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Editors
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GENERAL INFORMATION

Languages

Papers will be published in English, French or German.

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Papers should be sent to: Prof. Philip W. West, Coates Chemical Laboratories, College of Chemistry and Physics, Louisiana State University, Baton Rouge 3, La. 70803 (U.S.A.) or to
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Authors should submit two copies in double-spaced type with adequate margins on pages of uniform size. Acknowledgements, summary and references should be placed at the end of the paper.

Tables should be typed on separate pages and numbered in Roman numerals in the order in which they are mentioned in the text. All Tables should have descriptive titles. The use of chemical formulae and conventional abbreviations is encouraged in Tables and Figures but chemical formulae should not be used in the text unless they are necessary for clarity. Units of weight, volume, etc., when used with numerals should be abbreviated and unpunctuated (*e.g.*, 2%, 2 ml, 2 g, 2 μl, 2 μg, 2 ng, 2 cm; 200 nm).

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1. J. J. Lingane and A. M. Hartley, *Anal. Chim. Acta*, 11 (1954) 475.
2. F. Feigl, *Spot Tests in Organic Analysis*, 7th Ed., Elsevier, Amsterdam, 1966, p. 516.

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Soeben erscheint

Massenspektrometrie

Herausgegeben von Hermann Kienitz. Verfaßt von Fritz Aulinger, Gerhard Franke, Karleugen Habfast, Hermann Kienitz und Gerhard Spiteller.

Vor etwa 10 Jahren zeichnete sich in der Massenspektrometrie eine neue Arbeitsrichtung ab, die sie zu einem sehr wertvollen Hilfsmittel zur Aufklärung der Struktur chemischer Verbindungen werden ließ. Der Mechanismus des Abbaues von Molekülen organischer Substanzen in der Ionenquelle des Massenspektrometers wurde systematisch an vielen Verbindungstypen vergleichend untersucht, und es wurden Regeln für ihren Abbau gefunden. Unter der naheliegenden Annahme, daß der Energiegehalt der neugebildeten Teilchen für die Fragmentierung ausschlaggebend ist, können die Abbaumechanismen mit den Erkenntnissen der modernen theoretischen Chemie in Übereinstimmung gebracht werden.

Die Monographie über Massenspektrometrie, behandelt besonders die analytischen Anwendungen der Massenspektrometrie, ihre Grenzen und Möglichkeiten, wie auch die Kombination mit anderen analytischen Methoden. Als Mikro- und Spurenmethode ist die Massenspektrometrie neben quantitativen Analysen von Gasen und Flüssigkeiten, der Gruppenanalyse von Kohlenwasserstoff-Gemischen, zur qualitativen Analyse organischer und anorganischer Verbindungen geeignet. Die in letzter Zeit mehr und mehr eingesetzten hochauflösenden Geräte ermöglichen eine Präzisionsbestimmung der relativen Massen von Molekülen und ihren Bruchstücken, die in vielen Fällen ihre elementare Zusammensetzung als Summenformel anzugeben gestattet und damit die Strukturanalyse von chemischen Verbindungen wesentlich unterstützt. Die Kombination mit der Gas-Chromatographie kann bei kompliziert zusammengesetzten Gemischen zu einem Hilfsmittel der Analyse werden, das ausgehend von Bruchteilen von Milligrammen die qualitative und quantitative Zusammensetzung, gegebenenfalls auch die Struktur einzelner Komponenten anzugeben erlaubt. Spuren in anorganischen festen Substanzen werden in Konzentrationen erfaßt, die kaum von einer anderen Methode erreicht werden.

Die Anwendungen der Massenspektrometrie, die für geochemische Prozesse und kosmologische Vorgänge, für die Isotopentrennung, wie auch mit der Isotopenverdünnungsanalyse für weite Bereiche der Forschung und Industrie besondere Bedeutung haben, sind verschiedene Abschnitte gewidmet. Tabellen, die bei der praktischen Arbeit im Labor eine Hilfe darstellen, beschließen die Monographie.

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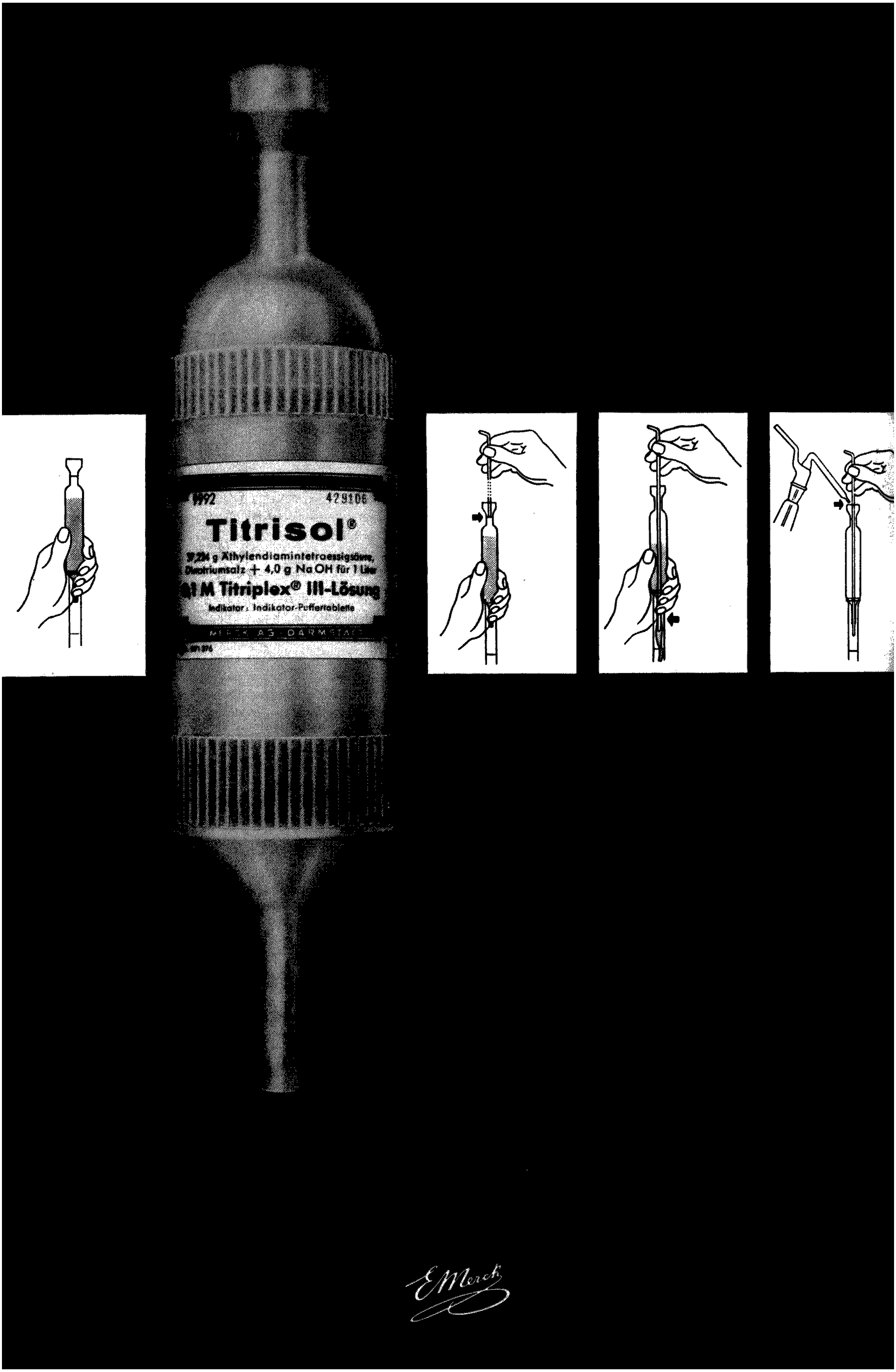
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Volume 42, No. 1, July 1968

NAPHTHENIC ACID EXTRACTION OF CALCIUM FOR DETERMINATION BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

A solvent extraction method with naphthenic acid and cyclohexylamine in MIBK is suggested for use in atomic absorption spectrophotometric analysis. The method is demonstrated for calcium in the presence of many known interfering ions.

