m	β^-, γ	203
Au	^{197}Au	100	(n, γ)	^{198}Au	96	2.70 d	β^-, γ	412, 676
Ag	^{107}Ag	51.3	(n, γ)	^{108}Ag	44	2.43 m	β^-, β^+ γ, EC	615, 434
	^{109}Ag	48.7	(n, γ)	^{110}Ag	113	24 s	β^-, γ	656, 940
				^{110m}Ag	3.2	253 d	β^-, γ, I.T.	655, 884, 935

[a] Reactions giving rise to stable isotopes have been omitted.
[b] Activation cross-sections.

For mercury the choice fell on ^{197}Hg, as ^{199m}Hg and ^{205}Hg have too short a half-life, whereas ^{203}Hg is too long-lived. The γ-rays of ^{197m}Hg are all highly converted and do not contribute visibly to the spectrum of mercury after a 1-day irradiation. As can be seen from Fig. 1, the most prominent peak in the spectrum is the 78 keV of ^{197}Hg. In fact this peak is the sum of the highly converted 78 keV peak and the 68.8 keV X-ray.

As gold is monoisotopic, only ^{198}Au is produced (Fig. 2). This isotope has a high thermal neutron cross-section, giving rise to ^{199}Au. Since successive neutron capture takes place in both the sample and the standard, no error is to be expected. ^{198}Au can also be produced by a (n,p) reaction on ^{198}Hg. The small concentration of mercury in the lead and the low cross-section[4] for this reaction rule out any interference from this effect.

In the case of silver, only ^{110m}Ag can be used, the half-lives of the other isotopes being too short. The long half-life of ^{110m}Ag and the fact that γ-rays are emitted with a wide variety of energies makes it a less convenient isotope for the purpose. ^{110m}Ag can also be produced by a (n,p) reaction on ^{111}Cd and a (n,α) reaction on ^{113}In. The low concentrations of these impurities and the small cross-sections make an interference from this source negligible. A spectrum of silver after a 1-day irradiation is shown in Fig. 3.



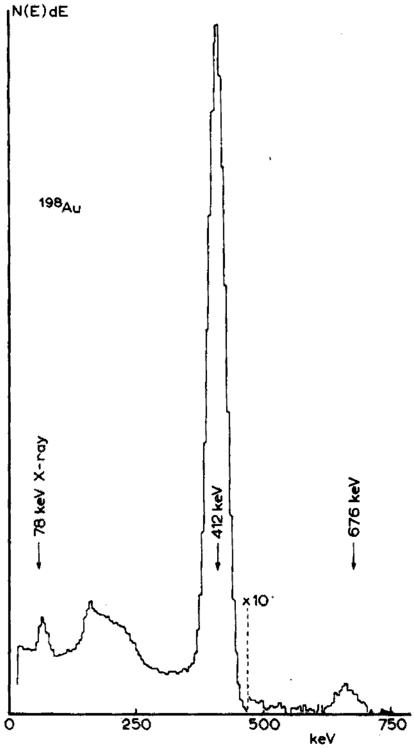


Fig. 1. Spectrum of neutron irradiated natural Hg.
Fig. 2. Spectrum of neutron irradiated natural Au.

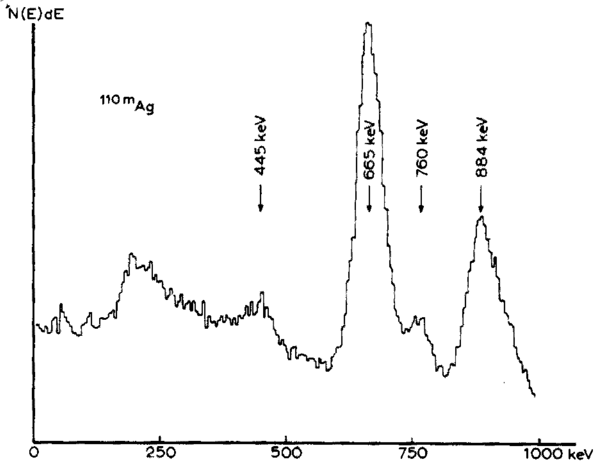


Fig. 3. Spectrum of neutron irradiated natural Ag.

The high elemental absorption cross-sections of the three metals, Hg (380 b), Au (98 b) and Ag (63 b), can be a source of strong self-shielding effects in the standards. Therefore it was decided to irradiate these metals in solution. For gold and mercury which have the highest cross-section (Table I), series of increasing amounts of these metals in solution (0.1–5 μg in 50 μl) were irradiated, and the obtained specific activities plotted as a function of the weight of the metal. No evidence for self shielding could be detected. It was subsequently decided to use ±2 μg of each metal dissolved in 40 μl.

When standards of elements, having large resonance peaks for neutron capture in the epi-thermal region, are irradiated in solution, it is possible that the linear correlation between the specific activities of samples and standards will no longer be valid. According to GIJBELS[5], this is due to the additional thermalization of the neutrons in the aqueous phase. For silver and gold the neutron capture cross-section is sufficiently well known[3] to conclude that this effect is not important. The neutron capture cross-section of ^{196}Hg being unknown, it was decided to investigate for any evidence of this phenomenon. Series of silica tubes containing 2 μg of mercury in 40 μl of water were irradiated together with artificial lead samples, made up of pellets pressed from lead powder on which a known amount of mercury had been homogeneously precipitated. The specific activities of mercury were compared for both cases, but no difference was noticed.

MATHEMATICAL METHOD

Compositional analysis of multi-component spectra with the aid of matrix calculus has been extensively described in the literature[6–13]. However, except in a few cases, only large-scale, computer-programmed, routine analyses have been developed. A less complicated method is derived here.

The complex γ-spectrum is considered as a superposition of the simple spectra of the pure isotopes. The contribution of each isotope in a certain region of the composite spectrum can be computed from n selected regions. If T_i represents the total activity in the region i, a set of n simultaneous equations can be written:

$$\left\{\begin{array}{lcl} T_1 & = & A_{11}+A_{12}+\ldots+A_{1n} \\ T_2 & = & A_{21}+A_{22}+\ldots+A_{2n} \\ \vdots & & \vdots \quad \vdots \quad \vdots \quad \vdots \\ T_n & = & A_{n1}+A_{n2}+\ldots+A_{nn} \end{array}\right. \tag{1}$$

where A_{ij} represents the contribution of the jth isotope in region i. This set of n equations has n^2 parameters A_{ij}. To reduce the number of parameters the set can be written as:

$$\left\{\begin{array}{lcl} T_1 & = & \frac{A_{11}}{A_{11}}A_{11} + \frac{A_{12}}{A_{22}}A_{22}+\ldots+ \frac{A_{1n}}{A_{nn}}A_{nn} \\ T_2 & = & \frac{A_{21}}{A_{11}}A_{11} + \frac{A_{22}}{A_{22}}A_{22}+\ldots+ \frac{A_{2n}}{A_{nn}}A_{nn} \\ \vdots & & \vdots \quad \vdots \quad \vdots \quad \vdots \\ T_n & = & \frac{A_{n1}}{A_{11}}A_{11} + \frac{A_{n2}}{A_{22}}A_{22}+\ldots+ \frac{A_{nn}}{A_{nn}}A_{nn} \end{array}\right. \tag{2}$$

or:

$$\begin{cases} T_1 = k_{11}A_{11} + k_{12}A_{22} + \ldots + k_{1n}A_{nn} \\ T_2 = k_{21}A_{11} + k_{22}A_{22} + \ldots + k_{2n}A_{nn} \\ \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ T_n = k_{n1}A_{11} + k_{n2}A_{22} + \ldots + k_{nn}A_{nn} \end{cases} \tag{3}$$

The coefficients k_{ij} are the ratios of the activities in the same regions i and j from the spectra of the pure isotopes which contribute to the spectrum. The set of equations can now be written as a matrix equation:

$$\begin{vmatrix} T_1 \\ T_2 \\ \vdots \\ T_n \end{vmatrix} = \begin{vmatrix} k_{11} k_{12} \ldots k_{1n} \\ k_{21} k_{22} \ldots k_{2n} \\ \vdots \; \vdots \; \vdots \; \vdots \\ k_{n1} k_{n2} \ldots k_{nn} \end{vmatrix} \times \begin{vmatrix} A_{11} \\ A_{22} \\ \vdots \\ A_{nn} \end{vmatrix} \tag{4}$$

After inversion of the matrix of coefficients this becomes:

$$\begin{vmatrix} A_{11} \\ A_{22} \\ \vdots \\ A_{nn} \end{vmatrix} = \begin{vmatrix} l_{11} l_{12} \, . \, . l_{1n} \\ l_{21} l_{22} \ldots l_{2n} \\ \vdots \; \vdots \; \vdots \; \vdots \\ l_{n1} l_{n2} \ldots l_{nn} \end{vmatrix} \times \begin{vmatrix} T_1 \\ T_2 \\ \vdots \\ T_n \end{vmatrix} \tag{5}$$

with $l_{ji} = (-1)^{i+j}(M_{ij}/D)$ (6)

M_{ij} being the minor of the element k_{ij} in the matrix of coefficients and D the algebraic value of that matrix. Thus the activities A_{ii} can easily be evaluated. For example:

$$A_{11} = l_{11}T_1 + l_{12}T_2 + \ldots + l_{1n}T_n \tag{7}$$

Since l_{ij} can be calculated from the pure isotopes, they are generally determined with a better precision than the T_i values deduced from irradiated samples. Usually the standard deviation on l_{ij} can be neglected compared to the standard deviation of T_i. Thus a comparatively simple expression can be deduced for the standard deviation of A_{ii}:

$$\sigma_{A_{ii}}{}^2 = \sum_{j=1}^{n} l_{ij}{}^2 \cdot \sigma_{T_j}{}^2 \tag{8}$$

It is obvious that $\sigma_{A_{ii}}{}^2$ increases with n. This means that the number of isotopes should not be too large. Indeed, with an increasing number of isotopes the contribution of an isotope in any part of the composite spectrum will finally become comparable to the statistical fluctuation of the total activity in that part. Therefore, in the case of an isotope j, the region i should be selected so that eqn. (9) is maximum

$$\frac{A_{ij}}{\sum\limits_{j=1}^{n} A_{ij}} \tag{9}$$

Moreover, the number of isotopes is already limited by the use of a desk-type calculator, the inversion of a matrix with a rank higher than 4 being too elaborate.

It is also clear that the l_{ij} values behave as important weighting factors in eqn. (8). If they reach values larger than unity the calculated standard deviation will quickly exceed the A_{ii} value itself. The value of l_{ij} is given by eqn. (6). To keep these as small as possible the k_{ij} values should be smaller or equal to unity and D as large as possible. Empirically it has been found that the first condition usually implies the second one. The first condition can be fulfilled when the region i, representative for isotope j, is selected so that

$$\frac{A_{mj}}{A_{ij}} \leqq 1 \text{ with } m = 1, 2, 3, \ldots n \tag{10}$$

Near or complete proportionality between two rows or columns of k_{ij} in the coefficient matrix should be avoided, since this will bring D near or equal to zero.

Optimal results will be obtained after careful examination of conditions (9) and (10), and consequent selection of the regions. These can be allowed to overlap or include the whole spectrum. Practically, narrow regions, including only the main photopeak areas of the individual isotopes, are in best agreement with conditions (9) and (10). As an example, in Fig. 4, a typical complex spectrum of mercury, gold and silver after separation from an irradiated lead sample is shown together with the selected regions.

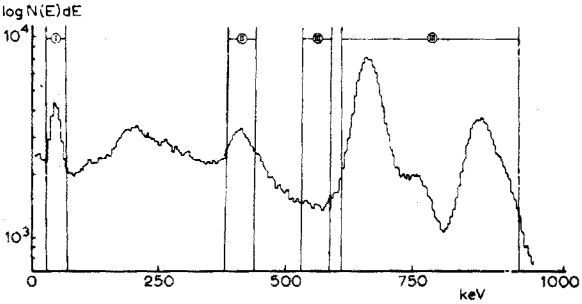


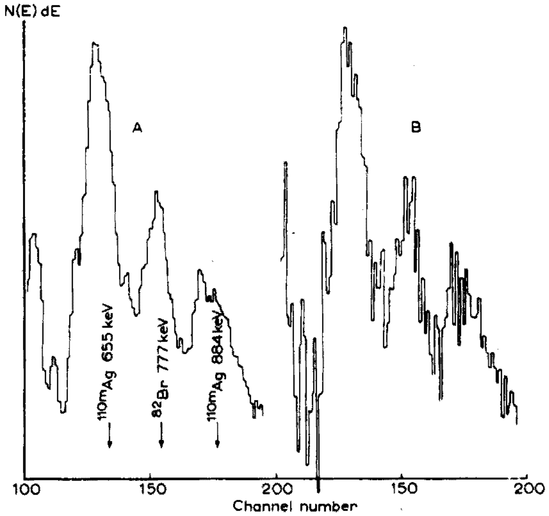
Fig. 4. Mixed spectrum of mercury, gold and silver, with selected regions.

When a multichannel analyzer is used, a spectrum can be obtained within a reasonable time from small activities. After substraction of the background, the random fluctuations are quite important and in extreme cases, smoothing of the data is necessary.

Savitzky and Golay[14] have derived sets of integers which provide weighting functions called convolutes. Smoothing becomes a convolution procedure, which is not an approximation, but an exact equivalent of the least squares procedure.

Although no well defined function can be found to describe a γ-spectrum, the smooth curve can be considered as quadratic in the vicinity of a peak, or cubic in the vicinity of a shoulder, if one takes sufficiently small intervals. Moreover, convolute integers are the same for quadratic and cubic functions, and the integers for a seven-point group are so simple that smoothing of a spectrum of 200 channels can be accomplished on a desk-type calculator within a matter of hours.

This procedure was used to determine the absence or presence of scarcely noticeable peaks in the spectra in order to take the full advantage of the sensitivity of a multichannel analyzer. A typical spectrum before and after the smoothing is given in Fig. 5.



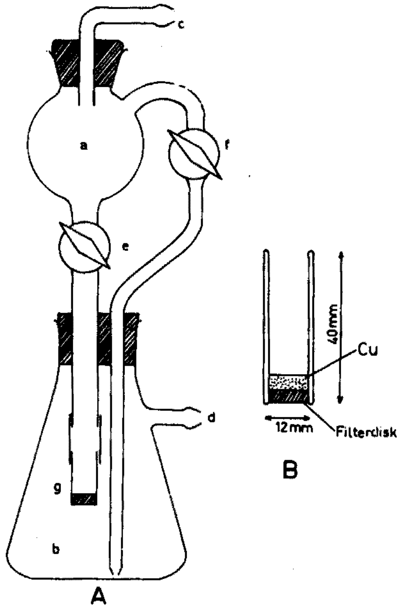


Fig. 5. Part of a typical spectrum after and before convolution.

Fig. 6. Modified EVANS percolator.

EXPERIMENTAL

Separation of mercury, gold and silver from lead

As at least 8 elements had to be determined in one lead sample, a radiochemical separation procedure had to be selected which introduced the lowest possible amount of foreign reagents into the sample solution. An electrochemical method was therefore chosen. The procedure is based on the determination of mercury by EVANS AND CLARKE[15,16] and can be carried out in a modified EVANS percolator as shown in Fig. 6A. The lead solution containing the noble metals is transferred into funnel (a). Valve (e) is opened and (f) closed. By applying a vacuum at (d), the liquid is sucked slowly through filter tube (g) into (b). After removing the vacuum, (e) is closed and (f) opened. The vacuum is now applied to (c) and the liquid is sucked up again into (a), after which the procedure can be repeated. The filter tube is connected to the funnel with a piece of P.V.C. tubing.

When a Jena G3 fritted glass filter and a 2-mm layer of copper powder (60-200 mesh) were used as shown in Fig. 6B (before use the copper powder was etched with 3 *N* nitric acid, to remove the surface layer of copper(I) oxide), tracer experiments demonstrated that in 0.2 *N* nitric acid, copper was not exchanged between the solution and the powder, the reduction of gold, mercury and silver was complete, and bismuth and antimony were co-deposited on the copper powder. By increasing the nitric acid concentration to 1 *N* and oxidizing antimony to the pentavalent state with permanganate, the co-deposition of bismuth was completely avoided and that of antimony reduced to 0.1%. Other reducible elements such as selenium, tellurium and the platinum metals were not detectable in high-purity lead.

Detailed separation procedure

Dissolve the irradiated lead sample in a covered beaker in a hot mixture of 5.7 ml of 14 *N* nitric acid + 0.7 ml of 14 *N* nitric acid for every gram of lead metal. Add 1 ml of each of the carrier solutions of mercury, gold and silver containing *ca.* 50 μg of the metal, and 2 ml of water. Add dropwise 0.1 *N* potassium permanganate, until the pink colour no longer disappears. Transfer the mixture to funnel (a) of the percolator, while valve (e) is closed. To the funnel, fit a filter tube containing 1 g of freshly etched and rinsed copper powder. Suck the solution slowly (5 min) into flask (b). Add 1 ml of the carrier solutions of mercury, gold and silver to flask (b). Mix and suck the solution back into (a). Repeat two times. Care should be taken to leave a layer of solution on top of the copper powder between the cycles, as on contact with the air, the wet copper is easily oxidised with formation of copper(I) oxide, which easily reduces bismuth and antimony. Any gold, mercury and silver activity is concentrated in the upper part of the copper layer. Finally, rinse the filter with a few ml of water.

Activation analysis of mercury, gold and silver in lead

The determination of silver in lead, using the short-lived isotopes ^{108}Ag, ^{110}Ag, by activation analysis, with thermal neutrons[17-19], as well as with bremsstrahlung[20] has been reported in the literature. Gold can be determined in Au–Pb intermetallic diffusion systems[21], or together with arsenic in high-purity lead[22]. Up to now activation analysis of mercury in lead has not been reported.

The specifications of the analysed lead samples, as provided by the manufacturer, are summarized in Table II. Samples varying from 0.5 to 3 g, according to impurity concentration and irradiation time, were cut from the metal and wrapped in aluminium foil. Standards were prepared by pipetting 40 μl of carrier solution of the pure metals with the aid of a Hamilton 710N precision micro syringe into small silica

TABLE II

SPECIFICATIONS OF SAMPLES

Impurity element	*1* 99·97% (*p.p.m.*)	*2* 99·999% (*p.p.m.*)	*3* 99·9995% (*p.p.m.*)	*4* 99·9999% (*p.p.m.*)	*5* 99·999% (*p.p.m.*)
Bi	270	5	1	0.3	<5
Cu	$\leqslant 1$	<1	<1	<0.1	<0.5
Cd	3	<1	<2	<0.2	—
Ag	9	<1	$\leqslant 1$	<0.1	<0.5
Tl	2	<2	<1	<0.3	—
Sb	0.1	0.1	0.1	$\leqslant 0.1$	—
Sn	0.1	0.1	0.1	$\leqslant 0.1$	—
As	0.1	0.1	0.1	$\leqslant 0.1$	—
Fe	—	—	—	—	<1
Au	—	—	—	—	—
Hg	—	—	—	—	—

ampoules. The standard solutions contained *ca.* 50 mg of metal/liter. The silica tubes were sealed and together with the lead samples, enclosed in an aluminium capsule.

Samples 1, 2 and 3 were irradiated in BR-1 during periods ranging from 2.5 to 8 days, with fluxes from $4 \cdot 10^{11}$ to $1.2 \cdot 10^{12}$ n/cm²/sec. Technical reasons imposed an irradiation time in BR-1 of only 2 h with a maximum flux of $5.5 \cdot 10^{11}$ n/cm²/sec, for sample 5. Sample 4 was irradiated in BR-2 during 24 h at a flux of $\pm 10^{13}$ n/cm²/sec.

After irradiation, the lead samples were etched in 6 *N* nitric acid, rinsed with water, dried and weighed. They were dissolved, and mercury, gold and silver separated as described above. The silica tubes with the standards were cleaned externally with boiling concentrated nitric acid. They were opened and heated together with the necessary carrier solution and a little nitric acid. For the gold standards, aqua regia was added to remove the activity completely from the silica capsule. The solutions were cooled, diluted to 100 ml, transferred to the percolator and treated exactly in the same way as the lead samples solutions. In this way, activities from both samples and standards were obtained with complete identical geometry. This was important, since the activity is concentrated in the upper part of the copper powder and this could lead to a noticeable attenuation of the weaker γ-rays.

The filter tubes with the activities of samples and standards were placed in standard 5-ml counting vials.

Although WESTERMARK AND SJÖSTRAND[23] have demonstrated the high volatility of mercury compounds in several media, tracer studies showed that in pure nitric acid no losses occurred.

Instrumental

A flat 3″ × 3″ cylindrical NaI(Tl) crystal with a resolution of 7.9% was used for all measurements. Although a well-type crystal would improve the sensitivity, good resolution is more important for multi-element analysis.

The samples were placed directly in the centre on top of the crystal. A 400-channel analyzer was used and the data were printed out in digital form. In order to obtain the necessary standardization, the temperature of the counting room was stabilized to 22 ± 0.5°. Slight variations in the high voltage of the multiplier phototube and the amplification of the linear amplifier were carried out manually before each counting period in order to minimize channel shift and to make 200 channels correspond exactly with 1 MeV.

RESULTS AND DISCUSSION

Five different high-purity lead metals (Table II) were analysed as described above. The results are shown in Table III. Each result is the average of 6–10 separate determinations. The listed errors are standard deviations.

Sample 1 (99.97% purity) was chosen for further consideration of the mathematical method for resolving complex spectra. In Table III, values obtained by the method described above, are listed under *a*. The matrix equation was as follows:

$$\begin{vmatrix} A_{\mathrm{Hg}} \\ A_{\mathrm{Au}} \\ A_{\mathrm{Ag}} \end{vmatrix} = \begin{vmatrix} 1 & -0.1344 & -0.07979 \\ 0 & 1 & -0.1498 \\ 0 & 0 & 1 \end{vmatrix} \times \begin{vmatrix} T_{\mathrm{I}} \\ T_{\mathrm{II}} \\ T_{\mathrm{III}} \end{vmatrix} \qquad (11)$$

TABLE III

RESULTS

Metal code	*Purity (%)*	*Concentration Hg (p.p.m.)*	*Concentration Au (p.p.m.)*	*Concentration Ag (p.p.m.)*
1	99.97	*a* 0.0233 ± 0.0045 *b* 0.0238 ± 0.0043 *c* 0.0213 ± 0.0055	0.00092 ± 0.00013 0.00122 ± 0.00022 0.00135 ± 0.00019	8.47 ± 0.18
2	99.999	*a* 0.0177 ± 0.0036 *b* 0.0175 ± 0.0035	0.00037 ± 0.00025 0.00037 ± 0.00024	0.032 ± 0.042
3	99.9995	0.0323 ± 0.0045	0.00097 ± 0.00041	0.048 ± 0.014
4	99.9999	0.0251 ± 0.0051	$5 \cdot 10^{-6} \pm 4 \cdot 10^{-6}$	0.0009 ± 0.0012
5	99.999	⩽ 0.012	⩽ 0.0004	0.40 ± 0.19

TABLE IV

STANDARD DEVIATION ON Hg DETERMINATION

(Background 5050 c.p.h.)

Lead sample weight (g)	*Hg activity eqn. (7) (c.p.h.)*	*Stand. dev. eqn. (8)*		*Stand. dev. of pure activities*	
		(c.p.h.)	*(%)*	*(c.p.h.)*	*(%)*
0.59895	5244	± 238	± 4.5	± 175	± 3.3
0.44957	4222	± 230	± 5.5	± 169	± 4.0
0.56291	5396	± 216	± 4.0	± 176	± 3.3
0.49596	5532	± 210	± 3.8	± 177	± 3.2
0.92361	11666	± 344	± 3.0	± 208	± 1.8
0.75277	7474	± 308	± 4.1	± 188	± 2.5

TABLE V

STANDARD DEVIATION ON Au DETERMINATION

(Background 4812 c.p.h.)

Lead sample weight (g)	*Au activity eqn. (7) (c.p.h.)*	*Stand. dev. eqn. (8)*		*Stand. dev. of pure activities*	
		(c.p.h.)	*(%)*	*(c.p.h.)*	*(%)*
0.59895	4266	± 260	± 6.1	± 167	± 3.9
0.44957	2688	± 236	± 8.8	± 157	± 5.9
0.56291	3146	± 222	± 6.7	± 160	± 5.1
0.49596	3543	± 212	± 6.0	± 162	± 4.6
0.92361	13826	± 404	± 2.9	± 216	± 1.6
0.75277	11248	± 368	± 3.3	± 204	± 1.8

D was equal to unity. A_{Hg}, A_{Au}, A_{Ag} are the activities of mercury, gold and silver in the regions I, II and III (Fig. 4), whereas T_{I}, T_{II} and T_{III} are the total activities in those regions. The integer zero values of the coefficients are due to the regions where no contribution for the pure isotope is to be expected. The integer unity values are due to eqn. (10) when $m = i$. The element l_{32} is listed as equal to zero, although gold exhibits a small photopeak in the region III (Fig. 2). For the amounts of gold present in the lead metals, this peak is so small that it is negligible compared to the statistical deviation of the background in that region. The decimal elements in the matrix are averages of 9 determinations and have a standard deviation of less than 2%. According to eqn. (8) standard deviations for individual analyses were calculated (Tables IV and V). If Hg, Au and Ag were separated radiochemically from one another, the activities, calculated from eqn. (11), can be measured directly. As a comparison the standard deviations on these measurements were added to Tables IV and V. It is obvious that the somewhat smaller accuracy of the mathematical analysis compares favourably with the more tedious chemical separation. On the other hand, the standard deviations on the average results in Table III are much larger than the individual errors. This is believed to be due to the inhomogeneous distribution of the impurities.

The values listed under sample 1 *b* in Table III were obtained by the so-called "stripping-off" method. Starting from the high energy part of the composite spectrum, due to ^{110m}Ag only, the subtraction of the silver activity can be carried out with the aid of a pure ^{110m}Ag source, until the top of the 656-keV photopeak reaches zero level, leaving the 411-keV gold peak virtually undisturbed. With a pure ^{198}Au source the process can be repeated to remove the gold activity and produce a pure mercury spectrum. The entire procedure is time-consuming and not accurate since it is dependent upon the judgement of the experimenter.

The values listed under *c* were obtained by the addition method of analysis. Increasing amounts of mercury were added to separate lead samples. After irradiation, separation and measurement, the obtained mercury activities were plotted as a function of the added weight of mercury. With the aid of the least squares procedure, a line was plotted through the experimental points. The intercept of this line with the abscissa gives the original impurity concentration.

COVELL's method[24] was not applied, because of the coincidence of the 445-keV photopeaks of the ^{110m}Ag with the 411-keV ^{198}Au peak, and of the ^{198}Au 71-keV X-ray with the 78-keV peak of ^{197}Hg.

Since agreement was obtained for the sample showing the largest silver interference on the determination of mercury and gold, the mathematical analysis can be applied to the other lead samples without further control. Thus the concentrations for samples 3, 4 and 5 were obtained with the same matrix equation. The large standard deviations for these metals, were mainly due to the inhomogeneous distribution of the impurities, the errors of the individual analyses being much smaller. The above-mentioned convolution method was frequently used to prove the purity of the ^{110m}Ag part of the spectrum.

Sample 2 presented some special difficulties. Its antimony concentration was respectively 15, 25 and 1300 times larger than its silver, mercury and gold concentration, and was larger by a factor of 25 to 130 than in the other metals. Furthermore, this sample contained approximately 0.1 p.p.m. of bromine. It was pointed out above that only 0.1% of the antimony present co-deposits on the copper powder. For this case, this resulted in a relatively large interfering peak at 564 keV, situated between the main photopeaks of gold and silver in the composite spectrum. On the other hand, it was found experimentally that the larger part of the bromine activity accumulated on the copper powder.

Two procedures were subsequently compared to remove the bromine interference: the separation was carried out as usual and the spectrum recorded immediately. The same spectrum was recorded again after complete decay of the bromine activity (10 days for the 36-h ^{82}Br isotope). The difference of activity in the silver region T_{III} (Fig. 4) is due to the decay of ^{82}Br only, since the half-life of ^{110m}Ag is too long for a noticeable decay. Once the ^{82}Br activity is known in one part of the first spectrum, corrections can be calculated for any other region with the aid of a simultaneously irradiated pure bromine standard.

In the second procedure, the irradiated lead samples were dissolved, without addition of carrier, in a small flask fitted with a good reflux cooler, while a gentle air current was drawn through the mixture. After dissolution of the metal a few drops of a freshly prepared potassium bromide–bromate mixture was added and with the reflux cooler still working, bromine vapors were drawn off into a sodium hydroxide solution. After a few minutes all the bromine was removed. Carrier solutions of mercury, gold and silver were added to the lead solution, which could be treated in the usual manner. The receiver contained no other activity than ^{82}Br. No interference from bromine was noticed in the subsequently recorded spectrum of mercury, gold and silver.

Both procedures result in a spectrum which still contained the antimony interference. Therefore a fourth region was selected (IIII, Fig. 4) and the mathematical analysis carried out according to the new matrix equation:

$$\begin{vmatrix} A_{Hg} \\ A_{Au} \\ A_{Sb} \\ A_{Ag} \end{vmatrix} = \begin{vmatrix} 1 & -0.1365 & -0.1431 & -0.06721 \\ 0 & 1 & -0.07341 & -0.1421 \\ 0 & 0 & 1.0179 & -0.07966 \\ 0 & 0 & -0.2290 & 1.0179 \end{vmatrix} \times \begin{vmatrix} T_{I} \\ T_{II} \\ T_{IIII} \\ T_{III} \end{vmatrix} \qquad (12)$$

calculated with the aid of a simultaneously irradiated antimony standard. Since antimony gives rise to 2 radioactive isotopes with very different half-lives, the coefficients of this new matrix change with time and have to be calculated before each analysis.

TABLE VI

INFLUENCE OF NUMBER OF REGIONS ON STANDARD DEVIATION

(Background 5118 c.p.h.)

Lead sample weight (g)	*Hg activity eqn. (7) (c.p.h.)*	*Stand. dev. (4 region) (c.p.h.)*	*(%)*	*Hg activity eqn. (7) (c.p.h.)*	*Stand. dev. (3 region) (c.p.h.)*	*(%)*
0.6823	7372	202	2.74	7302	196	2.68
0.6566	6304	200	3.18	6053	188	3.10
0.9205	8689	161	1.85	8493	152	1.79
1.3218	15003	187	1.25	14576	175	1.20
1.4090	20826	243	1.16	21555	191	0.89
1.2358	11251	165	1.47	11208	157	1.40
1.4916	15772	185	1.17	15565	176	1.13
1.2232	10757	163	1.51	10695	154	1.44

The obtained average results for sample 2 are listed in Table III, under *a*. As a check, the antimony activity was subtracted from the composite spectrum using an antimony standard until the main photopeak had completely disappeared. The resulting spectrum can then be analysed by the original matrix eqn. (11). The average results are listed in Table III under *b*. In Table VI, the influence is illustrated of the additional fourth region on the calculation of the standard deviation, according to eqn. (8), in the case of mercury. Agreement between the 2 methods is excellent whereas the difference in standard deviation is negligible.

Equation (7) shows clearly that the calculated activities for the separate isotopes are a function of all the isotopes contributing to the complex spectrum. Therefore no effort was made to give a definition of the sensitivity of the applied method since the latter is entirely dependent on the composition of the individual samples.

This work was partly supported by the "Interuniversitair Instituut voor Kernwetenschappen" whose financial aid is gratefully acknowledged. Thanks are also due to the S.C.K. in Mol for the numerous irradiations of the samples and to Miss M. HELSEN for technical assistance.

SUMMARY

A radiochemical method was developed to separate the group of the noble metals simultaneously from a lead matrix after irradiation with thermal neutrons. The resulting complex γ-spectrum was resolved by matrix calculus. Smoothing of the obtained data to determine the presence of small photopeaks among the background fluctuations, was done by convolution, based on a least squares approximation. The interference of antimony and bromine was studied. Amounts as low as 20–30 p.p.b. of Hg and less than 1 p.p.b. of Au were determined in the presence of up to 9 p.p.m. of Ag.

RÉSUMÉ

Une méthode radiochimique est développée pour séparer le groupe des métaux nobles simultanément d'une matrice de plomb, après irradiation avec des neutrons thermiques. Le spectre γ complexe résultant est résolu par calcul de matrice. On examine l'influence de l'antimoine et du brome. On a pu doser jusqu'à 20–30 p.p.b. de mercure et moins de 1 p.p.b. d'or, en présence de quantités d'argent s'élevant jusqu'à 9 p.p.m.

ZUSAMMENFASSUNG

Es wurde eine radiochemische Methode entwickelt, um edle Metalle gleichzeitig von einer Bleimatrix abzutrennen, nachdem sie mit thermischen Neutronen angeregt worden ist. Durch Berechnungen wurden im γ-Spektrum kleine Fotopeaks zwischen den Untergrundschwankungen bestimmt. Störungen durch Antimon und Brom wurden untersucht. 20–30 p.p.b. Hg und weniger als 1 p.p.b. Au wurden in Gegenwart bis hinauf zu 9 p.p.m. Ag bestimmt.

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EMISSION INTENSITY OF STRONTIUM AND BARIUM IN FLAMES OF VARIOUS GAS COMPOSITIONS

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The flame emission photometry of strontium and barium has been studied extensively and summarized repeatedly[1-3]. Little investigation, however, has been made of these elements in air–hydrogen flames, in spite of the fact that in the more conventional oxy–hydrogen flame the calibration curve for barium at 553.6 mμ is known to be concave upward. It has been suggested[1,3] that the ionization of barium atoms, which leads to the non-linear calibration at the atomic line, can be reduced by lowering the flame temperature.

In a study of the flame photometric analysis of strontium and barium in sea water[4], it was found that the atomic emission properties of these elements changed markedly when, in order to obtain a lower flame temperature, air was used as the aspirating gas instead of oxygen in a burner of the total consumption type. Even though the change in temperature was not great, the data indicate that air–hydrogen and oxy–hydrogen flames are very close to critical compositions at which the flame emission properties of the 2 elements are altered. Experiments were therefore made using aspirating gas mixtures having oxygen to nitrogen ratios of 4:1, 3:2, and 2:3 for comparison with the air–hydrogen and oxy–hydrogen flames.

EXPERIMENTAL

Apparatus and materials

Emission measurements were made using a Zeiss PMQ II spectrophotometer with flame attachment. A Radiometer pH meter model PHM-4 was used for pH measurements.

Strontium and barium chloride stock solutions were prepared from spectroscopically pure strontium carbonate and barium chloride dihydrate supplied by Johnson, Matthey and Co. Ltd. All other reagents were of analytical reagent grade. Water redistilled from all-Pyrex glass apparatus was used throughout. Oxygen–nitrogen mixtures were obtained in tanks from Corp Bros., Hyannis, Mass. and were guaranteed to be accurate in composition to within 1% of the stated value.

Methodology

Barium chloride solutions were prepared for atomization in water, in 0.10 *M*

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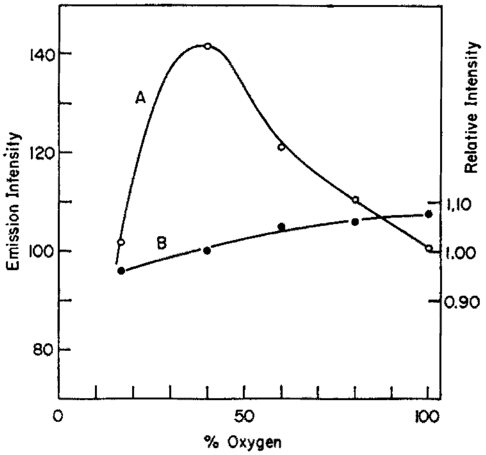
hydrochloric acid, and in 0.01 M EDTA buffered to pH 10.0 with ammonia–ammonium chloride. The latter contained 0.43 g of ammonium chloride and *ca.* 10 ml of concentrated aqueous ammonia per liter, the amount of ammonia being adjusted to give the exact pH. Strontium carbonate, dissolved in a minimum amount of hydrochloric acid, was then diluted with water or with 0.03 M acetic acid to provide working solutions. For the purpose of this study, a barium concentration of 11.40 p.p.m. and a strontium concentration of 6.20 p.p.m. were usually used in order to obtain convenient galvanometer deflections. The emission intensity of a given concentration of the element in EDTA, hydrochloric acid, or acetic acid is expressed either in arbitrary units or relative to the intensity observed for the same concentration of the element in water, as indicated in the figures.

The solutions were atomized into the hydrogen flame of a Zeiss PMQ II spectrophotometer with a fixed slit width of 0.10 mm. The atomizing gas, which also provides the oxygen necessary for combustion, was one of 5 oxygen–nitrogen mixtures containing respectively the following percentages of oxygen: (1) 100%, (2) 80%, (3) 60%, (4) 40%, and (5) 20%. The latter mixture was simply compressed dry air. In each case the gases were fed at flow rates which gave maximum emission intensity with the solution being atomized. Measurements were made only of the intensity at the strontium atomic line (460.7 $m\mu$) and at the barium atomic line (553.6 $m\mu$). Previous experiments[1–4] had shown these to be most promising for the precision flame analysis of these elements.



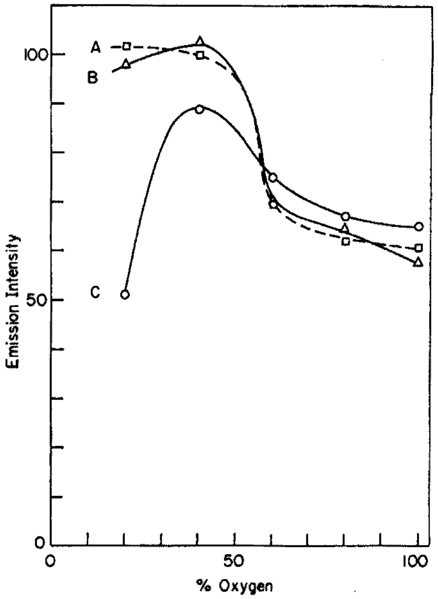


Fig. 1. Strontium emission intensity at 460.7 $m\mu$ (arbitrary units) as a function of oxygen content of aspirating gas. (A) $SrCl_2$, in water (left ordinate scale). (B) Relative emission intensity of $SrCl_2$ in 0.03 M acetic acid compared to a solution of the same concentration in water (right ordinate scale).

Fig. 2. Barium emission intensity at 553.6 $m\mu$ as a function of oxygen content of aspirating gas. (A) $BaCl_2$ in water. (B) In 0.10 M hydrochloric acid. (C) In 0.01 M EDTA at pH 10.0.

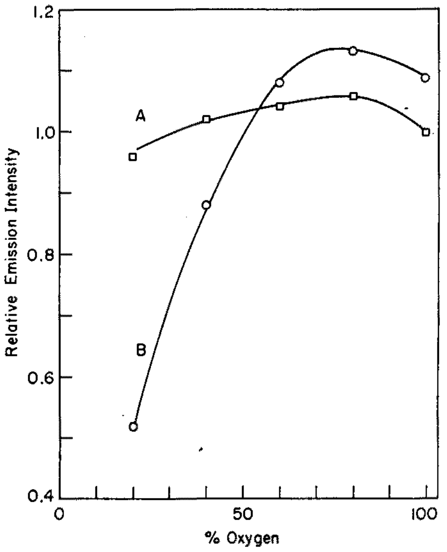
RESULTS

Effect of oxygen concentration on strontium emission

Figure 1 shows that there is a similar variation of the strontium emission in water and 0.03 *M* acetic acid solutions aspirated into flames of different oxygen composition. There is, however, a marked maximum in the resonance line emission of strontium at a 40% oxygen content of the carrier gas. The effect of acetic acid on the emission of strontium can be observed to change gradually from a slight depression in an air–hydrogen flame[4], to an enhancement in an oxy–hydrogen flame, as reported previously[1].

Effect of oxygen concentration on barium emission

Figure 2 summarizes the relation between barium emission and oxygen concentration for the three types of solutions used: pure water, 0.1 *M* hydrochloric acid, and 0.01 *M* EDTA at pH 10. Particularly striking are the depression of the barium line in EDTA solutions at low oxygen contents and the falling off in sensitivity for all the solutions due to ionization in high oxygen content flame mixtures.



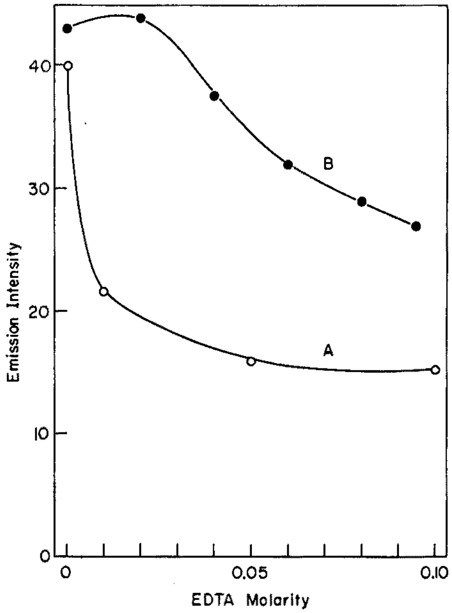


Fig. 3. Relative emission intensity of barium chloride solutions compared to solutions in water, at 553.6 mμ, as a function of oxygen content of aspirating gas. (A) 0.10 *M* hydrochloric acid. (B) 0.01 *M* EDTA at pH 10.0.

Fig. 4. Barium emission intensity at 553.6 mμ, as a function of EDTA concentration. Air–hydrogen flame. (A) At pH 10.0. (B) At pH 6.0.

In Fig. 3 the ratio of intensity in EDTA or hydrochloric acid solutions to the intensity in water alone is plotted against the oxygen content of the carrier gas. The effect of EDTA at pH 10.0 changes from depression in an air–hydrogen flame to the enhancement in an oxy–hydrogen flame reported previously[1]. The effect of 0.01 *M* hydrochloric acid, usually considered to be a depressant, is actually one of enhancement at 80% oxygen.

Effect of complexation on barium in an air–hydrogen flame

Figure 4A shows that there is a very marked depression of the barium emission at 553.6 mμ with increasing concentration of EDTA buffered at pH 10.0 with ammonia–ammonium chloride buffer. This is in contrast to reports of the oxy–hydrogen flame characteristics of the alkaline earths in the presence of complexing agents[1]. The depression might result either from an increase in the viscosity of the solution causing an appropriate decrease in the sample flow, or from an inhibition of the excitation of the barium atom caused by complexation with EDTA. The solution flow rate was checked and found to be diminished by the presence of EDTA, but only to the extent of about 1%, even by concentrations as high as 0.2 *M*. This, therefore, could not have caused the serious decrease (about 60%) observed in the emission intensity of the neutral barium atom.