L. SZEGO AND J. M. CALVERT,
Anal. Chim. Acta, 42 (1968) 1–6

ACTIVATION ANALYSIS OF RARE EARTHS

PART I. SEPARATION OF RARE EARTHS FROM ACCOMPANYING ELEMENTS

A scheme for the separation of rare-earth elements from gadolinite and tantalocolumbite minerals is discussed. The possibility of interference from traces of non-separated elements in the subsequent separation of rare-earth elements from each other by cation exchange with α-hydroxyisobutyrate as the eluting agent is investigated.

D. L. MASSART AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 7–14

ACTIVATION ANALYSIS OF RARE EARTHS

PART II. DETERMINATION OF LUTETIUM IN GADOLINITE

Two precise and accurate methods for the determination of lutetium in the presence of other rare earths and after separation from a mineral, gadolinite, are described. Both methods require separation of the lutetium and ytterbium from the other rare earths. A complete separation of Lu and Yb is necessary when integral counting is used. The other method differentiates between the two elements by γ-spectrometry.

D. L. MASSART AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 15–20

ACTIVATION ANALYSIS OF RARE EARTHS

PART III. THE DETERMINATION OF RARE EARTHS IN MINERALS BY THE SINGLE COMPARATOR TECHNIQUE

The determination of rare earths in minerals by activation analysis is described. The rare earths are separated as a group from the bulk of the material before irradiation. After irradiation the rare earths are separated from each other by gradient elution with ammonium α-hydroxyisobutyrate on a cation-exchange column. The elements are determined by the single comparator technique. This method permits a practical application of activation analysis to the routine determination of rare earths in complex matrices.

D. L. MASSART AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 21–28

ATOMIC-FLUORESCENCE SPECTROSCOPY OF MAGNESIUM WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP AS LINE SOURCE

Atomic fluorescence of magnesium is possible in air–propane or air–acetylene flames at 285.21 nm, using a high-intensity hollow-cathode magnesium lamp for excitation. The technique permits determinations of magnesium in the range 0.01–5 p.p.m., *i.e.* with more than 10 times the sensitivity of the atomic absorption method even for this most sensitive element. The detection limit in either flame is 1 ng/ml (signal: noise ratio 1 : 0.75). In a nitrous oxide–acetylene flame, atomic fluorescence may be carried out with linear signal/concentration dependence up to 100 p.p.m. without interference even from metals such as aluminium, titanium, etc. at a 1000-fold excess ratio to magnesium. A brief comparison is made with atomic absorption using the same source and equipment.

T. S. West and X. K. Williams,
Anal. Chim. Acta, 42 (1968) 29–37

ANALYSIS OF CHROMIUM BY γ-SPECTROMETRY AFTER SEPARATION OF THE RADIOELEMENTS BY ION EXCHANGE

(in French)

In activation analysis, matrices such as Al, Be or Nb are essentially inactive a few hours after irradiation. This is not the case for chromium which is very easily activated, the lower limit of determination being *ca.* 0.01 μg. A procedure is given for the determination of 9 elements in this matrix. After neutron irradiation, all separations, on Dowex 1 resin with chloride or fluoride–chloride eluants, can be done in a "cold" laboratory. Fe, Co, Ni, Cu, Zn, W, Mo, Ga and Ta can be determined. The lower limit of determination is *ca.* 1 p.p.m., except for Fe. The reproducibility is about 10%.

F. Dugain (avec la collaboration de C. Castre et B. Beyssier),
Anal. Chim. Acta. 42 (1968) 39–50

ON THE SEPARATION MECHANISM OF GEL PERMEATION CHROMATOGRAPHY

The separation mechanism of gel permeation chromatography was investigated by static experiments. It was found that the solute molecule is excluded from part of the inner space of the gel particle, which is entirely available to the solvent molecule. The excluded volume, ΔV, increases with increase of molecular size of the solute. A linear relationship was observed between the ΔV and the logarithm of molecular size. Excluded volume was found to be independent of solute concentration as was expected. Absorption effect was negligible with polystyrene gel. However, a strong effect was observed between acids and polydextran gel. The possibility of using absorption effects to increase the separability of GPC is suggested.

T.-L. Chang,
Anal. Chim. Acta, 42 (1968) 51–57

THE CHROMATOGRAPHIC PROPERTIES OF TRANSITION METAL COMPLEXES OF PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

A scheme has been devised whereby PAQH complexes of iron, nickel, copper and cobalt can be separated chromatographically and determined semiquantitatively in presence of up to tenfold excesses of interfering metal ions. The visual detection limits for iron, nickel and copper were found to be 0.01 μg and for cobalt 0.007 μg per spot. Interesting relationships were observed between R_F values, decomposition temperatures and position of the absorption maxima of the adsorbed complexes.

R. W. Frei, D. E. Ryan and C. A. Stockton,
Anal. Chim. Acta, 42 (1968) 59–65

DISTRIBUTION COEFFICIENTS FOR TWELVE ELEMENTS IN OXALIC ACID MEDIUM ON A STRONG ANION-EXCHANGE RESIN

The distribution coefficients were determined for twelve elements, namely As(III), Ce(III), Cr(III), Co(II), Cu(II), In(III), Lu(III), Mn(II), Hg(II), Mo(VI), Sc(III) and Zn(II), on a strong base anion exchanger in pure oxalic acid solutions. The K_D curves are given. A scheme was developed for the chromatographic separation of five elements, namely As(III), Mn(II), Co(II), Zn(II) and Cu(II). Ce(III) can be separated from Lu(III).

F. De Corte, P. Van den Winkel, A. Speecke and J. Hoste,
Anal. Chim. Acta, 42 (1968) 67–77

THE EXTRACTION OF COPPER(II) FROM HYDROCHLORIC ACID BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE

In marked contrast to the behaviour of copper(I), the extraction of copper(II) by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride is very small from 1.0 *M* chloride and although it increases with concentration it does not reach 90% until the chloride concentration exceeds 4 *M*. By varying such parameters as $[Cl^-]$, $[NR_4^+Cl^-]_{org.}$ and the total amount of copper in the system, it was shown that the distribution equilibria could best be explained by postulating the presence of binuclear complexes $Cu_2Cl_6^{2-}$ and $Cu_2Cl_7^{3-}$ in addition to mononuclear complexes in the aqueous phase, while only mononuclear species such as $NR_4^+CuCl_3^-$ and $(NR_4^+)_2CuCl_4^{2-}$ are extracted. A linear relationship is predicted between the reciprocal of the distribution ratio and the total amount of copper present at equilibrium in the aqueous phase and confirmed by the experimental results.

H. M. N. H. Irving and A. H. Nabilsi,
Anal. Chim. Acta, 42 (1968) 79–86

SOLVENT EXTRACTION SEPARATIONS WITH BPHA. APPLICATIONS TO THE MICROANALYSIS OF NIOBIUM AND ZIRCONIUM IN URANIUM

A detailed study of the benzoylphenylhydroxylamine (BPHA)–chloroform–hydrochloric acid solvent extraction system with 52 elements is described with emphasis placed on extraction of the easily hydrolyzed transition metals from strong hydrochloric acid. From this study, a separation procedure for hafnium, niobium, tantalum, titanium, vanadium, and zirconium from uranium was developed, and procedures are given for the microanalysis of niobium and zirconium in uranium. Niobium and zirconium are separated from uranium by extraction into BPHA–chloroform from 10 *N* HCl. The separated elements are then measured colorimetrically as the niobium–4-(2-pyridylazo)resorcinol and zirconium–arsenazo III complexes. The limit of detection is 1 μg/g U.

O. A. Vita, W. A. Levier and E. Litteral,
Anal. Chim. Acta, 42 (1968) 87–94

A NEW SPECTROPHOTOMETRIC DETERMINATION OF 1,1-DIALKYLHYDRAZINES

(in German)

1,1-Dialkylhydrazines after oxidation with mercury(II) sulfate in aqueous sulfuric acid split off one alkyl group as aldehyde and this reaction can be utilized for quantitative determination of 1,1-dialkylhydrazines by photometric estimation of the released aldehyde. The lower detection limit is 0.1–0.2 μmoles 1,1-dialkylhydrazine. The applicability and specificity of the analytical method are discussed.

R. Preussmann, H. Hengy and A. von Hodenberg,
Anal. Chim. Acta, 42 (1968) 95–99

DETERMINATION OF URANIUM IN PLUTONIUM BY DIFFERENTIAL LINEAR SWEEP OSCILLOGRAPHIC POLAROGRAPHY

The polarographic behavior of uranium in hydroxylamine hydrochloride was investigated by differential oscillographic polarography. A procedure is presented for the determination of uranium in plutonium for concentrations of uranium greater than 10 p.p.m. Analyses of solutions containing 22 common impurities found in plutonium metal revealed that antimony, copper, and titanium cause significant interference. A reversible peak corresponding to a one-electron reduction was obtained with a peak potential of -0.167 V *vs.* Hg pool electrode. The diffusion coefficient is $0.51 \cdot 10^{-5}$ cm^2/sec and the diffusion current constant is 1.59 with an average relative standard deviation of 2.28%. The peak current of uranium can be affected by hydrochloric, nitric, perchloric, and sulfuric acids, depending on the acid concentration.

C. E. Plock and J. Vasquez,
Anal. Chim. Acta, 42 (1968) 101–107

THE OSCILLOPOLAROGRAPHIC DETERMINATION OF URANIUM AND THORIUM IN SUPPORTING ELECTROLYTES CONTAINING CUPFERRON

Uranium(VI and IV) and thorium(IV) give cathodic indentations in supporting electrolytes prepared from 0.1 *M* perchloric acid, 0.5 *M* ammonium thiocyanate and $5 \cdot 10^{-3}$ *M* cupferron (solution A) or from 0.1 *M* succinic–succinate buffer pH 4, 0.1 *M* sodium chloride, 10^{-3} *M* cupferron and 0.05% gelatine (solution B). The uranium indentation on the $dE/dt = f(E)$ curve ($Q = 0.75$ and 0.73) permits its detection at the $3 \cdot 10^{-7}$ *M* level. The thorium indentation ($Q = 0.78$) permits its detection at the $4 \cdot 10^{-7}$ *M* level in solution B. Methods for the elimination of interfering ions for the uranium determination are described. In the determination of thorium, Ga(III), Fe(III), Ti(IV) and U(VI) interfere.

G. Donoso N., M. A. Santa Ana V. and I. Chadwick W.,
Anal. Chim. Acta, 42 (1968) 109–118

DETERMINATION OF FLUORINE IN SILICATE AND PHOSPHATE ROCKS, MICAS AND STONY METEORITES

By making certain modifications to a published procedure for fluorine in rocks, it has been possible to improve stability and extend the range of the method. The modified method has been successfully applied to silicate and phosphate rocks, micas, glass and stony meteorites, containing from 60 p.p.m. to 8% fluorine. Some precautions are recommended for reliable determination of chlorine.

J. G. Sen Gupta,
Anal. Chim. Acta, 42 (1968) 119–125

TRACE FLUORIDE DETERMINATION WITH SPECIFIC ION ELECTRODE

A method is described for determining 10^{-5}–10^{-4} *M* fluoride in a variety of solutions potentiometrically with a fluoride-specific electrode, by a standard addition method. Any change of ionic strength or the nature of the solution that might alter activity coefficients or junction potentials is minimized. The relationship between potential and fluoride *concentration* thus follows the Nernst equation, and the unknown concentration can be calculated. Experimental data are given for solutions of sodium chloride, sodium nitrate, acidified sodium silicate and sodium hydroxide, lithium chloride, and phosphoric acid. Metal ions (*e.g.*, Al^{3+}, UO_2^{2+}, Fe^{3+}, Th^{4+}) that interfere by forming complexes with fluoride can be precomplexed with phosphoric acid. The relative error is estimated at 10%, and the relative standard deviation is less than 5% over the concentration range 10^{-5}–10^{-4} *M* fluoride.

E. W. Baumann,
Anal. Chim. Acta, 42 (1968) 127–131

VACUUM-FUSION DETERMINATION OF OXYGEN IN ALUMINIUM AND ALUMINIUM–ALUMINIUM OXIDE COMPOSITES

A copper bath–vacuum fusion method for the determination of oxygen in aluminium was modified because the extensive evaporation of copper at the operating temperature gave trouble in a commercial instrument with unlidded crucibles. The evaporation can be decreased by making use of graphite capsules, where the samples and the copper are sealed before being dropped into the hot crucible. The procedure gives good results for specimens of aluminium and of aluminium–aluminium oxide composites, the oxygen content of which ranged from some tens of p.p.m. to some weight percent. The sensitivity of the method is of the order of 20 p.p.m. for sample weights of 100 mg, if copper of very low oxygen content is used.

A. Colombo and E. Rodari,
Anal. Chim. Acta, 42 (1968) 133–141

MODULAR SOLID-STATE UNIT FOR ELECTROCHEMICAL STUDIES

A relatively inexpensive unit based upon solid-state operational amplifiers is described; its modular design makes it an extremely versatile instrument for many electrochemical techniques, *e.g.*, normal direct current polarography and linear sweep voltammetry, cyclic voltammetry, alternating current polarography, and coulometry and electrolysis at controlled electrode potential. It can be readily adapted to many other functions.