Figure 4B illustrates the effect of the EDTA concentration on the emission intensity of the barium atom in a solution of pH 6. It was observed that at 0.02 *M*, EDTA caused a slight enhancement of the 553.6 mμ resonance line of barium with a decrease at higher EDTA concentrations. This decrease is associated with an increase in the background intensity.

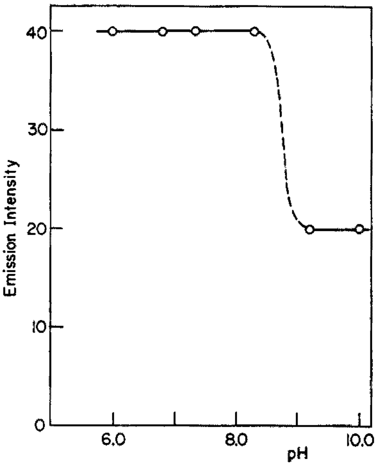


Fig. 5. Barium emission intensity at 553.6 mμ for 0.02 *M* EDTA solutions as a function of pH. Air–hydrogen flame.

The emission characteristics of the neutral barium atom were investigated at various pH values of the EDTA solution. Figure 5 summarizes the results; at pH values from 6 to 8.4 emission intensity was uniformly high whereas at pH 9.1 and 10 it was reduced by about 40%.

DISCUSSION

These experiments have shown that the flame characteristics of strontium and barium change drastically when flames in which the oxygen percentage of the carrier gas is varied, are used. Previous observations[4] comparing the flame emission properties of strontium and barium in air–hydrogen and oxy–hydrogen flames have been confirmed. The sensitivity of the emission intensities of barium and strontium, both to flame composition and to solution composition, warrant very careful consideration in practical analytical work.

Figure 2 graphically illustrates how the sensitivity of the barium determination is adversely affected by increasing the temperature of the flame, causing equilibrium (1) to be shifted to the right.

$$Ba^0 \rightleftarrows Ba^+ + e^- \qquad (1)$$

The population of neutral barium atoms in the flame is decreased, thus causing a corresponding decrease in emission observed at 553.6 mμ.

Figure 5 clearly illustrates that, with an air–hydrogen flame, the emission intensity of complexed barium is significantly depressed. Figure 3B shows that a high flame temperature is necessary for good efficiency in the volatilization and excitation of complexed barium.

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SUMMARY

The emission intensity of strontium at 460.7 mμ and barium at 553.6 mμ has been studied in hydrogen flames burning with varying mixtures of oxygen and nitrogen. With solutions of barium and strontium chloride in water and in various concentrations of EDTA, acetic and hydrochloric acids, it was found that the emission depended significantly on the oxygen:nitrogen ratio in the atomizing gas. Under some conditions, maximum emission intensity is found at compositions intermediate between air and pure oxygen. The emission of barium was found to be decreased significantly by EDTA at high pH under some flame conditions.

RÉSUMÉ

Les auteurs ont examiné l'intensité d'émission du strontium à 460.7 mμ et du baryum à 553.6 mμ dans des flammes d'hydrogène, brûlant avec divers mélanges oxygène–azote. On constate que l'émission dépend du rapport oxygène/azote d'après les expériences effectuées avec des solutions de chlorure de baryum et de chlorure de strontium dans l'eau, en présence de diverses concentrations d'EDTA, d'acide acétique et d'acide chlorhydrique. L'émission du baryum diminue considérablement en présence d'EDTA à pH élevé, dans certaines conditions.

ZUSAMMENFASSUNG

Die Emissionsintensität von Strontium bei 460.7 mμ und Barium bei 553.6 mμ wurde in Wasserstoffflammen untersucht, die mit variierenden Mischungen von Sauerstoff und Stickstoff brannten. Mit Lösungen von Barium- und Strontiumchlorid in Wasser und bei verschiedenen Konzentrationen von AeDTE, Essig- und Salzsäure fand man, dass die Emission bemerkenswert von dem Sauerstoff–Stickstoffverhältnis im atomisierenden Gas abhängt. Für einige Bedingungen wurde eine maximale Emissionsintensität bei Zusammensetzungen gefunden, die zwischen Luft und reinem Sauerstoff lagen. Die Emission des Bariums nahm bei einigen Flammenbedingungen durch AeDTE bei hohen pH-Werten deutlich ab.

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ALTERNATING CURRENT POLAROGRAPHY OF SOME COMPLEXES IN PRESENCE OF IONIC SURFACTANTS

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Small amounts of surface-active substances (surfactants) are often used in conventional d.c. polarography in order to suppress maxima on the waves. In a.c. polarography, however, the presence of surfactants must usually be avoided because the rate of the electron-transfer reaction is markedly decreased and a large decrease in, or even disappearance of, the a.c. polarographic wave may occur. Recent investigations of the effect of ionic surfactants on d.c. polarographic waves[1,2] showed that the electrode reaction in certain cases is practically unaffected or even accelerated in the presence of large amounts of a surfactant having a charge opposite to that of the depolarizer. These phenomena have been interpreted by assuming that the depolarizer can penetrate through certain surface films[2] and by the formation of a bridge which accelerates the electron-transfer between the electrode and the depolarizing species[3]. Preliminary experiments indicated that this electron-transfer through a surface film gives rise to well-defined a.c. polarographic waves. The object of the present communication is to discuss briefly such a.c. waves and the possible application of ionic surfactants in analytical a.c. polarography.

EXPERIMENTAL

Apparatus

A.c. and d.c. polarograms were obtained manually by a polarograph built in this laboratory. The circuit was the one described by BREYER AND BAUER[4]. The superimposed sinusoidal voltage was of the mains frequency (50 c/sec) and the amplitude was adjusted by means of a step-down transformer together with a resistive voltage divider. The amplitude of the alternating voltage was 15 mV (r.m.s.) in all experiments. The current measuring device consisted of a 10-ohm voltage dropping resistor, a Philips G.M. 6012 millivoltmeter and a Philips P.M. 6041 pre-amplifier. The conventional type of dropping mercury electrode (d.m.e.) was used. The capillary characteristics measured in 0.1 *M* potassium nitrate (open circuit) at a corrected mercury height of 49.0 cm were $m = 2.578$ mg/sec and $t = 3.54$ sec. An external saturated calomel electrode (S.C.E.) served as reference electrode. The polarographic cell was a so-called "pool condenser" electrode[5]. A shunt capacitor of 2000 μF was connected between the mercury pool in the cell and the calomel electrode.

Materials

Diethylenetriaminepentaacetic acid (DTPA) was obtained from Geigy Chemical Corp., New York. Ethylenediaminetetraacetic acid (EDTA) and ethyleneglycolbis-(β-aminoethylether)-tetraacetic acid (EGTA) were obtained from Fluka A.G., Switzerland. Stock solutions of these reagents and of copper(II) were prepared and standardized as described previously[6,7]. Phosphate buffer (0.2 M) was used as supporting electrolyte in most experiments. The pH of the electrolyte was adjusted to the desired value by adding potassium hydroxide or hydrochloric acid and the pH checked by a pH meter. Dodecylamine perchlorate (Armeen) and sodium dodecyl sulphate (SDS) were used as surface-active agents. Solutions of these surfactants were prepared as described earlier[2].

RESULTS AND DISCUSSION

Preliminary experiments showed that the a.c. base current was not affected by addition of EDTA, EGTA or DTPA to the supporting electrolyte. No tensammetric peak and no depression of the base current was observed at any pH value, indicating that these reagents are not adsorbed at the d.m.e. Addition of 0.01% Armeen or SDS to the electrolyte resulted in a great depression of the base current in the potential range 0 to −1.5 and 0 to −1.1 V *vs.* S.C.E., respectively, indicating that these surfactants are strongly adsorbed over a considerable potential range. A negative tensammetric peak was observed at the desorption potential of SDS (−1.1 V), whereas no tensammetric peak of Armeen was observed in the available potential range. These results are in perfect agreement with the electrocapillary curves described previously[2].

In the absence of surfactants, the copper–EDTA complex gives rise to a well-defined a.c. polarographic wave and the summit potential (E_s) coincides with the d.c. half-wave potential. When small amounts of the anionic surfactant SDS were added to the electrolyte, the a.c. wave was considerably depressed and in the presence of 0.005% SDS the whole a.c. wave was shifted to the desorption potential of SDS, indicating that the electrode reaction is completely inhibited in the presence of this surfactant. The a.c. polarographic wave of the copper–EDTA complex was affected also by the presence of Armeen. Upon addition of 0.004% of this cationic substance to the electrolyte, the wave-height decreased to about 1/3 of its original value and the summit potential was 60 mV more negative than in the absence of surfactants. The wave was, however, not obliterated upon a further increase in the Armeen concentration. Polarograms obtained from 0.2 M phosphate buffer with pH 7.0 showed that the summit potential ($E_s = -0.47$ V *vs.* S.C.E.) and the height of the wave were constant, independent of the Armeen concentration in the range 0.005 to 0.02%.

As shown in Fig. 1 this a.c. polarographic wave is accompanied by a d.c. polarographic step, which indicates that the a.c. current is brought about by an electron-transfer process through the adsorbed Armeen layer. The summit potential ($E_s = -0.47$ V *vs.* S.C.E.) is more negative than the d.c. half-wave potential ($E_{\frac{1}{2}} = -0.44$ V *vs.* S.C.E.) as in the case of an organic depolarizer of which the oxidized form is more strongly adsorbed than the reduced one. Further experiments showed another interesting feature of this a.c. wave. The a.c. current increased markedly with increasing height of the mercury column above the capillary. Thus, the current at the summit potential (measured half-way through the life of the drop) increased from 12.6 to 14.9 μA on increasing the mercury head from 25 to 55 cm. The height of the original a.c. wave measured in the absence of Armeen was 42.0 μA and was completely independent of the height of the mercury column.

D.c. polarograms of the copper–DTPA complex exhibit 2 waves in neutral and alkaline medium[6]. As indicated in Fig. 2 this electrode reaction gives rise to 2 well-defined a.c. waves in phosphate buffer with pH 6.95. On addition of Armeen to the electrolyte the first wave ($E_s = -0.40$ V *vs.* S.C.E.) decreased whereas the second wave ($E_s = -0.72$ V *vs.* S.C.E.) increased and was shifted to more positive potentials.

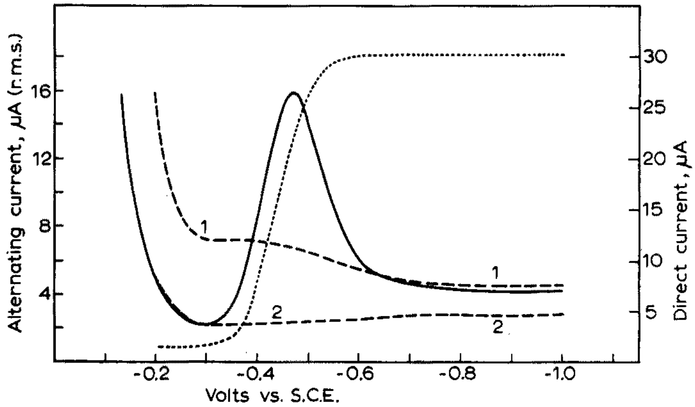

Fig. 1. A.c. polarogram (solid curve) and d.c. polarogram (dotted curve) of 0.005 *M* copper and 0.02 *M* EDTA in 0.2 *M* phosphate buffer of pH 7.0 with 0.01% Armeen present. Dashed lines are the a.c. base currents in absence (curve 1) and in presence (curve 2) of 0.01% Armeen.

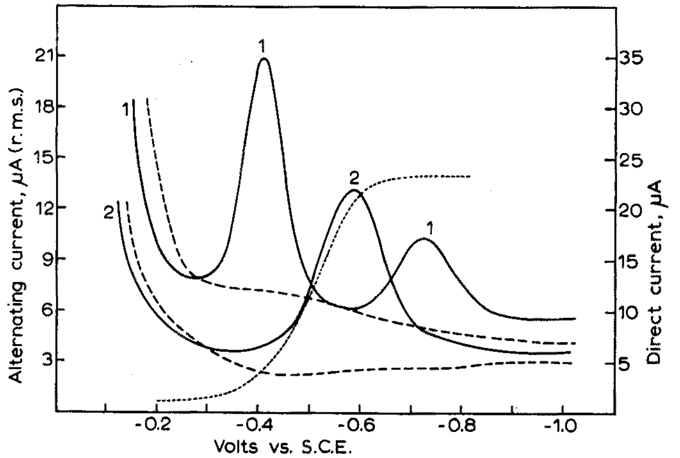

Fig. 2. A.c. polarograms of 0.004 *M* copper and 0.01 *M* DTPA in 0.2 *M* phosphate buffer of pH 6.95 in absence (curve 1) and in presence (curve 2) of 0.01% Armeen. Dashed lines are a.c. base currents of the same solutions and the dotted curve the d.c. polarogram of the copper–DTPA complex in the presence of 0.01% Armeen.

In the presence of 0.008% Armeen only one wave ($E_s = -0.58$ V *vs.* S.C.E.) appeared on the polarogram. The single a.c. wave obtained in the presence of Armeen (Fig. 2) was accompanied by an apparently irreversible d.c. wave. (The slope of the plots of log $i/i_d - i$ *vs.* the potentials was -0.100 V per log unit, compared to -0.029 V for a

TABLE I

EFFECT OF PRESSURE OF MERCURY ON THE HEIGHT OF THE A.C. WAVE OF $4 \cdot 10^{-3}$ *M* COPPER AND 10^{-2} *M* DTPA IN PHOSPHATE BUFFER WITH pH 6.95 AND 0.01% ARMEEN PRESENT

(A.c. current measured at the middle-age of the drop at −0.58 V *vs.* S.C.E.)

Height of Hg above the capillary (cm)	*Corrected height of Hg column (cm)*	i_s *(μA) (r.m.s.)*	$\Delta i_s/\Delta h$ *(μA/5 cm)*
25	39	10.9	
30	44	11.2	0.3
35	49	11.5	0.3
40	54	11.8	0.3
45	59	12.1	0.3
50	64	12.5	0.4
55	69	12.8	0.3
60	74	13.1	0.3

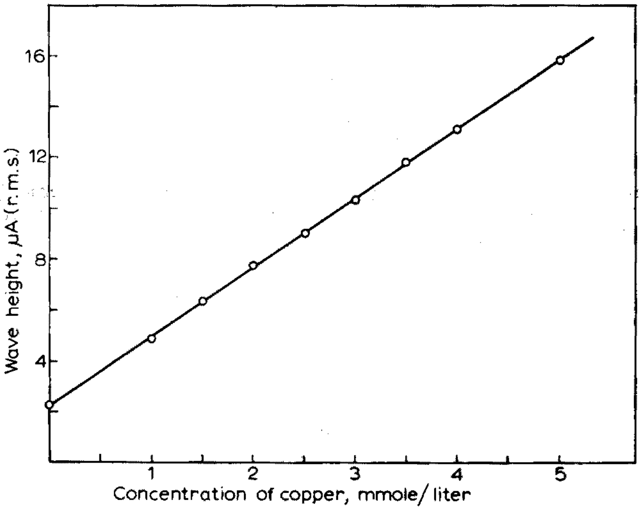

Fig. 3. Calibration curve of copper in 0.2 *M* phosphate buffer of pH 6.95 with 0.01 *M* DTPA and 0.01% Armeen present. The a.c. current was measured at −0.58 V *vs.* S.C.E. at a corrected mercury height of 54 cm.

reversible 2-electron reduction.) The a.c. wave with a summit potential about 60 mV more negative than the d.c. half-wave potential indicates, however, a reversible electron-transfer in the overall electrochemical reaction.

The height of the a.c. wave was measured at several different heights of the mercury column. As indicated in Table I the current increased almost linearly with increasing height of mercury above the capillary. The same result was also obtained at other copper concentrations. The a.c. current increased about 30% on raising the mercury head from 20 to 60 cm above the capillary.

The current, i_s, at the summit potential was not affected upon increasing the Armeen concentration from 0.008 to 0.02%, provided that the height of the mercury column was kept constant. Polarograms obtained from the same supporting electrolyte (0.01 *M* DTPA and 0.01% Armeen in 0.2 *M* phosphate buffer with pH 6.95), but with various amounts of copper present, showed that the height of the a.c. wave increased proportionally to the bulk concentration of copper. The results are shown in Fig. 3 and indicate that the presence of surfactants may be of analytical value also in a.c. polarography. In the present case only a single wave was observed on the polarogram, whereas the ordinary a.c. polarogram exhibits 2 waves and the height of these waves is extremely dependent on the pH of the solution.

Similar results were also obtained with the copper–EGTA complex. Polarograms of $5 \cdot 10^{-3}$ *M* copper and $2 \cdot 10^{-2}$ *M* EGTA in phosphate buffer of pH 8.55 showed 2 waves with summit potentials at -0.36 and -0.65 V *vs.* S.C.E., respectively. When 0.01% Armeen was added to the electrolyte, only a single wave with $E_s = -0.70$ V *vs.* S.C.E. was observed on the polarogram. The wave was followed by a d.c. polarographic step and the height of the a.c. wave increased linearly with the height of mercury above the capillary.

A.c. polarograms of the copper–DTPA and the copper–EGTA complex in 0.2 *M* phosphate buffer and with 0.01% SDS present showed that the electrode reactions are completely inhibited by this anionic surfactant.

CONCLUSION

The present investigation shows that well-defined a.c. polarographic waves are obtained in the presence of certain ionic surfactants. It is proposed to call this type of wave an "a.c. penetration wave", because the a.c. current is brought about by an electron-transfer through an adsorbed layer. In contrast to ordinary a.c. waves, the height of the penetration wave increases linearly with the height of the mercury column above the capillary. This drop-time dependence of the peak height indicates that the concentration of the depolarizer at the electrode surface is time-dependent[8] and that the current is partly controlled by the rate of adsorption or by the rate of penetration through the adsorbed layer.

The a.c. penetration wave is accompanied by a d.c. polarographic step, but the summit potential is more negative than the d.c. half-wave potential, indicating that the oxidized form of the depolarizer is strongly adsorbed at the electrode. The adsorption of the depolarizer is confirmed by the lowering of the a.c. base current at potentials more positive than the summit potential (Fig. 2).

An a.c. penetration wave of negatively charged complexes was not observed in the presence of the anionic surfactant SDS. When the surfactant has the same charge as that of the depolarizer, the latter is probably electrostatically repelled from the adsorbed layer. On the other hand, if the adsorbed layer has a charge opposite to that of the depolarizer (as in the case of Armeen and negatively charged complexes) the electrostatic attraction produces a more tightly packed layer which may accelerate the electron-transfer and give rise to a penetration wave.

Provided that the mercury head is kept at a constant level, the height of the a.c. penetration wave increases proportionally to the bulk concentration of the depolarizer. Hence, in addition to its theoretical importance, the a.c. penetration waves may also be of analytical value.

Further work is now in progress in order to investigate the effect of charged surfactants on various depolarizers and the possible application of ionic surfactants as electrochemical masking agents[9–12] in a.c. polarography.

SUMMARY

Well defined a.c. polarographic waves are obtained in the presence of certain ionic surfactants. The current is brought about by an electron-transfer through the adsorbed layer, probably by the formation of a bridge which accelerates the electron-transfer between the electrode and the depolarizer. The resulting a.c. wave is accompanied by a d.c. polarographic step and the height of the wave increases proportionally to the bulk concentration of the depolarizer. In contrast to ordinary a.c. waves, the a.c. current of these waves increases linearly with increasing height of the mercury column above the capillary.

RÉSUMÉ

Des vagues bien définies ont été obtenues par polarographie à courant alternatif, en présence de certains agents tensioactifs ioniques. Le courant est produit par un transfert d'électrons à travers la couche adsorbée, probablement par formation d'un pont accélérant de transfert entre l'électrode et le dépolariseur. Contrairement aux vagues ordinaires à courant alternatif, l'intensité augmente linéairement avec la hauteur de la colonne de mercure au-dessus du capillaire.

ZUSAMMENFASSUNG

In Gegenwart bestimmter ionischer, oberflächenaktiver Substanzen erhält man gut definierte Stufen bei der Wechselstrompolarographie. Der Stromtransport erfolgt durch einen Elektronenübergang durch die adsorbierte Schicht; wahrscheinlich wird eine Brücke gebildet, die den Elektronentransport zwischen der Elektrode und dem Depolarisator beschleunigt. Die Wechselstrom-Stufe wird von einem Gleichstrom-Schritt begleitet; die Höhe der Stufe wächst proportional mit der Konzentration des Depolarisators. Im Gegensatz zu gewöhnlichen Wechselstrom-Stufen steigt der Strom dieser Stufen linear mit steigender Höhe der Quecksilbersäule über der Kapillare.

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ZUM EINFLUSS DES LEITELEKTROLYTEN AUF DIE POLAROGRAPHISCHE REDUKTION DES METHYLBROMIDS

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Methylbromid wird polarographisch wie die Mehrzahl der Alkylmonohalogenide in wässrig-alkoholischer Lösung unter Ausbildung einer einzigen irreversiblen Stufe reduziert[1]:

$$CH_3Br + 2\,e^- + H^+ \rightarrow CH_4 + Br^- \qquad (1)$$

Das Halbstufenpotential (HSP) ist in alkalischer bis schwach saurer Lösung nicht pH-abhängig; als potentialbestimmender Teilschritt wird deshalb der Vorgang

$$CH_3Br + e^- \rightleftarrows (CH_3Br)^- \qquad (2)$$

angesehen[2,3]. Dieser Teilschritt entspricht einem gehemmten Durchtritt von Elektronen durch die Phasengrenze Hg/Lösung. Damit bestimmen die Eigenschaften der Phasengrenze, z.B. Ladungsdichte und Potentialverlauf der Doppelschicht das Potential und damit die Irreversibilität der Redoxelektrode $(Hg)e^-/CH_3Br$, $(CH_3Br)^-$. Da sich die elektrochemische Doppelschicht aus den Lösungspartnern des Depolarisators aufbaut, ist durch deren Variation die Durchtrittsüberspannung der Reaktion (2) und damit das HSP der Gesamtstufe veränderlich. Solche Wirkungen werden durch Kationen und Anionen des Leitelektrolyten als auch besonders durch grenzflächenaktive Substanzen hervorgerufen, wenn das Elektrodenpotential eine Mitwirkung dieser Stoffe am Aufbau der Phasengrenze erlaubt[4].

Infolge des stark negativen HSP des Methylbromids kann der Anioneneinfluss in erster Näherung vernachlässigt werden. Damit sollte eine klare Korrelation zwischen den Eigenschaften der Kationen des Leitelektrolyten und dem irreversiblen Potential nach (2) möglich werden. Dieser erwartete Einfluss auf das HSP des Methylbromids wurde an wässrigen Lösungen verschiedener Tetraalkylammonium-, Alkali- und Erdalkalisalze sowie kationaktiver Netzmittel in Gegenwart von Alkalisalzen untersucht.

EXPERIMENTELLE ANGABEN

Die Strom–Spannungs-Kurven wurden in einer konventionellen Anordnung mit thermostatierter Zelle gegen Bodenquecksilber erhalten. Anschliessend erfolgte die Potentialmessung der grossflächig ausgebildeten Anode gegen eine ges. Kalomelelektrode (+241.0 mV bei 25°). Alle Potentialangaben sind mit diesem Wert auf die Standard-Wasserstoffelektrode umgerechnet.

Bei allen Polarogrammen wurde vor Zugabe des Depolarisators der Reststrom des Leitelektrolyten registriert. Die Zugabe des Methylbromids erfolgte in Form frisch bereiteter *ca.* 0.1 molarer wässriger bzw. methanolischer Lösung zur vorentlüfteten Leitsalzlösung[5]. Im allgemeinen wurden CH_3Br-Konzentrationen von $2 \cdot 10^{-3}$ Mol/Liter eingestellt, eine Zugabe von Maximadämpfern war nicht vorgesehen.

Die HSP wurden bei völlig ausgebildeten Stufen graphisch in der üblichen Paralleltangenten-Konstruktion, bei unvollständiger Trennung der Stufe vom Endanstieg jedoch durch Vergleich des Diffusionsstromes mit einer Lösung gleicher CH_3Br-Konzentration in Tetraalkylammoniumsalzlösung ermittelt.

Die Standardabweichung der so erhaltenen HSP lag bei ±5 mV. Der Durchtrittsfaktor α wurde aus der Neigung der Geraden $\lg(i_d - i)/i$ gegen das Potential über die Gesamtstufe bestimmt[6].

Die benutzte Kapillare hatte bei einer Länge von 15 cm einen Innendurchmesser von 0.08 mm; bei einer Tropfzeit von 2.56 sec entsprach das z.B. einem Quecksilberfluss von 2.72 mg/sec.

ERGEBNISSE

Tetraalkylammoniumsalze (TAA-Salze)

Das HSP des Methylbromids ist meist in wässrig-organischer Lösung (Äthanol, Butanol, Dioxan) mit TAA-Salzen als Leitelektrolyte bestimmt worden[1,3]. In Jodidlösungen treten Störungen der Polarogramme durch die Austauschreaktion

$$CH_3Br + J^- \rightleftarrows CH_3J + Br^- \qquad (3)$$

auf.

Bei 25° ergeben sich in 0.1 *M* Leitsalzlösungen die folgenden Halbstufenpotentiale (Tropfzeit beim HSP *ca.* 2.4 sec):

	HSP:	α:
Tetramethylammoniumbromid (TMABr)	−1.436 V	0.23
Tetraäthylammoniumbromid (TÄABr)	−1.290 V	0.27
Tetra-*n*-butylammoniumchlorid (TBACl)	−1.238 V	0.38

In TMABr- und TÄABr-Lösungen tritt die polarographische Stufe in normaler Gestalt auf, in TBACl-Lösungen besitzt sie ein abbrechendes Maximum, das durch die üblichen Dämpfer zu beseitigen ist.

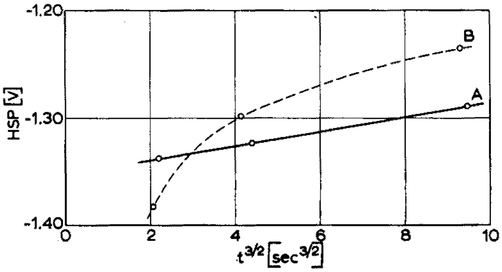
Das Halbstufenpotential wird ausser durch die Art des Kations in geringerem Umfange durch die Leitsalzkonzentration, die Tropfzeit des Quecksilbers und die Temperatur beeinflusst; es ist jedoch unabhängig von der Depolarisatorkonzentration.

In Lösungen von TÄABr wird dabei eine Positivierung des HSP mit steigender Leitsalzkonzentration bis zu einem schwachen Maximum beobachtet (25°, Tropfzeit *ca.* 2.45 sec):

	HSP:
0.02 *M* TÄABr	−1.368 V
0.05 *M*	−1.327 V
0.075 *M*	−1.310 V
0.10 *M*	−1.290 V
0.125 *M*	−1.306 V
0.25 *M*	−1.314 V
0.50 *M*	−1.323 V

Eine Abhängigkeit des konzentrationsproportionalen Grenzstromes von der Leitsalzkonzentration ist nicht feststellbar.

Eine von VON STACKELBERG[1] getroffene Feststellung zu niedriger Stufenhöhen des Methylbromids konnte für die Reduktion in wässrigen Lösungen nicht bestätigt werden.



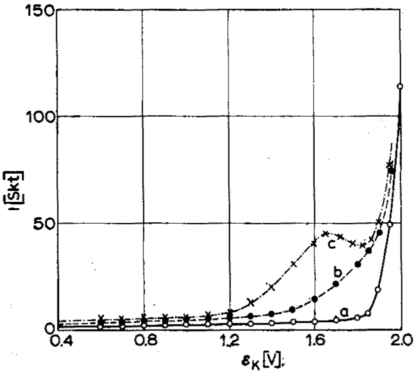


Fig. 1. Halbstufenpotential HSP des Methylbromids gegen Bodenquecksilber in verschiedenen Leitelektrolyten bei Variation der Tropfzeit *t* der Hg-Elektrode. (A) 0.1 *M* TÄABr in H_2O; (B) 0.09 *M* KBr, Zus. Peregal OK spez.

Fig. 2. Polarogramm des Methylbromids gegen Bodenquecksilber in 0.1 *M* KBr-Lösung (b) vor und (c) nach Zugabe von 0.02 *M* TÄABr. (a) Grundlösung.

Die Verschiebungen des HSP durch eine Änderung der Tropfzeit der Quecksilberkathode liegen in der gleichen Grössenordnung wie die durch Variation der Leitsalzkonzentration. Dabei bewirkt eine Verminderung der Tropfzeit eine Negativierung des HSP (Fig. 1).

Der Temperaturkoeffizient des HSP in 0.1 *M* TÄABr-Lösung beträgt +4.4 mV/° im Bereich 25–55°.

Alkali-, Erdalkali-, partiell alkylierte Ammoniumsalze

Mit diesen Verbindungen aufgebaute Leitelektrolyte zeigen allgemein Überlagerungen des CH_3Br-Grenzstromes mit dem Endanstieg des Leitelektrolyten. Die Auswertung der Polarogramme muss deshalb (ungenauer) indirekt erfolgen; einige Werte des so erhaltenen HSP für 0.1 molare Leitsalzlösungen bei 25° sind:

LiCl	HSP: nicht erreicht	NH_4Cl	HSP: −1.57 V
KCl	−1.62 V	$(C_2H_5)NH_3Cl$	−1.59 V
$CaCl_2$	−1.74 V	$(C_2H_5)_2NH_2Cl$	−1.59 V
$SrCl_2$	−1.65 V	$(C_2H_5)_3NHCl$	−1.49 V
$BaCl_2$	−1.62 V		

Das HSP ist auch hier abhängig von der Konzentration des Leitsalzes. An Lösungen von Kaliumbromid ergaben sich Verschiebungen des HSP von −1.74 V bis −1.58 V im Konzentrationsbereich 0.01 bis 1.0 *M* KBr.

Mischleitelektrolyte mit Tetraäthylammoniumbromid

Von der üblichen Form abweichende Reduktionsstufen des Methylbromids treten in Lösungen von Kaliumbromid bei gleichzeitiger Anwesenheit von TÄABr auf. Der Diffusionsstrom des Methylbromids folgt bis zu einem Potential von *ca.* −1.2 V gegen Standardwasserstoff etwa dem in reiner, gleichkonzentrierter TÄABr-Lösung beobachteten Verlauf, jedoch mit verringerter Steilheit des Stromanstieges.

Dann durchläuft die Strom–Potential-Kurve ein stark gerundetes Maximum (Potential ε_{max}) und sinkt in einem charakteristischen Bereich kontinuierlich ab. Nach Passieren eines Minimalwertes (Potential ε_{min}) mündet die Kurve in den durch die Entladung der Kalium-Ionen des Leitelektrolyten bedingten Endanstieg ein (Fig. 2).

Diese Potentialwerte ε_{max}, ε_{min} erweisen sich als von der Konzentration der TÄA-Ionen in der Lösung etwa logarithmisch abhängig, z.B. für TÄABr in 0.1 *M* KBr-Lösung (Tabelle I).

TABELLE I

ABHÄNGIGKEIT DES POTENTIALWERTES VON DER TÄA-IONENKONZENTRATION

Konz. TÄABr (M)	*Potentialwerte (V)*		*Konz. TÄABr (M)*	*Potentialwerte (V)*	
	Max	*Min*		*Max*	*Min*
0.005	−1.456	−1.536	0.025	−1.570	−1.682
0.01	−1.496	−1.596	0.05	−1.606	−1.704
0.02	−1.558	−1.668	0.1	normale Stufe	

Der Diffusionsstrom beim Potential ε_{max} steigt mit der Konzentration der grenzflächenaktiven Tetraalkylammoniumionen im Mischleitelektrolyt. Selbst im Falle des Erreichens der normalen Stufenform (z.B. mit 0.1 *M* TÄABr) wird aber nicht der in reinen TÄABr-Lösungen beobachtete Betrag des Grenzstromes erhalten.

Mischleitelektrolyte mit kationaktiven Netzmitteln

Die in Mischelektrolyten aus Alkali- und Tetraalkylammoniumsalzen erhaltenen Ergebnisse machen es wahrscheinlich, dass in Gegenwart höherer Konzentrationen an Alkaliionen die spezifische Adsorption der Tetraalkylammoniumionen bei stark negativen Potentialen nicht mehr ausreicht, um im gesamten Bereich der polarographischen Stufe einen gleichbleibenden Positivierungseffekt auf das HSP zu erreichen.

Das sollte aber bei Verwendung stärker grenzflächenaktiver Verbindungen, insbesondere ausgesprochen kationaktiver Netzmittel möglich sein. Bei der Untersuchung derartiger Systeme (0.09 *M* KBr, 1 g/Liter Netzmittel) konnte bei der Mehrzahl der geprüften Netzmittel jedoch keine ausreichende Trennung der CH_3Br-Stufe vom Endanstieg des Elektrolyten erhalten werden. Dieses Verhalten, das einem wenig ausgeprägten Positivierungseffekt entspricht, wiesen besonders Alkylpyridinium- und andere Ammoniumsalze auf.

Eine weitere Gruppe, die die als potentielle kationaktive Verbindungen anzusehenden "nichtionogenen" Polyglykolderivate Seral S, Sapal P, Bunegal O hochkonz. und Diazopal O (alle VEB Chemische Werke Buna) umfasst, entsprach in ihrem Verhalten der Kombination Alkalisalz–TÄABr. Der Übergang vom Maximum bei ε_{max} zum Minimum erfolgte jedoch abrupt innerhalb weniger Millivolt.

Dagegen zeigte das als quartäres Produkt bezeichnete Netzmittel Peregal

OK spezial (BASF) einen erheblichen Einfluss auf das HSP des Methylbromids. Bereits relativ geringe Konzentrationen dieses Netzmittels in Mischleitelektrolyten mit 0.09 *M* KBr führten zum Auftreten völlig separierter CH_3Br-Stufen, deren Grenzströme i_d die für die Diffusion kennzeichnende Abhängigkeit von der Höhe H des Hg-Vorratsgefässes mit $d(\lg i_d)/d(\lg H) = 0.46$ aufwiesen. Auch die Stufenhöhe zeigte sich in Übereinstimmung mit der ILKOVIC-Gleichung.

Bei verschiedenen Netzmittelkonzentrationen in einem KBr-Elektrolyten der erwähnten Konzentration wurden die in Tabelle II aufgeführten Halbstufenpotentiale des Methylbromids beobachtet (25°, Tropfzeit *ca.* 2.8 sec).

TABELLE II

HALBSTUFENPOTENTIALE DES METHYLBROMIDS IN EINEM KBr-ELEKTROLYTEN

Netzmittel-konzentration (mg/l)	*Halbstufen-potential (V)*	*Durchtrittsfaktor*
0	−1.66	Nicht bestimmbar
34	−1.477	Nicht bestimmbar
68	−1.425	0.26
136	−1.316	0.32
272	−1.260	0.38
544	−1.234	0.40

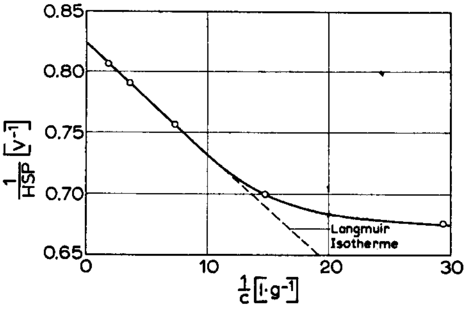


Fig. 3. Reziprokes Halbstufenpotential des Methylbromids in 0.09 *M* KBr-Grundlösung als Funktion der Verdünnung 1/c des Netzmittels Peregal OK spezial. Potentialangaben gegen die Standard-Wasserstoffelektrode.

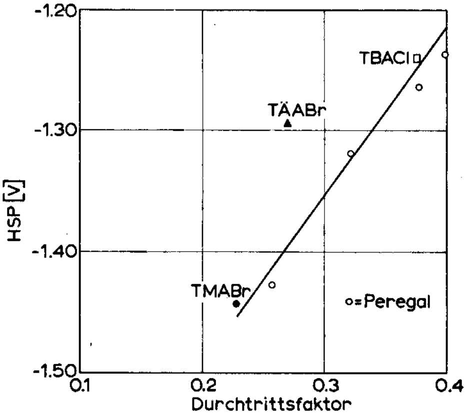


Fig. 4. Halbstufenpotential des Methylbromids (gegen Standard-Wasserstoffelektrode) in Elektrolyten mit quartären Ammoniumsalzen und Mischelektrolyten aus KBr und Netzmittel Peregal OK spezial bei verschiedenen Netzmittelkonzentrationen. Auf der Abszisse ist der experimentell ermittelte Durchtrittsfaktor aufgetragen.

Die Netzmittelkonzentration bezieht sich dabei auf Trockensubstanz der etwa 15%-igen handelsüblichen Lösung. Mit steigender Netzmittelkonzentration wird ein Grenzwert des HSP erreicht, der sich aus der Darstellung 1/HSP gegen die reziproke Konzentration (Adsorptionsisotherme nach LANGMUIR) unter den o.a. Bedingungen zu -1.207 V ergibt (Fig. 3).

Der Temperaturkoeffizient des HSP im Bereich 25–55° liegt bei $+5.0$ mV/°.

Die Art des eigentlichen Leitelektrolyten beeinflusst das sich einstellende Halbstufenpotential nur wenig, so ergibt der Austausch des Kaliumbromids gegen Lithiumchlorid lediglich eine Negativierung des HSP um 10 mV.

In grösserem Ausmass ist dagegen die Bildungsgeschwindigkeit der Tropfenoberfläche von Einfluss auf das HSP, wobei eine Verringerung der Tropfzeit der Elektrode unter sonst identischen Bedingungen eine Negativierung des HSP zur Folge hat (vgl. Fig. 1).

Bei einem Zusatz von 136 mg/l Trockensubstanz (entsprechend 0.9 ml/l des technischen Netzmittels Peregal OK spezial) zur Kaliumbromidlösung ergeben sich in dem weiten Konzentrationsbereich von 50–1000 mg/l CH_3Br gut auswertbare, der Methylbromidkonzentration proportionale Stufen, die zur analytischen Bestimmung des Halogenids geeignet sind.

DISKUSSION

Die beobachtete, z.T. erhebliche Variation des HSP der irreversiblen Reduktion des CH_3Br muss auf die Beeinflussung der Durchtrittsreaktion Gl. (2) zurückgeführt werden.

Daran sind wesentlich zwei Faktoren beteiligt:

(*a*) Beeinflussung der Aktivierungsenergie des Primärschrittes nach Gl. (2) bei gegebenem Potential;

(*b*) Änderung der Einflussnahme des elektrischen Feldes auf diese Aktivierungsenergie durch Veränderung des Potentialverlaufes ϕ (x) in der Doppelschicht.

Nach HUSH[3,7] ist die Dissoziationsenergie des Vorganges $(RX)^- \rightarrow R + X^-$ (X Halogen) bestimmend für die gegenseitige Lage der HSP der Methylhalogenide. Sie kann innerhalb der hier gemachten Voraussetzungen als konstant angesehen werden.

Dann ist der Einfluss des Leitelektrolyten durch die Veränderung des Potentialverlaufes ϕ (x) an der Phasengrenze Hg/Lösung zu beschreiben. Tatsächlich ergibt sich eine etwa lineare Beziehung zwischen dem Halbstufenpotential und dem Durchtrittsfaktor α mit verschiedenen kationaktiven Verbindungen (Fig. 4).

Bei Annahme des Reaktionsortes innerhalb der HELMHOLTZ-Doppelschicht ist die Potentialdifferenz über der Schicht in die Anteile $\Delta\phi_{eh} = \alpha \cdot \Delta\phi$ und $\Delta\phi_{hl} = (1 - \alpha)\Delta\phi$ (e Elektrode, h Reaktionsort, l Lösung) zerlegbar[8].

Bei konstantem Gesamtpotential bedingt eine Erhöhung der Ladungsdichte der Kationen in der Schicht eine Erhöhung der Potentialdifferenz $\Delta\phi_{eh}$ und damit des Durchtrittsfaktors α[9].

Mit diesem Modell kann die Positivierung des HSP in der beobachteten Reihenfolge

$$Li^+ < K^+, Ca^{2+}, Sr^{2+} \ll (CH_3)_4N^+ < (C_2H_5)_4N^+ < (C_4H_9)_4N^+$$

verstanden werden, wenn unter Berücksichtigung der Hydratation die wirksame Ladungsdichte dieser Ionen betrachtet wird. Unter diesem Gesichtspunkt ordnet sich auch die erhebliche Wirksamkeit des kationaktiven Netzmittels Peregal OK spezial durch dessen starke Anreicherung an der Phasengrenze infolge starker spezifischer Adsorption und genügender Ladungsdichte zwanglos ein.

Bei Netzmitteln mit über die Gesamtmolekel verschmierter Ladung, wie im Falle der "nichtionogenen" Verbindungen, ist durch Überlagerung der Einflüsse der Grenzflächenaktivität und der Coulomb-Energie bei Mischelektrolyten eine Desorption des grenzflächenaktiven Stoffes aus der Doppelschicht möglich.

In einem charakteristischen Potentialbereich erfolgt die Verdrängung des Netzmittels aus der Doppelschicht durch die dann wirksam werdende Coulomb-Anziehung der Ionen des eigentlichen Leitelektrolyten mit ihrer höheren Ladungsdichte.

Die unterschiedliche Form der Polarogramme in der Umgebung des Potentials ε_{min} bei TÄA-Salzen und Polyglykolderivaten kann dann auf die Kombination von Grenzflächenaktivität und wirksamer Ladungsdichte dieser Ionen zurückgeführt werden:

TÄA-Salze	hohe Ladungsdichte mässige Grenzflächenaktivität	allmähliche Desorption
nichtionogene Netzmittel	geringe Ladungsdichte hohe Grenzflächenaktivität	spontane Desorption
Netzmittel Peregal OK spezial	hohe Ladungsdichte hohe Grenzflächenaktivität	keine Desorption

Modifiziert wird das Verhalten der Netzmittel durch die mit der Bildungsgeschwindigkeit der Tropfenoberfläche veränderlichen Diffusionsprozesse. Der Einfluss der endlichen Diffusionsgeschwindigkeit der das HSP des Methylbromids beeinflussenden Ionen ist aus dem Vergleich der beiden Kurven in Fig. 1 und in der Abweichung der LANGMUIR-Isotherme vom linearen Verlauf in Fig. 3 bei geringen Netzmittelkonzentrationen erkennbar.