G. Dryhurst, M. Rosen and P. J. Elving,
Anal. Chim. Acta, 42 (1968) 143–152

THE COULOMETRIC TITRATION OF TETRAPHENYLBORATE ION WITH ELECTROGENERATED SILVER ION AND A BIAMPEROMETRIC END-POINT

APPLICATION TO THE DETERMINATION OF POTASSIUM AND POLYETHYLENEGLYCOLS

Microequivalent amounts of TPB in a 40% acetone generating electrolyte were titrated with coulometrically generated silver ions. With a biamperometric end-point, samples of 0.1–4 μeq of NaTPB were determined with a precision with 1%. The technique was applied to the determination of potassium in potassium chloride alone and in mixtures with other salts. The overall accuracy ranged from -3 to -7% for samples of 4 μeq to 1 μeq of potassium, respectively. Artificial serum samples gave somewhat discordant results, because of difficulty in removing all interfering protein. A method was developed for the determination of 0.1–1.0 mg of PEG 600 to 4000 with excess TPB in the presence of barium ions. With reasonable care errors may be held to within 5%.

J. R. Moody, G. D. Christian and W. C. Purdy,
Anal. Chim. Acta, 42 (1968) 153–159

SOLVENT EXTRACTION OF SOME ACTINIDES AND FISSION PRODUCTS BY NITROMETHANE

(Short Communication)

N. B. Milić,
Anal. Chim. Acta, 42 (1968) 160–162

RAPID SPECTROPHOTOMETRIC DETERMINATION OF LOW-MOLECULAR-WEIGHT DEXTRAN IN BLOOD

(Short Communication)

R. E. JENSEN, A. LANGSJOEN, R. LEWANDOWSKI AND J. BORTZ,
Anal. Chim. Acta, 42 (1968) 162–165

ACTIVATION ANALYSIS OF RARE EARTHS

PART IV. DETERMINATION OF TRACES OF RARE-EARTH IMPURITIES IN Gd_2O_3

(Short Communication)

D. L. MASSART AND J. HOSTE,
Anal. Chim. Acta, 42 (1968) 166–170

INTERFERENCE OF PERCHLORIC ACID WITH THE ANTHRONE REACTION FOR CARBOHYDRATES

(Short Communication)

E. P. BACHELARD,
Anal. Chim. Acta, 42 (1968) 171–173

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM AND OTHER COLOUR REACTIONS WITH 3, 5, 6, 7, 3′, 4′-HEXAHYDROXYFLAVONE

(Short Communication)

M. KATYAL, B. P. GUPTA, D. K. BHARDWAJ AND R. P. SINGH,
Anal. Chim. Acta, 42 (1968) 173–176

ESTIMATION OF CARBOXYL GROUP CONTENT OF COPOLYMERS BY THE INFRARED ABSORBANCE RATIO METHOD

(Short Communication)

A. J. SCISM,
Anal. Chim. Acta, 42 (1968) 177–180

THE DETERMINATION OF TRACE AMOUNTS OF PHOSPHORUS BY A DOUBLE AMPLIFICATION METHOD

(Short Communication)

R. BELCHER AND P. C. UDEN,
Anal. Chim. Acta, 42 (1968) 180–182

Molecular Vibrations and Mean Square Amplitudes

by SVEN J. CYVIN

The mean amplitudes have proved to play an increasingly important role as structural parameters (in addition to the rigid-molecule parameters) in modern studies of molecular structure. These parameters have been applied most extensively in gas electron diffraction, and also calculated by spectroscopic methods from infrared and Raman data.

The book reviews completely the previous work on mean amplitudes of vibration, including 476 references. Furthermore the spectroscopic analysis of harmonic vibrations of polyatomic molecules is reconsidered. The survey includes known methods based on the Wilson G and F matrices, but also supplementary aspects and new material, particularly as regard to the compliants ('inverse' force constants), Coriolis coupling and Σ matrices.

Seventeen molecular models are treated in great detail, giving G and C^{α} matrix elements and other useful expressions for subsequent applications and future reference.

Throughout the book special emphasis is laid on the calculation and properties of mean amplitudes of vibration and related quantities such as the generalized mean-square amplitudes and shrinkage effects. An additional 380 references are cited.

As a whole the book is to be regarded as a standard reference for spectroscopic analysis of polyatomic molecules based on the approximation of small harmonic vibrations with its application to mean amplitudes as one of the particular features. The last chapter contains eome proposals on future work in the field, including higher order approximations.

The book is believed to be of interest for advanced students and research workers on molecular structure (especially by gas electron diffraction), and spectroscopists interested in theoretical aspects and applications of spectral data.

CONTENTS: 1. Introduction - 2. Review of previous work - 3. Molecular vibrations: survey and notation - 4. Theory of compliance matrices - 5. Quantum–mechanical considerations - 6. Coriolis coupling of vibration–rotation: a survey - 7. Theory of the mean–square amplitude matrix - 8. Preliminary treatment of simple molecular models - 9. Mean–square amplitude matrices of simple molecular models - 10. Numerical examples of mean–square amplitude quantities and their variations - 11. Arbitrary interatomic distances and mean amplitudes of vibration - 12. Mean amplitudes of vibration of individual molecules - 13. Perpendicular displacements and generalized mean–square amplitudes - 14. Theory of the Bastiansen–Morino shrinkage effect - 15. Bastiansen–Morino shrinkage effects of individual molecules - 16. Coriolis constants and mean–square amplitude quantities - 17. Conclusion and future prospects - Bibliography - References and author index - Subject index

7x10", viii + 430 pages, 157 tables, 45 illus., 1968, Dfl. 75.00, US$27.00

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This 7th edition has involved complete revision and reorganisation of the subject in orde to present a still clearer picture of the multitudinous applications open to organic spo test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot tes techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis* and by limiting the number of tables and structural formulae.
Comparison with the 6th edition reveals the following differences:

	Number in	
	6th Edn.	7th Edn.
Preliminary tests	32	45
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.

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It is the author's hope that this work will help to correct the widespread impression that physical instrumentation is always superior to chemical methods for solving analytical problems. Each of the chapters presents instances of problems for which no solutions by physical means have yet been developed, or for which the rapid spot tests are equal or superior to the expensive instrumental procedure.

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

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Laboratory Practice

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NAPHTHENIC ACID EXTRACTION OF CALCIUM FOR DETERMINATION BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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The determination of the alkaline earth elements by atomic absorption spectrophotometry is subject to a number of interferences. Some of these can be substantially eliminated by suitable additions to the test solutions[1-3], and most can be overcome by high temperature flames, such as the nitrous oxide–acetylene flame[4]. A solvent extraction of magnesium with oxine in methyl isobutyl ketone can be used for trace amounts contained in brine, aluminium metal, etc.[5].

The present work was undertaken in order to find a suitable extraction procedure for calcium. Not many such extraction systems are known and the use of oxine in chloroform[6] was not successful, mainly because of the solvent's unsuitability for injection into the flame. Naphthenic acid was chosen as the extractant; this had been suggested for many elements by FLETCHER AND FLETT[7]. A detailed procedure was developed and is described here.