Dem Direktor des Institutes für Elektrochemie und Physikalische Chemie der TU Dresden, Herrn Prof. Dr. h.c. K. SCHWABE, sei an dieser Stelle besonders herzlich für seine Unterstützung dieser Arbeit gedankt.

ZUSAMMENFASSUNG

Die stark irreversible polarographische Reduktion des Methylbromids wurde in wässrigen Lösungen in Gegenwart verschiedener Leitelektrolyte untersucht. Deren Kationen positivieren mit steigender Ladungsdichte und Grenzflächenaktivität das Halbstufenpotential. Mischleitelektrolyte mit Alkalisalzen und Tetraalkylammoniumsalzen oder kationaktiven Netzmitteln zeigten teilweise Verdrängungseffekte der aktiven Komponente aus der Reaktionsschicht unter Aufhebung der Positivierung des HSP. Bei Netzmitteln hoher Aktivität und ausreichender Ladungsdichte ist mit derartigen Mischelektrolyten eine normale polarographische Bestimmung des Methylbromids möglich. Die endliche Diffusionsgeschwindigkeit der aktiven Komponente ist gleichfalls von erheblichem Einfluss auf das Halbstufenpotential, sodass HSP derartiger Systeme nicht allein durch die Lösungszusammensetzung zu kennzeichnen sind.

SUMMARY

The irreversible polarographic reduction of methyl bromide was studied in aqueous solution in the presence of various base electrolytes. $E_{\frac{1}{2}}$ values became more positive with increasing charge density and surface activity of the cations. Mixed electrolytes with alkali metal salts and tetraalkylammonium salts or cationic surfactants suppressed this increase in $E_{\frac{1}{2}}$ values. With such mixed electrolytes containing highly active surfactants of sufficient charge density, a normal polarographic determination of methyl bromide is possible. The final diffusion rate of the active component has also a considerable effect on $E_{\frac{1}{2}}$ values so that the $E_{\frac{1}{2}}$ values of such systems cannot be characterized by the solution composition alone.

RÉSUMÉ

L'auteur a effectué une étude sur la réduction polarographique irréversible du bromure de méthyle, en solution aqueuse, en présence de divers électrolytes de base. Les valeurs $E_{\frac{1}{2}}$ deviennent plus positives avec l'augmentation de la densité de courant et l'activité de surface des cations. Un mélange d'électrolytes, sels de métaux alcalins et sels de tétraalkylammonium, ou des agents tensioactifs cationiques suppriment cette augmentation de la valeur $E_{\frac{1}{2}}$. Un dosage polarographique normal du bromure de méthyle est alors possible.

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AN AUTOMATIC APPARATUS FOR SIMULTANEOUS THERMOGRAVIMETRIC AND MAGNETIC SUSCEPTIBILITY MEASUREMENTS

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During the past several years, the use of magnetic susceptibility measurements for studying the thermal dissociation of transition metal ammine complexes has become a useful thermoanalytical technique[1,2]. These measurements, at elevated temperatures, indicate the temperature ranges at which changes of structure of the complex or changes of oxidation state of the central metal ion occur, hence aiding in the elucidation of the reaction mechanism.

A survey of the various methods employed for the determination of the high temperature magnetic susceptibility of a substance, according to recent reviews[3-5], indicates that the Faraday method is perhaps the most convenient to use. At elevated temperatures, however, the sample generally undergoes a loss in mass so that it is often more convenient to measure the mass-changes simultaneously with magnetic susceptibility measurements. MULAY AND KEYS[6] have described a manually recording helical spring microbalance for simultaneous magnetic susceptibility, adsorption, and thermogravimetric measurements. A more elaborate apparatus has been described by RICHARDSON AND BEAUXIS[7] in which the sample mass, apparent mass-change caused by the magnetic field, and the temperature were recorded during short-timed cycles at any temperature from −196° to 500°.

The apparatus described here was designed to record automatically the continuous sample mass-change curve, the apparent mass-change caused by the magnetic field, and the sample temperature, all simultaneously from room temperature to 500°. Thus, the thermogravimetric analysis (TGA) curve, the sample mass susceptibility, and the magnetic moment of the central metal ion may be obtained from a single sample under the same carefully controlled conditions of pyrolysis.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is given in Fig. 1. The apparatus consisted of an Ainsworth Model RV-AU-2K semi-micro automatic recording balance which was equipped with a two-pen strip-chart potentiometric recorder; a 4-inch Alpha Instrument aluminum-foil wound electromagnet fitted with Heyden type pole pieces; a 0–10 A regulated (0.1%) magnet power supply; a Pyrex glass tube furnace chamber, non-inductively wound with Nichrome resistance wire (maximum ambient resistance of 20 ohms), and insulated with several layers of asbestos paper and

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Sauereisen cement; a furnace temperature programmer[8] consisting of a motor-driven variable transformer; and a magnet platform which could be raised or lowered by means of a 2-ton capacity hydraulic piston and pump assembly. The sample was contained in a small (0.4 × 1.0 cm) Pyrex glass bucket which was attached to the left balance pan by a platinum wire. The temperature of the furnace (and hence, sample) was detected by a Chromel–Alumel thermocouple placed in the furnace at a position just below the sample bucket. The sample mass was recorded on one channel of the recorder while the furnace temperature was recorded on the other; both were recorded as a function of time. The enclosed balance and sample chambers permitted the use of various controlled gaseous atmospheres (nitrogen, helium, ammonia, etc.) at pressures from ambient to approximately 10^{-2} torr.

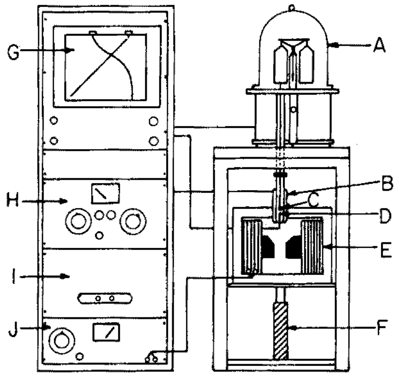

Fig. 1. Schematic diagram of apparatus. (A) Ainsworth semi-micro recording balance; (B) tube furnace; (C) sample container; (D) furnace thermocouple; (E) electromagnet; (F) hydraulic piston; (G) two-pen recorder; (H) furnace temperature programmer; (I) voltage regulator; (J) magnet power supply.

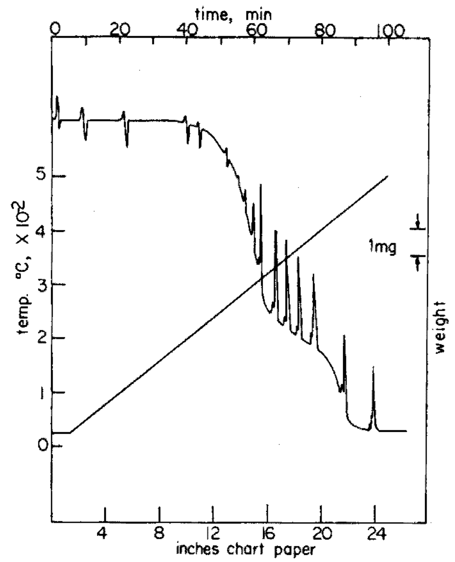

Fig. 2. Mass-change curve of $[Co(NH_3)_6]Cl_3$ (air atmosphere).

Procedure

From 10–30 mg of the sample was placed in the sample bucket. The furnace assembly was positioned about the sample and the sample and bucket mass determined automatically by the balance. From the total mass of the bucket, the sample mass could then be obtained. The magnet power supply was turned on and adjusted so that a maximum magnetic field of 4000 gauss was obtained. By manual operation of the hydraulic pump, the magnet was raised about the furnace and then lowered at a slow rate, at the same time recording the apparent mass-change of the sample. The furnace temperature programmer was then turned on and allowed to heat the sample at a temperature increase of approximately 5°/min. At various temperature intervals, the magnet was raised and lowered about the furnace and sample assembly. Thus, the mass-change curve was continuously recorded while the apparent mass-change, due to the presence of the magnetic field, was recorded at periodic intervals.

Calculations

In the Faraday method, the apparent mass-change as the sample passes through an inhomogeneous field is

$$g\Delta m = XmH\frac{\mathrm{d}H}{\mathrm{d}x} \qquad (1)$$

where g is the gravitational constant, Δm the apparent mass-change, X the sample mass susceptibility, m the mass of the sample, H the magnetic field, and $\mathrm{d}H/\mathrm{d}x$ the magnetic field gradient. The field can be plotted for $H(\mathrm{d}H/\mathrm{d}x)$ as a function of the sample position in the magnetic field using a sample of known susceptibility. However, by eqn. (1), when $H(\mathrm{d}H/\mathrm{d}x)$ is at a maximum, the apparent mass-change, Δm, is also at a maximum. This position in the magnetic field is fixed so that only the maximum apparent mass-change of a known sample and of the empty container need be known in order to calculate the mass susceptibility of an unknown sample. By replacing $H(\mathrm{d}H/\mathrm{d}x)$ in eqn. (1) by $[H(\mathrm{d}H/\mathrm{d}x)]_{\mathrm{max}}$, the following is obtained

$$X_{\mathrm{u}} = X_{\mathrm{s}}\left(\frac{\Delta m_{\mathrm{u}} - \Delta m_{\mathrm{c}}}{\Delta m_{\mathrm{s}} - \Delta m_{\mathrm{c}}}\right)\frac{m_{\mathrm{s}}}{m_{\mathrm{u}}} \qquad (2)$$

where the subscripts u, s, and c refer to the unknown sample, the standard sample, and the container, respectively. Such a procedure is well suited for the Ainsworth automatic balance since it is not a null-type instrument and the exact position of the sample in the field is not always known. The standard compound used in this investigation was $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$; $X = 32.3 \cdot 10^{-6}$ c.g.s. units.

The magnetic moment, μ, of the central metal ion in the complex is obtained from the equation

$$\mu = 2.84[X_{\mathrm{n}}'(T+\theta)]^{\frac{1}{2}} \qquad (3)$$

where T is the absolute temperature, θ is the Weiss constant, and X_{n}' is the corrected molar susceptibility in c.g.s. units.

RESULTS AND DISCUSSION

The use of the apparatus is illustrated by the thermal dissociation of the cobalt(III) ammine complex, $[Co(NH_3)_6]Cl_3$, which undergoes a change in oxidation state of the cobalt(III) ion on heating to elevated temperatures. The complex dissociates according to the equation[9]:

$$6\,[Co(NH_3)_6]Cl_3(s) \rightarrow 6\,CoCl_2(s) + 28\,NH_3(g) + 6\,NH_4Cl(s) + N_2(g) \qquad (4)$$

The initial complex is diamagnetic due to a d^6 configuration of the cobalt(III) ion in a spin-paired d^2sp^3 octahedral structure. On reduction from Co(III) → Co(II), the cobalt(II) ion has a d^7 configuration with three unpaired electrons so that it is paramagnetic.

The mass-change curve of $[Co(NH_3)_6]Cl_3$ is given in Fig. 2. At ambient temperature and up to about 200°, the negative apparent mass-change of the compound, at $[H(\mathrm{d}H/\mathrm{d}x)]_{\max}$, indicates that it is diamagnetic and that there was no loss in mass of the sample as a function of temperature. Above 200°, however, the compound began to lose mass and also became slightly paramagnetic as indicated by the smaller negative apparent mass-changes. At 250°, the deflections became positive and increased in intensity until the cobalt(III) ion was completely reduced to cobalt(II) at about 320°. The deflections then began to decrease slightly as the temperature was increased, due to the inverse temperature dependence of the mass susceptibility. Additional mass loss was observed above 320°, due to the sublimation of ammonium chloride, which was formed during the reaction as shown in eqn. (4). The residue at 475° consisted of cobalt(II) chloride. The magnetic moment of the cobalt(II) ion in this compound at this temperature, as calculated using eqn. (3), and a Weiss constant of −35°K, was 4.85 B.M. This is in fair agreement with the literature value of approximately 4.6 B.M.[10].

Recalculation of the above data to obtain the mass susceptibility of the complex as a function of temperature is shown in Fig. 3. The sample mass susceptibility increased very rapidly between 200° and 320° and then remained fairly constant to 400°. It increased again between 400° and 425° due to the loss of the ammonium chloride. Actually, very little information can be obtained from such a plot because X_u is dependent upon the sample mass and the temperature.

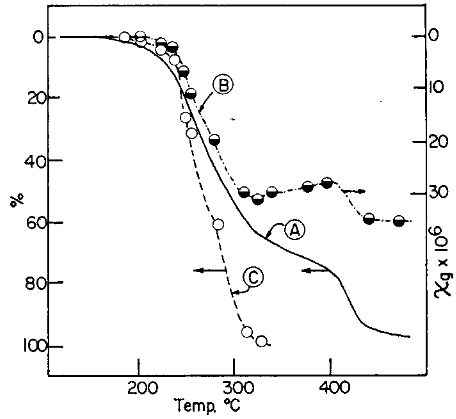

Fig. 3. Mass-change, susceptibility, and molar percent reduction of $[Co(NH_3)_6]Cl_3$. (A) Mass-change curve; (B) mass susceptibility curve; (C) mole percent cobalt(III) reduced curve.

Perhaps a more useful parameter is the mole percent of cobalt(III) reduced, as a function of temperature, as is also shown in Fig. 3. This parameter is calculated as follows. The apparent mass-change, Δm, due to the presence of the magnetic field at any given temperature, consists of three components: that contributed by (*a*) the empty container, Δm_c; (*b*) the original compound, Δm_o; and (*c*) the product compound, Δm_p, or

$$\Delta m = \Delta m_c + \Delta m_o + \Delta m_p \qquad (5)$$

If the diamagnetic corrections are considered to be negligible, then eqns. (2), (3), and (5) can be combined to give

$$N_p = \frac{\left[\frac{\Delta m\ -\ \Delta m_c}{\Delta m_s\ -\ \Delta m_c} m_s X_s - N \frac{\mu_{o2}}{(2.84)^2 (T+\theta)}\right](2.84)^2 (T+\theta)}{\mu_p{}^2 - \mu_o{}^2} \tag{6}$$

where N is the total number of moles of compound, N_p is the number of moles of product, and the subscripts o and p refer to the original compound and product, respectively. The mole percent reduced is then

$$\text{mole percent reduced} = \frac{100 N_p}{N} \tag{7}$$

In the case of $[Co(NH_3)_6]Cl_3$, the original compound is diamagnetic so that μ_o is negligible. Combining eqns. (6) and (7) then

$$\text{mole percent reduced} = 100 \frac{\left[\frac{\Delta m\ -\ \Delta m_c}{\Delta m_s\ -\ \Delta m_c} m_s X_s (2.84)^2 (T+\theta)\right]}{\mu_p{}^2} \tag{8}$$

The quantity,

$$100 \frac{m_s X_s (2.84)^2}{\mu_p{}^2 (\Delta m_s\ -\ \Delta m_c)} = \text{constant} = K \tag{9}$$

so that the reduced form of eqn. (8) becomes

$$\text{mole percent reduced} = K(\Delta m - \Delta m_c)(T+\theta) \tag{10}$$

From eqn. (10), the curve as shown in Fig. 3 was calculated. This curve thus indicates that the cobalt(III) ion is completely reduced at 320°. By comparison of the mass-change curve and the mole percent cobalt(III) reduced curve, the relationship between the mass-change and the reduction reaction, both taking place during the thermal dissociation reaction, may be ascertained. These data are very helpful in elucidating the mechanism of the dissociation reaction.

The apparatus also provides a fast and simple method for the determination of the constants in the Curie–Weiss equation,

$$X_n{}' = \frac{C}{T+\theta} \tag{11}$$

These constants can be determined by simply heating the sample at a linear heating rate and calculating the susceptibility values at various temperature intervals. Then by eqn. (11), a straight line curve is obtained if $1/X_n{}'$ is plotted against T. The constants, C and θ, are then calculated from the slope and the intercept of the curve.

This apparatus has proven very useful in studying the thermal dissociation of transition metal ammine complexes. The advantages of the apparatus are its apparent accuracy, the rapidity at which a run and calculations can be made due to automatic recording, and the furnace atmosphere control. The apparatus could also be used to study dehydration and other types of reactions not involving a change in oxidation state of some metal ion or adsorption processes using the method described by Mulay and Keys[6].

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SUMMARY

An apparatus is described which records automatically the continuous sample mass-change curve, the apparent mass-changes caused by the magnetic field, and the sample temperature, all simultaneously over the temperature range from room temperature to 500°. The use of the apparatus is illustrated by the thermal dissociation of $[Co(NH_3)_6]Cl_3$. Data obtained from the apparatus permit the plotting of mass-change, mass susceptibility, and molar percent reduction of cobalt(III) curves, all as a function of temperature. Such information is useful in elucidating the mechanism of the thermal dissociation reaction.

RÉSUMÉ

Un appareil est décrit pour enregistrer automatiquement les courbes de variation de masses en fonction de la température (20 à 500°) et du champ magnétique. On a choisi comme exemple la dissociation thermique de $[Co(NH_3)_6]Cl_3$. Les valeurs obtenues permettent le relevé des courbes de changement de masse, de susceptibilité et de pourcentage de réduction de cobalt(III), en fonction de la température. Ces renseignements sont utiles pour expliquer le mécanisme de la réaction de dissociation thermique.

ZUSAMMENFASSUNG

Es wird ein Apparat beschrieben, der von einer Probe über den Temperaturbereich von 20–500° automatisch und gleichzeitig die kontinuierliche Änderung des Gewichts, die scheinbare Gewichtsänderung durch ein magnetisches Feld und die Probentemperatur aufzeichnet. Die Apparatur wird am Beispiel der thermischen Dissoziation von $[Co(NH_3)_6]Cl_3$ beschrieben.

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THE SOLVENT EXTRACTION OF SOME THALLIUM(I) CHELATES

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Several investigations of the solvent extraction of neutral chelates of thallium(I) have been carried out in recent years. MORRISON AND FREISER[1] make reference to articles describing the use of thenoyltrifluoroacetone, diphenylthiocarbazone, sodium diethyldithiocarbamate, mercaptobenzothiazole, and thiosalicylidene-ethylenediimine as chelating agents. BAGREEV AND ZOLOTOV[2] have reported on extractions involving 8-hydroxyquinoline, sodium diethyldithiocarbamate, thenoyltrifluoroacetone, and 8-mercaptoquinoline in a variety of solvents. ALIMARIN AND ZOLOTOV[3] have investigated extractions of thallium(I) with 8-hydroxyquinoline into 7 organic solvents. They found that extraction is more efficient if a polar oxygen-containing solvent is employed than if a non-polar solvent is used. SCHWEITZER AND NORTON[4] have examined the use of 14 different chelating agents and found that bidentate 4- and 5-membered chelates bonding through nitrogen and sulfur seem to show the best characteristics for extraction into chloroform. SCHWEITZER AND COCHRAN[5] have performed extractions employing several reagents with both chloroform and methyl isobutyl ketone as the organic phase. They also investigated the effects of various adducts on the different extraction systems. SCHWEITZER AND MATTHEWS[6] have studied the influences of various complexing anions on the extraction of thallium(I) into chloroform containing mercaptobenzothiazole.

The present study was undertaken to find a good chelating reagent–solvent pair for the efficient extraction of thallium(I) from aqueous solutions. A system which would give very high extraction at relatively low pH values was desired. In addition, it was hoped that the species predominating in the extractions could be identified and that association and partition constants could be calculated for both the reagent and for the complexes.

THEORETICAL CONSIDERATIONS

In the extraction of tracer thallium(I) from an aqueous phase into an organic phase containing a chelating reagent HR at a concentration $[HR]_o$, the most likely organic species formed will be $TlR(HR)_a$ and the most likely aqueous species will be TlR_r where both a and r can take integer values including zero. The organic/aqueous distribution constant of the thallium D may be represented as $D = [TlR(HR)_a]_o/[TlR_r]$ where the subscript o indicates an organic phase concentration and the unsubscripted brackets indicate an aqueous phase concentration. Charges have been omitted for simplicity. Substitution of appropriate association and partition constants yields $D = K_{1a}P_{1a}[HR]_o^{1-r+a}/C_rK_r^{1-r}P_r^{1-r+a}[H]^{1-r}$ where K_{1a} is the association constant and P_{1a} the partition constant for $TlR(HR)_a$, K_r is the acid association constant and P_r the partition constant for HR, C_r is the association constant of TlR_r, and [H] is the hydrogen ion concentration. A plot of log D against pH at constant $[HR]_o$ will result in a curve of slope $1-r$ and a plot of log D against log $[HR]_o$ at constant pH will yield a curve with a slope of $1-r+a$.

When plots of experimental data are made, it is often discovered that there are regions with constant slope indicating that r and a are constant and there are regions of changing slope giving indications that the value of r or a is changing, which means that more than one aqueous or organic species is involved. Usually such curves can be represented by a series of terms of the type indicated in the previous paragraph, each term varying in the values of a and/or r. By proper slope analysis and curve fitting, all terms necessary to describe the extraction can be determined and often the constants K_{1a}, P_{1a}, and C_r can be estimated. SCHWEITZER[7] has presented a more detailed treatment in a previous paper.

EXPERIMENTAL

Reagents

Thallium-204 in dilute nitric acid, as obtained from the New England Nuclear Corporation, was converted to the perchlorate by successive evaporations with perchloric acid. From this a stock solution was prepared such that the final thallium(I) concentration used in the extraction experiments would be 10^{-6} M. All other chemicals, chelating reagents, and solvents were either reagent grade, were purified from technical-grade material, or were prepared directly from reagent-grade chemicals. The water employed was double distilled in an all-glass apparatus.

Procedure

Samples of 7 ml of aqueous phase plus 7 ml of organic phase placed in 20-ml glass bottles were tumbled at 27.0 ± 0.5° until equilibrium was reached. The aqueous phase contained 10^{-6} M thallium and was 10^{-1} M in sodium perchlorate, and the pH was adjusted with perchloric acid and sodium hydroxide. Measurements of pH were made with a Leeds and Northrup 16253 Combination Electrode coupled with a Beckman Research pH Meter which was frequently calibrated with buffers at pH values of 2.00, 4.00, 7.00, 9.00, and 11.00. After equilibration and pH measurement, samples were drawn from each phase, placed on planchets, dried, and counted using standard radioactivity detection equipment. From the counting results D values could be calculated.

Several xanthate chelating agents were prepared by refluxing stoichiometric amounts of sodium and the appropriate alcohol in toluene, triturating the resulting alkoxide with ether, and, after cooling, adding a slight excess of carbon disulfide. The product was filtered, washed with ether, and vacuum dried over Drierite.

The product K_rP_r for each of the xanthates was determined by titrating a known amount of the compound dissolved in 10^{-1} M aqueous sodium perchlorate in contact with an equal volume of chloroform. Aliquots of standard hydrochloric acid sufficient to react with one-tenth the total xanthate were added and the pH was measured after equilibration. At all points up to 50% completion it was assumed that essentially all the xanthic acid formed partitioned into the organic phase. This is reasonable since, for example, the value of log P_r for ethylxanthic acid has been independently[8] determined as 3.1. The amount of xanthate anion in the aqueous phase was taken to be the difference between the initial anion concentration and the amount of xanthic acid in the organic phase. The product K_rP_r was calculated from $K_rP_r = [HR]_o/[H]([X] - [HR]_o)$ where [X] is the initial xanthate concentration.

RESULTS

The values of log K_rP_r determined experimentally are 4.6 for ethylxanthic acid, 6.7 for amylxanthic acid, 6.9 for benzylxanthic acid, 6.2 for 2-phenylethylxanthic acid, and 5.8 for 3-phenylpropylxanthic acid. The value for ethylxanthic acid compares favorably with that obtained from other determinations, KIRK AND OTHMER[9] giving a value of 1.5 for log K_r and VON HALBAN AND HECHT[8] reporting 3.1 for log P_r.

Table I presents extraction data for numerous systems, log *D* being presented as a function of pH, log $[HR]_o$, or log [R]. Following the system number and the experimental parameters, the data are presented, then the integer slopes through which a curve plotted according to the parameters passes, are indicated.

TABLE I

EXPERIMENTAL EXTRACTION RESULTS

System number—Experimental parameter—Data—Slopes

1. $10^{-2.5}$ *M* thionalide in MIBK[a]: pH (log *D*), 6.7 (−1.20), 6.9 (−1.17), 7.8 (−0.38), 8.5 (0.26), 9.4 (0.80), 9.5 (1.05); slope 1
2. $10^{-2.0}$ *M* thionalide in MIBK: pH (log *D*), 5.8 (−1.68), 6.1 (−1.30), 6.2 (−1.51), 8.0 (0.61), 8.8 (0.88), 9.2 (1.41), 10.3 (2.47); slope 1
3. $10^{-1.5}$ *M* thionalide in MIBK: pH (log *D*), 6.55 (−0.36), 6.6 (−0.45), 7.55 (0.40), 7.6 (0.58), 8.7 (1.50), 9.9 (2.74), 10.2 (2.78); slope 1
4. Thionalide in MIBK, pH 7.5: log $(HR)_o$ (log *D*), −2.5 (−0.65), −2.0 (−0.12), −1.5 (0.40); slope 1
5. $10^{-2.0}$ *M* thionalide in chlorobenzene: pH (log *D*), 6.9 (−1.99), 7.4 (−1.57), 8.5 (−0.78), 8.8 (−0.52), 9.0 (−0.42), 9.4 (0.02), 9.7 (0.25), 10.5 (0.44), 10.75 (0.47), 11.9 (0.37), 12.3 (0.51); slopes 1, 0
6. $10^{-2.0}$ *M* thionalide in 1,2-dichloroethane: pH (log *D*), 7.7 (−0.90), 8.55 (−0.36), 9.0 (−0.02), 9.4 (0.39), 10.65 (1.01), 11.05 (1.00); slopes 1, 0
7. $10^{-2.0}$ *M* thionalide in benzyl ether: pH (log *D*), 4.9 (−0.79), 5.7 (−0.14), 5.8 (−0.19), 6.0 (0.08), 6.75 (0.67), 8.7 (1.60), 10.0 (1.58), 11.8 (1.59), 12.4 (1.60); slopes 1, 0
8. $10^{-2.0}$ *M* thionalide in benzyl alcohol: pH (log *D*), 7.8 (−0.41), 8.3 (−0.13), 8.9 (0.19), 9.6 (0.80), 10.55 (1.33), 11.05 (1.49), 12.0 (1.73); slope 0.5
9. $10^{-2.0}$ *M* dithiooxamide in $CHCl_3$: pH (log *D*), 3.4 (−1.34), 6.2 (−1.97), 7.65 (−1.69), 7.7 (−1.73), 10.0 (−0.50), 10.5 (−0.36), 11.5 (0.27); slope 0.5
10. $10^{-3.0}$ *M* dibutylphosphorodithioic acid in CCl_4: pH (log *D*), 2.3 (−0.67), 3.15 (−0.25), 3.3 (−0.21), 5.4 (0.17), 6.8 (0.35), 6.95 (0.33), 7.85 (0.35), 7.95 (0.26), 11.05 (0.33), 12.0 (0.22); slopes 0.5, 0
11. $10^{-3.0}$ *M* dithizone in $CHCl_3$: pH (log *D*), 7.4 (−0.25), 8.1 (0.42), 9.2 (1.18), 9.45 (1.38), 9.7 (1.54); slopes 1, 0
12. $10^{-2.5}$ *M* dithizone in $CHCl_3$: pH (log *D*), 7.2 (0.17), 7.6 (0.30), 8.1 (0.90), 8.2 (0.88), 9.05 (1.54), 11.3 (1.55); slopes 1, 0
13. $10^{-2.0}$ *M* dithizone in $CHCl_3$: pH (log *D*), 6.75 (0.62), 6.8 (0.81), 7.0 (0.85), 7.2 (0.96), 7.5 (1.16), 8.3 (1.41), 9.1 (1.56), 10.3 (1.54); slopes 1, 0
14. Dithizone in $CHCl_3$, pH 7.1: log $(HR)_o$ (log *D*), −3.0 (−0.45), −2.5 (0.14), −2.0 (0.38); slope 1

15. Dithizone in $CHCl_3$, pH 10.0: log $(HR)_o$ (log *D*), −3.0 (1.54), −2.5 (1.54), −2.0 (1.54); slope 0
16. $10^{-3.0}$ *M* dithizone in MIBK: pH (log *D*), 6.3 (0.05), 6.8 (0.34), 7.5 (1.00), 8.6 (1.47), 9.9 (1.67), 10.7 (1.68), 11.2 (1.68), 11.45 (1.68), 12.0 (1.70); slopes 1, 0
17. $10^{-1.3}$ *M* oxine in isobutanol: pH (log *D*), 4.7 (−0.81), 5.75 (−0.73), 6.0 (−0.75), 6.4 (−0.70), 7.5 (−0.69), 9.15 (−0.07), 9.25 (0.00), 9.7 (0.34), 10.35 (0.52), 11.0 (0.66), 11.1 (0.64), 11.6 (0.63), 11.8 (0.65); slopes 0.6, 0
18. $10^{-0.5}$ *M* oxine in isobutanol: pH (log *D*), 6.1 (−0.61), 6.7 (−0.55), 6.8 (−0.53), 7.4 (−0.32), 8.4 (−0.12), 9.6 (0.62), 9.7 (0.65), 10.2 (0.64), 10.5 (0.64), 10.9 (0.68), 11.4 (0.68); slopes 0.6, 0
19. Oxine in isobutanol, pH 9.0: log $(HR)_o$ (log *D*), −1.3 (−0.17), −0.5 (0.30); slope 0.6
20. Oxine in isobutanol, pH 11.0: log $(HR)_o$ (log *D*), −1.3 (0.65), −0.5 (0.68); slope 0
21. $10^{-2.0}$ *M* thiooxine in $CHCl_3$: pH (log *D*), 5.8 (−1.83), 7.4 (−0.81), 8.55 (−0.08), 10.8 (1.30); slope 0.6
22. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in $CHCl_3$: pH (log *D*), 3.0 (−1.75), 3.1 (−1.73), 5.0 (−1.36), 5.8 (−0.75), 6.1 (−0.41), 6.3 (−0.17), 6.6 (0.24), 7.3 (0.48), 8.9 (0.68), 10.0 (0.70), 11.0 (0.70), 11.95 (0.74); slopes 1, 0
23. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in $CHCl_3$, $10^{-1.0}$ *M* in CS_2: pH (log *D*), 6.0 (−0.84), 6.5 (−0.68), 7.5 (0.25), 7.6 (0.19), 7.8 (0.40), 8.0 (0.63), 8.15 (0.75), 8.5 (0.80); slopes 1, 0
24. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in $CHCl_3$, $10^{0.0}$ *M* in CS_2: pH (log *D*), 7.25 (−0.80), 7.7 (−0.15), 8.15 (0.05), 8.15 (0.11), 8.3 (0.43), 8.35 (0.60); slopes 1, 0
25. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in benzene: pH (log *D*), 3.5 (−1.67), 4.9 (−0.59), 5.6 (−0.18), 6.2 (0.21), 6.25 (0.27), 6.6 (0.50), 6.7 (0.58), 6.8 (0.63), 7.0 (0.70), 7.0 (0.80), 7.45 (0.83), 8.25 (0.83), 8.4 (0.80), 8.5 (0.88), 10.6 (0.81), 11.5 (0.83), 12.0 (0.83); slopes 0.7, 0
26. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in benzene, $10^{-1.0}$ *M* in CS_2: pH (log *D*), 3.15 (−1.40), 6.15 (0.62), 6.4 (0.88), 6.85 (1.02), 6.95 (1.03), 7.05 (1.07), 7.2 (1.15), 7.4 (1.23), 8.5 (1.24), 10.2 (1.25), 12.0 (1.10); slopes 0.7, 0
27. $10^{-1.0}$ *M* thenoyltrifluoroacetylacetone in benzene, $10^{-0.4}$ *M* in CS_2 (saturated): pH (log *D*), 5.9 (0.53), 6.3 (0.83), 7.3 (1.20), 8.5 (1.30), 10.2 (1.30), 11.8 (1.10); slopes 0.6, 0
28. $10^{-1.0}$ *M* acetylacetone in $CHCl_3$: pH (log *D*), 8.9 (−1.18), 9.2 (−1.10), 9.35 (−0.90), 10.0 (−0.33), 10.45 (−0.08), 10.85 (−0.10); slopes 1, 0
29. $10^{-1.0}$ *M* acetylacetone in $CHCl_3$, $10^{0.0}$ *M* in CS_2: pH (log *D*), 8.75 (−1.30), 8.9 (−1.00), 9.2 (−0.86), 9.9 (−0.25), 10.4 (−0.23); slopes 1, 0
30. $10^{-2.5}$ *M* sodium diethyldithiocarbamate in water in contact with CCl_4: pH (log *D*), 6.35 (0.60), 7.2 (0.90), 8.1 (0.81), 8.65 (0.90), 9.4 (0.92); slopes –, 0
31. $10^{-2.0}$ *M* sodium diethyldithiocarbamate in water in contact with CCl_4: pH (log *D*), 6.8 (1.17), 6.8 (1.28), 7.2 (1.25), 7.3 (1.42), 7.5 (1.42), 7.7 (1.37), 8.5 (1.35), 9.25 (1.40), 10.4 (1.37), 11.0 (1.44); slopes –, 0
32. $10^{-1.0}$ *M* sodium diethyldithiocarbamate in water in contact with CCl_4: pH (log *D*), 8.3 (1.53), 8.5 (1.55), 8.75 (1.55), 8.9 (1.55), 9.0 (1.55), 10.1 (1.53), 11.0 (1.52); slopes –, 0
33. $10^{-1.5}$ *M* sodium diethyldithiocarbamate in water in contact with isobutanol: pH (log *D*), 9.0 (1.06), 10.05 (1.03), 10.4 (1.03), 11.6 (1.05); slopes –, 0
34. $10^{-2.0}$ *M* diethylammonium diethyldithiocarbamate in water in contact with $CHCl_3$: pH (log *D*), 1.8 (−2.19), 2.2 (−1.70), 2.6 (−1.49), 2.6 (−1.49), 2.8 (−1.28), 2.8 (−1.20), 3.1 (−0.79), 3.2 (−0.97), 3.3 (−0.84), 3.5 (−0.81), 3.6 (−0.48), 3.9 (−0.41), 4.2 (−0.05), 4.6 (0.42), 4.8 (0.27), 5.0 (0.48), 5.4 (0.58), 5.5 (0.89), 6.0 (1.28), 6.4 (1.48), 6.6 (1.58), 6.9 (1.80), 6.9 (1.97), 7.1 (2.09), 7.3 (2.20), 7.6 (2.14), 8.4 (2.30), 8.75 (2.51), 9.45 (2.47), 9.5 (2.58), 9.7 (2.55), 10.35 (2.57), 10.9 (2.49); slopes 0.8, 0
35. $10^{-1.0}$ *M* diethylammonium diethyldithiocarbamate in water in contact with $CHCl_3$: pH (log *D*), 1.6 (−2.09), 2.5 (−2.21), 5.0 (−1.05), 5.9 (0.60), 6.0 (0.81), 8.0 (2.53), 8.5 (2.65), 8.8 (2.64), 8.9 (2.66), 9.2 (2.73), 10.0 (2.71), 10.3 (2.61), 10.3 (2.78), 10.4 (2.84), 10.55 (2.54), 10.8 (2.57), 11.15 (2.64); slopes 0.9, 0
36. $10^{-2.0}$ *M* diethylammonium diethyldithiocarbamate in water in contact with $CHCl_3$ (shaken by hand 5 min): pH (log *D*), 1.05 (0.32), 1.65 (−0.06), 2.95 (1.02), 3.6 (1.18), 4.0 (1.14), 4.15 (1.03), 4.5 (1.46), 4.95 (1.87), 5.25 (1.81), 5.35 (1.99), 5.65 (2.22), 5.8 (2.52), 6.35 (2.46), 6.95 (2.56); slopes 0.8, 0
37. $10^{-1.0}$ *M* diethylammonium diethyldithiocarbamate in water in contact with $CHCl_3$ (shaken by hand 5 min): pH (log *D*), 1.6 (−0.47), 2.2 (0.01), 2.6 (0.60), 3.45 (1.58), 4.35 (1.47), 4.6 (2.01), 4.8 (2.76), 5.0 (1.84), 5.3 (2.00), 5.35 (2.56), 5.55 (1.92), 5.7 (2.22), 6.7 (2.25), 8.0 (2.90), 8.1 (3.07), 8.5 (3.19), 8.65 (3.08), 8.8 (3.02), 9.0 (3.07), 9.5 (2.95), 9.9 (3.03), 10.15 (3.02); slopes 0.9, 0
38. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.35 (−1.98), 2.7 (−1.79), 3.55 (−1.06), 3.8 (−0.74), 4.8 (−0.10), 5.35 (0.16), 5.4 (0.26), 5.6 (0.29), 6.2 (0.40), 7.05 (0.38), 8.7 (0.38), 10.45 (0.47); slopes 0.8, 0

39. $10^{-2.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.55 (−1.15), 2.8 (−0.95), 3.15 (−0.65), 3.75 (−0.11), 4.15 (0.06), 4.3 (0.08), 5.45 (0.61), 6.0 (0.63), 6.4 (0.61), 7.9 (0.56), 8.1 (0.70), 9.15 (0.66), 9.5 (0.62), 10.2 (0.64), 10.55 (0.69), 10.95 (0.68), 11.25 (0.68); slopes 0.8, 0
40. $10^{-1.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 1.95 (−1.16), 2.15 (−0.75), 2.9 (0.16), 3.6 (0.23), 3.95 (0.58), 4.9 (0.90), 5.5 (0.90), 5.75 (1.01), 6.0 (1.09), 6.2 (1.08), 7.0 (0.99), 7.6 (0.88), 7.9 (0.93), 8.8 (0.93), 9.6 (0.92), 10.7 (0.94); slopes 0.8, 0
41. Potassium ethylxanthate in water in contact with $CHCl_3$, pH 3.5: log $(HR)_o$ (log *D*), −3.03 (−1.05), −2.03 (−0.30), −1.03 (0.35); slope 0.7
42. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −5.6 (−2.27), −5.2 (−1.92), −4.8 (−1.65), −4.45 (−1.35), −4.05 (−1.05), −3.7 (−0.72), −3.4 (−0.40), −3.2 (−0.10), −3.1 (0.12), −3.04 (0.30), −3.0 (0.40); slope 1
43. $10^{-2.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −4.6 (−1.62), −4.2 (−1.26), −3.8 (−0.95), −3.4 (−0.60), −3.05 (−0.25), −2.7 (0.06), −2.4 (0.31), −2.2 (0.48), −2.04 (0.62), −2.0 (0.62); slope 1
44. $10^{-1.0}$ *M* potassium ethylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −3.6 (−0.89), −3.2 (−0.57), −2.8 (−0.24), −2.4 (0.11), −2.05 (0.40), −1.7 (0.65), −1.4 (0.81), −1.2 (0.91), −1.1 (0.93), −1.04 (0.94), −1.0 (0.94); slope 1
45. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with benzene: pH (log *D*), 2.35 (−2.20), 3.4 (−1.08), 3.65 (−0.86), 5.0 (0.12), 5.4 (0.24), 6.0 (0.52), 7.0 (0.45), 8.2 (0.50), 9.2 (0.51), 9.95 (0.46), 11.4 (0.53); slopes 1, 0
46. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with CS_2: pH (log *D*), 3.4 (−1.90), 4.0 (−1.36), 5.1 (−0.45), 5.5 (−0.40), 6.45 (−0.13), 7.9 (0.01), 8.6 (−0.04), 9.55 (0.03), 10.05 (0.05), 10.35 (−0.28), 10.9 (−0.35), 11.1 (−0.50), 11.6 (−0.82); slopes 0.9, 0, −0.7
47. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with CCl_4: pH (log *D*), 2.5 (−2.48), 3.95 (−1.66), 5.2 (−1.20), 6.2 (−0.89), 6.7 (−0.95), 8.05 (−0.83), 8.95 (−0.75), 9.85 (−0.87), 10.75 (−0.67); slopes 0.6, 0
48. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with chlorobenzene: pH (log *D*), 2.25 (−2.12), 2.8 (−1.66), 3.45 (−1.18), 4.75 (−0.45), 5.15 (−0.25), 6.3 (−0.16), 7.0 (−0.15), 7.7 (−0.12), 9.0 (−0.06), 9.9 (−0.08), 10.55 (−0.15); slopes 0.8, 0
49. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with heptane: pH (log *D*), 2.05 (−2.79), 4.45 (−2.54), 5.95 (−2.33), 6.8 (−2.38), 7.65 (−2.51), 8.95 (−2.47), 10.9 (−2.52)
50. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with isobutanol: pH (log *D*), 2.45 (−1.03), 3.45 (−1.02), 3.8 (−1.01), 4.95 (−1.01), 6.5 (−0.98), 7.05 (−0.96), 7.8 (−0.98), 10.1 (−0.96)
51. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with methylene chloride: pH (log *D*), 2.7 (−1.76), 3.8 (−0.75), 4.9 (−0.14), 5.5 (0.19), 6.55 (0.38), 7.7 (0.46), 8.35 (0.48), 10.6 (0.48); slopes 0.7, 0
52. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with methylisobutyl ketone: pH (log *D*), 2.55 (−2.20), 3.55 (−2.13), 4.5 (−2.18), 5.0 (−2.06), 6.7 (−2.09), 8.15 (−2.12), 8.95 (−2.04), 9.65 (−2.09)
53. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with nitrobenzene: pH (log *D*), 2.5 (−1.80), 3.75 (−0.90), 4.75 (−0.21), 5.75 (0.45), 5.9 (0.49), 6.25 (0.58), 6.4 (0.55), 7.4 (0.53), 7.65 (0.51), 8.85 (0.52), 9.05 (0.56), 9.5 (0.61), 10.85 (0.58); slopes 0.7, 0
54. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with toluene: pH (log *D*), 2.65 (−1.76), 3.85 (−0.75), 4.75 (−0.18), 5.45 (−0.15), 6.05 (0.12), 7.35 (0.16), 7.7 (0.22), 7.8 (0.11), 10.25 (0.16); slopes 0.9, 0
55. $10^{-3.0}$ *M* potassium ethylxanthate in water in contact with 1,1,1-trichloroethane: pH (log *D*), 2.4 (−2.48), 3.2 (−2.12), 3.9 (−1.75), 4.9 (−1.06), 5.2 (−1.07), 6.0 (−0.80), 6.1 (−0.90), 6.8 (−0.92), 7.0 (−0.89), 7.55 (−0.82), 7.95 (−0.84), 8.5 (−0.84), 8.75 (−0.79), 10.0 (−0.88); slopes 0.6, 0
56. $10^{-4.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.85 (−2.70), 4.0 (−2.16), 5.15 (−1.45), 5.85 (−1.01), 6.45 (−0.57), 6.95 (−0.35), 7.5 (−0.30), 9.0 (−0.33), 9.75 (−0.33), 10.85 (−0.30), 11.2 (−0.34); slopes 1, 0
57. $10^{-3.5}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: pH (log *D*), 4.05 (−1.79), 4.3 (−1.64), 4.4 (−1.39), 5.55 (−0.74), 5.75 (−0.68), 6.1 (−0.50), 6.3 (−0.27), 6.8 (−0.09), 7.3 (0.02), 7.45 (0.06), 7.6 (0.10), 8.25 (0.16), 9.45 (0.15), 10.5 (0.19), 11.0 (0.18); slopes 1, 0
58. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.6 (−3.03), 3.05 (−2.57), 3.05 (−2.48), 3.1 (−2.45), 3.3 (−2.30), 3.9 (−1.52), 4.4 (−1.01), 5.35 (−0.16), 5.65 (0.15), 5.8 (0.13), 5.95 (0.27), 6.45 (0.56), 6.85 (0.74), 7.3 (0.83), 7.9 (0.92), 8.7 (0.95), 9.4 (0.94), 9.5 (0.96), 9.6 (0.90), 9.8 (0.89), 9.9 (0.95), 10.4 (0.96), 10.5 (0.91), 11.05 (0.94), 11.3 (0.89); slopes 1, 0
59. $10^{-2.5}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.3 (−2.00),

3.75 (−1.55), 4.0 (−1.22), 4.6 (−0.55), 5.3 (0.08), 6.35 (0.79), 7.1 (1.15), 8.0 (1.20), 8.8 (1.15), 10.0 (1.24), 10.55 (1.26), 10.8 (1.27); slopes 1, 0

60. $10^{-2.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$; pH (log *D*), 2.75 (−2.23), 2.9 (−1.96), 3.0 (−1.55), 3.5 (−1.55), 3.85 (−0.56), 5.25 (0.71), 5.85 (1.32), 6.8 (1.25), 7.15 (1.52), 7.7 (1.40), 7.8 (1.66), 8.45 (1.49), 9.65 (1.60), 9.95 (1.65), 10.2 (1.58), 10.3 (1.65), 10.65 (1.60), 11.0 (1.67); slopes 1, 0
61. $10^{-4.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −7.5 (−3.40), −7.1 (−3.00), −6.7 (−2.58), −6.3 (−2.20), −5.9 (−1.78), −5.5 (−1.40), −5.1 (−1.11), −4.8 (−0.83), −4.5 (−0.60), −4.25 (−0.42), −4.15 (−0.35), −4.1 (−0.35), −4.0 (−0.35); slope 1
62. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −6.5 (−2.35), −6.1 (−1.90), −5.7 (−1.45), −5.3 (−1.00), −4.9 (−0.65), −4.55 (−0.26), −4.12 (0.05), −3.76 (0.35), −3.47 (0.59), −3.25 (0.75), −3.11 (0.85), −3.05 (0.93), −3.0 (0.95); slope 1
63. $10^{-2.0}$ *M* potassium amylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −5.5 (−1.35), −5.1 (−0.95), −4.7 (−0.55), −4.3 (−0.15), −3.9 (0.25), −3.5 (0.68), −3.12 (1.07), −2.76 (1.32), −2.46 (1.50), −2.25 (1.60), −2.12 (1.60), −2.05 (1.60), −2.0 (1.60); slope 1
64. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with benzene: pH (log *D*), 3.55 (−1.75), 3.6 (−1.71), 3.65 (−1.66), 4.45 (−1.31), 5.05 (−0.85), 5.6 (−0.68), 6.1 (−0.01), 6.2 (0.00), 6.75 (0.30), 7.1 (0.45), 8.25 (0.49), 8.7 (0.34), 9.65 (0.53), 10.55 (0.64), 11.35 (0.54); slopes 0.6, 0
65. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with CS_2: pH (log *D*), 2.65 (−2.50), 3.35 (−1.94), 5.2 (−0.66), 6.2 (0.13), 7.3 (0.45), 8.55 (0.59), 9.45 (0.61), 9.95 (0.59); slopes 0.8, 0
66. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with CCl_4: pH (log *D*), 3.1 (−2.15), 4.1 (−1.60), 5.2 (−1.15), 6.7 (−0.47), 6.95 (−0.34), 7.8 (0.12), 8.5 (−0.15), 10.45 (0.19), 11.5 (0.11); slopes 0.5, 0
67. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with chlorobenzene: pH (log *D*), 2.6 (−2.84), 2.95 (−2.54), 3.35 (−2.17), 5.4 (−0.13), 7.8 (0.51), 8.85 (0.50), 9.6 (0.46), 10.5 (0.49); slopes 1, 0
68. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with heptane: pH (log *D*), 3.15 (−3.00), 3.6 (−2.25), 4.55 (−2.10), 6.1 (−2.05), 7.8 (−2.01), 8.6 (−2.00), 9.4 (−2.07), 10.7 (−2.03)
69. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with isobutanol: pH (log *D*), 2.8 (−1.05), 3.1 (−1.02), 3.8 (−0.96), 4.4 (−0.97), 6.7 (−0.99), 7.25 (−0.95), 7.45 (−0.99), 10.0 (−0.96)
70. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with methylene chloride: pH (log *D*), 3.0 (−1.95), 3.4 (−1.80), 3.9 (−1.45), 4.55 (−0.89), 5.45 (−0.45), 6.1 (0.08), 6.75 (0.45), 7.1 (0.75), 7.65 (0.62), 7.95 (0.61), 8.2 (0.72), 8.35 (0.73), 9.2 (0.71), 9.65 (0.70), 9.95 (0.82), 10.35 (0.70); slopes 0.7, 0
71. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with methylisobutyl ketone: pH (log *D*), 2.7 (−1.85), 3.4 (−1.83), 5.4 (−2.08), 7.75 (−1.95), 8.25 (−1.95), 11.3 (−1.76)
72. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with nitrobenzene: pH (log *D*), 2.2 (−1.86), 3.25 (−1.48), 3.85 (−1.38), 6.25 (−0.52), 7.45 (−0.24), 7.9 (−0.15), 9.15 (−0.06), 10.35 (−0.11); slopes 0.4, 0
73. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with toluene: pH (log *D*), 2.4 (−2.55), 3.8 (−1.95), 5.5 (−1.21), 6.45 (−0.89), 7.4 (−0.37), 7.9 (−0.34), 9.1 (−0.38), 9.8 (−0.21), 10.6 (−0.32); slopes 0.6, 0
74. $10^{-3.0}$ *M* potassium amylxanthate in water in contact with 1,1,1-trichloroethane: pH (log *D*), 3.3 (−2.36), 4.45 (−1.72), 5.3 (−1.48), 6.4 (−1.35), 7.1 (−1.22), 8.0 (−1.08), 8.25 (−1.20), 8.8 (−1.21), 9.85 (−1.35), 11.0 (−1.20); slopes 0.6, 0
75. $10^{-4.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: pH (log *D*), 4.15 (−1.18), 4.7 (−0.60), 6.6 (0.56), 7.7 (0.60), 10.05 (0.65), 11.05 (0.64); slopes 1, 0
76. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.5 (−1.62), 4.65 (0.55), 5.0 (0.81), 5.95 (1.30), 6.3 (1.49), 6.75 (1.51), 7.55 (1.56), 8.05 (1.54), 9.4 (1.61), 10.35 (1.55), 10.95 (1.52); slopes 1, 0
77. $10^{-2.5}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.4 (−0.58), 3.75 (−0.33), 4.5 (0.55), 5.75 (1.68), 6.25 (1.93), 6.45 (1.93), 6.95 (1.80), 8.6 (1.85), 9.4 (1.83), 10.1 (1.83), 11.3 (1.84); slopes 1, 0
78. $10^{-2.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.3 (−1.04), 2.85 (−0.55), 3.25 (0.13), 5.75 (1.98), 6.7 (2.29), 6.95 (2.21), 7.3 (2.27), 9.7 (2.26), 9.95 (2.24), 10.5 (2.24); slopes 1, 0

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79. $10^{-1.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.05 (0.55), 3.55 (0.80), 5.65 (2.35); slope 1

80. $10^{-4.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −7.7 (−2.17), −7.3 (−1.75), −6.9 (−1.34), −6.5 (−0.91), −6.1 (−0.50), −5.7 (−0.12), −5.3 (0.24), −4.9 (0.44), −4.6 (0.57), −4.3 (0.60), −4.2 (0.62), −4.1 (0.62), −4.0 (0.62); slope 1

81. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −6.7 (−0.90), −6.3 (−0.50), −5.9 (−0.10), −5.5 (0.30), −5.1 (0.67), −4.7 (1.00), −4.3 (1.24), −3.9 (1.40), −3.6 (1.50), −3.3 (1.55), −3.2 (1.55), −3.1 (1.55), −3.0 (1.55); slope 1

82. $10^{-2.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −5.7 (−0.20), −5.3 (0.20), −4.9 (0.59), −4.5 (0.97), −4.1 (1.35), −3.7 (1.66), −3.3 (1.92), −2.9 (2.10), −2.6 (2.20), −2.3 (2.25), −2.2 (2.25), −2.1 (2.25), −2.0 (2.25); slope 1

83. $10^{-1.0}$ *M* sodium benzylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −4.7 (−0.50), −4.3 (0.88), −3.9 (1.26), −3.5 (1.65), −3.1 (2.00), −2.7 (2.25), −2.3 (2.42), −1.9 (2.55); slope 1

84. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with benzene: pH (log *D*), 2.4 (−1.22), 4.0 (0.16), 4.65 (0.74), 5.8 (1.59), 6.8 (2.00), 7.75 (1.98), 8.95 (1.98); slopes 0.9, 0

85. $10^{-2.0}$ *M* sodium benzylxanthate in water in contact with benzene: pH (log *D*), 3.1 (−0.35), 4.5 (0.85), 5.7 (1.91), 6.8 (2.27), 7.0 (2.38), 7.55 (2.09), 9.0 (2.19), 9.05 (2.16), 9.5 (2.12), 10.15 (2.12), 11.0 (2.11); slopes 0.9, 0

86. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with CS_2: pH (log *D*), 2.4 (−1.95), 4.55 (0.12), 5.2 (0.53), 5.25 (0.63), 6.55 (1.27), 7.65 (1.31), 8.75 (1.33), 10.3 (1.36); slopes 1, 0

87. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with CCl_4: pH (log *D*), 2.6 (−1.63), 4.65 (−0.42), 5.45 (−0.17), 6.45 (0.43), 7.2 (0.47), 7.6 (0.41), 7.75 (0.43), 10.45 (0.47); slopes 0.5, 0

88. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with chlorobenzene: pH (log *D*), 2.3 (−1.52), 3.45 (−0.47), 4.15 (−0.14), 6.0 (1.13), 6.7 (1.30), 7.6 (1.44), 8.4 (1.39), 10.15 (1.45); slopes 0.7, 0

89. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with heptane: pH (log *D*), 2.35 (−3.16), 4.35 (−1.81), 5.4 (−1.49), 6.6 (−1.38), 7.9 (−1.36), 8.4 (−1.34), 9.4 (−1.48), 10.9 (−1.32)

90. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with isobutanol: pH (log *D*), 2.65 (−1.00), 3.75 (−0.95), 4.95 (−0.95), 5.85 (−0.96), 6.3 (−0.69), 7.05 (−0.13), 7.15 (−0.21), 8.3 (−0.10), 9.8 (0.06); slopes 0.8, 0

91. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with methylene chloride: pH (log *D*), 2.65 (−1.35), 3.8 (−0.21), 5.1 (1.08), 6.5 (1.83), 7.2 (1.86), 7.5 (2.00), 8.5 (2.13), 9.8 (1.88); slopes 1, 0

92. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with methylisobutyl ketone: pH (log *D*), 2.35 (−1.93), 3.7 (−2.10), 5.1 (−2.05), 5.2 (−2.07), 6.15 (−2.02), 7.4 (−2.06), 7.6 (−2.15), 7.8 (−2.16), 8.7 (−1.72), 9.2 (−1.95), 10.35 (−1.65), 10.95 (−1.47); slopes 0.3 (?)

93. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with nitrobenzene: pH (log *D*), 2.45 (−1.59), 3.65 (−0.77), 4.35 (−0.34), 5.4 (0.57), 6.75 (1.46), 7.35 (1.60), 7.6 (1.83), 8.2 (1.90), 9.2 (1.95), 10.0 (1.93), 10.65 (1.76); slopes 0.8, 0

94. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with toluene: pH (log *D*), 2.35 (−1.51), 4.75 (0.24), 5.0 (0.57), 6.35 (1.49), 7.05 (1.49), 8.8 (1.38), 9.8 (1.40), 11.5 (1.36); slopes 0.8, 0

95. $10^{-3.0}$ *M* sodium benzylxanthate in water in contact with 1,1,1-trichloroethane: pH (log *D*), 2.6 (−1.78), 4.2 (−0.36), 5.35 (0.21), 6.45 (0.55), 7.6 (0.64), 7.7 (0.70), 8.6 (0.66), 9.35 (0.76), slopes 0.9, 0

96. $10^{-3.0}$ *M* sodium *t*-butylxanthate in water in contact with $CHCl_3$: pH (log *D*), 5.9 (−1.35), 6.65 (−0.92), 6.7 (−1.00), 7.5 (−0.63), 7.5 (−0.60), 8.0 (−0.46), 9.1 (−0.50), 9.65 (−0.23), 10.55 (−0.18); slopes 0.5, 0

97. $10^{-4.0}$ *M* sodium 2-phenylethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.25 (−1.49), 4.25 (−0.35), 4.9 (0.35), 6.05 (1.44), 8.1 (1.80), 9.25 (1.80), 10.9 (1.80); slopes 1, 0

98. $10^{-3.0}$ *M* sodium 2-phenylethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 2.5 (−2.08), 2.9 (−1.23), 3.55 (−0.65), 4.5 (0.48), 6.6 (2.05), 6.65 (2.12), 7.05 (2.19), 7.35 (2.21), 8.1 (2.37), 9.7 (2.33), 11.8 (2.35); slopes 1,0

99. $10^{-2.0}$ *M* sodium 2-phenylethylxanthate in water in contact with $CHCl_3$: pH (log *D*), 3.15 (−0.44), 3.2 (−0.37), 4.9 (1.60), 7.4 (2.79), 8.5 (2.89), 8.55 (2.82), 9.4 (2.87), 10.5 (2.90); slopes 1, 0

100. $10^{-4.0}$ *M* potassium 2-phenylethylxanthate in water in contact with $CHCl_3$: log (R) (log *D*), −7.0 (−1.35), −6.6 (−0.95), −6.2 (−0.55), −5.8 (−0.15), −5.4 (−0.15), −5.0 (0.65), −4.7 (1.00), −4.4 (1.29), −4.2 (1.50), −4.1 (1.64), −4.04 (1.70), −4.02 (1.73), −4.0 (1.73); slope 1

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101. $10^{-3.0}$ *M* potassium 2-phenylethylxanthate in water in contact with CHCl$_3$: log (R) (log *D*), −6.0 (−0.95), −5.6 (−0.50), −5.2 (−0.05), −4.8 (0.40), −4.4 (0.85), −4.0 (1.25), −3.7 (1.60), −3.4 (1.85), −3.2 (2.03), −3.1 (2.15), −3.04 (2.21), −3.02 (2.29), −3.0 (2.35); slope 1

102. $10^{-2.0}$ *M* potassium 2-phenylethylxanthate in water in contact with CHCl$_3$: log (R) (log *D*), −5.0 (−0.35), −4.6 (0.10), −4.2 (0.55), −3.8 (1.04), −3.4 (1.50), −3.0 (1.87), −2.7 (2.15), −2.4 (2.38), −2.2 (2.55), −2.1 (2.67), −2.04 (2.76), −2.02 (2.82), 2.0 (2.90); slope 1

103. $10^{-3.0}$ *M* sodium 2-phenylethylxanthate in water in contact with benzene: pH (log *D*), 3.15 (−0.45), 4.45 (0.87), 8.6 (1.94), 10.35 (1.95); slopes 1, 0

104. $10^{-3.0}$ *M* sodium 2-phenylethylxanthate in water in contact with carbon disulfide: pH (log *D*), 3.65 (−0.65), 4.6 (0.36), 7.7 (1.56), 9.25 (1.62); slopes 1, 0

105. $10^{-3.0}$ *M* sodium 2-phenylethylxanthate in water in contact with chlorobenzene: pH (log *D*), 2.75 (−1.57), 3.9 (−0.50), 4.9 (0.46), 5.75 (1.25), 7.8 (2.25), 9.75 (2.25); slopes 1, 0

106. $10^{-3.0}$ *M* sodium 2-phenylethylxanthate in water in contact with methylene chloride: pH (log *D*), 2.6 (−1.60), 3.3 (−0.86), 4.4 (0.27), 5.5 (1.54), 7.55 (2.60), 10.2 (2.60); slopes 1, 0

107. $10^{-4.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with CHCl$_3$: pH (log *D*), 3.2 (−2.35), 4.25 (−1.40), 5.5 (−0.26), 6.8 (0.95), 9.05 (2.05), 10.45 (2.05); slopes 1, 0

108. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with CHCl$_3$: pH (log *D*), 2.8 (−2.17), 3.8 (−1.45), 4.35 (−0.75), 5.0 (−0.19), 5.05 (−0.10), 7.0 (1.20), 9.55 (2.60), 10.3 (2.60); slopes 1, 0

109. $10^{-2.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with CHCl$_3$: pH (log *D*), 3.35 (−1.01), 3.9 (−0.56), 4.05 (−0.41), 5.25 (0.65), 6.45 (1.65), 7.8 (2.82), 8.3 (3.15), 9.45 (3.13), 9.75 (3.13), 12.4 (3.15); slopes 1, 0

110. $10^{-4.0}$ *M* potassium 3-phenylpropylxanthate in water in contact with CHCl$_3$: log (R) (log *D*), −7.0 (−2.38), −6.6 (−2.00), −6.2 (−1.62) −5.8 (−1.24), −5.4 (−0.82), −5.0 (−0.50), −4.7 (−0.12), −4.4 (0.25), −4.2 (0.61), −4.1 (0.96), −4.05 (1.30), −4.02 (1.60), −4.0 (1.81), −4.0 (2.06); slope 1

111. $10^{-3.0}$ *M* potassium 3-phenylpropylxanthate in water in contact with CHCl$_3$: log (R) (log *D*), −6.0 (2.22), −5.6 (−1.80), −5.2 (−1.45), −4.8 (−1.06), −4.4 (−0.72), −4.0 (−0.32), −3.7 (0.05), −3.4 (0.41), −3.2 (0.80), −3.1 (1.15), −3.05 (1.52), −3.02 (2.15), −3.0 (2.60); slope 1

112. $10^{-2.0}$ *M* potassium 3-phenylpropylxanthate in water in contact with CHCl$_3$: log (R) (log *D*), −5.0 (−1.48), −4.6 (−1.14), −4.2 (−0.80), −3.8 (−0.44), −3.4 (−0.10), −3.0 (0.25), −2.7 (0.60), −2.4 (0.93), −2.2 (1.28), −2.1 (1.61), −2.05 (1.96), −2.02 (2.65), −2.0 (3.15); slope 1

113. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with benzene: pH (log *D*), 3.5 (−0.40), 4.35 (0.51), 9.8 (2.04), 11.0 (2.06); slopes 1, 0

114. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with carbon disulfide: pH (log *D*), 4.8 (0.20), 5.25 (0.66), 8.35 (1.75), 9.65 (1.76); slopes 1, 0

115. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with chlorobenzene: pH (log *D*), 2.7 (−1.65), 3.25 (−1.25), 4.3 (−0.55), 6.1 (1.25), 7.0 (1.75), 8.15 (2.55), 9.15 (2.73), 11.15 (2.75); slopes 0.8, 0

116. $10^{-3.0}$ *M* sodium 3- phenylpropylxanthate in water in contact with heptane: pH (log *D*), 4.9 (−1.31), 9.5 (−1.29); slope 0

117. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with isobutanol: pH (log *D*), 4.0 (−1.00), 9.0 (−1.01); slope 0

118. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with methylene chloride: pH (log *D*), 2.65 (−1.80), 3.4 (−0.95), 4.0 (−0.52), 4.4 (0.20), 5.45 (1.45), 6.6 (2.38), 7.6 (2.75), 10.3 (2.75); slopes 1, 0

119. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with nitrobenzene: pH (log *D*), 3.1 (−1.45), 3.65 (−1.16), 6.0 (0.90), 8.5 (2.15), 9.25 (2.15), 10.4 (2.16); slopes 0.8, 0

120. $10^{-3.0}$ *M* sodium 3-phenylpropylxanthate in water in contact with 1,1,1-trichloroethane: pH (log *D*), 2.75 (−1.41), 3.95 (−0.76), 5.4 (0.14), 7.05 (0.71), 9.4 (0.70), 10.75 (0.70); slopes 0.6, 0

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[a] MIBK stands for methyl isobutyl ketone.

Systems 1–4 give data for extractions using thionalide in methyl isobutyl ketone. The log-*D*-against-pH curve rises with a slope of 1, indicating that 1−r, the exponent of [H] is equal to 1, making r equal 0. The predominant species is therefore probably Tl. The log-*D*-against-log-[HR]$_0$ plot has a slope of 1, indicating that n − r + a, the exponent of $[HR]_o$ is equal to 1. This gives a value of 0 to a, and identifies the predominant organic species as TlR. D then turns out to be given by $[TlR]_o/[Tl]$ or $D = K_{10}P_{10}[HR]_o/K_rP_r[H]$. Using the data and a known value of K_rP_r, log $K_{10}P_{10}$ turns out to be 4.3. Reagent decomposition at pH values greater than 10.3 prevented the accumulation of data which would indicate the attainment of a plateau region of slope 0.

Systems 5–7 involve extractions using thionalide in chlorobenzene, 1,2-dichloroethane, and benzyl ether. The predominant organic species in every case appears to be $TlR(HR)_a$, a being undetermined since $[HR]_o$ was not varied. The aqueous species are Tl at low pH values where the slope is 1 and TlR at higher pH values where the slope is 0. In the benzyl alcohol case, no region of slope 0 was attained.

System 9, a study of extraction with dithiooxamide in chloroform, gives a log-D-against-pH curve with a slope of 0.5, indicating the existence of a mixture of Tl and TlR in the aqueous phase along with $TlR(HR)_a$ in the organic phase. System 10, dibutylphosphorodithioic acid in carbon tetrachloride, probably involves an organic species $TlR(HR)_a$ and aqueous species Tl and TlR, the former predominating at slope 0 and the latter at slope 1. Assuming a to be 0, log P_{10} is 0.3 and log K_{10} is 0.5 if an expression of the following form is used to fit the curve: $1/D = [Tl]/[TlR]_o + [TlR]/[TlR]_o = K_rP_r[H]/K_{10}P_{10}[HR]_o + 1/P_{10}$.

Dithizone in chloroform as an extracting medium is employed in systems 11–15. The organic species is seen to be TlR, and the aqueous species at low pH values is Tl which changes to TlR at higher values. If the equation employed in the previous paragraph is invoked for these data, the curves are very readily fitted by using a value of 1.5 for log P_{10} and 4.5 for log K_{10}. The log-D-against-pH curve for dithizone in methyl isobutyl ketone which may be obtained from system 16 is shifted about 1.4 pH units in relation to the chloroform curve, but there is little change in the plateau level.

Systems 17–20 are concerned with the use of oxine in isobutanol. The slopes of the log-D-against-pH curves start at 0.6 and then move to 0, indicating a mixture of Tl and TlR in the aqueous phase which changes to TlR alone. The organic species appears to be TlR. These species lead to an expression similar to the one describing the dithizone data, log P_{10} being 0.7 and log K_{10} 3.5. Thiooxine in chloroform, system 21, has an upslope similar to that for oxine, but no plateau is seen. Treatment of the type given to systems 1–3 gives log $K_{10}P_{10}$ a value of 3.5.

Systems 22–24 involve log-D-against-pH data for thenoyltrifluoroacetone in chloroform plus varying amounts of carbon disulfide. KUROVSKII[10] indicates that thallium(I) forms a complex involving one molecule of a β-diketone, one molecule of carbon disulfide, and 2 thallium ions. It was thought that such a species might partition but the data indicate that the addition of carbon disulfide has scant effect on the extraction. Examination of the results indicates the organic species to be TlR and the aqueous species to be Tl, then TlR. Log P_{10} is 0.7 without carbon disulfide and 0.8 with either 0.1 M or 1.0 M carbon disulfide. Log K_{10} is 1.9 without carbon disulfide and 0.9 with 0.1 M and 0.4 with 1.0 M carbon disulfide. These values were calculated using K_r and P_r values for thenoyltrifluoroacetone in pure chloroform. As carbon disulfide is added, the value of P_r undoubtedly changes, perhaps explaining the apparent variations in log K_{10}. The slight alteration in log P_{10} may also be assigned to differences in extractability brought about by changes in the solvent.

Systems 25–27 involve similar experiments with benzene as the organic medium. Some enhancement of extraction is realized, a maximum log D of 0.8 being seen without the carbon disulfide and 1.3 with it. Log P_{10} values are 0.8 without and 1.2 with carbon disulfide and log K_{10} is 2.2 without and 2.3 with carbon disulfide. As with systems 22–24, these changes can be assigned largely to solvent alterations of P_r and P_{10}. Systems 28–29 concern acetylacetone in chloroform with and without carbon disulfide. No enhancement is seen. Log P_{10} is found to be -0.1 without and -0.2 with 1.0 M carbon disulfide and log K_{10} has corresponding values of 1.3 and 1.8.

Sodium diethyldithiocarbamate in water in contact with carbon tetrachloride is the subject of systems 30–32. Reagent decomposition below pH 7 prevented accurate determination of an upslope. On the plateau, $1-r$ is 0, thus r is 1. The organic species is therefore probably $TlR(HR)_a$ and the aqueous species is TlR. Isobutanol was substituted for carbon tetrachloride in system 33 with no essential improvement of data. The diethylammonium salt of the reagent was used in systems 34–37 in an attempt to prevent decomposition at low pH values. Even so, decomposition was still in evidence, though the samples in systems 36–37 were equilibrated for only 5 min.

Systems 38–44 involve the extraction of thallium(I) from an aqueous solution containing potassium ethylxanthate into chloroform. The log-D-against-pH plots exhibit slopes of 0.8 and 0.0 giving values of 0.2 and 1 to r. A plot of log D against log $[HR]_o$ at a pH value of 3.5 (system 41) shows a slope of 0.7. This would yield a negative value for a and suggests that the simple relation $D=[TlR(HR)_a]_o/[TlR_r]$ does not fully represent the situation. Plots of log D against log [R] show greater extraction at constant [R] by the system having a lower [HR] suggesting the existence of an aqueous species other than Tl or TlR. In addition, the slope of the log-D-against-log-[R] curve increases sharply as the limiting value for log [R] is approached. This suggests that the unknown aqueous species decreases as the pH is raised. An aqueous species agreeing with these observations is TlHR since it would lower the extraction instead of enhancing it and would be transformed to Tl or TlR as the pH value is raised. The D would then be given by $D=[TlR(HR)_a]_o/[TlR_r(HR)_f]$ and substitution of proper constants would lead to $D=K_{1a}P_{1a}[HR]_o^{1-r+a-f}/C_{rf}K_r^{1-r}P_r^{1-r+a-f}[H]^{1-r}$, where C_{rf} represents the association constant of $TlR_r(HR)_f$. A plot of log D against log $[HR]_o$ would now show a slope of $1-r+a-f$, and since r has been shown to be 0, $a-f$ is -0.3 for system 41, making a equal to 0 and f 0.3. This corresponds to an organic species of TlR and an aqueous mixture of Tl and TlHR on the rising portion of the curve and TlR on the plateau. D is thus given by $D = [TlR]_o/[Tl]+[TlHR]+[TlR]$ and substitution of proper constants yields

$$D = K_{10}P_{10}[R]/1+(C_{01}/P_r)[HR]_o+K_{10}[R]$$

When known values of D, [R], and $[HR]_o$ are placed in this equation, log P_{10} has a value of 0.9, log K_{10} 2.1, and log C_{01} 4.6. SCHWEITZER AND NORTON[4] report a value of 0.8 for log P_{10} and SCHWEITZER AND COCHRAN[5] give 0.9.

Systems 45–55 involve log-D-against-pH data for 10^{-3} M solutions of potassium xanthate in water in contact with 11 organic solvents. In all cases the predominant organic species appears to be TlR and the aqueous species seem to be a mixture of Tl, TlHR, and TlR.

Extractions involving potassium amylxanthate in water in contact with chloroform are examined in systems 56–63. Curves similar to those for the ethylxanthate are seen and they are found to be amenable to a similar interpretation. Log P_{10} is 1.5, log K_{10} 2.8, and log (C_{01}/P_r) 2.0. Extractions with potassium amylxanthate and 11 other organic solvents are examined in systems 64–74. In these the species appear to be the same as those with potassium ethylxanthate.

Systems 75–83 give data for extractions involving sodium benzylxanthate in water in contact with chloroform. Curves similar in form to those for the previous xanthates are seen and the species identification is quite similar. Log P_{10} is 2.3, log K_{10} 3.4, and log (C_{01}/P_r) 1.0. Eleven other organic solvents used with this reagent yielded the results as given in systems 84–95.

System 96 involves the extraction of thallium with sodium *t*-butylxanthate in water in contact with chloroform. Extraction was small and the decomposition of the reagent so rapid that no theoretical interpretation of the data was warranted. Sodium 2-phenylethylxanthate and chloroform are the reagent and organic phase, respectively, presented in systems 97–101. Curves with the expected xanthate-type shapes are seen, log P_{10} being 2.6, log K_{10} 2.8, and log (C_{01}/P_r) 2.5. Extractions into 4 other solvents are given in systems 103–106.

Extractions involving sodium 3-phenylpropylxanthate and chloroform are shown in systems 107–112. The expected xanthate-type features are seen, and the plots of log D against the various parameters give evidence for the same species as seen in the other xanthate extractions. The values determined for the constants are 3.2 for log P_{10}, 2.5 for log K_{10}, and 4.6 for log (C_{01}/P_r). Systems 113–120 list data for extractions employing 8 other organic solvents. These appear to involve the same species as do all the other xanthate extractions.

GENERAL REMARKS

The extracting species in all systems examined appears to be TlR while the predominant aqueous species appear to be Tl and/or TlR depending on the pH region. In addition, the aqueous species TlHR seems to be important at low pH values when a xanthate is employed as the chelating agent. When isobutanol, heptane, or methyl isobutyl ketone was used in connection with any of the xanthates, a low, virtually constant amount of extraction was noted throughout the entire pH range studied. This might be attributed to the solvent acting to form an extracting species since the amount of extraction into isobutanol was the same both with and without xanthate.

A comparison of the extractions by any one of the xanthate reagents into the variety of solvents employed indicates that extraction is more complete if polar solvents are used rather than non-polar solvents. This agrees with the results of ALIMARIN AND ZOLOTOV[3]. For example, consistently greater extraction into methylene chloride than into chloroform is seen and greater extraction into chloroform than into carbon tetrachloride. In addition, extraction into nitrobenzene is generally more complete than extraction into chlorobenzene, and extraction into chlorobenzene is generally more complete than extraction into toluene. This effect may be explained by considering the thallium(I) ion to be coordinately unsaturated[2]. If it is assumed that thallium(I) has a coordination number greater than 2, there will be open coordination sites after chelation with a monobasic bidentate ligand such as the xanthates. These positions will be occupied by water molecules and the relative ability of the solvent molecules to replace the water molecules will influence the amount of extraction. The more polar solvents will more readily coordinate with the chelate and thus produce greater extraction. The low extractions obtained with solvents like isobutanol and methyl isobutyl ketone may be assignable to the large solubilities of water in these organic media, these large amounts of water not favoring the replacement of water by isobutanol or the ketone.

From all the results it is recommended that the best extraction systems for thallium(I) are the ones involving 3-phenylpropylxanthate and chloroform, chlorobenzene, or methylene chloride. These systems evidence high *D* values at relatively low pH values.

SUMMARY

Studies of the extraction of thallium(I) from aqueous solution into an immiscible organic solvent have been made using 71 chelating reagent–solvent pairs involving 16 reagents and 17 solvents. The data have been analyzed to identify the predominant species involved, and association and partition constants have been estimated in many cases. The best extraction systems seem to be those involving 3-phenylpropylxanthate and chloroform, chlorobenzene or methylene chloride.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du thallium(I) en solution aqueuse, au moyen d'un solvant organique non-miscible, en utilisant 71 réactifs chélatants et des couples réactif–solvant comprenant 16 réactifs et 17 solvants. Les meilleurs systèmes semblent être ceux comprenant 3-phénylpropylxanthate et chloroforme, chlorobenzène ou chlorure de méthylène.

ZUSAMMENFASSUNG

Es wurden Versuche zur Extraktion des Thalliums(I) aus wässriger Lösung mit einem nicht mischbaren organischen Lösungsmittel durchgeführt. Dazu wurden mit 16 Reagenzien und 17 Lösungsmitteln 71 Kombinationen aus chelatbildendem Reagenz und Lösungsmittel untersucht. Die vorherrschenden Spezies wurden identifiziert und in vielen Fällen die Assoziations- und Verteilungskonstanten geschätzt. Die besten Extraktionssysteme scheinen die mit 3-Phenylpropylxanthat und Chloroform, Chlorobenzol oder Methylenchlorid zu sein.

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THE SPECTROPHOTOMETRIC DETERMINATION AND SOLVENT EXTRACTION OF OSMIUM WITH *o*-(β-BENZOYLTHIOURIDO)BENZOIC ACID AS REAGENT

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Thiourea[1-3] and its derivatives[4,5] give coloured complexes with osmium due to the presence of a =CS group linked to $-NH_2$ or $-NHR$. In this paper is reported the use of a new thiourea derivative, *o*-(β-benzoylthiourido)benzoic acid, which behaves as a highly selective spectrophotometric reagent and under certain conditions permits the determination of even 3 p.p.m. of osmium in the presence of almost all ions.

In strong hydrochloric acid medium, osmium forms with the reagent a brownish yellow complex, which is soluble in alcohol and in a number of organic solvents. The reaction is sensitive[9] and the colour system obeys Beer's law at 410 mμ from 3 to 18 p.p.m. of osmium. The extraction of the complex into organic solvents allows the determination of 3 p.p.m. of osmium, even when moderate amounts of many other ions including other platinum metals are present.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer was used with 10-mm corex glass cells.

A standard solution of osmium from its tetroxide was prepared as suggested by AYRES AND WELLS[5].

Standard solutions of other cations were prepared from their chlorides or nitrates and of anions from their ammonium or sodium salts; the strengths were determined by standard methods.

The reagent was prepared by the method of DOUGLASS AND DAINS[6]. A 1% (w/v) solution of the reagent in 95% ethanol was used.

All other reagents were of the highest chemical purity.

Absorbance curves

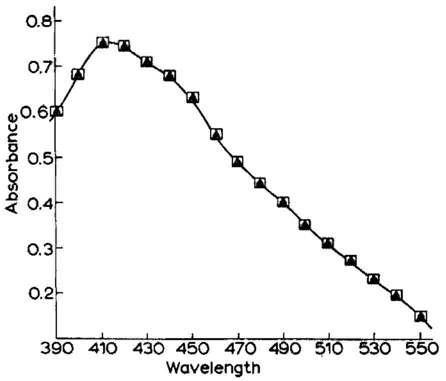
To a measured quantity of the osmium solution, 3 ml of the reagent were added and the acidity of the solution was adjusted to 4–6 *N* with respect to hydrochloric acid. The solution was then either diluted to 25 ml with 95% ethanol, or extracted and diluted to 25 ml with an organic solvent such as ethyl acetate, chloroform, benzene or tributyl phosphate. The absorbance of the solution was then measured against a reagent blank prepared in the same way. The absorbance curves (Fig. 1) show that the colour system has a maximum at 410 mμ, whether the solvent is ethanol, benzene, ethyl acetate, chloroform or tributyl phosphate.

Acidity, reagent and time

The optimum acidity of the colour system was studied with a definite amount of the metal solution and with varying concentrations of hydrochloric acid. The maximum colour intensity developed at 4–6 N hydrochloric aeid, and all subsequent measurements were therefore made in this range.

For 1.5–20 p.p.m. of osmium, 2 ml of the reagent were found sufficient to give full colour intensity. However, addition of more reagent had no effect.

Colour development was instantaneous at room temperature (30°) and the absorbance remained stable for 4 h.



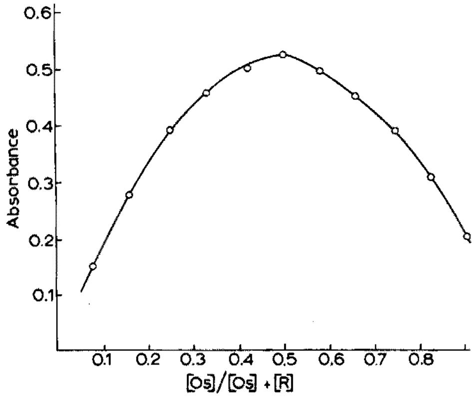


Fig. 1. Absorbance spectra for the osmium complex in various solvents.

Fig. 2. JOB's method.

Beer's law, optimum range, accuracy and sensitivity

The colour system was found to obey Beer's law from 3 to 18 p.p.m. of osmium. A RINGBOM plot[7] showed that the optimum range for measurement is 3.0–15.0 p.p.m. of osmium; in this range, the relative error per 1% absolute photometric error[8] is 2.75%.

Spectrophotometric sensitivity, calculated by the SANDELL method[9], was found to be 0.0157 μg/cm^2.

Composition of the complex

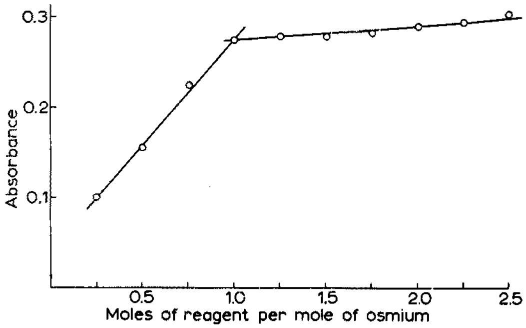
The composition of the coloured complex was determined by JOB's method of continuous variation[10] and the mole ratio method[11].

For the continuous variation method, equimolar solutions ($5.0 \cdot 10^{-4}$ M) of osmium and reagent were mixed in different proportions (12 ml of total mixture). The acidity of the mixtures was then adjusted and either the volumes were diluted to 25 ml with 95% ethanol or the colour species was extracted and diluted to 25 ml as described for the absorbance curve. The absorbances of the solutions were measured at 410 mμ. The maximum (Fig. 2) indicated that in solution the metal and the reagent combine in a ratio of 1:1.

For the mole ratio method, equimolar solutions ($5 \cdot 10^{-4}$ M) of the metal and the reagent were mixed in ratios varying from 1:0.25 to 1:2.5. After adjustment of acidity to the optimum value, the mixtures were diluted to 25 ml as mentioned earlier and the absorbances measured at 410 mμ. The plot obtained (Fig. 3) confirmed the formation of a 1:1 complex.

Dissociation constant

To evaluate the dissociation constant of the osmium complex, mixtures of non-equimolar solutions of the metal and the reagent were prepared as described for JOB's method and their absorbances were measured at 410 mμ. From the data obtained (Fig. 4) the dissociation constant, K, was evaluated by an equation reported previously[10]. Since the values of m and n are both equal to 1, K as calculated by substituting the values of X, p and c (Table I) is $1.7 \cdot 10^{-5}$.



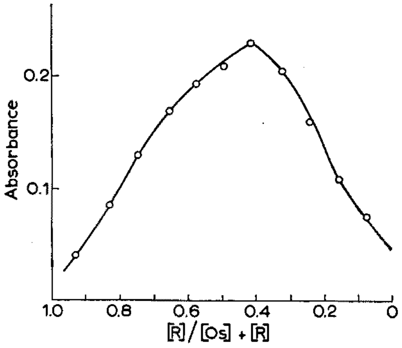


Fig. 3. Mole ratio method of composition.

Fig. 4. Measurement of dissociation constant (Os $= 1.5 \cdot 10^{-4}\ M$; reagent $= 7.5 \cdot 10^{-4}\ M$).

TABLE I

CALCULATION OF DISSOCIATION CONSTANT

Concn. of Os ($M \cdot 10^4$)	*Concn. of reagent ($M \cdot 10^4$)*	X	p	$K \cdot 10^5$
1.5	7.5	0.42	5	1.7

The degree of dissociation, α, and the dissociation constant, K, of the coloured osmium complex were also calculated from the equation of HARVEY AND MANNING[12] as given below.

$$K = \frac{(m\alpha c)^m (n\alpha c)^n}{c(1-\alpha)}, \quad \text{where} \quad \alpha = \frac{E_m - E_s}{E_m}.$$

The values of E_m and E_s being 0.305 and 0.275, $\alpha = 0.098$ and therefore $K = 4.17 \cdot 10^{-5}$.

Extraction and separation from other ions

The coloured complex on extraction into any of the organic solvents tested (chloroform, ethyl or amyl acetate, carbon tetrachloride, amyl alcohol, benzene or tributyl phosphate) has the same optical density and the same region of maximum absorption as it has in alcohol solution. Accordingly, any of those solvents may be used for the extraction and separation of osmium from other ions before its determination.