EXPERIMENTAL

Apparatus

A "Techtron AA-100" Atomic Absorption Spectrophotometer was used, fitted with an "AB-41" laminar-flow burner. An air–acetylene flame was used, very lean for the organic phase and fuel-rich for the aqueous work.

The instrument settings were:
Wave length: 4227 Å
Lamp current: 3 mA
Gain: 4
Acetylene flow: 4 (org.)
Acetylene flow: 6 (aq.)
Air pressure: 15 psi
Burner height: 4.5 (arbitrary scale)

Reagents

Naphthenic acid. A commercially distilled acid mixture, pale straw in colour, was used. It contained less than 10% unsaponifiable matter, had an "acid value" of 230 and a specific gravity of 0.961/20°. A solution was prepared by shaking 20 ml of naphthenic acid and 84 ml of MIBK with 20 ml of 1 *M* hydrochloric acid, and washing 3 times with 50 ml of distilled water.

Cyclohexylamine. Laboratory-reagent grade material was redistilled and kept well stoppered to exclude carbon dioxide.

Methyl isobutyl ketone (MIBK). The commercial product was used after distillation.

Naphthenate solution. 50 ml of naphthenic acid solution, 3 ml of cyclohexylamine and 47 ml of MIBK were mixed. This solution, when shaken with an equal volume of distilled water should give a pH of 8.5 in the aqueous phase. A slight change in the cyclohexylamine quantity may be necessary for a different "acid value".

Pre-extracting solution. 2.5 ml of naphthenate solution and 97.5 ml of naphthenic acid solution were mixed.

Other reagents. A.R. quality was used and all reagents were dissolved in distilled water. Unless otherwise indicated the cations were added as chlorides, the anions as sodium salts.

Extraction

Three procedures were developed. Procedure 1 was suitable for comparatively pure calcium solutions in the absence of strong complexing agents. Up to 1000 p.p.m. of phosphate, sulphate, or vanadate can be present and any quantity of nitrate or chloride of the alkali metals. Procedure 2 was used in the presence of up to 100 p.p.m. of all ions listed in Table I, with the exception of Ti^{4+}, Zr^{4+}, Al^{3+} and Sb^{3+}. In the presence of these ions Procedure 3 was used. However, no satisfactory result was obtained in the presence of Ti^{4+}.

TABLE I

EFFECT OF VARIOUS IONS IN SAMPLE SOLUTION

Ion added	*Ca found (µg/ml)*		*Ion added*	*Ca found (µg/ml)*		
	Proc. 1	*Proc. 2*		*Proc. 1*	*Proc. 2*	*Proc. 3*
At level	*1000 p.p.m.*	*100 p.p.m.*	*At level*	*1000 p.p.m.*	*100 p.p.m.*	*100 p.p.m.*
None	(5.0)	(5.0)	Ti^{4+}	1.2	3.0	2.9
PO_4^{3-}	5.1	5.0	Zr^{4+}	1.8	3.5	4.9
SiO_3^{2-}	3.2	5.1	Al^{3+}	3.2	3.9	5.1
WO_4^{2-}	—	4.9	Cr^{3+}	4.3	4.8	5.0
MoO_4^{2-}	—	5.1	Fe^{3+}	4.7	5.0	5.1
CO_3^{2-}	3.9	5.0	Sb^{3+}	4.0	4.7	5.0
SO_4^{2-}	5.0	5.0	Sn^{2+}	1.8	4.8	4.9
VO_3^-	5.0	5.0	Zn^{2+}	4.8	5.0	—
NO_3^-	5.0	5.1	Sr^{2+}	4.9	5.0	—
Cl^-	4.9	5.0	Mg^{2+}	5.0	5.1	—
F^-	5.0	4.9	Li^+	5.1	5.0	—
Oxalate	1.7	5.0	Na^+	5.1	5.0	—
Lactate	2.4	5.1	K^+	5.1	5.1	—

Procedure 1

Put 10 ml of a solution containing less than 60 µg of calcium into a separating funnel, add 1 ml of 1 *M* sodium chloride solution and sufficient sodium hydroxide or hydrochloric acid to give a pH between 6.0 and 9.0. Add 10 ml of naphthenate solution and shake for 2 min.

After separation, measure the pH of the aqueous phase; if it is between 8 and 9, centrifuge the organic layer and aspirate it into the flame; if not, adjust the pH and repeat the shaking before measuring the absorbance.

Procedure 2

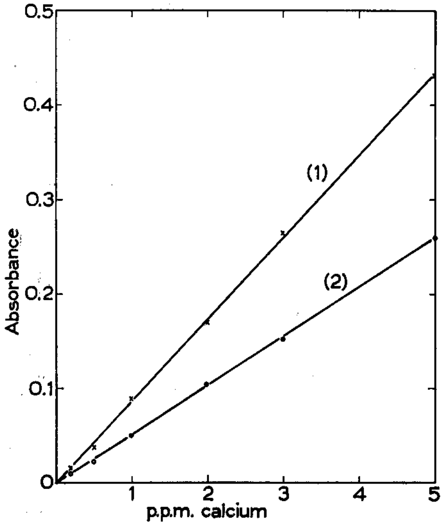
Put an aliquot containing less than 30 μg of calcium into a 250-ml separating funnel. Add 10 ml of 1 *M* sodium chloride solution and sufficient distilled water to make 100 ml. Adjust the pH to 8 or as close to it as possible without causing precipitation. Add 8 ml of naphthenate solution, shake for 2 min and continue as in Procedure 1.

Procedure 3

Treat the sample as in Procedure 2 but adjust the pH to about 5 (instead of 8). Add 50 ml of pre-extracting solution. Shake for 2 min, allow to separate, and check the pH of the aqueous phase. If necessary, add cyclohexylamine (in dilute aqueous solution) to bring the pH between 5 and 6 and repeat the extraction, using the same solutions. Discard the organic layer (after the pH has been checked again), adjust the pH to 8.5 and place all of the aqueous phase including the portion used for the pH determination into a clean 250-ml separating funnel. Add 8 ml of naphthenate solution and continue as for Procedure 1.

RESULTS AND DISCUSSION

The extraction of calcium from pure chloride solutions is shown in Fig. 1, where the absorbance of the organic phase is plotted against the initial calcium contents of the aqueous solutions. With Procedure 1, the extraction was approxi-



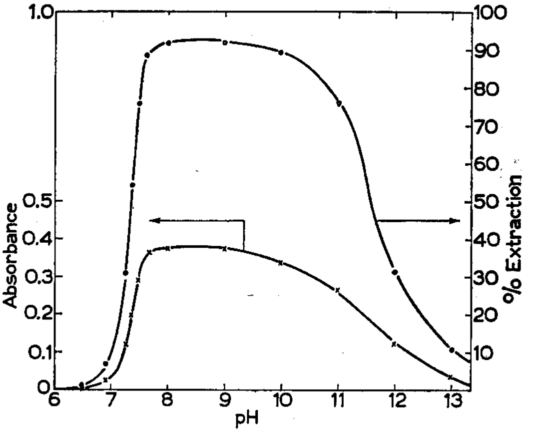


Fig. 1. Absorbance of organic phase after extraction of calcium from a chloride solution at pH 8.5 following procedure 1 (x) and procedure 2 (o).

Fig. 2. Dependence of absorbance (x) and extraction (o) on pH after extraction of 5 p.p.m. calcium from a chloride solution with 10% naphthenic acid and cyclohexylamine in MIBK.

mately 92%, and with Procedure 2 the extraction was only about 66%, as a result of the less favourable phase ratio. Both curves show very satisfactory linearity over the range tested.

Figure 2 shows the dependence of absorbance on the final pH of the aqueous phase when using Procedure 1. The pH was varied by changing the cyclohexylamine contents of the naphthenate solution. Also shown is the percentage extraction calculated from the aqueous absorbances before and after extraction. It can be seen that optimum accuracy is at pH 8–9. At very high pH values the absorbance decreases; the readings were found to be somewhat scattered, tending to be quite unreliable over pH 12, owing to the absorption of carbon dioxide from the atmosphere.

The effect of naphthenic acid concentration is shown in Fig. 3. The extraction increases with the concentration as expected, but there is a maximum of absorbance at 15%. This is due to the increased viscosity of the more concentrated solutions, which causes a decrease in the quantity of sample aspirated into the flame. The total concentration range covered at constant pH gives a very limited free ligand concentration range, but this indicates the expected 2 : 1 naphthenic acid to calcium ratio.

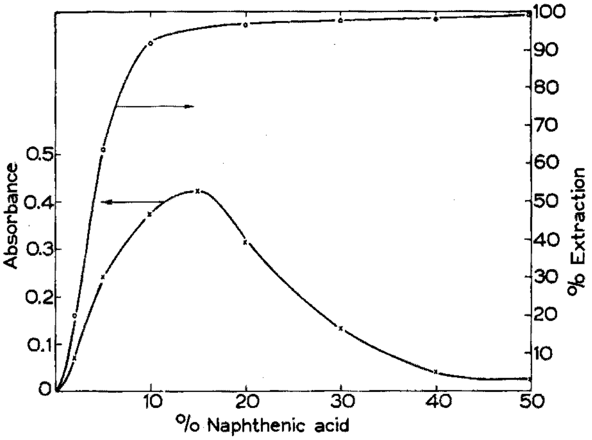


Fig. 3. Effect of naphthenic acid concentration on extraction (o) and absorbance (x) after extraction of an equal volume of 5 p.p.m. calcium solution at pH 8.5.

The ratio is deduced from the slope of the logarithm of calcium concentration ratios in the two phases, plotted against the logarithm of the total naphthenic acid present (not shown). It should be noted that the diluent (MIBK) is markedly soluble in water, and under our conditions the solubility is *ca.* 3%. In Procedure 2, 8 ml of 10% extractant is used, but after separation only about 5 ml of 15% naphthenic acid is obtained. This must be borne in mind when changes of procedure are made for special purposes.

The effect of interfering ions is shown in Table I. The ions tested were mainly those known to interfere in the atomic absorption of calcium, but others which were thought to impede the extraction were also included. The mechanism of the interferences was not further considered. It is quite obvious that anions which form strong calcium complexes will suppress the extraction. Similarly large amounts of competing cations will also suppress extraction. The alkali metals do not interfere at all and of the anions tested, phosphate, vanadate, sulphate, nitrate, and chloride do not interfere up to the 1000 p.p.m. level. This means that, in Procedure 1, any of these ions may be present in concentrations up to 200 times that of calcium without interference, while the range of absorbance can be kept between 0.2–0.7. In this range, the results had a coefficient of variation of 3% for 5 extractions. When Procedure 1 is used, the sensitivity is enhanced by a factor of two, compared to direct measurements on the aqueous sample.

Procedure 2 was found adequate for up to a 20-fold excess of all ions tested, with the exception of Ti^{4+}, Zr^{4+}, Al^{3+}, Sb^{3+} and Sn^{2+}. Larger excesses can also be handled, but dilution may be necessary with the result that the absorbance will be lower with a correspondingly larger coefficient of variation. For Procedure 2 the sensitivity can be enhanced by a factor as high as 30 for very dilute samples.

For the cationic interferences mentioned above, a pre-extraction step may be used. Care must be taken not to extract any calcium and not to leave dissolved in the aqueous layer any traces of foreign materials which may affect the extraction or absorbance. Repeated washing with MIBK may be necessary to remove traces of reagents used in the pre-extraction, such as chloroform and acetyl acetone. A pre-extraction step proved successful for Zr^{4+}, Al^{3+}, Zn^{2+} as described in Procedure 3. Titanium was present as an oxalate complex and could not be removed by this method.

The extractant was chosen because the constituents are combustible, easily purified and stable. Naphthenic acid of different specification may also be used but the higher acid value gives better extraction and is also less viscous. It can be distilled *in vacuo* and the fraction 140–170° at 5 mm Hg may be used. However, with a reasonably pure commercial product, the acid washing is quite sufficient and distillation was found unnecessary.

Cyclohexylamine and MIBK were used in preference to sodium hydroxide and kerosene because of better compatibility in all proportions. Although octanol and butanol overcame turbidity and third phase formation in the kerosene system, allowing its successful use, the system chosen allows an easier adjustment of standard conditions, especially for weakly buffered calcium solutions. The extraction system described is also of interest for flame spectrophotometric work, the absence of an emitting cation being a definite advantage.

The system can be adapted for the determination of other cations besides calcium. The procedure described in this paper was tried for magnesium determination but, owing to the less complete extraction and less severe original interferences, it showed disadvantages compared to previously published methods of AAS determination. However, it is useful for magnesium in the presence of up to 100 p.p.m. of silicate.

The method described is suitable for the determination of calcium in the presence of many interfering substances within the given limits without appreciable error. Among the many additions tested only titanium was found to interfere, but this element was present in complex form and is not likely to be encountered often. Both in the case of titanium and also with interfering ions at higher levels, the absorbance is still sufficient to allow determination of calcium by the method of standard additions.

This method can be recommended for the determination of calcium and magnesium in the presence of silicate, for calcium in the presence of large quantities of other salts, and for very low level calcium determinations. It is not as accurate as direct AAS-analysis in the absence of interfering ions.

SUMMARY

A solvent extraction method with naphthenic acid and cyclohexylamine in MIBK is suggested for use in atomic absorption spectrophotometric analysis. The method is demonstrated for calcium in the presence of many known interfering ions.

RÉSUMÉ

Une méthode d'extraction est proposée pour usage en dosage spectrophotométrique à absorption atomique, utilisant l'acide naphténique et cyclohexylamine dissous en MIBK. La méthode fût démontrée pour le dosage du calcium en présence de plusieurs ions interférents.

ZUSAMMENFASSUNG

Für die Verwendung bei der Flammenabsorptionsspektralphotometrie wird eine Flüssigextraktionsmethode mit Naphthensäure und Zyklohexylamin in Methylisobutylketon vorgeschlagen. Die Brauchbarkeit der Methode wird am Beispiel des Calciums in Gegenwart zahlreicher störender Ionen demonstriert.