When 5 ml of ethyl acetate were used, as little as 3 p.p.m. of osmium could be extracted as the coloured species from Ir^{4+} (100), Ru^{3+} (100), Pt^{4+} (100), Rh^{3+} (100), Ni^{2+} (400), Co^{2+} (400), Ti^{4+} (400), Fe^{3+} (200), Mn^{2+} (400), Zr^{4+} (400), Cr^{3+} (400), UO_2^{2+} (400), Th^{4+} (400), Be^{2+} (400), Sr^{2+} (400), Ba^{2+} (400), Ca^{2+} (400), Mo^{6+} (400), Al^{3+} (400), W^{6+} (400), La^{3+} (400), Tl^{+} (400), Bi^{3+} (400), As^{5+} (400), Sb^{3+} (400), Cd^{2+} (400), Pb^{2+} (400), Zn^{2+} (400), Mg^{2+} (400), V^{5+} (400), Hg^{2+} (400) and rare earths (400). In parentheses are given the amounts in p.p.m. of ions taken. Palladium interfered but was removed as the azide complex by extraction with *n*-butanol[13] before the solvent extraction of osmium. Even 400 p.p.m. of each of the anions, citrate, oxalate, EDTA, tartrate and phosphate had no action on the colour system. Cu^{2+}, Ag^{+}, Au^{3+}, cyanide and fluoride, however, interfered.

Coordination complexes of other ions with this reagent and their analytical applications will be described later.

SUMMARY

o-(*β*-Benzoylthiourido)benzoic acid is proposed as a spectrophotometric reagent for the determination of osmium. The brownish yellow complex formed is soluble in alcohol and in other organic solvents. The colour system obeys Beer's law from 3 to 18 p.p.m. of osmium at 410 mμ with an optimum range of 3–15 p.p.m., where the percent relative error per 1% absolute photometric error is 2.75%. A 1:1 complex is formed and the dissociation constant is of the order of 10^{-5}. With prior extraction of palladium as the azide complex with *n*-butanol, osmium can be separated from almost all ions, including those of platinum metals, by extraction with ethyl acetate.

RÉSUMÉ

L'acide *o*-(*β*-benzoylthiourido)benzoïque est proposé comme réactif spectrophotométrique pour le dosage de l'osmium. Le complexe jaune brunâtre formé est soluble dans l'alcool et dans d'autres solvants organiques. La loi de Beer s'applique pour des concentrations de 3 à 18 p.p.m. d'osmium à 410 mμ. Il se forme un complexe (1:1) avec une constante de dissociation de l'ordre de 10^{-5}. Après une extraction préalable du palladium, l'osmium peut être séparé de presque tous les ions, y compris ceux du groupe du platine, par extraction au moyen d'acétate d'éthyle.

ZUSAMMENFASSUNG

o-(*β*-Benzoylthiourido)benzoesäure wird als spektralphotometrisches Reagenz für die Bestimmung von Osmium vorgeschlagen. Der gebildete braungelbe Komplex ist in Alkohol und in anderen organischen Lösungsmitteln löslich. Das Beersche Gesetz wird bei 410 mμ im Bereich von 3–18 p.p.m. Os befolgt. Der prozentuale relative Fehler beträgt etwa 3%. Es wird ein 1:1-Komplex gebildet; die Dissoziationskonstante liegt in der Grössenordnung von 10^{-5}. Nach vorhergehender Extraktion des Paladiums kann das Osmium von den meisten Ionen einschliesslich denen der Platinmetalle durch Extraktion mit Äthylacetat abgetrennt werden.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH FERRON

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7-Iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) is a well-known reagent for the detection and determination of iron. Neither the iron(III)–ferron complex nor the analogous inner complexes of other metals are soluble in chloroform or other organic solvents, so that it was initially believed[1] that they cannot be extracted from their aqueous solutions. It was later reported[2] that the iron(III) complex can be extracted with amyl alcohol, but no other information seems to be available. In the present work, it was observed that the ferron complexes of vanadium(V), iron(III), uranium(VI), molybdenum(VI), and tungsten(VI) can be extracted selectively into immiscible alcohols. Preliminary experiments showed that *n*-butanol gave the most satisfactory results. In this paper, investigations on the extraction and spectrophotometric determination of vanadium(V) with ferron as the chelating agent are described.

EXPERIMENTAL

Apparatus

A Beckman Model DU spectrophotometer was used with 1-cm corex cells. A Kaycee potentiometer with a Cambridge "Spot" galvanometer was used for potentiometric titrations; a saturated calomel half-cell and a bright platinum rod were used as reference and indicator electrodes with a saturated ammonium nitrate salt bridge.

Reagents

Vanadium(V) solution. A 0.01 *M* solution was prepared by dissolving the requisite amount of ammonium vanadate (Merck) in twice distilled water. The strength of the solution was checked by titration with a standard iron(II) solution.

Ferron solution. An aqueous 0.005 *M* solution was prepared from A.R. grade ferron (B.D.H.). More concentrated solutions could not be prepared due to solubility limitations.

Where necessary, sodium acetate–hydrochloric acid buffers were used. All chemicals used were of AnalaR quality.

Procedures

The following method was used to determine the vanadium in the two phases during the investigation of the optimum conditions and in the determination of the distribution ratio.

A solution (50.0 ml) containing the requisite amounts of vanadium(V) and ferron was equilibrated with 25.0 ml of *n*-butanol at the appropriate pH for 2 min. After separation, the vanadium content in the organic phase was back-extracted with 2 *M* ammonia until the organic phase became completely colorless. It was then washed twice with water and the back-extract and the washings were evaporated to dryness. Organic matter was destroyed by adding nitric acid and again evaporating to dryness. The residue was dissolved in 1 *M* sulphuric acid and dilute permanganate solution was added dropwise to the boiling solution until a slight excess was present, in order to oxidise any vanadium(IV). The solution was then titrated potentiometrically with standard iron(II) solution, the difference between the first and second breaks giving the vanadium content.

Effect of acidity

The most satisfactory extraction was obtained when the acidity was adjusted with sulphuric acid. The effect of pH (adjusted with sulphuric acid) on the extraction is shown in Fig. 1; the overall concentration of vanadium(V) was 0.001 *M* and that of ferron 0.003 *M*. It can be seen that the optimum pH is 1.

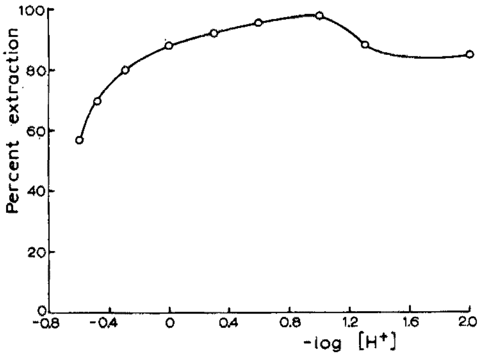


Fig. 1. Effect of pH on the extraction of vanadium(V).

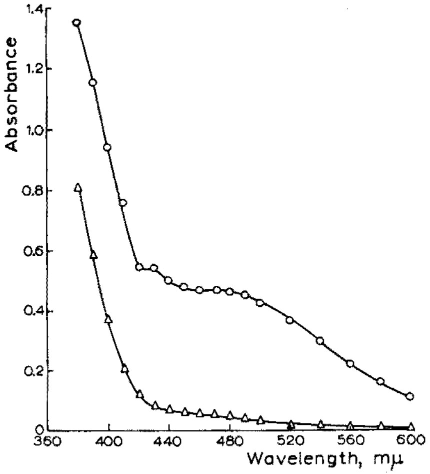


Fig. 2. Absorption spectrum of vanadium(V)–ferron complex extracted into *n*-butanol. Vanadium(V) $1.0 \cdot 10^{-4}$ *M*, ferron $2.0 \cdot 10^{-3}$ *M*. (○) vanadium(V)–ferron complex extracted into *n*-butanol; (△) reagent alone extracted into *n*-butanol. Acidity 0.05 *M* (H_2SO_4).

Effect of the concentration of alcohol and ferron on the extraction

The concentration of *n*-butanol in the organic phase was varied for a vanadium(V) concentration of 0.001 *M*, by preparing solutions of *n*-butanol in benzene. Benzene extracted neither the vanadium(V)–ferron complex nor pure vanadium(V) in the absence of alcohol under the experimental conditions. Extraction of vanadium(V) increased with the concentration of *n*-butanol and a maximum of 98% was achieved only when 100% alcohol was used. It was shown that with an aqueous phase of 50.0 ml, 25 ml (*i.e.* half of the aqueous phase) of *n*-butanol sufficed for the extraction.

The effect of the ferron concentration on the recovery of 0.05 millimoles of vanadium(V) was studied by carrying out extractions from 0.05 *M* sulphuric acid solutions. Maximum extraction of vanadium was achieved when the molar concentration of reagent was 2.5 times that of vanadium(V) and a further increase in the reagent concentration (up to a 5-fold excess) had no effect on the extraction.

Recovery of vanadium(V)

The effect of salting-out reagents such as sodium chloride, sodium sulphate, ammonium chloride, potassium chloride, magnesium sulphate, etc. on the extraction of vanadium was investigated in order to make the extraction quantitative in a single extraction step; unfortunately, no salting-out effect was apparent. However, it was found that the percentage extraction was improved to about 99 when a second extraction with another 25.0 ml of *n*-butanol was done. The results are presented in Table I.

TABLE I

PERCENTAGE RECOVERY OF VANADIUM(V)

Amount of vanadium(V) taken (millimoles)	*Recovery (%)*	
	Single extraction	*After second extraction*
0.025	98.2	99.0
0.050	97.8	99.2
0.075	97.6	99.1
0.100	97.5	99.2

Spectrophotometric determination of vanadium(V)

When aqueous solutions of vanadium(V) and ferron are mixed, a green soluble complex is produced with maximum absorbance at 530–550 mμ, the optimum pH being 1.85. The color is stable only for about 1 h and Beer's law is obeyed up to 41 μg of vanadium per ml. However, the absorbance increases with increasing concentration of ferron. BENT AND FRENCH's method and JOB's method indicated a 1:2 complex. In view of the interference of various other elements and low sensitivity, this method has no advantage over existing methods. On the other hand, the red color of the *n*-butanolic phase obtained by extracting vanadium(V) from 0.05 *M* sulphuric acid solution in presence of ferron was found to be very selective and sensitive. The absorption spectrum of this extract along with that for the reagent is given in Fig. 2. A very similar absorption spectrum was obtained when *n*-amyl alcohol was used in place of *n*-butanol. The color of the *n*-butanol extract was stable for more than 24 h. Under the optimum experimental conditions Beer's law was obeyed up to 15.3 μg of vanadium per ml. The sensitivity of the color reaction[2] and the molar absorptivity of the extract as calculated from the Beer's law plot at 430 mμ are 0.011 μg of vanadium per cm^2 and 4262 respectively.

Recommended procedure

Transfer an aliquot of vanadium(V) solution containing up to 15.3 μg of vanadium per ml to a 100-ml separatory funnel along with 15.0 ml of 0.005 *M* ferron solution. Dilute the contents to 25 ml with redistilled water maintaining the acidity at

0.05 *M* with respect to sulphuric acid; equilibrate with 25 ml of *n*-butanol for 2 min. After separation dry the organic phase over solid anhydrous sodium sulphate to remove the last traces of moisture and measure the absorbance of the extract at 430 mμ against a reagent blank, obtained by carrying out the extraction under identical conditions without vanadium. The results obtained were found to be accurate to within ±0.5%.

Study of interferences

The interferences of various substances were studied by extracting 127.4 μg of vanadium from 25.0 ml of aqueous phase in presence of the foreign substance under the optimum experimental conditions.

Complexing ions such as citrate, tartrate, phosphate, pyrophosphate, fluoride, etc., had no effect on the extraction and determination of vanadium even when present in 1000-fold amounts, whereas oxalate and EDTA seriously inhibited the extraction if present in more than 100-fold amounts. Al, Be, Cd, Ce(III), Co(II), Cr(III), Mg, Mn(II), Ni, Th, U(VI), V(IV) and Zn in 1000-fold amounts did not interfere with the determination of vanadium. Copper(II), at high concentrations (>100 times) formed a precipitate with the reagent but did not interfere with the vanadium determination provided that the reagent was present in large excess. Molybdenum(VI) and tungsten(VI) formed extractable yellow ferron complexes and hence interfered with the determination of vanadium although not with its recovery. The interference of iron(III), which formed a green extractable complex with ferron, was completely suppressed by adding excess of pyrophosphate. Reducing substances such as iron(II) should not be present, because they reduce vanadium(V) to vanadium(IV) which is not extracted under the experimental conditions.

COMPOSITION OF THE EXTRACTED SPECIES

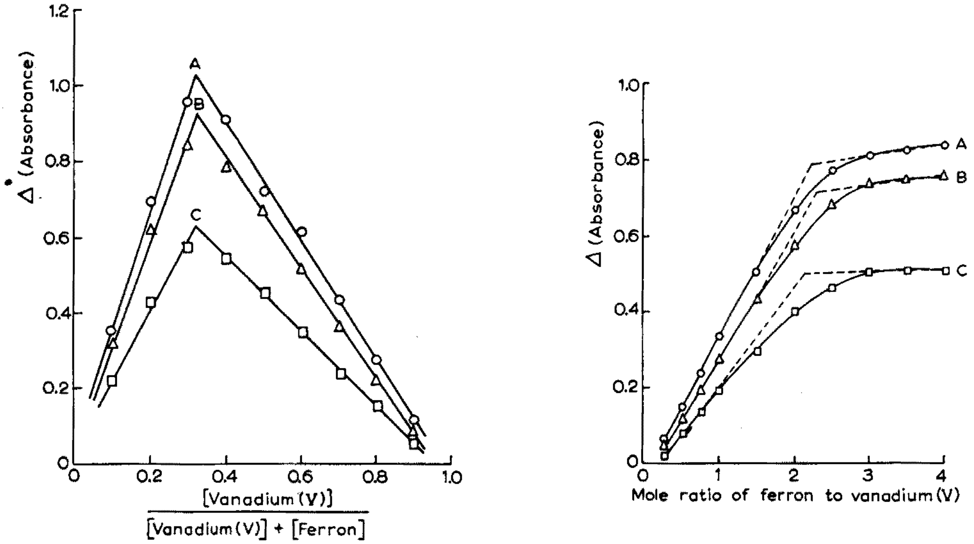
The ratio of vanadium(V) to ferron in the extracted species was determined by JOB's method of continuous variations[3] modified for the two-phase system[4,5]. Equimolar (0.001 *M*) solutions of vanadium(V) and ferron were mixed so that the mole-fraction of vanadium(V) varied from 0.0 to 1.0 keeping the total concentration of the two variables equal to $4 \cdot 10^{-4}$ *M*; the mixtures were made 0.05 *M* with respect to sulphuric acid and the total aqueous phase of 25.0 ml was then extracted for 2 min with 25.0 ml of *n*-butanol. After separation, the alcoholic layer was dried over anhydrous sodium sulphate and the absorbance measured against a blank obtained by carrying out the extraction under the same conditions without vanadium. The curves thus obtained at 430 mμ, 470 mμ and 540 mμ (Fig. 3) clearly indicated the formation of a 1:2 vanadium–ferron complex.

The JOB's curves give a sharp peak showing that the extracted species is a strong complex. Calculation by the slope ratio method[5,6] confirmed the formation of the 1:2 complex.

The composition of the extracting species was further examined by the molar ratio method[5,7] using the same technique for extraction and measurement of absorbance at 430 mμ, 470 mμ and 540 mμ. The overall concentration of vanadium in these experiments was $2 \cdot 10^{-4}$ *M*. The curves in Fig. 4 clearly show that the species contained vanadium and ferron in the ratio 1:2.

Figure 5 shows the graphs obtained by plotting log (distribution ratio) against log (ferron concentration) for a constant vanadium(V) concentration of 0.002 *M*; for the sake of completeness, data were obtained for extractions from aqueous phases which were 0.05 *M* and 0.5 *M* in sulphuric acid, the extraction being carried out with *n*-butanol. The slopes of the straight line portions show that the ratio vanadium : ferron was 1 : 2.

Similar experiments were carried out with fixed concentrations of vanadium(V)



Figs. 3–4. Nature of the vanadium(V)–ferron extracted species: Fig. 3, JOB's method; Fig. 4, molar ratio method. λ: (○) A = 430 mμ; (△) B = 470 mμ; (□) C = 540 mμ. Acidity 0.05 *M* (H_2SO_4).

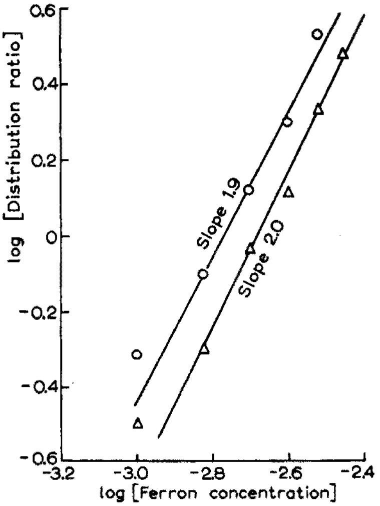
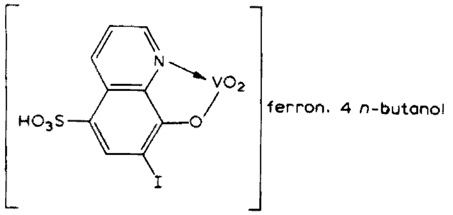


Fig. 5. Nature of the vanadium(V)–ferron extracted species: log–log plot. Acidity: (○) 0.05 *M* (H_2SO_4); (△) 0.50 *M* (H_2SO_4).

(0.001 *M* overall) and ferron (0.003 *M* overall) in the aqueous phase but the extraction was done with a solution of *n*-butanol in benzene. The curves showed that the ratio of vanadium to *n*-butanol in the extracted species was 1:4. Evidently the composition of the extracted species is vanadium:ferron:*n*-butanol = 1:2:4.

Since in solutions of pH below 2, vanadium(V) exists unambiguously as VO_2^+ [8,9] it may be assumed that the original complex is a neutral vanadyl–ferron species and this extracts with another molecule of ferron attached as an adduct. However, this species would be highly hydrophilic in view of the $-SO_3H$ group present, and has to be rendered hydrophobic before considerable extraction takes place. For the species to be rendered hydrophobic, the addition of 4 *n*-butanol molecules is apparently required. It is possible that the alcohol molecules merely replace 4 water molecules associated with the complex. The extracted species can probably be represented as



Two of us (N.K. and D.S.) are grateful to the Council of Scientific and Industrial Research (India) for the award of Research Fellowships.

SUMMARY

Various metal complexes of 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) were found to be selectively extracted into immiscible alcohols. Vanadium(V) is almost completely extracted into *n*-butanol in a single extraction from solutions which are 0.05 *M* in sulphuric acid. A sensitive and selective spectrophotometric method can be based on this extraction. Beer's law is obeyed up to 15.3 μg of vanadium per ml; the sensitivity of the color reaction is 0.011 μg of vanadium per cm^2 at 430 mμ. The interference of iron(III) can be eliminated by adding excess pyrophosphate. The extracted species appears to contain vanadium, ferron and *n*-butanol in the ratio 1:2:4.

RÉSUMÉ

Divers complexes métalliques de l'acide iodo-7-hydroxy-8-quinoléine sulfonique-5 (ferron) peuvent être extraits sélectivement dans des alcools non miscibles. Le vanadium(V) est extrait presque complètement dans le *n*-butanol en une simple extraction, à partir de solution 0.05 *M* en acide sulfurique. Une méthode spectrophotométrique, sensible et sélective, est proposée. La loi de Beer s'applique jusqu'à 15.3 μg/ml de vanadium. Sensibilité: 0.011 μg de vanadium par cm^2 à 430 mμ. Le fer(III) est masqué par un excès de pyrophosphate.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Vanadium(V) vorgeschlagen, bei der der Metallkomplex der 7-Jodo-8-hydroxychinolin-5-sulfonsäure (Ferron) selektiv mit Alkoholen extrahiert wird. Vanadin wird fast vollständig in einem Schritt mit *n*-Butanol aus 0.05 *M* Schwefelsäure extrahiert und spektralphotometrisch bestimmt. Das Beersche Gesetz wird bis hinauf zu 15.3 μg V/ml befolgt; die Empfindlichkeit der Farbreaktion beträgt 0.011 μg V/cm^2 bei 430 mμ. Störungen durch Eisen(III) können durch einen Überschuss an Pyrophosphat eliminiert werden. Die extrahierten Spezies scheinen Vanadin, Ferron und *n*-Butanol im Verhältnis 1:2:4 zu enthalten.

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DETERMINATION OF ZIRCONIUM IN ZIRCONIUM METAL AND ZIRCONIUM POWDER BY USE OF MANDELIC ACID

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There is presently no satisfactory method for the determination of zirconium in zirconium metal or zirconium powder. The comprehensive works on the analysis of zirconium metal[1-3] do not give a method for the determination of zirconium. A method for the determination of zirconium in zirconium powder by use of selenious acid[4] is inaccurate according to the experiences of this and other laboratories. A method for zirconium in zirconium powder whereby the zirconium is separated with cupferron and is ignited to the oxide[5] is troublesome because corrections must be made for iron, titanium, and other elements precipitated by cupferron. A method for zirconium in zirconium powder whereby the zirconium is precipitated with ammonium hydroxide and is ignited to the oxide[6] has the disadvantage that corrections must be made for iron, titanium, aluminum, and other elements precipitated by ammonium hydroxide.

In view of the need for a method for the determination of zirconium in zirconium metal and zirconium powder, this laboratory undertook the development of a satisfactory method.

Various approaches to the problem were considered. The EDTA titration method[7] was not found to be satisfactory for the determination of zirconium in zirconium metal or zirconium powder because of interferences. The zirconium phosphate method[7] gave low results when applied to the determination of zirconium in zirconium metal or zirconium powder. The use of mandelic acid or its derivatives seemed to offer the best possibilities.

The use of mandelic acid for the determination of zirconium was first proposed by KUMINS in 1947[8]. Since that time mandelic acid has been used for the determination of zirconium in all kinds of materials, containing traces to fairly large amounts of zirconium[7,9-22]. No study has been made of the use of mandelic acid or its derivatives for the determination of zirconium in zirconium metal or zirconium powder.

Previous investigators have generally agreed that the acidity for the precipitation of zirconium by mandelic acid or its derivatives is not critical (acidities of 0.1 to 8 M have been used). Hydrochloric acid is the preferred medium although small amounts of sulfuric acid have been found not to interfere. The precipitation is usually made from a hot solution. *p*-Bromomandelic acid and to a lesser extent *p*-chloromandelic acid have been recommended by some investigators for the determination of smaller amounts of zirconium, because zirconium *p*-bromomandelate and zirconium *p*-chloromandelate are somewhat less soluble than zirconium mandelate. Mandelic acid, however, is much more widely used than the halomandelic acids. Zirconium mandelate is usually washed with a solution containing mandelic acid and hydrochloric acid, while zirconium *p*-bromomandelate and zirconium *p*-chloromandelate are usually washed with water. The precipitate is ordinarily ignited to the oxide. The technique of weighing as zirconium mandelate, zirconium *p*-bromomandelate, or zirconium *p*-chloromandelate, after washing with ethanol and drying at 100–120°, is troublesome because the composition of the precipitate is not exactly stoichiometric.

EXPERIMENTAL

Reagents

Mandelic acid solution (15%). Dissolve 75 g of DL-mandelic acid in water and dilute to 500 ml.

Mandelic acid wash solution. Dissolve 25 g of DL-mandelic acid in 400 ml of water, add 10 ml of hydrochloric acid, and dilute to 500 ml.

Procedure

If the sample is a powder, transfer a portion of it to a Buchner funnel containing a Whatman No. 41H filter paper, wash with acetone and ether, transfer to a watch glass, dry in an oven at 60° for 1 h, and store in a stoppered bottle.

Transfer a 0.23–0.25-g sample (weighed to 0.1 mg) to a large platinum dish. Add 15 ml of water, 10 ml of sulfuric acid (1:1), 5 ml of nitric acid, and 2 ml of perchloric acid. Cover with a plastic (or wax-covered) watch glass. Add 5 ml of hydrofluoric acid in 0.5-ml portions from a plastic medicine dropper, while swirling the platinum dish and allowing about 1 min between additions. After the final addition, allow to stand for 5 min to complete the dissolution and then wash down the watch glass with water. Evaporate to fumes of sulfuric acid at gentle heat without the watch glass, remove the dish from the hot plate, cool it in water, wash down the sides with water, and swirl. Again evaporate to fumes of sulfuric acid at gentle heat, then raise the temperature of the hot plate to moderate heat, and evaporate to dryness and the disappearance of fumes. Cool somewhat, add 50 ml of water and 10 ml of hydrochloric acid, swirl, and heat on the hot plate at gentle heat until the solution is clear. Wash into a 400-ml beaker and police the platinum dish.

Dilute to *ca.* 100 ml, put in a stirring rod, and heat to about 80° on the hot plate. Add 75 ml of mandelic acid solution (15%) from a graduate over a period of 15–30 sec while stirring with a stirring rod. Stir frequently during the next 5 min. Cover with a watch glass and allow to stand at about 80° for 40 min while stirring occasionally. Wash down the cover lid with water, filter through a Whatman No. 40 filter paper, and collect the filtrate in a clean 400-ml beaker. Police the stirring rod and beaker, and wash the filter paper and precipitate with mandelic acid wash solution. Place the filter paper and precipitate into a tared platinum crucible and heat on the hot plate at highest heat for 1 h or more.

Within 30 min after the filtration, wash the filtrate into the original 400-ml beaker, cover with a watch glass (but do not insert a stirring rod), and heat to about 80° on the hot plate. Place the beaker in an oven at about 80°, cover with an inverted 1-l beaker, and allow to stand overnight. Filter through a Whatman No. 40 filter paper and transfer and wash with mandelic acid wash solution. Place the filter paper into the crucible containing the first precipitate and heat on the hot plate at the highest heat for 1 h or more. Burn off the carbonaceous material over the low flame of a Meker burner, then heat over the full flame of the Meker burner until the precipitate is white. Ignite over a blast burner for 20 min, cool in a desiccator, and weigh.

Calculate as follows:

$$\% \text{ Zr} (+\text{Hf}) = \frac{74.03 \times \text{g of precipitate}}{\text{g of sample}}$$

RESULTS AND DISCUSSION

Dissolution of the sample

Zirconium can only be dissolved by treatment with a medium containing hydrofluoric acid or by fuming with a mixture of sulfuric acid and a sulfate. The latter method of attack gave erratic results for the mandelic acid precipitation, hence a hydrofluoric acid medium was selected.

At first, the sample was dissolved in a mixture of hydrofluoric and sulfuric acids and the solution evaporated to fumes of sulfuric acid. Subsequently, in order to destroy organic matter (carbides) perchloric and nitric acids were added and the solution was evaporated to a low volume in order to drive off the perchloric and nitric acids. Later it was found that more complete precipitation of the zirconium was obtained if the sulfuric acid solution was evaporated to dryness and the residue dissolved in dilute hydrochloric acid (10 ml of hydrochloric acid and 50 ml of water). The barest trace of fluoride caused low results, hence to ensure complete removal of fluoride the sides of the platinum dish were washed down after the initial fuming and the solution was again evaporated to fumes. Dissolution of the sample in a mixture of hydrofluoric and perchloric acids, followed by evaporation to fumes of perchloric acid caused low results for reasons that were not clear.

Precipitation with mandelic acid

The manner of adding the mandelic acid was not critical. The same result was obtained whether the mandelic acid solution was added dropwise from a buret, slowly from a graduate over a period of 15–30 sec, or at one stroke from a graduate. The addition of the mandelic acid solution from a graduate over a period of about 15 to 30 seconds is recommended.

The digestion time for the precipitation at 80° was 40 min; allowing the solution to digest for 1½, 3, and 7 h did not give a better recovery. In fact, the recovery was less, since prolonged heating caused the precipitate to adhere to the sides of the beaker. Allowing to stand for several hours at room temperature did not give a better recovery. The acidity had no significant effect.

Regardless of the method of precipitation used or whether *p*-bromomandelic acid or *p*-chloromandelic acid was used in place of the mandelic acid, complete precipitation of the zirconium could not be obtained (1–3 mg of zirconium was always found in the filtrate). The probable reason for incomplete precipitation is that a portion of the large amount of precipitate always dissolved during the transferring and washing operation, particularly since many treatments with a policeman were necessary to remove the precipitate from the beaker. There is no information available concerning the solubility of zirconium mandelate in the mandelic acid–hydrochloric acid wash solution. However, BELCHER, SYKES AND TATLOW[10] give the solubility of zirconium mandelate and zirconium *p*-bromomandelate in water at 25° as 0.1560 and 0.0446 g/l, respectively.

Experiments were conducted on the use of a wash solution prepared by saturating the usual mandelic acid–hydrochloric acid solution with zirconium mandelate and filtering. However, the results obtained for zirconium by use of such a wash solution were inclined to be erratic, so the technique is not recommended. One difficulty with using a saturated solution of zirconium mandelate is that saturation depends upon the temperature, a factor that changes during the washing. It is to be noted that the variation in results for the solubility of zirconium mandelate and zirconium *p*-bromomandelate in water (for 5 determinations) was ±0.01 g/l[10].

Attempts were made to determine the unprecipitated zirconium in the filtrate spectrophotometrically after the mandelic acid precipitation with the intention of determining the total zirconium. However, the technique did not give satisfactory results with the spectrophotometric reagents tested (alizarin and morin[23]). Before using the spectrophotometric method it was necessary to destroy the mandelic acid in the filtrate. This could only be done by the tedious procedure of fuming with sulfuric acid and repeatedly adding nitric acid. Attempts to destroy the mandelic acid by treatment with nitric and perchloric acids and evaporation to fumes of perchloric acid caused a mild explosion.

In view of the failure of the spectrophotometric technique it was decided to recover the residual zirconium by other means. It was found that the zirconium in the filtrate could be completely recovered by allowing the filtrate to stand overnight at 80° (in an oven). Heating at 80° for 6 h or allowing to stand overnight at room temperature did not give complete recovery of the zirconium.

The mandelic acid–hydrochloric acid solution used to wash the precipitates contained 5% mandelic acid and 2% hydrochloric acid. Too high a hydrochloric acid concentration increased solubility losses on washing.

Ignition of the precipitate

The manner of charring and burning off the organic matter and igniting the precipitate offered problems in working with large amounts of zirconium.

At first, the filter paper and precipitate were charred and the organic matter was burned off by heating over the low flame of a Meker burner. However, it was found that low results were obtained by this technique, probably because of mechanical expulsion of some of the precipitate by the cloud of carbon produced. It was found that the losses could be eliminated by heating the platinum crucible containing the paper and precipitate on the hot plate at highest heat for 1 h so as to decompose the zirconium mandelate. The organic matter that was left was then readily burned off over a Meker burner without the formation of a cloud of carbon. It is believed that the reason for the effectiveness of the hot plate technique is that it controls the decomposition of the zirconium mandelate over the temperature range at which the decomposition is vigorous.

Previous investigators have usually recommended 800° to 1000° for the final ignition of the precipitate to zirconium dioxide, although some do not specify a temperature. The findings from thermogravimetric studies of previous investigators are not necessarily applicable to the present problem, since in thermogravimetric studies much less zirconium dioxide is handled than in the proposed method. According to the thermogravimetric studies of STACHTCHENKO AND DUVAL[24] on zirconium mandelate, there is an extremely rapid decrease in weight from 200° to 300°, then a moderately rapid decrease to about 550°, then a slower decrease to 700°, and finally a slow increase to 959°, at which point constant weight is obtained. The thermogravimetric studies of ADAMS AND HOLNESS[9] on zirconium mandelate show an extremely rapid decrease from 200° to 350°, then a moderately rapid decrease to about 600°, and finally a very slight decrease to 1000°, at which point constant weight is obtained.

According to experiences in this laboratory it is necessary when working with larger amounts of zirconium to ignite over a blast burner (temperature 1100°–1200°) to obtain constant weight. If the precipitate obtained in the determination of zirconium in zirconium metal or zirconium powder is first ignited at 1000° for 1 h and then over a blast burner for 20 min, there will be a decrease in weight between the two ignitions of approximately 1 mg. This amount of zirconium dioxide represents 0.3% zirconium (on a 0.25-g sample). Twenty minutes is an adequate length of time for the ignition over the blast burner. Heating for additional 30 min caused an insignificant loss of 0.1 mg.

HILL AND MILES[14] and OESPER AND KLINGENBERG[17] recommended filtering the zirconium mandelate through a Selas filtering crucible and igniting at 1000°. This technique cannot advantageously be applied to the method described in the present paper since two crucibles would have to be used, thus doubling the error due to weighing. Also, Selas crucibles lose a significant amount of weight when heated in a blast burner. Ignited zirconium dioxide is non-hygroscopic.

Size of sample

A 0.23- to 0.25-g sample was found to be ideal for obtaining maximum accuracy. When a sample much larger than 0.25 g was used, the zirconium sometimes hydrolyzed before the mandelic acid was added.

Effect of hafnium and other elements

Hafnium, the sister element of zirconium, is quantitatively precipitated by mandelic acid and is counted with the zirconium. There is an error caused by the determination of zirconium plus hafnium, since the factor for converting zirconium dioxide to zirconium is 0.7403, whereas the factor for converting hafnium dioxide to hafnium is 0.8481. The amount of hafnium found in ordinary commercial zirconium is about 2%. This amount of hafnium will cause a negative error in the result for zirconium plus hafnium of about 0.25%. There is a considerable amount of zirconium containing less than 0.02% hafnium being produced for atomic energy purposes. Much of the scrap from this purified metal is available for producing zirconium powder for normal civilian uses.

Ordinarily, it will suffice to determine the total of zirconium plus hafnium calculated as zirconium. This is particularly true of zirconium powders which have a minimum requirement for zirconium plus hafnium calculated as zirconium (usually 95% or 96%[4,6]). For materials for which separate results for zirconium and hafnium are desirable, this laboratory determines the percent hafnium in the sample spectrographically[1] on the ignited and weighed mixed oxides from the mandelic acid precipitation. The amount of hafnium dioxide in the precipitate is then deducted and the percent of zirconium is calculated.

No other elements found in zirconium metal or zirconium powder interfered with the method. This was to be expected from the studies on interferences by previous investigators.

Recovery of mandelic acid

Zirconium mandelate and other mandelates were not extractable with organic solvents. It would seem feasible, therefore, to recover the mandelic acid by extracting with an organic solvent. It was found that about 7 g of the 11.25 g of mandelic acid originally added could be recovered by extracting twice with 75-ml portions of diethyl ether and evaporating to dryness. The recovered material was white and had a melting point of 114° (the m.p. listed in the handbooks is 118°). Whether recovery of the mandelic acid would be worthwhile under usual circumstances is questionable since that reagent is only moderately expensive. Recovery might be worthwhile for the more expensive *p*-bromomandelic or *p*-chloromandelic acids.

Results for zirconium in zirconium metal and zirconium powder

The results obtained for zirconium on typical samples of zirconium metal and zirconium powder are shown in Table I. The results show good precision and are in satisfactory agreement with the results obtained for zirconium (plus hafnium) calculated by difference.

TABLE I

RESULTS FOR ZIRCONIUM (PLUS HAFNIUM) IN SAMPLES OF ZIRCONIUM METAL AND ZIRCONIUM POWDER

Sample	*Contains (%)*	*% Zr (+ Hf) by difference*	*% Zr (+ Hf) found*
Zr wire	0.01 Hf; $<$ 0.1 impurities	$>$99.9	99.86, 99.96, 99.92 Av. 99.91
Zr powder 1	0.01 Hf; 0.63 O, 0.01 H, 0.03 C, 0.01 Fe, 0.07 N, 0.00 Si, 0.02 Cl, 0.01 Ti, 0.00 Mo, 0.00 Al	99.22	99.32, 99.36, 99.39 Av. 99.35
Zr powder 2 (Zircaloy)	0.01 Hf; 1.43 O, 0.46 H, 0.13 C, 0.26 Fe, 0.04 N, 0.00 Si, 0.01 Cl, 0.01 Ti, 0.00 Mo, 0.00 Al, 0.02 Ni, 0.05 Cr, 1.10 Sn	96.49	96.46, 96.33, 96.39 Av. 96.39
Zr powder 3	2.0 Hf; 0.82 O, 0.05 H, 0.16 C, 0.44 Fe, 0.03 N, 0.22 Si, 0.03 Cl, 0.06 Ti, 0.21 Mo, 0.50 Al	97.5	97.24, 97.29, 97.19 Av. 97.24
Zr powder 4	1.8 Hf; 0.77 O, 0.08 H, 0.19 C, 1.00 Fe, 0.52 N, 0.08 Si, 0.02 Cl, 0.06 Ti, 0.31 Mo, 0.00 Al	97.0	96.91, 96.86, 96.79 Av. 96.85

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SUMMARY

An accurate gravimetric method is proposed for the determination of zirconium in zirconium metal and zirconium powder by use of mandelic acid. The sample is dissolved in a mixture of hydrofluoric, nitric, perchloric and sulfuric acids, the solution is evaporated to dryness, and the salts are dissolved in dilute hydrochloric acid. Zirconium mandelate is precipitated at 80°. The residual zirconium in the filtrate is recovered by heating at 80° overnight and the combined precipitates are ignited to zirconium dioxide. An investigation was made of the factors involved in the dissolution of the sample, precipitation with mandelic acid, ignition of the precipitate, and size of sample. The effect of hafnium is discussed.

RÉSUMÉ

Une méthode gravimétrique précise est proposée pour le dosage du zirconium dans le zirconium métal et dans de la poudre de zirconium, en utilisant l'acide mandélique. L'échantillon est traité par un mélange d'acides fluorhydrique, nitrique, perchlorique et sulfurique; la solution est évaporée à sec; les sels sont dissous dans l'acide chlorhydrique dilué. Le mandélate de zirconium est précipité à 80°. Le zirconium restant dans le filtrat est récupéré par chauffage à 80° pendant une nuit. Les deux précipités combinés sont calcinés en oxyde de zirconium.

ZUSAMMENFASSUNG

Es wird eine genaue gravimetrische Methode zur Bestimmung von Zirkonium in Zirkoniummetall und Zirkoniumpulver mit Hilfe von Mandelsäure vorgeschlagen. Die Probe wird in einer Mischung von Salz-, Salpeter-, Perchlor- und Schwefelsäure gelöst, die Lösung bis zur Trockne eingedampft und die Salze wieder in verdünnter Salzsäure gelöst. Zirkoniummandelat wird bei 80° gefällt. Das in dem Filtrat zurückbleibende Zirkonium wird durch Erwärmen auf 80° über Nacht gewonnen und die vereinigten Niederschläge zu Zirkoniumdioxid verglüht. Folgende Faktoren wurden untersucht: Die Auflösung der Probe, die Fällung mit Mandelsäure, das Verglühen des Niederschlages und die Grösse der Probe. Der Einfluss des Hafniums wird diskutiert.

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A VOLUMETRIC DETERMINATION OF ARSENIC AND ANTIMONY IN MIXED MANGANESE ARSENIDE, ANTIMONIDE AND PHOSPHIDE COMPOUNDS

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In order that reliable measurements of the thermomagnetic and crystallographic properties of a series of compounds manganese arsenide–phosphide and manganese arsenide–antimonide could be made[1], considerable care was required in their preparation. Because of the sensitivity of the magnetic properties to stoichiometry and impurities, and because of the strong tendency of these materials to be nonstoichiometric in the direction of excess manganese, it was necessary to develop suitable analytical procedures to establish the quality of the compounds and the preparation procedure.

Past procedures for arsenic and antimony have generally called for their separation before determination, *e.g.* by precipitation as sulfides or by fractional distillation of the trichlorides. A volumetric procedure without separation was preferred to circumvent the errors and the involved procedure of separation.

According to HILLEBRAND AND LUNDELL[2], the most accurate method for the determination of antimony, in amounts greater than a few milligrams, is the permanganate oxidation of antimony(III) to the pentavalent form in sulfuric–hydrochloric acid solution. Further, the arsenic(III) oxide–permanganate reaction is of such dependable character that it is considered one of the best for standardization of permanganate solutions[3]. Thus, if antimony could be selectively reduced in the presence of arsenic, permanganate titration appeared to be a desirable procedure.

MCCAY[4] achieved selective reduction of antimony(V) in the presence of arsenic(V) and other metal ions using mercury in hydrochloric acid. The method involved violent shaking of the antimony solution with mercury in a closed flask thoroughly purged of air. Attempts to use this procedure did not yield satisfactory results, but re-evaluation of techniques, materials, and procedures indicated that these tests may not have been entirely reliable.

One of the outstanding features of the oxidation–reduction methods for arsenic is the need for effective catalysts. Iodide and osmic acid are the 2 most commonly used, but iodide is often complexed by other ions, *e.g.* mercury(II), and osmic acid is rendered ineffective by even moderate concentrations of chloride.

Oxidation and reduction of antimony in aqueous solution is generally carried out in the presence of chloride and the concentration of chloride appears to be important to satisfactory results. PUGH[5] indicates that the concentration of hydrochloric

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acid and sulfuric acid are interdependent and he gives optimum concentrations of each. The acid concentration is also important because of the tendency of antimony to hydrolyze and precipitate.

Mercury(I) chloride appeared advantageous over mercury for the selective reduction of antimony because of a somewhat lower oxidation potential than the mercury–mercury(I) couple. The large surface area of a fine powder should lead to considerably better rates of reaction without need of shaking.

EXPERIMENTAL

Reagents

Arsenic(III) oxide. Baker and Adamson, primary standard grade. General Chemical Div., Allied Chemical and Dye Corp., New York.

Antimony metal. The Consolidated Mining and Smelting Co. of Canada, Ltd., Grade H.P., 99.999%.

Potassium permanganate solution. Certified reagent solution (concentrated) (Fisher Scientific Company, Fairlawn, New Jersey) was diluted, filtered and standardized against arsenic(III) oxide.

Other chemicals used were of analytical reagent grade.

Total combined arsenic and antimony

Arsenides, antimonides and phosphides are often difficult to dissolve, usually requiring a strong oxidizing attack. This treatment also minimizes the loss of the elements as hydrides. Acidic bromate solutions, which will dissolve many such transition metal compounds, serve well for the compounds of these elements with manganese.

Antimony metal, used as a standard in this work, does not dissolve in acidic bromate media, but is best dissolved in hot, concentrated sulfuric acid[5]. After cooling, the solution was diluted with water approximately 1:1 and purged of excess sulfur dioxide by heating. Arsenic(III) oxide, when used, was dissolved in this antimony solution. Solid potassium permanganate was added until a slight pink color remained. This oxidized the lower valent compounds of sulfur and promoted the arsenic and antimony to the pentavalent state. The solution was then diluted with water to yield 5 M sulfuric acid.

General procedure

To the finely ground Mn (P, As) or Mn (As, Sb), containing about 1 millimole of (As + Sb), were added 10 ml of water, an excess of saturated aqueous sodium bromate solution (usually 1–2 ml depending on the phosphide content) and 1 ml of 10 M (1:1) sulfuric acid. This was warmed until the compound was dissolved. Care was needed to dissolve occluded particles in the manganese dioxide formed, and total solution sometimes required several hours. Concentrated sulfuric acid (11 ml) was added to decompose the excess of bromate. To drive out the bromine formed, the solution was concentrated by gentle heating for a few hours in an air stream yielding a purple solution containing manganese(III). Except in the determination of antimony, traces of bromine (or iodine) do not interfere, since they are reduced later and complexed by the mercury(II) added. To this solution was added 20 ml of water, followed by 1–2% hydrogen peroxide dropwise to reduce manganese(III) compounds; the solution was then gently heated to destroy the excess of hydrogen peroxide. The solution was diluted to 40 ml to produce 5 *M* sulfuric acid.

To the 5 *M* sulfuric acid solutions containing the arsenic and antimony standards or the unknowns (the manganese compounds), as prepared above, was added 1 drop of aqueous 0.1 *M* potassium iodide as catalyst. The arsenic(V) and antimony(V) were next reduced to the trivalent state by adding 275 mg of solid tin(II) chloride dihydrate and heating at 75° for 2 h. (For *Variation 1* below with arsenic alone, use 300 mg of $SnCl_2 \cdot 2\ H_2O$; see discussion.)

Variation 1 (with or without antimony). Instead of destroying the large excess of tin(II) with mercury(II) chloride, as is done in the well-known procedure for iron, it was eliminated by allowing the solution to stand overnight. Since a little arsenic(III) might be reoxidized, 0.6–0.8 ml of fresh 0.05 *M* tin(II) chloride in 5 *M* sulfuric acid was added and the solution was maintained at 75° for 1 h and then cooled to 15° (see discussion). On adding 2.7 ml (1.5 ml if antimony present) of 1.3 *M* sodium chloride and 2 ml of 0.1 *M* mercury(II) chloride, very little mercury(I) chloride precipitated; this precipitate was allowed to age for 1.5 h at 15–20°. The solution was then diluted to about 150 ml, and 10 drops of 0.01 *M* osmic acid solution in 0.1 *M* sulfuric acid were added for the titration.

When arsenic but not antimony was present, titration with 0.1 *N* potassium permanganate was carried out dropwise at 25–30° with good stirring and in the presence of the mercury(I) chloride. In this case the end-point was taken as the first color lasting about 10 sec. Ferroin could not be used since it is adsorbed by mercury(I) chloride.

When antimony was present, the amount of permanganate required was estimated and titration carried out in the presence of the mercury(I) chloride until all the arsenic and one-quarter to one-half, but no more, of the antimony was oxidized. No arsenic end-point appeared. (During the reduction with tin(II), some antimony may hydrolyze where condensed moisture runs down into the solution. To minimize this, the water-bath level was maintained above the liquid level.) The solution was allowed to stand for 30 min at 20°–25°, then 30–35 ml of concentrated hydrochloric acid were added, and the solution stood for 30 min at 15°–20°. It was then filtered through medium-fine sintered glass, the mercury(I) chloride washed with a little 2 *M* hydrochloric acid, and the filtrate cooled to 0°–5° and titrated potentiometrically[6] with 0.1 *N* permanganate using platinum–calomel electrodes. The sum of the 2 titrations gives the total combined arsenic and antimony in moles. Two blanks were included.

Variation 2 (no antimony). The reduced solution was cooled to 15° and 2.7 ml of aqueous 1.3 *M* sodium chloride and 3 ml of aqueous 0.1 *M* mercury(II) chloride were added. The solution was allowed to stand at least 15 min at 15° in a water bath to precipitate mercury(I) chloride. Chloride slows the precipitation of $SnO_2 \cdot xH_2O$ during the titration, but too much chloride leads to bad end-points, apparently by poisoning the osmic acid catalyst which is added later. The mercury(I) chloride was filtered off on medium sintered glass and washed with water. The filtrate was then diluted to about 150 ml and 3 drops of 0.01 *M* osmic acid solution in 0.1 *N* sulfuric acid were added. (Iodide is complexed by mercury(II) and rendered ineffective as a catalyst.) The solution was then titrated dropwise with 0.1 *N* permanganate to a little before the end-point, one drop of 0.025 *M* ferroin then being added and the titration continued to the complete decolorization of the ferroin. Two blanks were done, starting from the bromate step. Only a little tin(II) chloride was needed here.

Total antimony

Antimony may be selectively reduced and determined in the presence of arsenic(V). A new sample was prepared (using 0.1 millimole Sb), reducing most of the manganese(III) with 1–2% hydrogen peroxide. After addition of 105 ml of water, 30 ml of concentrated hydrochloric acid, 1 g of solid mercury(II) chloride and 3 g of mercury(I) chloride (total vol. 165 ml; contains 11 ml of 18 *M* sulfuric acid), the solution was heated for a total of 12 h at 95° in a 500-ml flask covered by a beaker with swirling every 45 min while the flask was being heated. It may be allowed to stand overnight between heatings. After cooling and standing for 1 h, the solution was filtered, washing with 2 *M* hydrochloric acid. Titration was done potentiometrically at 0°–5° as in *Variation 1*. No blanks were necessary since they amounted to only 0.01–0.02 ml.

Unless a mat of mercury(I) chloride is present, traces of this salt can pass through a sintered glass filter and will add to the antimony titre. This means refiltering the first solution to remove traces of the precipitate (also in *Variation 1* when antimony is present but not in *Variation 2*).

Total manganese

The bismuthate procedure in 1 *M* sulfuric acid was used[7] after fusion of the compound with 5 g of potassium pyrosulfate in a porcelain crucible. A drop of hydrogen peroxide was added when dissolving the melt. Interference by arsenic was eliminated by extending the oxidation time to 45 min at 35°–40°, and then 30 min more when cool. The determination of total manganese in compounds with more antimony than $MnAs_{0.96}Sb_{0.04}$ was unsuccessful without separation of antimony.

Total phosphorus

Standard procedures were followed for phosphates[8]. Antimony, mercury, tin and some arsenic were first precipitated with sodium sulfide in acid solution. The phosphate was freed from the large excess of chloride and sulfate by co-precipitation with iron(III), using zinc oxide to neutralize the excess acid and to control pH. The precipitate was dissolved in nitric acid and the phosphorus precipitated as the phosphomolybdate. That amount of arsenic which followed to this point was volatilized by boiling to near dryness twice with hydrochloric acid in the presence of a little sodium iodide. A double precipitation as magnesium ammonium phosphate followed. The second precipitate was dried and weighed as $MgNH_4PO_4 \cdot 6H_2O$.

DISCUSSION

The procedure described here for the determination of the total combined arsenic and antimony and of arsenic by *Variation 2* was adapted from the well-known procedure for total iron. In this procedure careful consideration must be given to the proper functioning of catalysts and to the control of acidity and chloride concentration.

In the determination of total combined arsenic and antimony by *Variation 1*, osmic acid was used as a catalyst for the oxidation of arsenic(III), since the iodide added during the reduction procedure was complexed by the mercury(II) present. As osmic acid would be rendered ineffective as a catalyst in the chloride ion concentrations necessary for satisfactory titration of antimony(III), this determination was carried out in two steps: (*1*) complete oxidation of the arsenic(III), and (*2*) adjustment of the acidity and chloride concentration for the oxidation of antimony(III).

It is advisable to titrate in the presence of only a very small amount of mercury(I) chloride. This was accomplished by destroying the large excess of tin(II) in the first reduction by allowing air to oxidize it overnight. A small measured excess of tin(II) chloride was then added in a second step to re-reduce any arsenic(III) which may have been re-oxidized also. Since there are indications that the oxidation by air proceeds faster in the absence of antimony[3], slightly more tin(II) chloride was added when no antimony was present. The quantities of tin(II) chloride used were somewhat empirical, being dependent upon sample size, laboratory temperature and other conditions influencing the rate of oxidation of tin(II) and arsenic(III) by air.

It is important to allow sufficient time for the precipitation and coagulation of the mercury(I) chloride. High blank values (over 0.05–0.06 ml) or high results for unknowns may be due to insufficient coagulation or incomplete filtration. High results can also be produced by a very rapid addition of permanganate.

It is advisable to delay the filtration of the mercury(I) chloride precipitate until after adding the hydrochloric acid. If filtered earlier, some antimony is lost, possibly by hydrolysis and/or adsorption by the precipitate. Some time must be allowed after addition of the hydrochloric acid for equilibrium to be established.

TABLE I

TOTAL ARSENIC AND ANTIMONY

Sample	*Method*	*As present theor. (mg)*	*Sb present theor. (mg)*	*As + Sb found % of theor.*
As_2O_3 std.	Var. 1	78.1	None	100.0
As_2O_3 std.	Var. 1	76.6	None	99.8
As_2O_3 std.	Var. 1	76.0	None	100.2
As_2O_3 std.	Var. 1	77.2	None	100.1
As_2O_3 std.	Var. 1	77.1	None	100.1
As_2O_3 std.	Var. 1	78.4	None	99.9
Sb metal, As_2O_3 std.	Var. 1	70.2	13.1	100.0
Sb metal, As_2O_3 std.	Var. 1	71.1	15.1	100.0
Sb metal, As_2O_3 std.	Var. 1	68.9	12.9	99.9
As_2O_3 std.	Var. 2	74.9	None	99.7
As_2O_3 std.	Var. 2	75.0	None	99.9
As_2O_3 std.	Var. 2	75.1	None	99.9
As_2O_3 std.	Var. 2	75.4	None	99.7

In Table I are shown representative results of the application of the above procedure. The results with mixtures of arsenic and antimony are highly satisfactory. Those with arsenic alone tended to vary slightly, but are still satisfactory.

In the absence of antimony, the shorter procedure of *Variation 2* can be used. Since ferroin is used here, ions yielding strongly colored solutions tend to give less interference. The technique of allowing air to oxidize the excess tin(II) to some

TABLE II

TOTAL ANTIMONY BY REDUCTION WITH MERCURY(I) CHLORIDE

Sample	*Catalyst present* $5 \cdot 10^{-6}$ *mol* I^-	*Sb theor. (mg)*	*Sb found % of theor.*	*As theor. (mg)*	*As reduced*[b] *approx. % of total*	$HgCl_2$ *added (g)*
Sb metal, As_2O_3 std.	Yes	14.2	148 (av. of 2)	68	5.9 (av. of 2)	1
Sb metal, As_2O_3 std.	Yes	13.7	130 (av. of 2)	68	4.0 (av. of 2)	2
Sb metal, As_2O_3 std.	Yes	13.2	116 (av. of 2)	68	1.9 (av. of 2)	4
Sb metal, As_2O_3 std.	Yes	13.7	114 (av. of 2)	68	1.8 (av. of 2)	10
Sb metal, As_2O_3 std.	Yes	12.8	108 (av. of 2)	68	1.0 (av. of 2)	20
Sb metal std.	No	15.0	99	None		1
Sb metal std.	No	13.4	101	None		1
Sb metal, As_2O_3 std.	No	14.1	103	68	0.4	1
Sb metal, As_2O_3 std.	No	14.5	101	68	0.1	1
Sb metal, As_2O_3 std.	No	14.1	99	68	—	1
Sb metal, As_2O_3 std.	No	14.3	97	68	—	1
Sb metal, As_2O_3 std.	No	13.5	98	68	—	1
Sb metal, As_2O_3 std.	No	13.7	98	68	—	1
Sb metal, As_2O_3 std.	No	13.0	101	68	0.2	1
$MnAs_{0.96}Sb_{0.04}$[a] (147.5 mg)	No	5.45	101	80.5	?	0.14
$MnAs_{0.96}Sb_{0.04}$[a] (142.0 mg)	No	5.25	101	77.5	?	0.14
$MnAs_{0.96}Sb_{0.04}$[a] (149.3 mg)	No	5.52	100	81.5	?	0.14

[a] Same cpd. included in Table III. [b] All reductions were carried out at 95° for 12 h.

degree could be used, as followed in *Variation 1* above. However, it is less important in this case.

As indicated in the procedure of *Variation 2*, control of the chloride concentration is important to obtain good end-points. It is better to use less chloride and accept some flocculent precipitate of $SnO_2 \cdot xH_2O$ than risk catalyst poisoning and an attendant failure of the ferroin indicator.

The above titrations of antimony solutions are carried out in strong acid in accordance with the recommendations of PUGH[5]. The acidity is critical since too little leads to hydrolysis of the antimony while too much can lead to oxidation of chloride. The acidity during the reduction step must also be controlled. Increased acid concentration reduces the arsenic(III)/arsenic(V) oxidation potential and increases reaction rates to such an extent that tin(II) reduces arsenic(V) to the element in 10 *M* sulfuric acid. The acid concentration in the reduction step of this procedure is approximately 5 *M*.

The oxidation potential of antimony(III) is also lowered by higher acid concentrations, increasing the ease with which antimony is reduced by even weak reducing agents such as mercury(I) chloride. Under the conditions necessary to the reduction of antimony(V), mercury(I) chloride is a sufficiently strong reducing agent to reduce the arsenic(V). The kinetics in the case of arsenic are very slow in the absence of catalysts, and the selective and quantitative reduction of antimony(V) to antimony(III) occurs. Very little catalyst is needed for the reduction of arsenic(V) because of the long time allowed for this to take place. As little as $5 \cdot 10^{-6}$ moles of iodide (one drop of 0.1 *M* potassium iodide) is active as a catalyst even in the presence of mercury(II). This is in contrast to the failure of the iodide catalyst in the permanganate titration of arsenic(III) in the presence of mercury(II) ion where a rapid reaction is required.

The half-cell reaction acting as the reducing agent here is probably

$$6\ Cl^- + Hg_2Cl_2(s) \rightleftharpoons 2\ HgCl_4^{2-} + 2\ e\ ;\ \text{or}\ 3\ Cl^- + Hg_2Cl_2(s) \rightleftharpoons 2\ HgCl_3^- + 2\ e$$

No reliable values of the potential of this half-cell are available because of the complex nature of mercury(II) chloride solutions[9], but this can be roughly estimated to be about -0.5 V. The oxidation potential of the mercury(I)/mercury(II) reaction in the absence of complexing of the mercury(II) (perchloric acid solution) is $E_0 = -0.905$ V[9]. In the former reactions, the chloride concentration enters the potential calculation to a high power and the influence of chloride ion on the potential of this half-cell would be quite marked. Thus a relatively small chloride concentration may be sufficient to favor reduction of arsenic(V). It appears that the most effective means of controlling the potential of this half-cell is by controlling the chloride concentration, but the concentration necessary for the proper reduction of antimony(V) does not permit this.

Before the discovery of the failure of mercury(II) to destroy the catalytic activity of iodide during reduction, attempts were made to reduce the oxidation potential of the mercury(I) chloride/mercury(II) half-cell by additions of mercury(II) chloride. The results of this are shown in Table II. Although some advantage was gained by its use, the amounts required for effective control would be large. Elimination of catalysts eliminated the need for the mercury(II) chloride additions. A small amount was added in all cases, however, to control the potential of the couple in the early stages of reduction when the mercury(II) generated would be small. This was considered advisable because of the possibility of some reduction of arsenic(V) under such conditions.

Table II also gives the results of the procedure described for the determination of antimony selectively in the presence of arsenic. In view of the small amount of antimony taken and the large amount of arsenic (molar ratios As:Sb > 8:1), these results are considered quite satisfactory. Also represented in Table II is the performance of the procedure when applied to an unknown material.

Under more ideal conditions of greater amounts of antimony and relatively smaller amounts of arsenic, improved performance could be expected. Although it is not practical to lower the chloride concentration sufficiently to control the oxidation potential of the mercury(I) chloride/mercury(II) half-cell, some reduction is possible. This coupled with the use of mercury(II) additions to the solution may aid in improving the results.

The various steps taken in the analysis for the phosphorus are generally known. The values found (Table III) for the unknown materials show some deviation from those intended in the preparation of these materials. This discrepancy is not large in view of the numerous steps necessary for the determination of phosphorus and the very small amount present. Since the arsenic and phosphorus used to prepare these materials showed oxide contamination, this discrepancy and that in the arsenic values may be due in part to this. There is no assurance that these compounds had the composition intended in preparation, since these materials show a strong tendence to be non-stoichiometric in the direction of excess manganese (equivalent to anion deficiency).

TABLE III

APPLICATION TO UNKNOWN MATERIALS

Composition[a] *attempted*	$MnAs_{0.90}P_{0.10}$		$MnAs_{0.95}P_{0.05}$		$MnAs_{0.96}Sb_{0.04}$	
	Theor.	*Found*	*Theor.*	*Found*	*Theor.*	*Found*
Mn	43.79	43.80 ± 0.05	43.04	42.97 ± 0.10	41.70	41.46 ± 0.11
As	53.74	53.36 ± 0.06	55.75	55.49 ± 0.06	54.61	54.71 ± 0.04
Sb	—	—	—	—	3.70	3.73 ± 0.04
P	2.47	2.36 ± 0.10	1.21	1.13 ± 0.10	—	—
Total	100.0	99.5 ± 0.2	100.0	99.6 ± 0.3	100.0	99.9 ± 0.2
As, Sb method	Variation 2		Variation 2		Variation 1	

[a] These materials were not necessarily stoichiometric and are believed to be contaminated with oxygen.

As shown in Table III, excellent results were obtained in recovery and determination of manganese except in the case of the antimony-containing compound. Antimony appears to interfere in this procedure but the reason is not known.

The process of bringing many phosphides and arsenides into solution in acids involves risk of loss of the elements as hydrides. Such compounds must be brought into solution under conditions which lead to immediate oxidation to positive formal valence states; bromate was found to serve this purpose well in the case of all the compounds with manganese. Elemental arsenic is readily dissolved whereas metallic antimony is not attacked.

SUMMARY

A procedure is described for the titrimetric determination of arsenic and antimony without separation. Total combined arsenic and antimony were determined by reduction with tin(II) chloride and titration with permanganate; antimony is found by selective reduction with mercury(I) chloride and titration with permanganate. A precision of 0.1–0.2% was obtained for total combined arsenic and antimony, and approximately 1% for antimony alone (small amounts in the presence of large amounts of arsenic). The procedure was developed for and applied to the analysis of synthesized compounds of the type $MnAs_{1-x}P_x$ and $MnAs_{1-y}Sb_y$.

RÉSUMÉ

On décrit un procédé pour le dosage titrimétrique de l'arsenic et de l'antimoine sans séparation. Le total arsenic et antimoine sont dosés par réduction avec le chlorure d'étain(II) et titration au moyen de permanganate. L'antimoine est obtenu par réduction sélective à l'aide de chlorure de mercure(I) et titration au moyen de permanganate. Ce procédé peut être appliqué à l'analyse de composés synthétisés du type $MnAs_{1-x}P_x$ et $MnAs_{1-y}Sb_y$.

ZUSAMMENFASSUNG

Es wird ein Verfahren beschrieben, das ohne Trennung die massanalytische Bestimmung von Arsen und Antimon gestattet. Arsen und Antimon werden durch Reduktion mit Zinn(II)-chlorid und Titration mit Permanganat gemeinsam bestimmt; Antimon wird durch selektive Reduktion mit Quecksilber(I)-chlorid und Titration mit Permanganat ermittelt. Die Genauigkeit beträgt für Arsen und Antimon zusammen 0.1–0.2% und etwa 1% für Antimon allein (kleine Anteile in Gegenwart von grossen Mengen Arsen). Das Verfahren wurde entwickelt und angewandt bei der Analyse von synthetischen Verbindungen des Typs $MnAs_{1-x}P_x$ und $MnAs_{1-y}Sb_y$.

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DOSAGE DU PLUTONIUM PAR POTENTIOMETRIE A INTENSITE CONSTANTE

APPLICATION AU COMBUSTIBLE DE RAPSODIE

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Le combustible de Rapsodie est constitué de pastilles frittées d'oxyde mixte de plutonium et d'uranium contenant de 20 à 25% de plutonium. Il est nécessaire de contrôler cette teneur au moyen d'une méthode d'analyse chimique dont la précision soit au moins de 1%, compte tenu des spécifications imposées au combustible. Ce résultat peut être obtenu en utilisant une méthode de titrage faisant intervenir la réaction de réduction du plutonium(VI) par le fer(II), puisqu'une telle méthode n'est pas sujette à l'interférence de l'uranium et du fer. Le procédé a déjà été appliqué par Waterbury et Metz[1] sous forme de dosage en retour, puis par Shults[2] qui utilise le même principe en coulométrie. Les auteurs oxydent le plutonium à la valence(VI) au moyen d'acide perchlorique. Récemment, un nouvel agent, l'oxyde argentique, a été utilisé par Seils, Meyer et Larsen[3] qui effectuent le titrage par ampérométrie en milieu sulfurique.

La méthode la plus courante pour la dissolution de l'oxyde mixte UO_2PuO_2 est une attaque par l'acide nitrique concentré en présence d'acide fluorhydrique. Il était donc intéressant de développer un mode opératoire utilisable en milieu nitrique, afin d'éviter des opérations de changement de milieu par ébullition en présence d'acides sulfurique ou perchlorique. En effet, ces opérations sont toujours délicates à effectuer, et d'autant plus quand l'échantillon contient une quantité appréciable de sels étrangers au plutonium.

PARTIE EXPÉRIMENTALE

Reactifs

Oxyde argentique. Dissoudre 72 g de soude en pastilles dans 1 litre d'eau maintenue à 85°. Ajouter 75 g de persulfate de potassium à la solution alcaline chaude. Ajouter 51 g de nitrate d'argent dissous dans le minimum d'eau. La température du mélange atteint 90°. Continuer à agiter pendant 15 min. Filtrer sur Buchner le précipité noir d'oxyde argentique. Laver par une solution de soude à 1% et sécher à l'air.

Mode opératoire

Dissoudre à chaud, dans un ballon d'attaque surmonté d'un réfrigérant à reflux, une pastille de 2 à 3 g par 10 ml de solution HNO_3 11 *N*/HF 0.1 *N*. Laisser refroidir, transvaser dans une fiole jaugée de 100 ml, rincer et amener à volume avec de l'acide nitrique 0.1 *N*. Effectuer une prise d'essai de 5 ml dans un bécher de 100 ml. Diluer à environ 20 ml avec l'acide nitrique 0.1 *N*.

Ajouter en agitant une première portion de 50 mg d'oxyde argentique. Attendre 5 min en maintenant l'agitation. Ajouter une deuxième portion, attendre 5 min. Ajouter une troisième portion, attendre 15 min. La présence d'un excès d'oxydant est mise en évidence par une coloration brune de la solution et, éventuellement, la présence d'un précipité. Faire chauffer 5 min au voisinage de l'ébullition le bécher recouvert d'un verre de montre. Laisser refroidir.

Ajouter, en agitant, 2 ml de solution de nitrate d'aluminium 0.1 *M*. Ajouter, en agitant, 2 ml de solution d'acide sulfamique 1 *M*. Pipeter exactement 10 ml de solution de fer(II) $3 \cdot 10^{-2}$ *N* dans l'acide sulfurique 2 *N*. L'ajouter dans la solution de Pu(VI) en agitant.

Faire tremper la double électrode de platine dans la solution obtenue et titrer l'excès de fer(II) par une solution titrée de sulfate cérique 10^{-2} *N*.

Le point équivalent est déterminé par potentiométrie avec un courant d'électrolyse constant de 3 μA entre les deux électrodes de platine. Il correspond à la valeur maxima du potentiel mesuré entre les deux électrodes. La courbe donnant la différence de potentiel en fonction du volume de solution de sulfate cérique peut être enregistrée au moyen d'un titrimètre qui fournit aussi le courant d'électrolyse constant.

Effectuer le dosage à vitesse moyenne jusqu'à ce que la différence de potentiel atteigne une valeur d'environ 200 mV. Terminer le dosage goutte à goutte en laissant se stabiliser la différence de potentiel avant chaque nouvelle addition de solution titrée.

Titrer chaque jour de la même façon une aliquote de 5 ml de la solution de fer(II) $3 \cdot 10^{-2}$ *N*.

RÉSULTATS ET DISCUSSION

Choix de la méthode de titrage

Le choix de la méthode de titrage s'est porté sur le principe du dosage en retour, plutôt que sur le titrage direct du plutonium(VI) par le fer(II). Des essais de titrage direct avec détermination ampérométrique du point équivalent avaient été entrepris sur le chrome sous forme de dichromate de potassium et donnaient des résultats satisfaisants. La transposition de ces essais au plutonium a donné des courbes moins bien définies. Le courant ne se stabilise que lentement après chaque addition de fer(II), ce qui présente 2 inconvénients: le titrage demande de 30 à 45 min et la méthode se prête mal à l'enregistrement.

Le titrage en retour a l'avantage d'utiliser des systèmes oxydoréducteurs rapides, qui permettent une détermination potentiométrique du point équivalent. Le type de potentiométrie choisi est une potentiométrie à intensité constante au moyen de deux électrodes indicatrices de platine identiques. Ce mode de détermination se prête bien à l'enregistrement. L'appareillage ne présente qu'un encombrement très réduit dans la boite à gants et ne nécessite que l'entretien courant des électrodes de platine utilisées en potentiométrie. La position du point équivalent, qui correspond au maximum de différence de potentiel entre les deux électrodes, est facilement déterminée. Un exemple en est donné (Fig. 1). Il représente, sur le même graphique avec une origine décalée, le titrage de 2 prises d'essai identiques de fer(II) et le titrage de l'excès de fer(II) après réduction du plutonium(VI).

Les variations de la différence de potentiel ΔE entre les deux électrodes sont déterminées par la position des courbes intensité/potentiel et permettent de suivre les concentrations des différents constituants au cours du titrage[4].

Pour l'étalonnage de la solution de fer(II), le potentiel de chacune des électrodes est fixé au départ par le système mixte oxydation du fer(II)/réduction de l'oxygène ou par le système Fe(II)/Fe(III) suivant la concentration du fer(III) dans la solution de fer(II) utilisée. Ensuite, la différence de potentiel entre les deux électrodes passe par une valeur minima fixée par le système rapide Fe(II)/Fe(III). Avant et au voisinage du point équivalent, la valeur de ΔE croît, car elle est fixée par le potentiel mixte oxydation de Ce(III)/réduction de Fe(III). Après le point équivalent, la valeur de ΔE décroît car elle est déterminée par le système rapide Ce(IV)/Ce(III).

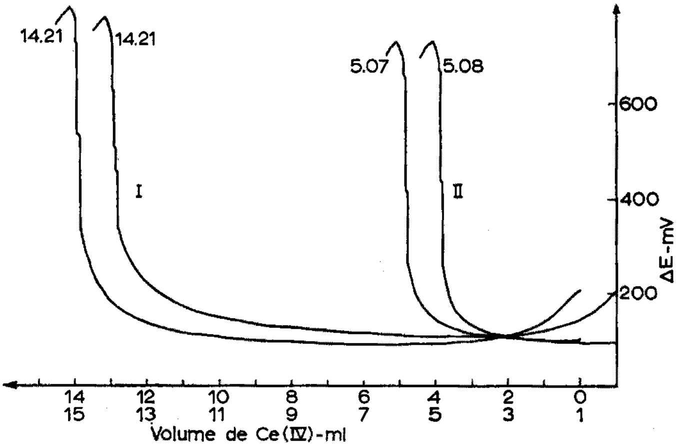

Fig. 1. Courbes de titrage potentiométrique à intensité constante. (I) titrage de la solution de fer(II); (II) titrage de l'excès de fer(II) après réduction du plutonium(VI).

Pour le titrage de la solution de plutonium, le raisonnement est le même, mais la différence de potentiel est fixée au début de la réaction par le système rapide Fe(II)/Fe(III).

Dissolution des échantillons

L'acide nitrique est le meilleur agent de dissolution des pastilles UO_2PuO_2 à condition d'opérer en présence d'acide fluorhydrique ou de fluorure d'ammonium à une concentration voisine de 0.1 *M*. Dans ces conditions, l'attaque des oxydes est réalisée en 2 heures environ pour une pastille de 3 g et, bien que les oxydes soient frittés à 1600°, la dissolution est plus facile que celle d'un oxyde de plutonium calciné à plus basse température.

La présence de fluorures dans la solution est gênante pour le titrage du plutonium et c'est pourquoi il est nécessaire de les complexer en ajoutant du nitrate d'aluminium avant le dosage. De même, l'action gênante des nitrites est évitée au moyen d'acide sulfamique.

Eléments gênants

Les interférences possibles sont dues à des éléments qui sont oxydés à une valence supérieure par l'oxyde argentique et réduits ensuite par le fer(II). Ces éléments ont déjà été décrits par de nombreux auteurs qui utilisent un principe de réaction voisin. Lingane et Davis[5] ont utilisé l'oxyde argentique et le fer(II) pour la détermination du chrome, du manganèse et du cerium. Dans le cas de l'oxydation par l'acide perchlorique, Waterbury et Metz[1] signalent l'interférence du vanadium, de l'or et du platine, Coleman et Hornsby[6] celle du neptunium. Bien que les essais n'aient pas été effectués dans le cas de la méthode à l'oxyde argentique, il est probable que ces éléments interfèrent de la même façon. Pour la méthode ampérométrique, Bergstresser et Waterbury[7] ont mentionné une action gênante et non quantitative de l'americium.

Dans le cas du combustible de Rapsodie, ces éléments sont en quantité suffisamment faible pour pouvoir être négligés. Une analyse d'impuretés déterminées par spectrographie d'émission est donnée dans le Tableau I.

TABLEAU I

TENEUR EN IMPURETÉS DE L'OXYDE MIXTE UO_2PuO_2 FRITTÉ

Eléments	*Teneur dans l'oxyde* UO_2PuO_2 *fritté (p.p.m.)*	*Eléments*	*Teneur dans l'oxyde* UO_2PuO_2 *fritté (p.p.m.)*
Ag	0.5	Mg	60
Al	20	Mn	5
B	0.1	Na	< 50
Ca	25	Ni	10
Cd	1	Pb	< 5
Cr	10	Si	80
Cu	10	Sn	< 5
Fe	30	Ti	< 50
K	< 50	Zn	80
Li	< 5		

TABLEAU II

TITRAGE DU PLUTONIUM EN PRÉSENCE DE DIFFÉRENTES QUANTITÉS D'URANIUM

(conditons opératoires: la solution de Pu(IV) est reduite par 14 ml de solution de Fe(II). 5 ml de Fe(II) correspondent à 14.98 ml de Ce(IV). L'excès de Fe(II) à titrer correspond à 3.5 ml environ de Ce(IV).

Prise d'essai uranium (mg)	*U/Pu*	*ml de Ce(IV) correspondant au titrage du Pu*				*Concentration de la solution de plutonium (mg/ml)*
		1er essai	*2e essai*	*3e essai*	*Valeur moyenne*	
0		38.54	38.59	38.57	38.57	8.910
45	1	38.57	38.54	38.51	38.54	8.903
90	2	38.57	38.54	38.57	38.56	8.907
225	5	38.59	38.54	38.54	38.56	8.907
450	10	38.57	38.61	38.59	38.59	8.914

La teneur en americium n'a pas été déterminée mais la composition isotopique du plutonium indique de 1 à 1.5% de ^{241}Pu. Comme le plutonium n'est lui-même présent dans le combustible qu'à une concentration comprise entre 20 et 25%, l'interférence de l'americium formé à partir de ^{241}Pu peut être négligée pour le contrôle de fabrication.

Selon le principe utilisé pour le dosage, l'uranium ne participe pas à la réaction. Des essais ont été effectués pour des rapports U/Pu variant de 0 à 10, correspondant à la composition du combustible de Rapsodie ou à celle de combustibles du même type. Les solutions utilisées pour ces essais sont, d'une part une solution de plutonium à environ 9 g/l et d'autre part, une solution d'uranium à environ 45 g/l, toutes deux en milieu nitrique 1 *N*. A une prise d'essai constante de 5 ml de la solution de plutonium, 1, 2, 5, 10 ml de la solution d'uranium ont été ajoutés. Les résultats sont rassemblés dans le Tableau II.

Solution titrante

La solution titrante utilisée était une solution de cerium(IV) qui avait été étalonnée au moyen d'un échantillon de plutonium du NBS. L'emploi du plutonium NBS ou du plutonium français de haute pureté (moins de 500 p.p.m. d'impuretés cumulées) nous a semblé la méthode la plus sûre pour l'étalonnage de la solution de cerium. Les résultats obtenus concordent d'ailleurs à mieux de 0.1% avec ceux donnés en utilisant comme produits étalons l'oxalate de sodium et l'anhydride arsénieux.

Résultats et applications

Ce mode opératoire a été appliqué à différents types d'oxyde mixte dont la composition variait de 10 à 30% en PuO_2 et de 70 à 90% en UO_2. Il est maintenant utilisé couramment pour le contrôle des différents lots de fabrication qui représentent plusieurs dizaines de kilogrammes de plutonium. Le Tableau III donne un exemple de résultats obtenus.

TABLEAU III

TITRAGE DU PLUTONIUM DANS LES OXYDES FRITTÉS

	No. de la pastille	*ml de Ce(IV) correspondant au titrage du Pu*	*Pu (%)*
UO_2PuO_2 à environ 11% PuO_2	1	36.27/36.23	9.92
	2	37.61/37.56	9.96
UO_2PuO_2 à environ 25% de PuO_2	1	34.14/34.08	22.89
	2	30.42/30.37	22.98
	3	30.52/30.57	22.22
	4	25.50/25.47	22.40
	5	27.87/27.84	22.58

Le temps total nécessaire pour l'analyse est d'environ 1 heure à partir du prélèvement de la solution. Les opérations d'oxydation à la valence(VI), de destruction de l'excès d'oxydant, d'addition des différents réactifs peuvent être menées en série et le titrage lui-même demande environ 5 min.

Appliquée en routine, la méthode donne une précision de ±0.5%. Elle peut être utilisée comme méthode de haute précision sous réserve du respect des conditions opératoires requises dans ce domaine: opérateur qualifié et entraîné, mesures des quantités de solution titrante au moyen de burettes calibrées ou par pesée, surveillance de la température, étalonnage des solutions titrantes par des produits de haute pureté.

En dehors du combustible de Rapsodie, le mode opératoire est appliqué à un grand nombre de solutions de plutonium provenant d'installations de traitement et contenant de l'uranium et du fer, ainsi qu'à différents alliages binaires ou ternaires.

RÉSUMÉ

Une nouvelle méthode a été développée pour l'analyse de plutonium dans le combustible de Rapsodie. Elle consiste à dissoudre l'échantillon dans un mélange d'acides nitrique 11 N et fluorhydrique 0.1 N. Le plutonium est oxydé au moyen d'oxyde argentique. Le plutonium(VI) est réduit en présence d'acide sulfamique par une quantité connue de fer(II) en excès, qui est titrée en retour par du sulfate cérique. Le point équivalent est déterminé par potentiométrie à intensité constante. L'uranium et le fer ne gênent pas et il n'est pas nécessaire d'effectuer de séparation. Appliquée en routine, la méthode donne une précision de 0.5%.

SUMMARY

A new method is proposed for the determination of plutonium in the UO_2PuO_2 pellets for Rapsodie. The sample is dissolved in a mixture of 11 N nitric acid and 0.1 N hydrofluoric acid, and the plutonium is oxidized with silver(II) oxide. Plutonium(VI) is reduced in the presence of sulphamic acid with an excess of iron(II) which is back-titrated with cerium(IV) solution to a constant-current potentiometric end-point. Uranium and iron do not interfere and no separation is required. In routine work, the method gives a precision of 0.5%.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Bestimmung von Plutonium in UO_2PuO_2-Pellets vorgeschlagen. Die Probe wird in einer Mischung von 11 N Salpetersäure und 0.1 N Fluorwasserstoffsäure gelöst und das Plutonium mit Silber-(II)-oxid oxydiert. In Gegenwart von Sulfaminsäure wird Plutonium(VI) mit einem Überschuss von Eisen-(II) reduziert und das Eisen mit einer Cer(IV)-Lösung zurücktitriert. Uran und Eisen stören nicht, so dass eine Trennung nicht erforderlich ist. Die Genauigkeit der Methode beträgt 0.5%.

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THE AUTOMATIC DETERMINATION OF SILICATE–SILICON IN NATURAL WATERS WITH SPECIAL REFERENCE TO SEA WATER

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The dissolved silicon in natural waters shows a considerable range of concentrations, from values of over 20 mg/l in hot springs down to very low levels in the surface waters of the sea at the time of the spring diatom bloom. Both geochemical and biochemical processes affect the silicon content of natural waters. A knowledge of the silicon content of the hydrosphere is therefore of use not only to biologists and geochemists, but also to physical oceanographers, who use the differing silicon contents of water masses as tags for studying movements of water masses and marine mixing processes. The ever-increasing numbers of samples collected during oceanographic and limnological investigations render essential the introduction of automatic methods of micronutrient analysis. This paper describes an automatic method for the determination of reactive silicate in natural waters, which is also of value in the analysis of boiler-feed waters.

Silicate is normally determined photometrically in sea water either as the yellow α- or β-silicomolybdic acids formed by reaction with molybdate at various pH values[1,2], or as the molybdenum blue formed by reduction of silicomolybdic acid with stannous chloride[3] or metol[4]. Aminonaphthol sulphonic acid has been used for the reduction in an automatic method for the determination of silicate in boiler-feed waters[5], but this reagent is liable to throw down a precipitate which interferes with the photometric determination. GRASSHOFF[6] has given a preliminary account of an automatic method for the determination of silicate in sea water which he has employed on the Research Vessel "Meteor" in 1965 during the International Indian Ocean Expedition.

In the method of MULLIN AND RILEY[4] for the analysis of natural waters silicate is converted principally to β-silicomolybdic acid by the addition of an acidic molybdate solution. The acid/molybdate ratio and the time of reaction must be controlled to minimize the formation of α-silicomolybdic acid. After 10 min an acidified solution of sodium sulphite and metol is added; this reduces the silicomolybdic acid to molybdenum blue, the absorption of which is measured at 815 mμ. The reduction is slow and rather surprisingly the time required for colour development depends on the amount of silicon present. At room temperature with a silicate concentration of 0.26 mg Si/l the reduction requires 1 h for completion in sea water and 2 h in distilled water. Interference of phosphate is prevented by the addition of oxalic acid.

In adapting this method to the AutoAnalyzer it was apparent that it would be necessary to accelerate the reduction by heating. The AutoAnalyzer manifold was connected up to give ratios of reagent volumes: sample volume similar to those used in the manual method. Colour development was carried out in a double coil heating bath. A series of calibration runs was made with both distilled water and sea water using various temperatures for the reduction. Even at temperatures as high as 90° the calibration curves were non-linear. This lack of linearity was attributed to incomplete development of the colour and a means of hastening the colour development was sought. A study of unpublished work by MULLIN[7] suggested that the reduction might be speeded up by increasing the proportions of both metol and sulphite in the reductant. Reducing solutions containing various proportions of these reagents were tested. It was found that a linear calibration graph resulted with both distilled water and sea water in the range 0–4 mg Si/l if a reagent containing 4 times the normal concentration of both metol and sulphite was used at 70°. The optical densities obtained were similar to those found in the manual method after correction for changes in cell length.

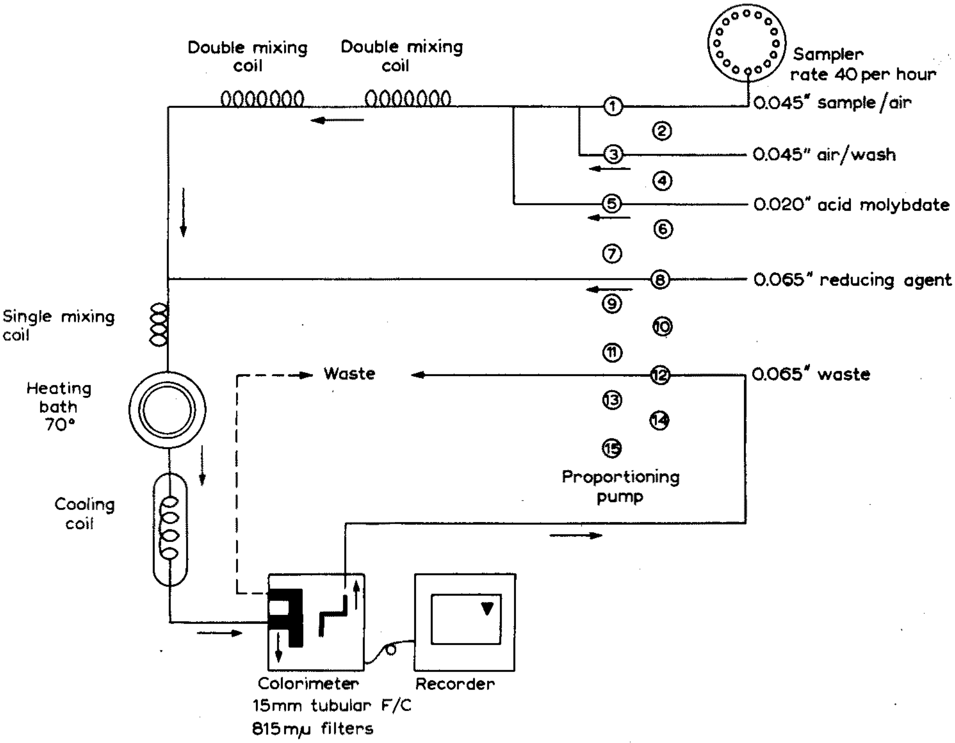

Fig. 1. AutoAnalyzer manifold for determination of silicate in natural waters.

In the manifold finally adopted (Fig. 1), the tube adding the water to dilute to volume was discarded and the reducing agent was diluted by a factor of 2 and added through a tube giving twice the flow rate.

EXPERIMENTAL

Reagents

Acid molybdate reagent. Dissolve 2 g of ammonium molybdate in *ca.* 70 ml of water, add 6 ml of concentrated hydrochloric acid (s.g. 1.18) and dilute to 100 ml with water. Store in a Pyrex glass bottle.

Metol–sulphite solution. Dissolve 5 g of metol (*p*-methylaminophenol sulphate) in *ca.* 240 ml of water containing 6 g of anhydrous sodium sulphite. Dilute to 250 ml with water. Store the reagent in a well stoppered amber glass bottle.