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ACTIVATION ANALYSIS OF RARE EARTHS

PART I. SEPARATION OF RARE EARTHS FROM ACCOMPANYING ELEMENTS

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The rare-earth content of gadolinite and tantalocolumbite can be determined by thermal neutron activation analysis. Although a non-destructive analysis is possible for some of the rare-earth elements in minerals by γ-spectrometric analysis using a Ge–Li detector, the determination of small constituents such as Lu, Tm and Er requires a chemical separation before the determination of the activity. This separation can be achieved in two steps: (1) separation of the rare earths as a group from other elements present in the mineral; (2) separation of individual rare earths from each other.

There are several reasons why the separation before irradiation is to be preferred. The short half-lives of ^{152m}Eu (9.2 h) and ^{171}Er (7.8 h) necessitate a rapid measurement. Because of the presence of gadolinium and samarium, neutron self-shielding would occur in solid samples. However, to maintain the samples in solution a pre-separation from the matrix is necessary for the tantalocolumbite mineral. Furthermore, the presence of large quantities of tantalum would give rise to very high activities.

The gross formula of gadolinite (origin: Iveland, Norway) is $2BeO \cdot FeO \cdot Y_2O_3 \cdot 2SiO_2$[1]. The tantalocolumbite (origin: Congo) was analysed by DAMS AND HOSTE[2]. It contains 0.99% SiO_2, 1.03%SnO_2, 12.05% FeO, 10.22% MnO, 5.46% TiO_2, 0.78% WO_3, 23.28% Ta_2O_5, 36.70% Nb_2O_5, 1.49% CrO_3, 4.50% rare-earth oxides.

The chemical yield of the separation is determined by adding ^{153}Gd isotope. This isotope has a convenient long half-life (230 days) and the element gadolinium can be determined through other isotopes (^{159}Gd or ^{161}Tb). The yield found for gadolinium is considered as representative for the total rare-earth group. A problem which arises in this context is the possible fractionation of the rare-earth group during chemical processing. This would cause a change in the ratio between individual rare earths and the element used for chemical yield determination, gadolinium. Such fractionations are caused for example by precipitation techniques classically used for group separations of rare earths.

SEPARATION OF THE RARE-EARTH GROUP

Silicates of rare earths, such as gadolinite, are easily decomposed with con-

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centrated hydrochloric acid. The residue is fused, after volatilisation of silicon with hydrofluoric acid, with potassium bisulfate.

Tantalocolumbite is not soluble in strong acids and has to be fused with potassium bisulfate. After cooling, the melt is dissolved in nitric acid. Tantalum and niobium are kept from precipitating by addition of peroxide[2,3].

The hydrochloric acid gadolinite solution contains potassium and sulfate as well as rare earths, iron and beryllium. To eliminate potassium and sulfate and other alkali metals present in smaller quantities, rare earths are precipitated with ammonia solution. Iron and beryllium accompany the rare earths. Since light rare earths are more soluble and hydrolyse at higher pH than heavy rare earths[4], the precipitation is carried out with concentrated ammonia solution ($\text{pH} > 10$). Less than 1% of the ^{140}La added in a tracer experiment is found in the filtrate under such circumstances.

The tantalocolumbite solution contains tantalum and tungsten in addition to rare earths. The former are separated by homogeneous precipitation of the earth acids after thermal decomposition of their peroxide complexes as described by DAMS AND HOSTE[2,3]. The presence of a chemical yield monitor (^{153}Gd) however, allows some simplifications to be made. After the separation of the earth acids, the solution contains, besides the rare earths, iron, titanium and some other minor constituents, potassium and sulfate; these can be separated from the rare earths and accompanying elements by precipitation with ammonia solution as discussed earlier.

From here, the separation of the rare earths from both minerals follows the same principles.

The method most used for the separation of rare earths from other metal ions is precipitation with oxalate. Under well defined circumstances of pH and concentration, it is very specific, only thorium precipitating with the rare earths. The solubility is low for light rare earths and lower still for the gadolinium group but increases rapidly with increasing atomic number in the heavy rare-earth group[5]. The possibility of fractionation within the rare-earth group during oxalate precipitation was investigated on a synthetic rare-earth mixture containing 12 mg La, 23 mg Ce, 6 mg Nd, 2 mg Gd, 5 mg Y, 0.5 mg Yb and 0.5 mg Lu in 10 ml of slightly acidified water. Such a mixture is more or less representative of natural rare-earth distributions. Tracers were added to determine the yield of individual elements.

The first method tested was the homogeneous precipitation technique described by WILLARD AND GORDON[6].

Procedure. To 10 ml of the rare-earth mixture, add 200 ml of water, 15 ml of 12 N hydrochloric acid and 15 ml of a 40% (w/v) dimethyloxalate solution in methanol. Stir the mixture, heat until precipitation takes place (30 min), and add 200 ml of a solution containing 8 g of oxalic acid. Stir the mixture, heat during 30 min and cool to room temperature. Adjust the pH to 0.4–0.5 with dilute ammonia. Filter and wash the precipitate.

The yields were: 98.0% for Ce (^{144}Ce), 98.5% for Nd (^{147}Nd), 99.3% for Gd (^{153}Gd), 89.8% for Lu (^{177}Lu). With the same mixture, to which 5 mg Lu more was added, a yield of 91.1% was obtained for this element.

Better results can be obtained with a method described by SCHOELLER AND POWELL[7] and modified by BROADHEAD AND HEADY[8].

Procedure. To 10 ml of the rare-earth mixture add 4 ml of 12 N hydrochloric acid and 65 ml of water. Cool in an ice bath and add 20 ml of saturated oxalic acid.

Digest the precipitate during 30 min, stir for 5 min and digest again overnight (20 h).

The yields were 99.6% for Gd, 97.0% for Yb (^{175}Yb) and 96.7% for Lu. The degree of fractionation obtained with this method is low enough for the activation analysis of all the rare-earths in minerals where a 10% precision is sufficient (Part III of this series). For more precise determinations of lutetium alone (Part II of this series), a method without any fractionation is to be preferred.

Specific separations of the rare-earth group, can be achieved by cation exchange with hydrochloric acid as the eluting agent. The rapidity of elution on cation exchangers is determined principally by two parameters, *i.e.* the affinity of the ion for the resin (which is highest for the ion with highest charge) and the formation of non-adsorbable neutral or negative chloride complexes. Since the rare earths are trivalent and since they do not form any neutral or negative complexes[9], the rare-earth group elements are adsorbed by the resin to a greater extent than most other metal ions. This is reflected in distribution coefficients quoted by STRELOW[10] and NELSON *et al.*[11]. A similar technique has been used for rare-earth separations by VOLFOVSKI *et al.*[12] and STRELOW[13].