Reducing agent. Mix 100 ml of metol–sulphite solution with 15 ml of 10% (w/v) oxalic acid and add while cooling, 30 ml of 25% (v/v) sulphuric acid. Dilute to 500 ml with water. The mixed reducing agent should be prepared as required.

Standard silicate solution. Fuse 0.2140 g of finely powdered pure silica with about 2 g of sodium hydroxide in a silver crucible at 600° for 20 min in a muffle furnace. Digest the cold residue with water. Using a polyethylene funnel, quantitatively transfer the solution to a 1-l graduated flask containing 10 ml of 5 *N* hydrochloric acid and dilute to 1 l. This solution which contains 100 μg silicate-Si/ml is used for the preparation of a working standard solution containing 1.0 μg Si/ml.

Explanation of flow diagrams

The layout of the AutoAnalyzer is shown schematically in Fig. 1. The samples are placed in 3-ml cups on the plate of a No. 1 sampler and alternated with cups of distilled water. The sampler is set to a sampling rate of 40 per h and the samples are pumped from the cups by means of a 0.045″ i.d. tube and segmented with air supplied from an identical tube connected to a reverse-acting crook. The sample stream is mixed in two double mixing coils with the acid molybdate reagent supplied through a 0.020″ i.d. tube. The reducing agent is then added through a 0.065″ i.d. tube and the combined stream is circulated through a single mixing coil, and then through a double coil heating bath at 70° for development of the colour. The solution is cooled by means of a water-jacketed coil, the segmenting air is removed by means of a debubbler and the liquid is passed through the 15-mm tubular flow cell of a photocell colorimeter (fitted with 90CV phototubes) for photometry at 815 mμ. If low silicate concentrations are expected, the 4 or 10 times range expansion facility on the recorder is employed. The solution is then pumped to waste through a 0.065″ i.d. tube.

At the beginning of each series of determinations the base line should be set with the instrument running continuously on distilled water plus reagents; the base line reading should also be checked in the same manner after a run.

Calibration of the method

The method should be calibrated at the beginning and end of each set of analyses by examining standard solutions of silicate in distilled water. A silicate concentration of 1000 μg Si/l is recommended if range expansion is not used; with 4 and 10 times range expansion silicate concentrations of 250 and 40 μg Si/l respectively are satisfactory. The results obtained with sea water samples should be corrected for salt error by means of the expression: Corrected optical density = optical density $(1 + 0.0028\ \mathrm{Cl}^{0}/_{00})$.

Correction for turbidity

With samples showing appreciable turbidity a parallel run should be made using a dilute hydrochloric acid solution (6 ml of concentrated acid/100 ml of water) instead of the acid molybdate reagent. The optical density readings obtained are deducted from those obtained by the full procedure to give the corrected optical densities. Alternatively, samples may be filtered using the AutoAnalyzer filtering module and analyzed in the normal manner.

RESULTS

Calibration curve and salt error

Using the conditions described above, symmetrically shaped AutoAnalyzer traces were obtained using the normal range on the recorder. When the 10 times range expansion facility was employed, satisfactory but not quite symmetrical curves were obtained. The relationship between silicate concentration and optical density was studied in both distilled water and sea water. Aliquots (40 ml) of both distilled water and Irish Sea surface water of low silicate content were spiked with known amounts of up to 200 μg of silicon and diluted to 50 ml. These samples were then run in duplicate through the AutoAnalyzer (see Table I). Similar runs were also carried out on spiked samples of artificial sea water in the range 0–80 μg Si/l using the 10 times range expansion facility (artificial sea water was employed since no natural water was available having a sufficiently low silicate content). The results of these experiments (Table II), and of those carried out without range expansion (Table I), indicated that there is close adherence to Beer's law in the range 0–4000 μg Si/l. This covers the range of silicate concentrations encountered in the sea.

TABLE I

OPTICAL DENSITIES FOUND IN CALIBRATION RUNS PERFORMED ON SEA WATER AND DISTILLED WATER SOLUTIONS OF SILICATE

Silicon concentration ($\mu g/l$)	*500*	*1000*	*1500*	*2000*	*2500*	*3000*	*3500*	*4000*
Distilled water								
Average optical density	0.143	0.284	0.427	0.566	0.706	0.842	0.993	1.127
Average increment per 500 μg/l	0.143	0.142	0.142	0.142	0.141	0.140	0.142	0.142
Sea water (final Cl = $18.44\,^0/_{00}$)								
Average optical density[a]	0.129	0.264	0.407	0.543	0.678	0.815	0.943	1.074
Average increment per 500 μg/l	0.129	0.132	0.136	0.136	0.136	0.136	0.135	0.135

[a] Less optical density for sea water (0.045).

TABLE II

CALIBRATION DATA FOR DETERMINATION OF SILICATE IN ARTIFICIAL SEA WATER (Cl = $15.2\,^0/_{00}$) USING 10 × RANGE EXPANSION

Silicon concentration (μg Si/l)	*20*	*40*	*60*	*80*	*100*
Average optical density[a]	0.0066	0.0129	0.0207	0.0274	0.0342
Optical density increment/100 μg Si/l	0.0330	0.0321	0.0345	0.00343	0.0342

[a] Less value for artificial sea water diluted 40 ml to 50 ml (0.0115).

The data in Tables I and II suggest that the method has a small salt error amounting to 4.3% at a chlorinity of 15.4‰. In fact, the salt error varies proportionally with chlorinity. Optical densities obtained with sea water samples should therefore be corrected by use of the expression: Corrected optical density = determined optical density × (1 + 0.0028 Cl‰).

The reproducibility of the procedure was tested with 2 sea waters by carrying out 18 replicate analyses. Coefficients of variation of 0.7% and 0.5% were found at silicate concentrations of 1000 and 66 μg Si/l respectively; in the latter instance the 10 times range expansion facility was employed. Similar results were obtained with fresh waters.

Interference of phosphate

Phosphate interferes in many molybdenum blue methods for the determination of silicon. In the present method its interference is minimized by the presence of oxalic acid in the reducing solution and by the conditions selected for the formation of the β-silicomolybdic acid. It was found that phosphate did not interfere in the automatic method for the estimation of silicon at its maximum known concentration in sea water (140 μg P/l).

SUMMARY

An automatic method using a Technicon AutoAnalyzer is described for the determination of silicate in natural waters in the range 0–4 mg Si/l. It is based on the conversion of silicate to β-silicomolybdic acid which is reduced by means of a metol–sulphite reagent to molybdenum blue. Interference of phosphate is prevented by oxalic acid. The relationship between silicate concentration and optical density is linear in both fresh waters and sea water. With sea water the salt error of the method is *ca.* 5% at a salinity of 35‰. A coefficient of variation of 0.8% was found at a silicate concentration of 1 mg Si/l with both fresh and sea waters.

RÉSUMÉ

On décrit une méthode automatique, utilisant un Auto Analyseur Technicon pour le dosage des silicates dans les eaux naturelles (0–4 mg Si/l). Elle est basée sur la transformation du silicate en acide β-silicomolybdique et réduction en bleu de molybdène au moyen d'un mélange métol–sulfite. Les phosphates ne gênent pas en présence d'acide oxalique. Avec l'eau de mer, l'erreur est d'environ 5% avec une salinité de 35‰. On a trouvé un coefficient de variation de 0.8% pour 1 mg Si/l soit avec les eaux douces, soit avec les eaux de mer.

ZUSAMMENFASSUNG

Es wird eine automatische Methode mit dem Technicon AutoAnalyzer zur Bestimmung von Silikat in natürlichen Wässern im Bereich von 0–4 mg Si/l beschrieben. Die Methode beruht auf der Umwandlung des Silikats zur β-Silicomolybdänsäure, welche mit einem Metol–Sulfit-Reagenz zum Molybdänblau reduziert wird. Störungen durch Phosphorsäure werden durch Zugabe von Oxalsäure vermieden. Der Variationskoeffizient betrug 0.8% bei einer Silikatkonzentration von 1 mg Si/l.

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HETEROMETRIC TITRATIONS OF GELATIN AND EGG ALBUMIN WITH HETEROPOLY ACIDS OR WITH SODIUM TETRAPHENYLBORATE

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From a previous study[1] of the reactions between large nitrogen compounds and heteropoly acids, it was learned that only those nitrogen atoms that are built in closed heterocyclic rings can be titrated heterometrically with heteropoly acids. An analogous study of proteins is now presented, for which 2 easily available and water soluble reagents were chosen, namely, gelatin and egg albumin. The results obtained show that both proteins can be determined by titration with the heteropoly acids: phosphotungstic, phosphomolybdic and silicotungstic, and also by sodium tetraphenylborate. The titrations take 10–20 min and the precision is satisfactory.

When the *total* nitrogen content of the proteins, as determined by the Kjeldahl method, was compared with the *active* nitrogen content, as found by the heterometric titrations, it was found that only a small part of the nitrogen atoms present in the proteins were active with the heteropoly acids.

EXPERIMENTAL

The instrumentation and working conditions have been described previously[2].

Chemicals

The silicotungstic, phosphomolybdic and phosphotungstic acids and the sodium tetraphenylborate were the same as those used in previous work with alkaloids[1,3].

Gelatin (Baker & Adamson gelatin powder, U.S.P.). Aqueous 0.5% solutions were prepared at about 70°, filtered through a sintered glass filter, and kept in the refrigerator. New solutions were prepared every few days.

Egg albumin (Soluble; Difco Laboratories, Detroit, Mich.). Aqueous 2% solutions were prepared at room temperature, filtered, and kept in the refrigerator. New solutions were prepared every few days.

Determination of proteins

20 ml of a 0.3–0.5% solution of egg albumin, or of a 0.075–0.125% solution of gelatin, were titrated heterometrically with a 0.0025–0.00125 *M* solution of heteropoly acid, or with a 0.01 *M* solution of sodium tetraphenylborate. The solutions titrated contained 1–5 ml of *M* hydrochloric or nitric acid, or were adjusted to pH 3–5 by acetic acid–acetate buffers. Titrations were also performed in the presence of 1–5 ml of *M* sodium chloride. Reverse titrations were performed in every case.

RESULTS AND DISCUSSION

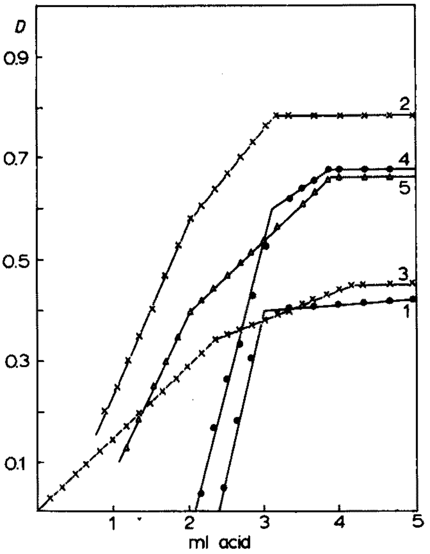
The course of some of the direct and reverse titrations is given in Figs. 1 and 2.

Egg albumin

Quantitatively, there was no difference in the results obtained whether the egg albumin was titrated with the heteropoly acids (HP) or with tetraphenylborate (TPB). Both in the direct and reverse titrations, the same stoichiometric relationship was always used, namely

$$1 \text{ ml of } 0.01\ N \text{ HP or TPB} = 1 \pm 0.05 \text{ ml of } 2\% \text{ egg albumin.}$$

The maximum optical density obtained, for the concentrations used, was 0.2–0.4 when the titrant was TPB, and 0.5–0.8 when the titrant was HP; phosphomolybdic acid proved to be the most sensitive reagent. In the reverse titrations the maximum optical density was higher. In the reverse titrations initial precipitation took place on the addition of the first drop of egg albumin, while in the direct titrations precipitation did not occur at the beginning of the titration.



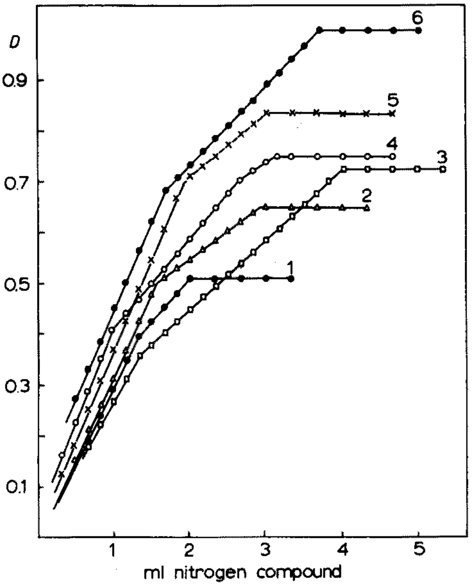


Fig. 1. (1) 3 ml 2% egg albumin + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.01 *M* sodium tetraphenylborate. (2) 4 ml 0.5% gelatin + 1 ml *M* HNO_3 + 15 ml H_2O + *x* ml 0.00125 *M* silicotungstic acid. (3) 3 ml 0.5% gelatin + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.00125 *M* phosphotungstic acid. (4) 3 ml 2% egg albumin + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.0025 *M* phosphomolybdic acid. (5) 3 ml 0.5% gelatin + 1 ml *M* HNO_3 + 16 ml H_2O + *x* ml 0.00125 *M* phosphomolybdic acid.

Fig. 2. (1) 4 ml 0.005 *M* sodium tetraphenylborate + 1 ml *M* HCl + 15 ml H_2O + *x* ml 2% egg albumin. (2) 3 ml 0.01 *M* sodium tetraphenylborate + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.5% gelatin. (3) 3 ml 0.00125 *M* silicotungstic acid + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.5% gelatin. (4) 4 ml 0.0025 *M* phosphotungstic acid + 1 ml *M* HCl + 15 ml H_2O + *x* ml 2% egg albumin. (5) 4 ml 0.00125 *M* phosphomolybdic acid + 1 ml *M* HCl + 15 ml H_2O + *x* ml 0.5% gelatin. (6) 4 ml 0.00125 *M* phosphomolybdic acid + 2 ml *M* acetic acid + 14 ml H_2O + *x* ml 0.5% gelatin.

Gelatin

The same values were obtained in the direct and reverse titrations of gelatin with tetraphenylborate, namely,

1 ml of 0.01 *N* TPB = 0.5 ± 0.01 ml of 1% gelatin.

But in the case of the heteropoly acids, different values were obtained in the direct and reverse titrations, and the amounts of gelatin used per ml of 0.01 *N* acid were different for silicotungstic acid, and phosphomolybdic or phosphotungstic acid. Direct titrations with phosphomolybdic or phosphotungstic acid gave the value: 1 ml of 0.01 *N* acid = 1 ± 0.05 ml of 1% gelatin; and for silicotungstic acid: 1 ml of 0.01 *N* acid = 1.2 ± 0.08 ml of 1% gelatin. In the reverse titrations, the ratio for phosphomolybdic and phosphotungstic acids was: 1 ml of 0.01 *N* acid = 1.3 ± 0.02 ml of 1% gelatin; and for silicotungstic acid, 1 ml of 0.01 *N* acid = 1 ± 0.05 ml of 1% gelatin.

The maximum optical density obtained with the heteropoly acids was 0.4–0.8, and initial precipitation took place at the beginning of the titration, both in the direct and reverse titrations. With tetraphenylborate, the maximum optical density was 0.2–0.3, and initial precipitation took place at the beginning of the titration only in the reverse titrations.

Generally, the egg albumin compounds obtained were distinctly more soluble than the corresponding gelatin compounds, and the titrations of egg albumin were about half as sensitive as those of gelatin. Also, the most reproducible results were obtained with phosphomolybdic and phosphotungstic acids; the values obtained for both these acids were nearly identical. Silicotungstic acid was in certain cases more sensitive, but the deviations between the results were greater.

Dilute hydrochloric acid and nitric acid acted in the same manner, and 1 ml of *M* acid in 20 ml of titrated solution was found to be the optimum amount; greater amounts of acid increased the sensitivity but the results obtained were not comparable. Almost no precipitate was obtained in the titration of tetraphenylborate with gelatin in excess of mineral acid. Addition of 2 ml of *M* acetic acid, or of 2 ml of *M* acetic acid and 2 ml of *M* sodium acetate did not affect the results. Sodium chloride increased the sensitivity but also increased the deviations.

The active nitrogen content of gelatin and egg albumin

Kjeldahl determinations of the total nitrogen content of the gelatin and egg albumin used gave the following results:

Gelatin: 16.35% nitrogen (16.3 and 16.4%)
Egg albumin: 13.35% nitrogen (13.3 and 13.4%)

On the basis of the titrations with the heteropoly acids, the ratios of the "heterometrically active" nitrogen content to total nitrogen content were calculated.

For the titration of 3 ml of 0.5% gelatin (15 mg of gelatin; total nitrogen content 2.45 mg), 4 ml of 0.00125 *M* acid (0.00375 *N*, conforming to 0.21 mg nitrogen) were needed. Thus a ratio of active to total nitrogen of 1:12 was obtained. This means that the heteropoly acids react with only *one* nitrogen atom for every 12 nitrogen atoms contained in gelatin. The same calculations applied for egg albumin: 60 mg of egg albumin showed a total nitrogen content of 8.01 mg, and the nitrogen content found to react with the heteropoly acids was 0.399 mg. A ratio of 1:20 was thus obtained for egg albumin, or *one* active nitrogen atom for every 20 nitrogen atoms.

These results may be explained by the different characters of the two proteins studied. Thus, the arginine, histidine and lysine content of both proteins is similar, but gelatin also contains 15% proline and 15% hydroxyproline. Both these heterocyclic compounds probably form insoluble compounds with the heteropoly acids.

Analytical aspect

From Fig. 1, it may be assumed that both gelatin and egg albumin can be successfully titrated with the heteropoly acids. The end-points of the titrations with phosphotungstic and phosphomolybdic acids, which always gave nearly identical results, are especially clear. The maximum density values obtained were somewhat higher with phosphomolybdic acid.

For gelatin, a suitable method would be to titrate 20 ml of aqueous solution containing 3 ml of 0.5% gelatin and 1 ml of *M* hydrochloric acid with 0.00125 *M* phosphomolybdic acid.

For egg albumin, a suitable procedure would be to titrate 20 ml of aqueous solution containing 3 ml of 2% egg albumin and 1 ml of *M* hydrochloric acid with 0.0025 *M* phosphomolybdic acid.

SUMMARY

Heterometric titrations of gelatin and egg albumin with sodium tetraphenylborate, silicotungstic, phosphotungstic and phosphomolybdic acids were carried out at low pH values. The ratio of the nitrogen content reacting with the heteropoly acids to the total nitrogen was found to be 1:12 for gelatin and 1:20 for egg albumin. Both egg albumin and gelatin could be determined heterometrically with phosphomolybdic acid.

RÉSUMÉ

Des titrages hétérométriques de gélatine et d'albumine d'oeuf ont été effectués au moyen de tétraphénylborate de sodium, et d'acides silicotungstique, phosphotungstique et phosphomolybdique. Le rapport teneur en azote réagissant avec l'hétéropolyacide/azote total est de 1:12 pour la gélatine et 1:20 pour l'albumine d'oeuf. L'albumine d'oeuf et la gélatine peuvent être dosées hétérométriquement avec l'acide phosphomolybdique.

ZUSAMMENFASSUNG

Es wurden heterometrische Titrationen von Gelatine und Eialbumin mit Natriumtetraphenylborat, Wolframkieselsäure, Wolframphosphorsäure und Molybdatophosphorsäure bei niedrigen pH-Werten durchgeführt. Das Verhältnis des Stickstoffs, der mit den Heteropolysäuren reagiert zum Gesamtstickstoff, wurde bei der Gelatine mit 1:12 und bei dem Eialbumin mit 1:20 gefunden. Sowohl Eialbumin als auch Gelatine konnten heterometrisch mit Molybdatophosphorsäure bestimmt werden.

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SHORT COMMUNICATIONS

A new application of atomic absorption spectrophotometry: determination of phthalic acid by solvent extraction with neocuproine–copper(I) chelate

In atomic absorption spectrophotometry, a hollow-cathode lamp which emits the spectral lines belonging to the element being determined is generally used as a light source. Because of this restriction, it has been impossible to determine organic compounds and most non-metals by atomic absorption methods.

In the course of studies on solvent extraction with metal chelate cations[1], it was found that cuproine (2,9-dimethyl-1,10-phenanthroline) dissolved in chloroform was a selective extractant for phthalic acid in aqueous solutions containing a moderate amount of copper(I), and that it was possible to determine a small amount of the organic acid by measuring the absorbance of the extracts spectrophotometrically. To apply these phenomena in atomic absorption spectrophotometry, chloroform was unsuitable because of incomplete combustion in the flame and the toxicity of the decomposed products such as phosgene. To find a suitable solvent for atomic absorption spectrophotometry, various ketones, alcohols and esters were tested for the extractions; methyl isobutyl ketone containing neocuproine proved to be a selective extractant for phthalic acid in the same way as chloroform containing cuproine. An indirect method for the determination of nitrate, based upon the same principle, has recently been reported[2].

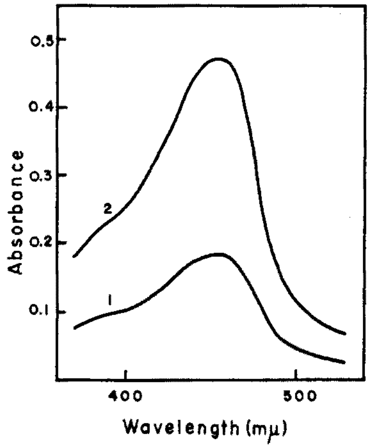

Fig. 1. Absorption spectra. (1) extracts by MIBK without phthalic acid; (2) extracts by MIBK with $2 \cdot 10^{-5} M$ phthalic acid (reference: MIBK).

This paper is concerned with the determination of phthalic acid by atomic absorption. Figure 1 shows the visible absorption spectra in the organic phase. It may be observed that the presence of phthalic acid in aqueous solution leads to a considerable increase in the extraction. The absorbance maximum of the extracted species is at 456 mμ. The chemical formula of the extracted species is assumed to be $\{[\mathrm{Cu(neocuproine)_2}] \cdot [\mathrm{C_6H_4(CO_2)_2}]\}$.

It therefore appeared possible to determine the phthalic acid as well as nitrate by spraying the extracted MIBK solution into the flame of an atomic absorption spectrophotometer with a copper hollow-cathode lamp.

To establish the optimum conditions for the determination of phthalic acid, various factors were studied: the effect of the concentrations of copper(II) ions (as copper sulfate) and hydroxylamine sulfate, the pH of the solution, the presence of the diverse ions, and also the effect of instrument settings such as fuel pressure and burner height on the intensity.

Recommended procedure for the calibration curve

The atomic absorption measurements of the organic phase were made with a Hitachi atomic absorption spectrophotometer (Model 139-0420).

Mix 1 ml of copper(II) sulfate solution ($1 \cdot 10^{-2}$ *M*), 2 ml of 5% hydroxylamine sulfate solution, 5 ml of 0.25 *M* phosphate buffer solution, and varying amounts of standard phthalic acid solution ($1 \cdot 10^{-4}$ *M*, 2–10 ml). Dilute the solution with water to 25 ml, and shake for 2 min with 10.0 ml of a MIBK solution containing neocuproine ($2 \cdot 10^{-3}$ *M*). Measure the absorption using a copper hollow-cathode lamp as light source at the 3247 Å copper line. Use an air–acetylene flame with an air flow-rate of about 7.0 l/min and an acetylene flow-rate of about 1.1 l/min.

Under the above conditions, the calibration curve was found to be linear for the tested range (0–$4 \cdot 10^{-5}$ *M*) of concentration of phthalic acid in the aqueous solution. Equal amounts of terephthalic and isophthalic acid did not interfere with the determination.

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The precipitation of calcium fluoride from homogeneous solution

A study has been made of a gravimetric procedure for the quantitative determination of calcium as the fluoride which presents certain advantages over the standard oxalate method. The method involves precipitation from homogeneous solution by means of the hydrolysis of the tetrafluoroborate ion from buffered media. Although the precipitation of calcium fluoride has been used as a gravimetric procedure for the determination of fluoride, this seems to be the first time that the same method has been used successfully for the determination of calcium. It should be noted, however, that SHAVER and GORDON[1] have precipitated calcium fluoride by hydrolyzing ethylene chlorohydrin in a solution containing potassium fluoride and the calcium complex of EDTA. Unfortunately, no information regarding the character of the precipitate and the kind of results obtained is given.

Calcium fluoride as usually prepared in the laboratory is gelatinous, difficult to filter and apt to become colloidal. TREADWELL AND HALL[2] state that the precipitate is slimy and clogs filter paper to such an extent that it is almost impossible to filter. Precipitation from homogeneous solution presented the possibility of minimizing such undesirable characteristics. Various methods were used to precipitate calcium fluoride homogeneously. Among them were the generation of the calcium ion from its complexes with ethylenediaminetetraacetic acid, diethylenediaminepentaacetic acid and nitrilotriacetic acid. The hydrolysis of β-hydroxyethylacetate was used to decrease the stability of such calcium complexes. The precipitates produced by such means, however, were extremely gelatinous and hydrated. The generation of calcium ions from solutions containing hexametaphosphate and urea also yielded unsatisfactory results as did other procedures.

Apparatus and reagents

Baker and Adamson's fluoboric acid (18–50%) and perchloric acid (60%) were used. Standard calcium solutions were prepared by dissolving 24.973 g of primary standard-grade calcium carbonate in hydrochloric acid and diluting the solution to 1 l. This solution contained 0.0100 g of calcium per ml. Solutions of magnesium oxide, lead nitrate, barium chloride, and sodium chloride were used for interference studies. They were prepared from reagent-grade chemicals.

A Perkin-Elmer model 303 atomic absorption spectrophotometer was used to follow the course of the investigation.

Recommended procedure

Add 1.0 ml of fluoboric acid and 5.0 g of ammonium chloride to 100 ml of a solution containing 0.1–0.2 g of calcium. Dilute to 200 ml and add 6.5 g of urea. Partially cover the beaker containing the solution and heat on a hot plate set at about 95°. Allow the precipitate which forms to stand for at least 3 h before filtering with Whatman No. 44 filter paper. Wash the precipitate 5 times with 10-ml portions of 3% ammonium fluoride and twice with 10-ml portions of distilled water. Transfer the filter paper to a previously weighed platinum crucible and carbonize it with the aid of a Tirrill burner. Place the crucible in a muffle furnace at 800° for approximately

20 min, then cool and weigh. The theoretical gravimetric factor for the resulting calcium fluoride is 0.5133.

Discussion

Factors such as pH, reaction temperature, buffer action, aging, excess precipitant, etc., had qualitative and/or quantitative effects upon the precipitate produced. Each of these factors was investigated before arriving at the optimum procedure. At a temperature of 60°, precipitation occurred after 1 h and at 88°, the precipitate formed settled very slowly. At 97° signs of precipitation were visible within 15–20 min and the precipitates settled quite rapidly.

The acidity of the solution affected the completeness of precipitation, as expected, and the data shown in Table I illustrate this. The final pH of the solution was regulated by varying the quantity of urea and ammonium chloride added. Quantities ranging from 2.0 to 8.0 g were used. Upon the first sign of turbidity, aliquots of the solution were taken and cooled in icewater baths to room temperature. The pH of each aliquot was then measured. At pH values of 4.6–6.1, the results obtained were within the normal experimental error allowed with gravimetric procedures. The final pH used in most determinations was 5.7 ± 0.1, which is obtained with the recommended procedure.

TABLE I

EFFECT OF pH ON THE PRECIPITATION OF CALCIUM FLUORIDE[a]

(Calcium taken: 0.2000 g)

Number	*pH at which turbidity appears*	*Final pH*[b]	*Difference (g)*
1	1.7	3.0–3.5	−0.0074
2	1.8	3.0–3.5	−0.0090
3	1.7	3.5–4.1	−0.0072
4	1.8	3.5–4.1	−0.0061
5	1.8	4.1–4.6	−0.0030
6	1.8	4.1–4.6	−0.0015
7	1.8	4.6–5.0	−0.0008
8	1.9	4.6–5.0	−0.0007
9	1.9	5.0–6.1	−0.0006
10	1.8	5.0–6.1	+0.0003

[a] Recommended procedure with modified amounts of buffer constituents to obtain varying final pH values.

[b] Initial pH of 1.6 for all determinations.

In the absence of ammonium ions, the precipitated calcium fluoride was slightly colloidal and exhibited a tendency to creep. Also, the precipitate when seen under the microscope was less crystalline than that produced in the presence of such ions. This indicated that the ammonium ion was perhaps acting as a buffering agent.

Table II illustrates the results obtained by using various amounts of fluoboric acid in excess of that used in the recommended procedure. Besides the greater increase in weight, the precipitates produced under such conditions were amorphous. Diaquocalcium fluoborate, $[Ca(H_2O)_2][BF_4]_2$, may possibly be formed in such instances. According to BERZELIUS[3], hot water dissolves the acidic component of

TABLE II

THE EFFECT OF EXCESS PRECIPITATING AGENT ON THE WEIGHT OF PRECIPITATE PRODUCED

Recommended volume of HBF_4 (ml)	*Volume of HBF_4 used (ml)*	*Weight of CaF_2 expected (g)*	*Weight of precipitate (g)*
0.7–1.0	1.5	0.1948	0.1965
0.7–1.0	1.5	0.1948	0.1950
1.0	2.0	0.3895	0.3932
1.0	2.0	0.3895	0.4889
1.5	3.0	0.4869	0.4915

TABLE III

DETERMINATION OF CALCIUM ALONE BY PRECIPITATION AS CALCIUM FLUORIDE

Ca taken (g)	*Ca found (g)*	*Ca in filtrate (g)*	*Difference (g)*
0.1000	0.0994	0.0002	−0.0006
0.1000	0.0996	0.0000	−0.0004
0.1000	0.1000	0.0001	0.0000
0.2000	0.1992	0.0003	−0.0008
0.2000	0.2004	0.0000	+0.0004
0.2000	0.1996	0.0002	−0.0004
0.2500	0.2507	0.0002	+0.0007
0.2500	0.2498	0.0001	−0.0002
0.2500	0.2500	0.0002	0.0000

TABLE IV

DETERMINATION OF CALCIUM AS THE FLUORIDE IN THE PRESENCE OF VARIOUS METALS

(Calcium fluoride taken: 0.3895 g)

Element added (g)	*Final pH*	*CaF_2 found (g)*	*Difference (g)*
0	5.7	0.3898	+0.0003
0.05 Mg	5.5	0.5045	+0.1150
0.05 Mg	5.3	0.5034	+0.1139
0.04 Pb[a]	5.6	0.4212	+0.0317
0.04 Pb	5.6	0.4236	+0.0341
0.04 Ba	5.7	0.3904	+0.0009
0.04 Ba	5.6	0.3907	+0.0012
0.05 Na	5.7	0.3906	+0.0011
0.05 Na	5.8	0.3903	+0.0008
0.1 Na	5.8	0.3923	+0.0022
0.1 Na	5.7	0.3920	+0.0019

[a] The calcium, lead and ammonium ions were in the nitrate form.

calcium fluoborate and leaves a residue of a basic salt containing an excess of calcium fluoride. What takes place may perhaps be formulated as

$$[Ca(H_2O)_2][BF_4]_2 \rightarrow HF + [Ca(H_2O)_2OH][BF_4\cdot BF_3] + [Ca(OH)_2][BF_3] + CaF_2$$

However, at temperatures between 300 and 500°, calcium fluoborate dissolves into boron trifluoride and calcium fluoride. This indicates that heating the fluoborate of calcium at 800° should leave only calcium fluoride behind since boron trifluoride would be volatilized. The results obtained did not agree with this explanation. The increased weights may be explained, however, if the formation of borates of calcium is postulated. These compounds are quite stable at temperatures just above 1000°.

The results obtained with the recommended procedure are illustrated in Table III. The amount of calcium in the filtrate was determined using atomic absorption spectrophotometry. Perchloric acid was used to eliminate the fluoride interference. Table IV shows the effect of selected interferences on the calcium determination.

Conclusions

The reactions involved in the formation of calcium fluoride are initiated by the hydrolysis of urea which facilitates the hydrolysis of the fluoborate anion and effects the subsequent precipitation of calcium, *i.e.*,

$$CO(NH_2)_2 + H_2O = CO_2 + 2\,NH_3 \quad (1)$$

$$BF_4^- + H_2O = BF_3(OH)^- + HF \quad (2)$$

$$2\,HF + Ca^{2+} = CaF_2 + 2\,H^+ \quad (3)$$

As a means for the gravimetric determination of calcium, the method presented offers advantages over the oxalate procedure. First, as much as 0.040 g of barium can be present with 0.2 g of calcium and not interfere with the initial precipitation of the latter. In the case of the oxalate method, the presence of any measurable amount of barium requires that the calcium be reprecipitated *at least* once in order that this interference be removed[4]. Furthermore, the presence of fluoride ions will not affect the results as would be the case with the oxalate procedure. The fluoride precipitate, moreover, is not hygroscopic, does not require a rigid control of ignition temperature, and need not be converted into another weighing form.

Magnesium interferes with the determination and thus this interference would have to be eliminated when employing the fluoride method. Lead interferes with both methods. Sodium can be tolerated in the amounts shown in Table IV.

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The routine determination of uranium in vegetation ash

The neutron activation technique is particularly suited to the determination of low concentrations of uranium and has 2 important advantages over other methods: high sensitivity and restriction of the possibility of contamination to the pre-irradiation stage.

The nuclear processes are

$$^{238}U \xrightarrow{n,\gamma} {}^{239}U \xrightarrow[23.5\ min]{\beta-} {}^{239}Np \xrightarrow[2.3\ days]{\beta-} {}^{239}Pu$$

Maximum sensitivity is obtained by counting uranium-239 soon after irradiation[1,2] but it is often more convenient for a routine programme to count the longer-lived neptunium-239 and this is the only course when irradiation facility and laboratory are widely separated.

Irradiation for 2 days in a thermal flux of about $1 \cdot 10^{12}$ n/sec/cm^2 produces several hundred disintegrations per minute of neptunium-239 from 10^{-9} g uranium, so that if the uranium concentration in the material under investigation is as low as 10^{-8} g/g, only 0.1 g or less of sample is required. At this low concentration contamination could preclude other analytical methods since typical laboratory dust may contain 10^{-6} g/g and many reagents contain more than 10^{-8} g/g. For the same reason pre-irradiation treatment, when an activation method is to be used, is kept to a minimum. After irradiation chemical treatment is concerned solely with the isolation of neptunium.

The isolation of chemically and radiochemically pure neptunium-239 from activated vegetation ash presents difficulties. Much of the literature concerning neptunium separation deals with pure or chemically simple solutions and it has been recognized that in the presence of other ions yields may be drastically reduced[3]. In the present work, the elements in vegetation ash were found to have this effect on extraction with thenoyltrifluoroacetone (TTA), reduced fluoride precipitation and ion-exchange processes, so that a purification scheme involving all 3 often gave an overall yield of less than 1%. MORGAN AND LOVERING[4] isolated neptunium from rock usually with a yield of 10–40% but for routine analysis of small samples a simpler procedure giving higher yields was needed.

To this end a procedure was devised in which interfering ions were systematically removed; this allowed high yields at all stages. At the same time the method was kept as short as possible, consistent with final source purity, both for maximum yield and for convenience. The experience obtained in a routine analytical programme (350 analyses) is incorporated in the detailed description.

Outline of the method

Irradiation conditions. Besides its thermal neutron capture cross-section of 2.74 barns, ^{238}U exhibits resonance peaks of very high cross-section at neutron energies in the epithermal region (0.1–100 eV)[5]. A high epithermal/thermal flux ratio therefore favours production of ^{239}Np relative to the formation of many other (n, γ) products. BEPO (AERE, Harwell) provides adequate conditions with a thermal flux $1.2 \cdot 10^{12}$ n/sec/cm^2 and epithermal flux $6 \cdot 10^{10}$ n/sec/cm^2. Irradiation for 2 days gives a growth factor of 0.45. Cooling for 2 days allows much of the ^{24}Na activity (15.4 h) to decay.

Neptunium separation. Silica and organic materials are removed with concentrated hydrofluoric and perchloric acids and the ash brought into solution. Gross amounts of highly active species, such as ^{24}Na and ^{42}K, are removed early in the process to reduce radiological hazard, by precipitation of insoluble hydroxides with sodium hydroxide; many other ions, some of which would interfere with later stages, are removed (aluminium) or their amounts reduced (calcium, magnesium). A reduced fluoride precipitation isolates rare earths and actinides and removes phosphates, troublesome as a complexing agent in the ion exchange and TTA stages and as ^{32}P (14.3-day β-emitter). Sparingly soluble hydroxides are removed in the supernate from a second hydroxide precipitation, this time using ammonia gas. An ion-exchange column removes most of the ^{233}Pa (daughter of ^{237}Np added as chemical yield tracer) and the final step is a TTA extraction prior to evaporation on a stainless steel disc for counting.

Low weight sources suitable for α-measurement of ^{237}Np are produced by this method so that electrodeposition is unnecessary.

Counting. The β-activity of ^{239}Np is measured on a continuous flow proportional counter (background about 30 counts/min, efficiency for ^{239}Np about 33%) at daily intervals during about 10 days. If activity is low, a VAN DUUREN counter fitted with an absorber to reduce the effects of α- and low γ-energies is used. This has a background of about 2 counts/min and an efficiency of about 25% for ^{239}Np. The decay curve is analysed by computer.

The activity of ^{237}Np added as a chemical yield indicator (about 100 d.p.m.) is measured via its α-emission in a scintillation counter. The α-emission from ^{239}Pu (daughter of ^{239}Np) is negligible.

Computer analysis of results. ^{237}Np tracer contributes to the β-count directly by the detection of a small fraction of its γ- and X-rays (about 1 count/min per 100 d.p.m. of ^{237}Np) and indirectly by the ingrowth of its daughter ^{233}Pa (a β-emitter). Each counter can be calibrated for these effects and a correction applied, but this is only necessary when the ^{239}Np activity is low enough to require a VAN DUUREN counter. The correction to be applied to PANAX VAN DUUREN counters fitted with a window of 2 mg/cm^2 mica plus 4.35 mg/cm^2 aluminium was found experimentally to be

$$C = \alpha\,[0.0113 + 0.23\,(1 - e^{-\lambda t})]$$

where C is the correction (counts/min) to be subtracted from the observed β-count rate, α is the ^{237}Np activity (d.p.m.), λ is the decay constant for ^{233}Pa ($=1.07 \cdot 10^{-3}$/h), t is ^{233}Pa ingrowth time (h).

In practice the correction was applied for ^{233}Pa only and the γ- and X-ray effect (a constant with respect to time) were incorporated in the constant component of the decay curve which was determined (see below).

Although the fully corrected decay curve usually fitted ^{239}Np accurately, in a few cases a small unidentified component of long half-life was present. A good fit was obtained by assuming this contribution to be constant. Consequently for simplicity all decay curves were analysed routinely for two components, ^{239}Np and a constant, and the purity of the source was inferred from the size of the constant. The contribution to this constant from γ- and X-radiation from ^{237}Np was less than 1 count/min (usually about 0.5 count/min). Duplicate analyses, one producing a pure ^{239}Np decay and the other contaminated with the long-lived impurity, gave the same value for ^{239}Np activity.

This approach has the advantage that the occasional contaminated sample, always likely in a long programme, still produces a valid result.

An IBM 7040 computer ("Stretch") operates a programme NEPRADCHEM of which the essential steps are:

(*1*) Calculate counts/min for each point and correct for counter paralysis.

(*2*) Subtract counter background.

(*3*) Subtract ^{233}Pa contribution which is currently

counts/min $= 0.23\,\alpha(1 - e^{-\lambda t})$

(*4*) Analyse the corrected decay curve for ^{239}Np + constant by a "maximum likelihood" method.

(*5*) Convert to zero time (common time for all samples in the same irradiation batch).

(*6*) Convert to activity (d.p.m.) in sample by multiplying by chemical yield factor and counter efficiency factor.

Procedure

Sample preparation. Ash the vegetation in a muffle furnace at 800° and thoroughly mix and grind in an agate mortar. Accurately weigh about 0.1 g into a weighed "Sellotape" envelope (*ca.* 0.1 g) of which the uranium content is known ($3.3 \cdot 10^{-8}$ g/g) and seal in a silica ampoule. Pack about 6 ampoules, one of which contains a known quantity of pure uranium as standard, into a standard aluminium irradiation can. Irradiate for 2 days (growth factor = 0.45) and allow to cool for 2 days.

Neptunium separation. Decontaminate the outside of the ampoules by boiling for 15 min in 8 *M* nitric acid and wash in distilled water. Break the ampoule into a platinum dish, add about 100 d.p.m. (accurately known) of ^{237}Np and about 0.1 mg of neodymium carrier, and cover with concentrated nitric acid. Heat gently to dissolve the "Sellotape" envelope and remove the pieces of ampoule, adding the washings to the main solution. Evaporate the solution to dryness. Add 5 ml of concentrated nitric acid, 10 ml of concentrated hydrofluoric acid and evaporate to dryness. Re-evaporate with concentrated nitric acid and 5 ml of perchloric acid, repeating if necessary. Dissolve the residue in 6 *M* nitric acid, transfer to a centrifuge tube and dilute to 15 ml. Add sodium hydroxide pellets until alkaline, centrifuge and discard the supernate. Again dissolve the residue in 6 *M* nitric acid, dilute, make alkaline, and centrifuge as before, finally washing the precipitate with a freshly prepared solution of sodium hydroxide.

Dissolve the precipitate in approximately 1 ml of 1.0 *M* nitric acid, add 0.1 ml of 0.5 *M* hydrazine nitrate and heat on a water bath for 15 min; cool and add 0.25 ml of 12% ammonium fluoride. Allow to stand for 5 min, centrifuge and discard the supernate. Dissolve the precipitate in 0.05 ml of saturated boric acid and 0.05 ml of concentrated nitric acid. Dilute, pass ammonia gas, centrifuge and discard the supernate. Wash the precipitate twice with water. *Thorough washing is essential.*

Dissolve the precipitate in concentrated hydrochloric acid and evaporate to dryness. Take up in the minimum of concentrated hydrochloric acid and transfer to a De-Acidite FF anion-exchange column (4 cm × 6 mm) and allow to pass through under gravity. Wash the column with ten 1-ml portions of concentrated hydrochloric acid (15 min). Wash the column with 4 × 1-ml portions of concentrated hydrochloric acid containing 1% hydriodic acid. Elute the neptunium with 4 M hydrochloric acid, add 1 drop of neodymium carrier (concentration about 1 mg/ml) and evaporate to dryness.

Take up the residue in 1.0 M hydrochloric acid, reduce with hydrazine nitrate for 15 min in a boiling water bath and dilute to 0.5 M in hydrochloric acid. Extract the neptunium with 2 × 1-ml portions of 0.25 M TTA in benzene, shaking vigorously in a polythene ampoule for 15 min. Wash the benzene solution with 2 × 1-ml portions of 0.5 M hydrochloric acid, discard the aqueous layer and note the time (^{233}Pa separation time). Back-extract the neptunium with 2 × 1-ml portions of 6 M nitric acid, shaking for 10 min each time. Wash the combined aqueous layers with 2 × 1-ml lots of benzene and discard the organic layers. Boil off the excess of benzene. Evaporate the aqueous solution to approximately 0.5 ml and mount totally on a previously flamed stainless steel disc for counting.

Results and discussion

The method is convenient for routine analysis. The time taken for the neptunium separation is about 6 h and one analyst can handle 2 samples at a time. Duplicates irradiated in different batches agreed to better than 10% and overall recoveries were better than 50%.

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Determination of thallium in cesium iodide scintillators

In an effort to correlate the response of thallium-activated cesium iodide scintillators with the thallium content, a method for analyzing thallium in concentrations of 0.001–0.5% was desired. Thallium(I) behaves ideally at the dropping mercury electrode to give reproducible waves with half-wave potentials very close to -0.47 V respective to the saturated calomel electrode. The remarkable constancy of this potential with changing solution media makes this ion a useful pilot ion for polarographic work. Measurable waves can be obtained with concentrations as low as a few tenths of a microgram per ml. These factors prompted the choice of a polarographic procedure for this analysis.

The cesium iodide sample was first dissolved in the minimum amount of water. When the thallium content was about 0.05% or more, a precipitate of thallous iodide was visible. The iodide, and subsequently the precipitate, were removed by oxidizing to free iodine with nitric acid. This was done by heating the solution and adding nitric acid dropwise. The rate of addition of the acid was controlled to avoid too rapid an evolution of iodine. After all the iodide and iodine had been removed as shown by the clear color of the solution, a few drops of sulfuric acid were added and the solution was evaporated to remove the nitric acid. The remaining salts were taken up in 0.1 *M* sulfuric acid, the solution was made to a known volume, and an aliquot of this volume was polarographed.

In the actual analysis, excellent waves were obtained until the thallium content dropped below 0.01% after which it became difficult to distinguish the thallium wave from the background. A separation of the thallium from the bulk of the cesium seemed to be a logical procedure to follow. The separation should also make possible the concentration of solutions very dilute with respect to thallium to the point where measurable waves can be obtained without increasing the total salt content to an unwieldy level.

Two separation schemes were considered and tested, an anion-exchange operation and solvent extraction. In either scheme it is necessary to oxidize the thallium(I) present in the solution prepared as above to thallium(III) because thallium(I) does not readily form complexes of stability great enough to be useful for these types of separations. Either sodium hypochlorite or chlorine water will readily bring about this oxidation; only a few drops of the former reagent are required. Chlorine water should be freshly prepared and at least 5 ml of this solution should be used. The oxidation should be performed in 3–6 *M* hydrochloric acid to insure the instant complexation of the thallium(III) as it is formed.

KRAUS AND NELSON[1] have shown that the thallium(III) chloro complex is retained on a Dowex-1 column through the entire range of hydrochloric acid concentration with the separation factors increasing with decreasing acid molarity. Since only a small amount of thallium needs to be sorbed, a column 1 cm in diameter and 5 cm long was found to be ample. The solution containing the oxidized thallium in hydrochloric acid medium was passed through this column as fast as gravity flow would allow. Since complete separation from all the cesium was not necessary, only one column volume of dilute acid wash was used. The original solution and the wash were discarded. The thallium was then eluted with 4 column volumes of 0.2% sulfurous acid. The eluate was evaporated nearly to dryness. If any organic matter was present as shown by charring, it was removed with the minimum amount of perchloric acid. The solution was made to volume with 0.1 M sulfuric acid and polarographed. The resin was discarded following the elution.

Solvent extraction was performed with the thallium in a 6 M hydrochloric acid medium. When chlorine water was used for the oxidant, it was necessary to add some concentrated acid to compensate for the dilution brought about by the addition of the oxidizing solution. Extraction with ethyl ether[2] was found to be incomplete. Even when 3 extractions were performed with a reoxidation between successive extractions, a maximum of 70% extraction was attained. Either hexone or methyl ethyl ketone was found to extract the thallium fully with one pass. These solvents form heavy emulsions with water. In order to minimize this emulsification, the extraction was performed by slowly swirling the extraction vessel. Even with this mode of extraction, complete extraction was obtained within 30 sec.

The organic phase can be evaporated to dryness, any residual organic material removed with perchloric acid, and the remainder taken up with 0.1 M sulfuric acid for the polarographic determination. An alternative procedure is to strip the thallium from the organic phase with a dilute sulfurous acid solution, acidifying this with sulfuric acid, and boiling to remove residual sulfurous acid.

Good recovery was obtained with either method, but the anion-exchange method is preferable from the standpoint of equipment required and ease of operation.

The limit of sensitivity of the polarographic method at 0.5 μA full scale is about 1 μg per ml when the cesium concentration does not exceed 0.1 M. If it is desired to increase the sensitivity by going to the lower ranges (0.2, 0.1 μA), it is necessary to cut down the total salt content. Wherever possible, it is preferable to concentrate the dilute solutions and polarograph at least at the 0.5 μA range. The precision in determining 3 μg per ml at 0.5 μA is better than 10% relative and improves with increasing thallium concentration, approaching 5% at the 10 μg per ml level. At the lower levels below 1 μg per ml, the precision drops to about 15%.

The thallium in cesium iodide containing 0.05 and 0.1% thallium was analyzed before and after the removal of the bulk of the cesium. The analyses agreed within 5 μg indicating that recovery was essentially complete.

Since the starting material was very pure, no interference from this source was expected and none was found. Interference can result from residual reductants which have to be removed before the polarographic step. The most troublesome interference is the organic material contributed by the resin column or the extracting liquids.

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The preparation and stability of uranium carbide samples for the determination of oxygen, hydrogen and nitrogen by vacuum fusion

Uranium carbide offers numerous advantages because of its relatively high uranium content, thermal conductivity, and low production cost compared to other uranium compounds; investigations of its applicability as the fuel element in nuclear reactors have therefore increased considerably, and numerous different techniques for its manufacture have been developed. Depending on the metallurgical, compacting and sintering processes used, the gaseous content of the uranium carbide will be different, particularly for O_2, H_2 and N_2 [1]. Moreover, the sintered UC is extremely moisture-sensitive, even in the absence of air, giving rise to the formation of UO_2, so that its oxygen content is increased[2,3].

Accordingly, the analysis of the O_2, H_2, N_2 and C contents of uranium carbide is of great importance, not only as a means of controlling and studying the methods of preparation, but also in controlling methods of storage and handling. Because of the importance of obtaining satisfactory and accurate analytical results, a detailed study of the variations in the analytical results for O_2, H_2 and N_2 contents of uranium carbide was undertaken. Particular attention was given to the procedures used to prepare the sample before its introduction to the unit for vacuum fusion; the variations shown by these gases as a function of time depending on the storage medium for the UC were also studied. The analytical method involved vacuum fusion with a platinum bath, as described previously for the analysis of uranium and some of its compounds[4,5].

Apparatus

The equipment utilized was a N.R.C. unit of the standard ASTM type, the basic parts consisting of an induction oven and the analytical system. The induction oven consisted of a Pyrex tube with a quartz tube suspended in its interior. A graphite crucible was placed inside the quartz tube, separated by a coating of powdered graphite[6]. The crucible served not only as a container to melt the samples, but also as a source of carbon for the formation of CO and CO_2. The power source was a 2.5 kW unit and the maximum temperature reached was 2400°.

The analytical system consisted of the following components: (a) two mercury diffusion pumps, one for extraction of gases from the oven, and the other in order to circulate the gas through the analytical system; (b) a Toepler pump for the quantitative transfer of gases to the measuring system; (c) a triple MacLeod gauge; (d) a copper oxide tube at 325° to catalyse the oxidation of hydrogen to water and of carbon monoxide to the dioxide, with a trap cooled by a dry ice–acetone mixture in order to retain the CO_2 formed; (e) an oil diffusion pump connected to another mechanical pump.

Procedure

Samples of *ca.* 100 mg were introduced into platinum foil cones, previously prepared from platinum foil squares 20 mm long and 0.01 mm thick, which had been completely degreased with acetone. The approximate weight of these cones was 250 mg[7]. The samples prepared in this manner, and which had a precisely known UC content, were placed into the arm of the oven, and then allowed to fall on to the melted platinum bath contained in the graphite crucible, heated by induction in the high-frequency oven. The temperature of the bath during and after the analysis was 1800–1850°, and the temperature at which the sample was introduced was 1650–1700°. The oven was degassed previously at 2200° for 2 h or more, until a blank value of 0.016 ml/h was obtained. After degassing the oven and checking that the analytical system was free from blank values, the temperature was reduced to the appropriate value for analysis.

The gases obtained from the samples during an interval of 15 min were collected and measured; they were then passed through the copper oxide tube at 325°, through the dry ice–acetone trap, and then through a trap cooled with liquid air to retain the CO_2 during the measurement of the nitrogen gas. Through the difference between these measurements, the percentage amounts of the O_2, H_2 and N_2 gases in the sample were readily obtained.

Results

Variation in the gaseous content of uranium carbide as a result of the cutting, grinding and powdering processes in various media. Approximately 100-mg portions were taken from a UC rod kept in a plastic enclosure under argon. Cutting was done under trichloroethylene[8]. The portions were dried, any contact with hands or greased surfaces being avoided, and then transferred to the platinum foil cones. The UC residue was again stored under an argon atmosphere in a tight container[9]. The prepared samples were weighed and then placed in the side-arm of the oven for analysis.

TABLE I

GASEOUS CONTENT OF THE Pt BATH UTILIZED

Sample	*Weight (g)*	*% Oxygen*	*% Nitrogen*	*% Hydrogen*
1	0.2046	0.0031	0.00005	0.00000
2	0.2387	0.0035	0.00010	0.00000
3	0.2740	0.0033	0.00020	0.00000

The gaseous content of the platinum bath proved to be very small, consisting mainly of oxygen as shown in Table I. The average results of the analyses of the recently cut samples are shown in Table II (Exp. 1). In order to improve the precision of these results, a greater homogenization of the sample was sought by powdering the UC samples, thereafter proceeding to their immediate analysis.

First the UC was ground under unpurified trichloroethylene of technical grade purity. In view of the deviations in the analytical results (Table II, Exp. 2), as well as of the characteristic smell of acetylene of the ground sample, a further grinding step was carried out with purified and dried trichloroethylene "Probus", containing 0.0086% of water (Table II, Exp. 3). From these results it became apparent that in both cases the oxygen and hydrogen contents varied, while the nitrogen content could be considered practically the same as at the starting point, since no improvement whatsoever was obtained in the precision of the results.

For comparative purposes, a dry pulverization was made with the certainty that a variation in the gaseous content should take place due to the fact that UC is highly pyrophoric; the results are shown in Table II, Exp. 4. These results were rather similar to those in Exp. 3, with the only difference that the nitrogen content was slightly higher.

Variation of the gaseous content of uranium carbide as a function of time under normal and argon atmospheres. In order to investigate the variation of the gaseous content of UC as a function of time, the tests were repeated, 40 days after the first analysis had been carried out, with fragments weighing *ca.* 100 mg, which had been stored under argon and only exposed to the atmosphere during the short time involved in the collection of the different samples. From the results obtained (Table II, Exp. 5), it can be seen that the oxygen and hydrogen contents varied, the later results being higher than the initial contents which indicated that the UC had altered considerably. The loss of precision in the results compared to those obtained in Exp. 1 can also be seen clearly. These tests were repeated with another sample of uranium carbide, by carrying out the analyses before and after storage without any kind of precautions in an atmosphere of air. The results given in Table II, Exps. 6 and 7 show that the disagreement was much more pronounced.

TABLE II

COMPARATIVE STUDY OF PREPARATION AND STORAGE CONDITIONS[a]

Exp. no.	*Conditions of the sample*	*Nitrogen (p.p.m.* $\pm ts/\sqrt{n}$*)*	*Oxygen (p.p.m.* $\pm ts/\sqrt{n}$*)*	*Hydrogen (p.p.m.* $\pm ts/\sqrt{n}$*)*	*Degrees of freedom (N − 1)*
1	In recently cut fragments	142 ± 28	708 ± 81	3.5 ± 1.8	6
2	Ground under technical grade purity trichloroethylene	226 ± 55	3507 ± 194	47.0 ± 24	4
3	Ground under purified and dried trichloroethylene	126 ± 15	1306 ± 57	12.0 ± 1.4	4
4	Dry ground	229 ± 14	1003 ± 85	12.0 ± 1.0	3
5	In fragments 40 days after cutting, kept under argon atmosphere	133 ± 68	1110 ± 312	10.0 ± 8.3	4
6	Recently prepared fragments	540 ± 87	1868 ± 223	34 ± 1.2	4
7	Stored under air atmosphere without precautions	550 ± 190	2134 ± 440	45 ± 8.6	6
8	Ground under argon atmosphere and exposed to atmosphere 0 h	112 ± 14	3129 ± 86	35 ± 23	7
9	Ground under argon atmosphere and exposed to atmosphere 15 h	127 ± 43	3280 ± 392	44 ± 17	5
10	Ground under argon atmosphere and exposed to atmosphere 72 h	106 ± 30	3054 ± 582	35 ± 15	5

[a] The values of this Table are calculated for a confidence level of 95%.

Because of the evidence that the gaseous content of UC, particularly those of oxygen and hydrogen, varied as a function of time, a study was made of this variation, starting with a sample pulverized under argon in order to facilitate the homogeneity of the reactions throughout the sample. Different portions of this UC sample were placed into glass tubes and sealed with a burner under an argon atmosphere. The tubes were opened and their contents were placed on watch glasses in a container open to the atmosphere; these operations were carried out so that time intervals of 0, 2, 4, 15, 24, 48 and 72 h, respectively, elapsed between the opening of the tubes and the introduction of the sample into the induction oven for analysis. However, these results showed no systematic variation with time at all; the analyses were therefore repeated at greater time intervals and also a greater number of experiments was made. For this purpose, three of the samples already prepared, pulverized under an argon atmosphere and sealed with a burner under the same atmosphere, were selected and opened at intervals of 0, 15 and 72 h. These samples were analysed as described above; the results are shown in Table II, Exps. 8–10, from which it can be seen that again no systematic variation was obtained.

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An analytical method for the "simultaneous" determination of deuterium and tritium

The use of isotope effects for the study of reaction mechanisms is now an established technique[1,2]. Deuterium and tritium are particularly valuable in this respect for several reasons. Firstly, isotope effects are greatest when a hydrogen atom is replaced by deuterium or tritium, since these substitutions correspond to large relative changes in the mass of the atom. Secondly, one-step methods are now available for either specific[3] or random double labelling[4] with both hydrogen isotopes.

It would thus be convenient to possess a technique for the "simultaneous" determination of deuterium and tritium in the same organic compound. The purpose of this paper is to describe the development of a method involving a single combustion and reduction process for the "simultaneous" analysis of the 2 hydrogen isotopes in organic compounds.

A number of combustion reactions have already been reported for the separate analysis of deuterium and tritium in organic materials, but few of these are applicable to the simultaneous determination of these isotopes. For example, consider the most commonly used one-step method for tritium gas analysis which was originally developed by WILZBACH *et al.*[5] and later modified by GARNETT *et al.*[6]. The procedure which gives a high precision in counting reproducibility consists in the quantitative conversion of organic-bound tritium into the gaseous state by combustion at 650° with nickel oxide and zinc catalysts in a sealed tube. The technique not only yields isotopic hydrogen but some hydrocarbons (predominantly methane) and carbon dioxide. For subsequent tritium analysis by the ion-current–vibrating reed electrometer method, the conversion procedure is satisfactory, but for deuterium assay, the method is unsatisfactory since the deuterated hydrocarbons and carbon dioxide interfere with the mass spectrometric analysis of deuterium.

The GRAFF AND RITTENBERG[7] combustion and reduction procedure for the analysis of deuterium produces only isotopic hydrogen gas and is thus potentially suitable for simultaneous deuterium–tritium estimation since the resulting isotopic hydrogen is amenable to analysis both by the vibrating reed electrometer (tritium) and mass spectrometric (deuterium) methods. The procedure consists of combustion of the organic compound in a stream of oxygen over copper oxide, and collection of the isotopic water followed by zinc reduction to hydrogen. However some modifications to the original GRAFF AND RITTENBERG deuterium procedure were necessary for the present work and these are included in the following detailed analytical method.

Analytical procedure

The organic compound (10–20 mg) is volatilized in a stream of dry oxygen into a copper oxide furnace maintained at 610°. The water from the combustion is collected in a cold trap (dry ice/acetone is satisfactory) and the combustion tube pumped out to approximately 10^{-1} mm to ensure complete conversion and collection of water. The isotopic water is reduced to hydrogen by repeated passes over zinc granules (20 mesh) at a temperature of *ca.* 410°. The gas is then toeplered into a sample vessel (ampoule A, Fig. 1) and first analysed for its deuterium content at 70 eV by conventional mass spectrometer techniques using the peak heights at M/e 2, 3 and 4. The remaining gas in the ampoule is then analysed for tritium by the vibrating reed technique. This involves delivery of a constant aliquot of gas to the ionization chamber (D), utilizing the apparatus shown in Fig. 1. The equipment is evacuated to sample tube A, taps T_1 and T_2 are closed and a fixed quantity of gas is toeplered into the space defined by taps T_1, T_2 and T_3. Taps T_1 and T_4 are opened and the gas expanded into the ionization chamber which is then filled with counting gas (propane) to a pressure of one atmosphere and the ion-current measured either by the technique of rate-of-charge of the capacitor or by the constant leak circuit[5,6].

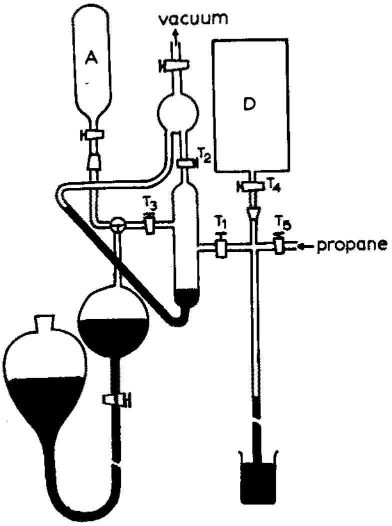

Fig. 1. Gas handling apparatus for tritium analysis. A, sample tube containing isotopic hydrogen from GRAFF–RITTENBERG combustion; D, ionization chamber.

Discussion of procedure

During the adaption of the GRAFF AND RITTENBERG procedure, several new features were discovered in the combustion and reduction processes which influence the accuracy of the analysis. The first of these concerns the existence of a critical operating temperature for the copper oxide furnace beyond which reproducible results are not obtained. It was found that copper oxide becomes suddenly unstable at approximately 630° with the liberation of large quantities of oxygen and the formation of copper. Combustions performed under these conditions lacked reproducibility and this is attributed to a side-reaction involving reduction of portion of the combustion water by copper.

$$Cu + H_2O \rightarrow CuO + H_2 \qquad (1)$$

This occurs with a large isotope effect and since, during the trapping of water, hydrogen is pumped away, a significant difference from the correct D/T ratio may ultimately be observed under these conditions.

A temperature of 610° was found to be satisfactory for the copper oxide.

Another source of error results from the isotope effect in the zinc reduction process which although not reported by GRAFF AND RITTENBERG, has also been detected by other authors[8]. It is important to recognise this isotope effect since it necessitates the complete reduction of the isotopic water. Failure to carry out this step satisfactorily even by several percent, produced very serious errors in the isotopic determination. The temperature of the zinc furnace is also critical since zinc sublimes at 410–420° under the conditions of combustion and this frequently leads to blockage of the furnace exit tube if the temperature is too high. The reduction reaction is markedly exothermic so that it is advisable to start combustion at temperatures of 385°. The heat of reaction will inevitably raise the furnace temperature to 400–410° after each major pass of water vapour.

For the deuterium analysis step in the mass spectrometer, particular care should be taken to construct a calibration graph by reducing water of known isotopic hydrogen content (diluted from 99.75% in this instance). This will essentially overcome the appreciable mass discrimination effects in both the mass spectrometer itself and the conversion procedure, although some mass spectrometers have recently been designed to reduce this to a minimum[9].

The accuracy of the present technique was tested using doubly labelled benzene by comparing the results with those obtained by established methods (Table I). For tritium the modified combustion and reduction over nickel oxide and zinc was employed[6], while deuterium was analysed by low voltage (10 eV) mass spectrometry[2] which is particularly suitable for volatile organic compounds. Standard benzene samples of varying isotopic composition were prepared by equilibrating[2] isotopic water with benzene in the presence of platinum catalyst for 24 h at 120°. Results of the "simultaneous" deuterium–tritium analytic technique are in excellent agreement with the separate methods of isotope analysis, a reproducibility of better than 1% being obtained. The analytical procedure was then used to determine isotope effects for the heterogeneous exchange between benzene and isotopic water in the presence of active platinum. Deuterium was found to exchange faster than tritium, the ratio[2] of the rate constants being 1.70 ±0.10 at 30°.

TABLE I

COMPARISON OF ANALYTICAL METHODS FOR THE DETERMINATION OF DEUTERIUM AND TRITIUM IN BENZENE

Isotope	*Method of analysis*	*Isotopic content*		
		Sample 1	*Sample 2*	*Sample 3*
Deuterium (%)	Low voltage (10 eV) mass spectrometry[2].	20.1	39.8	60.0
	"Simultaneous Deuterium–Tritium Analysis"	20.0	39.7	60.4
	"Graff–Rittenberg Deuterium Analysis" with CuO furnace[7] at 650°	26.2	44.9	69.3
Tritium (μC/g)	Combustion and reduction over nickelic oxide and zinc[6]	1.52	2.97	4.49
	"Simultaneous Deuterium–Tritium Analysis"	1.49	3.00	4.52

The authors thank the Australian Institute of Nuclear Science and Engineering (Mr. E. A. PALMER) for assistance in the purchase of the heavy water and Cdr. J. MASON for instrumentation advice. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

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Anal. Chim. Acta, 35 (1966) 540–543

The use of tetracycline as a fluorescent indicator in the compleximetric microdetermination of group II cations

The titration of micro quantities of calcium with EDTA is not satisfactory with eriochrome black T indicator unless magnesium is present[1]; visual titrations with murexide as indicator are difficult because the colour change starts before the equivalence point is reached[2]. Fluorescent indicators, being extremely sensitive, are very suitable for the compleximetric determination of micro quantities of metal ions[3]. KOHN[4] has described the fluorimetric determination of tetracyclines as their highly fluorescent calcium complexes. The possibility of using tetracycline as a fluorescent indicator was therefore investigated; it was shown to be highly sensitive in UV light for compleximetric titrations of calcium, strontium and magnesium in ammoniacal buffer at pH 10 and less sensitive for titrations of cadmium and zinc. Barium could not be titrated directly but a back-titration procedure was feasible. No fluorescent complex was formed in ammoniacal buffer at pH 10 between tetracycline and Ag, Cu, Pb, Bi, Sn(II), Hg(I), Hg(II), Mn(II) or Fe(III).

Apparatus

The titration assembly consisted of a 25-ml capacity transparent silica crucible and a Shandon UV Chromatolite 2537 Å source fitted with a cardboard shield which allowed the UV light to pass through a 1.5 × 5 cm slit into the solution, but prevented any direct viewing of the UV radiation during the titration. The use of pyrex titration vessels made the end-points less easy to detect. Titrations were carried out in the dark. The determinations could be carried out in daylight without loss of accuracy using a Fisher UV titration unit.

Reagents

Analytical-grade reagents and deionised water were used to prepare all solutions.

Tetracycline indicator. A $10^{-3}M$ indicator solution was prepared by dissolving 11 mg of tetracycline (Pfizer, Ltd.) in 25 ml of deionised water and adding two drops of chloroform. This solution was stable for at least 3 months; in dilute ammonia solution tetracycline is unstable, the clear yellow colour turning brown after several hours.

Titration of calcium, strontium, magnesium, cadmium and zinc

Procedure. To 2–3 ml of a neutral solution of the metal ion, add 3 drops of ammonia–ammonium chloride buffer pH 10 and 1 drop of tetracycline indicator. A yellowish-green fluorescence is obtained in UV light. Titrate with standard EDTA solution until the fluorescence is just extinguished. Results obtained by this method are shown in Table I.

The effect of pH on fluorescence. The fluorescence of free tetracycline under UV light cannot be visually detected in the pH range 6–12. The calcium–tetracycline complex does not fluoresce below pH 7.6, but above this value the fluorescence intensity increases with increase in pH, reaching a maximum in the pH range 9–11. Ammonia–ammonium chloride, monoethanolamine and sodium hydroxide solutions were all suitable for the adjustment to pH 10; the ammoniacal buffer was finally chosen for convenience.

The fluorescence of the zinc–tetracycline complex was weaker than that of the calcium–tetracycline complex and therefore tetracycline is not a suitable indicator for

TABLE I

DETERMINATION OF VARIOUS METALS

Metal titrated	*Metal present (µg)*	*No. of detns.*	*Metal found (µg)*	*Average error (µg)*	*Molarity of EDTA titrant*
Ca	1604	2	1594	—10	0.01755
	802	1	802	0	0.01755
	802	2	803	+1	0.00439
	401	2	401	0	0.00439
	40	6	42.7	+2.7	0.00439
	4	5	4.36	+0.36	0.00044
Sr	1753	3	1752	—1	0.01755
	1753	2	1741	—12	0.00439
	88	3	87	—1	0.00439
Ba [a]	1374	5	1306	—68	0.00990
Mg	487	2	488	+1	0.01755
	487	5	486	—1	0.00439
	48.5	2	50	+1.5	0.00439
	24.3	3	23.2	0.9	0.00439
Cd	2248	3	2238	10	0.00439
Zn	1308	4	1296	12	0.00439

[a] Determined by back-titration.

the determination of zinc in the 25-μg range. The determinations of cadmium and zinc were not investigated further because indicators more sensitive than tetracycline are already available for the determination of these metals.

Interfering ions. Tetracycline does not form fluorescent complexes with Cu, Bi, Sn(II), Pb, Fe(III) or Mn(II) in ammoniacal buffer but it was found that all of these ions interfered with the determinations. Attempts to determine calcium in the presence of copper or zinc by masking them respectively as their thiosulphate or cyanide complexes failed. The presence of phosphate ions and other reagents that precipitated or formed complexes with the ions interfered with the determinations. Alkali metals did not interfere.

Determination of barium

The direct titration of micro amounts of barium by the above method gave very poor end-points, which were not improved by addition of alcohol. A much improved end-point was obtained by adding excess of 0.01 *M* EDTA solution and back-titrating with standard 0.01 *M* calcium solution until the fluorescence first appeared. However, a negative error was found (see Table I) which was probably due to the fact that it was more difficult to detect the exact point of appearance of the fluorescence than that of its disappearance. Attempts were made to improve the end-point by the use of EGTA and DCyTA as complexing agents instead of EDTA in the direct and indirect titrations; back-titration of EGTA with magnesium solution was also examined. None of these attempts was successful.

The most consistent results were obtained by the following method.

Procedure. To 1–2 ml of neutral sample solution add an excess of 0.01 *M* EDTA solution keeping the total volume of solution as small as possible. Add 4 drops of ammoniacal buffer pH 10 and one drop of tetracycline solution and titrate with 0.01 *M* calcium solution under UV light until the fluorescence just appears.

Conclusion

Tetracycline is superior to murexide and eriochrome black T for the titration of micro quantities of calcium and strontium. Although its application is limited to the determination of ions in pure solutions, it could prove very useful in conjunction with separation techniques such as ion exchange and paper chromatography.

The author is grateful to Dr. J. J. T. Owen for his assistance with the literature survey and to Messrs. Pfizer Limited, Sandwich, Kent, for supplying the tetracycline.

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(Received January 19th, 1966)

BOOK REVIEWS

L. ERDEY, *Gravimetric Analysis**, translated by G. SVEHLA, edited by I. BUZAS, (International Series of Monographs on Analytical Chemistry, Vol. 7) Pergamon Press, Oxford.
Part I, 1963, vii + 324 pp., price 50 s.
Part II, 1965, xv +796 pp., price 120 s.
Part III, 1965, vii + 301 pp., price 50 s.

No other analytical technique can rival the accuracy of a gravimetric method chosen properly and applied with care and technical artistry. Gravimetric methods have, of course, fallen into disrepute because they require skill beyond the capacity of the average junior technician, and time beyond that allowable for skilled workers. However, such methods still cannot be ignored for they form the fundamental basis of comparison for many other analytical techniques and are without peer for standardization and certain other special purposes.

A variety of fairly recent books is available on other aspects of classical analytical chemistry but it is many years since any text has been devoted entirely to gravimetric analysis. These 3 volumes must therefore be welcomed unreservedly.

In Part I of this text, the principles and general practice of gravimetric analysis are described comprehensively, every step of the procedure from sampling to calculation of results being treated with a fine appreciation of its importance; the several types of thermogravimetric analysis are also described. Further chapters deal with methods of separation of all types from fractional precipitation through solvent extraction to paper chromatography, and with the determination of the water content of solids.

In Part II, gravimetric methods for the determination of cations are discussed in detail. The chapter dealing with cobalt provides a suitable example of the scale of treatment: after a brief general discussion of the occurrence of cobalt, the dissolution of samples and the main reagents utilized, the principal methods of precipitation (as metal, sulphide, hydroxide, tetrapyridinocobalt(II) thiocyanate, cobalt 1-nitroso-2-naphtholate, potassium cobaltinitrite and oxinate) are discussed with a wealth of practical information; thermogravimetric curves, many of which have not been previously published, are included. This is followed by an outline of the procedures suitable for the separation of cobalt from other cations or groups of cations. In all, 42 cations or groups of cations (*e.g.* rare earths) are dealt with. The final chapter of this Part contains much valuable information on the separation of the alkali metals.

In the third and final Part, the gravimetric determination of anions is similarly described. Possibly because there are far fewer available methods for anions, this Part contains a fair amount of material which, useful though it is, is not strictly relevant to gravimetry. The text ends with an excellent Appendix on cleaning of

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* This text is also available in a German edition: *Theorie und Praxis der gravimetrische Analyse,* Akademiai Kiado, Budapest.
Band I. Theoretischer Teil, 1964, 382 S., price $ 9.00.
Band II. Bestimmung der Metalle, 1964, 802 S., price Hfl. 65.—.
Band III. Bestimmung der Nichtmetalle, 1964, 340 S., price $ 13.00.

apparatus, purity and preparation of reagents, and calculations, followed by tables of solubility products and conversion factors.

This text will undoubtedly gain the status of a classic, for it is a fine amalgam of modern theoretical understanding and old and modern method. The author is a master of the analytical science in both its classical and instrumental aspects and his appreciation of the continuing importance of gravimetric techniques makes this an outstanding contribution to the literature of analytical chemistry.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 35 (1966) 546–547

Advances in Analytical Chemistry and Instrumentation, Vol. 3, Edited by C. N. REILLEY, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1964, vi + 523 pp., price 113 s.

Any attempt to assist chemists to keep abreast of the original literature is to be welcomed and this series of reviews is of great value in that respect. The present volume contains 8 reviews dealing with widely diverse types of analysis.

A review of atomic absorption spectroscopy (30 pp.) by R. LOCKYER, deals mainly with basic principles and general considerations; only a brief list of applications is given. Photometric titrations are considered by A. L. UNDERWOOD in a minor monograph (73 pp.) in which the theory of the titrations with and without indicators, instrumentation and techniques and selected applications are discussed in straightforward terms.

The review of enzyme-catalyzed reactions of analytical value by W. J. BLAEDEL AND G. P. HICKS (37 pp.) contains less utilitarian information from the point of view of the general analytical chemist but the indications given of the possibilities of these extremely sensitive methods should be widely appreciated.

Ion sources and detectors for the mass spectroscopic study of solids are discussed by L. F. HERZOG (39 pp.) and galvanic analysis is described by P. HERSCH (65 pp.); the latter chapter should be of particular interest to those concerned with continuous monitoring processes.

The final 3 chapters are devoted to various chromatographic separation techniques. L. R. SNYDER discusses linear adsorption chromatography (62 pp.) with emphasis on the development of a quantitative theory of adsorption chromatography. J. C. GIDDINGS then deals with column parameters in gas chromatography (52 pp.); basic principles are outlined and the information on the choice of conditions for gas–liquid, gas–solid, capillary column and programmed-temperature chromatography should be invaluable to workers not wholly acquainted with the techniques. Finally, R. MAIER AND H. K. MANGOLD have written a monograph (107 pp.) on thin-layer chromatography; this section comprises a full-scale survey of the whole technique from its origin to recent applications in organometallic separations.

The present volume must enhance the already high esteem in which this series of volumes is held. One can but lament that costs prevent the series from being available on every analytical bookshelf.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 35 (1966) 547

Absorption Spectra in the Ultraviolet and Visible Region, Edited by Dr. L. LANG, Vol. VI, Akademiai Kiado, Budapest, 442 pp., price 115 s.

Il s'agit du sixième volume du catalogue de spectres d'absorption visibles et ultraviolets édité par le Dr. LANG; ce volume est présenté de façon analogue aux précédents; il comprend 196 substances nouvelles dont il serait difficile de donner un aperçu sommaire étant donné la variété très grande. Ajoutons cependant qu'il comporte un grand nombre de composés hétérocycliques azotés et oxygénés.

Comme pour les volumes antérieurs, la présentation est très soignée et très commode pour le classement suivant les exigences de l'utilisateur.

G. DUYCKAERTS (Liège)

PUBLICATIONS RECEIVED

R. BERNHEIM, *Optical Pumping: An Introduction.* (Frontiers in Chemistry: An Advanced Monograph Series). W. A. Benjamin, New York, 1965. Pp. xi+272.

Chapter headings: Introduction; The Optical Pumping Experiment; The Dynamics of Optical Pumping; Optical Resonance Radiation; Magnetic Interactions; Electric Interactions; Magnetic Resonance Detection; Phenomenological Description of Oriented Systems; Energy Level Crossing Experiments; Spin Exchange; Pressure Shift of the Hyperfine Interaction; Spin-Relaxation Times; Chemical Applications of Optical Pumping; Optical Pumping in Solids; Selected Reprints.

F. ŠORM AND L. DOLEJŠ. *Guaianolides and Germacranolides.* (Collection: Chemistry of Natural Products). Hermann, Paris, 1965. Pp. 153. Price 48.— F.

Chapter headings: Introduction; The Guaianolides; The Germacranolides; Tables of Physical Constants and Infra-red Spectra.

J. R. DYER. *Applications of Absorption Spectroscopy of Organic Compounds.* (Foundations of Modern Organic Chemistry Series). Prentice-Hall, Inc., New York, 1965. Pp. x+143.

Chapter headings: Introduction; Ultraviolet Spectroscopy; Infrared Spectroscopy; Nuclear Magnetic Resonance Spectroscopy; Wavelength-Wave Number Conversion Table.

M. J. SIENKO AND R. A. PLANE. *Physikalische anorganische Chemie.* Übersetzt und ergänzt von F. Steinbach. S. Hirzel Verlag, Stuttgart, 1965. viii+169 S. Kart. DM 18.—.

Inhaltsverzeichnis: Einführung; Atombau; Moleküle; Der feste Zustande; Flüssigkeiten und Lösungen; Chemische Reaktionen.

ERRATUM

J. E. PORTMANN AND J. P. RILEY, The determination of bismuth in sea and natural waters, *Anal. Chim. Acta*, 34 (1966) 201–210.

On pp. 206 and 207, the strength of the ammonia solution used was 0.1 *N* and not 1 *N* as stated. Thus, line 8 (p. 206) should read: ... the use of 5 ml of 0.1 *N* ammonia gave the lowest reagent blank ...

The top line of Table IV should read:

Normality of ammonia (*N*) 0.05 0.1 0.125 0.15 0.2

On p. 207, under *Reagents*, the preparation of the ammoniacal cyanide reagent should read: Dissolve 1 g of potassium cyanide in 100 ml of 0.1 *N* ammonia solution.

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25wn. 10.

ANNOUNCEMENT

XXIst INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY

The XXIst International Congress of Pure and Applied Chemistry will be held in Prague on September 4–10, 1967, under the auspices of the Government of the Czechoslovak Socialist Republic. The Scientific Programme will be divided into three sections as follows.

1. *Automation in Analytical Chemistry.* Papers should show the contribution that automation can make to the study of chemical reactions and other phenomena, with particular reference to analytical chemistry but without emphasizing instrumental aspects. This section will be subdivided into automation of analytical methods based on *a*) electrical measurements, *b*) thermography, *c*) spectrochemical measurements at all wavelengths, *d*) separation methods, and *e*) radiochemical methods, together with *f*) automation and regulation of chemical processes based on analytical methods.
2. *Toxicological Chemistry.* This section will deal with industrial, forensic and clinical toxicology, and will cover the analytical chemistry and biochemistry of industrial poisons and of toxicologically important drugs.
3. *Chemistry of Nucleic Acid Components.* This section will deal with the present state of the chemistry and physical chemistry of purine and pyrimidine bases, their nucleosides and nucleotides.

Papers may be presented in any language but the Organizing Committee hopes that speakers will use a language that is widely understood, preferably English; no arrangements will be made for simultaneous translations, except for Plenary Lectures which will be translated into English.

Authors intending to take part in the Congress and to present papers must return application forms not later than September 1, 1966. It is expected that, apart from Plenary Lectures, only abstracts of submitted papers will be published.

A full programme of social events for the participants and a ladies' programme are planned. The registration fee for the Congress will be $35 for active participants and $20 for persons accompanying them.

Further information can be obtained from: The Chairman, Organizing Committee, XXIst International Congress of Pure and Applied Chemistry, P.O.B. 139 PRAHA 6 – Dejvice, Czechoslovakia.

ANALYTICA CHIMICA ACTA, VOL. 35 (1966)

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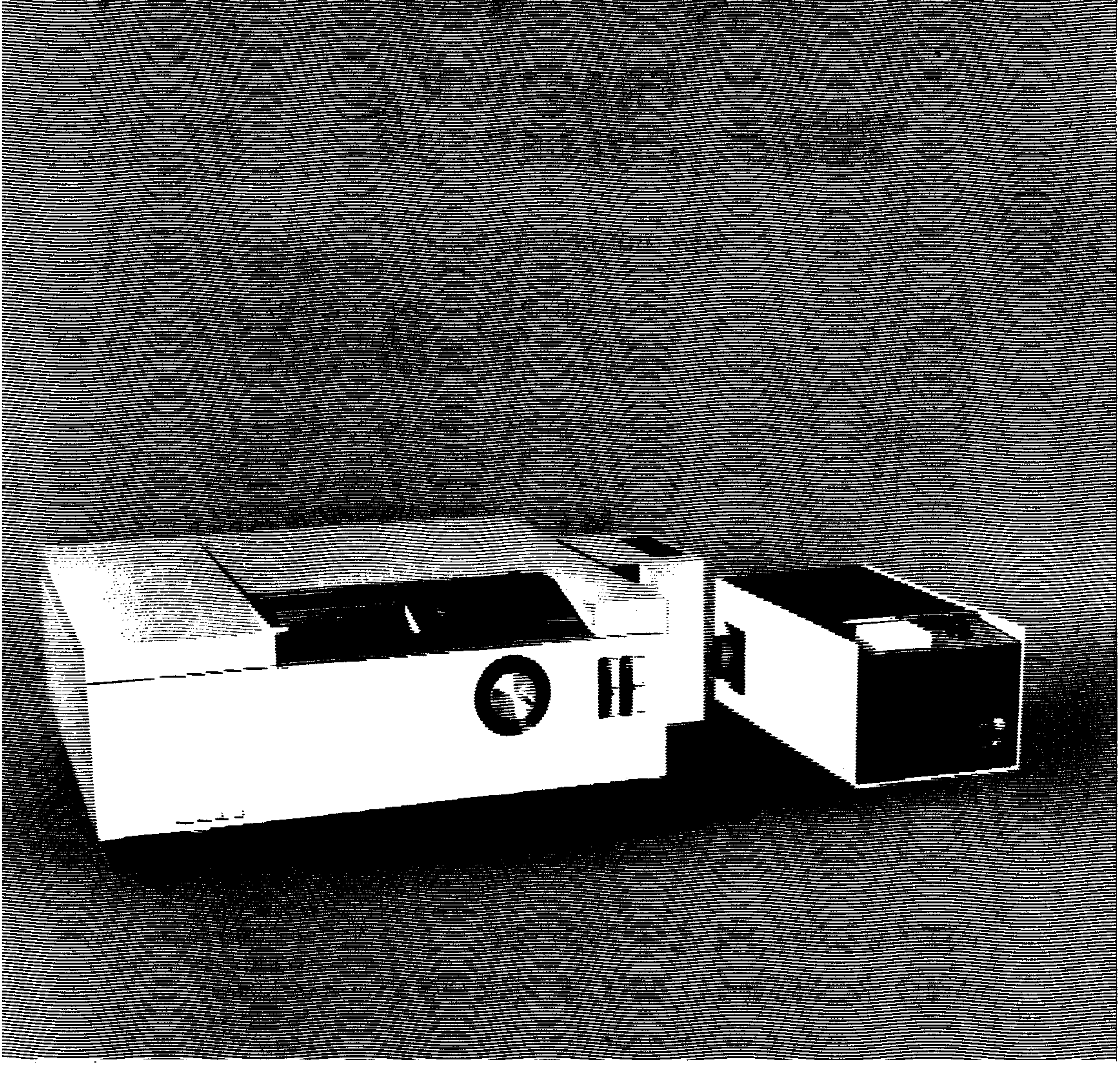

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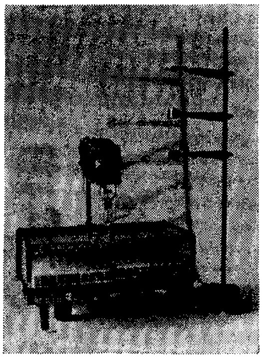

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