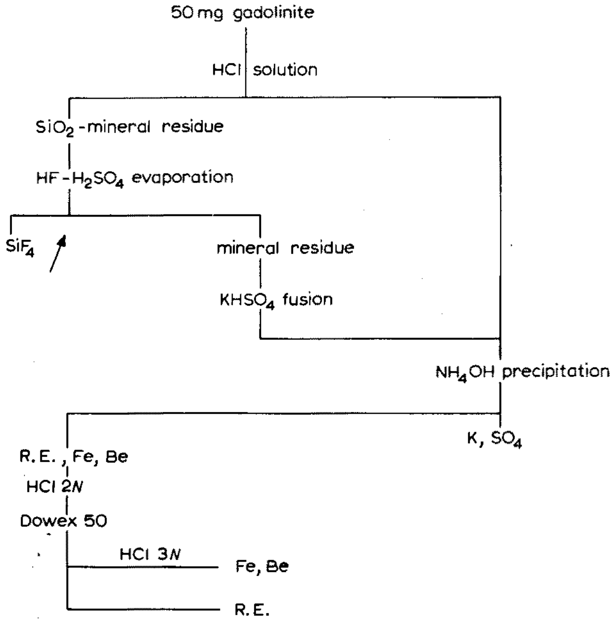

Fig. 1. Separation of rare earths (R.E.) from gadolinite.

The gadolinite and tantalocolumbite solutions are adsorbed on a cation exchanger in hydrochloric acid of low molarity; iron, beryllium, titanium and most other metal ions are eluted with 3 *M* hydrochloric acid. Rare earths are desorbed with 6 *M* hydrochloric acid. In tracer experiments with ^{177}Lu or ^{140}La (the rare earths with, respectively, the lowest and highest distribution coefficients) added to the mineral solutions, recoveries of 100% are obtained. Be, Fe, Ti, Al, Cr, Mn (identified by spot tests) are completely eluted.

The total yield of the separation of rare earths from gadolinite and tantalocolumbite is generally between 85 and 95%.

Separation schemes for the rare-earth group are shown in Figs. 1 and 2.

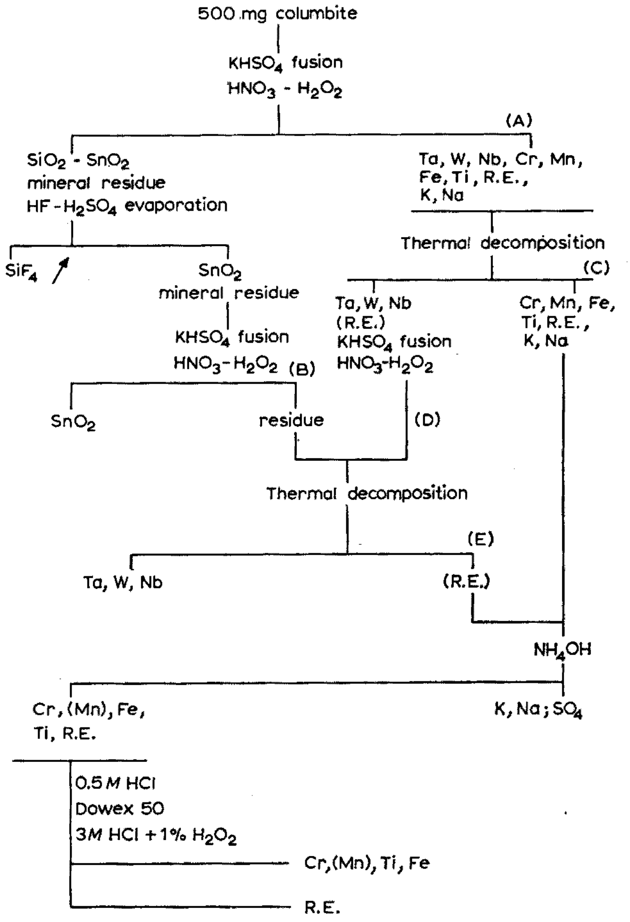

Fig. 2. Separation of rare earths (R.E.) from tantalocolumbite.

EXPERIMENTAL

Gadolinite

Decompose 50 mg of the powdered mineral with 30 ml of 12 *N* hydrochloric acid. Add ^{153}Gd (counting rate of 10,000 to 100,000 counts/min). Evaporate to dryness under an infrared lamp and dehydrate silica by heating at 110°–120° during 1 h.

Add 5 ml of 12 *N* hydrochloric acid, heat during 10 min and dilute with 25 ml of water. Keep hot for 15 min and let the solution boil for a few moments. Filter and wash with small portions hot 1:100 hydrochloric acid.

Ash the filter paper and the precipitate containing silica and mineral residue in a platinum crucible and heat for 30 min at 1000°. After cooling, add 4 ml of 28

N hydrofluoric acid and 1 ml of 35 N sulfuric acid, evaporate to dryness and fuse with 2 g of potassium bisulfate. Dissolve the melt in hot water and combine this solution with the first filtrate.

Precipitate by adding 14 N ammonia solution (pH > 10). Centrifuge and discard the supernatant, stir with water to which a drop of ammonia solution has been added, centrifuge and again discard the supernatant. Dissolve in a minimal amount of 2 N hydrochloric acid (about 10 ml) and place the solution on the top of a Dowex 50W-X8 column (20 cm × 2 cm^2). Elute iron and beryllium with 60 ml of 3 N hydrochloric acid. Elute the rare-earth fraction with 250 ml of 6 N hydrochloric acid.

Tantalocolumbite

Fuse 500 mg of the powdered mineral with 10 g of potassium bisulfate in a platinum crucible. Place the cooled melt in a 600-ml beaker and add successively 200 ml of water, 10 ml of 100-vol hydrogen peroxide and ^{153}Gd tracer. Add 80 ml of 14 N nitric acid and dissolve by heating. Filter (filtrate A). The residue contains silica and undissolved mineral. Ash and eliminate silicon by evaporating with 4 ml of 28 N hydrofluoric acid + 1 ml of 35 N sulfuric acid. The residue is fused with potassium bisulfate and dissolved as described above, using half of the indicated reagent quantities (solution B).

In filtrate A the earth acids are precipitated by thermal decomposition of hydrogen peroxide. Filter (filtrate C), ash, fuse the residue with potassium bisulfate and dissolve as described above but with half the reagent quantities (solution D). Combine B and D, reprecipitate by thermal decomposition of hydrogen peroxide and filter (filtrate E). Combine C and E, reduce the volume to 200–300 ml by evaporation and precipitate the hydroxides with concentrated ammonia solution (pH > 10). Filter on a porous-glass filter and wash with 10% ammonia solution. Dissolve the precipitate in 5–10 ml of 0.5 N hydrochloric acid to which a few drops of hydrogen peroxide have been added to keep titanium in solution.

Add the solution to the top of a 20 cm × 2 cm^2 Dowex 50 W-X8 column (100–200 mesh). Elute with 3 N hydrochloric acid containing 1% hydrogen peroxide until the orange-coloured titanium band has completely left the column (ca. 70 ml) and wash with 20 ml of 3 N hydrochloric acid. Elute the rare earths with 250 ml of 6 N hydrochloric acid.

Separation of impurities from rare earths after activation

The rare-earth fractions are evaporated to dryness, taken up in 0.1 N nitric acid and activated. After activation the individual rare-earth elements are separated from each other by cation exchange with 0.5 M α-hydroxyisobutyric acid (α-HIBA) as the eluting agent. The distribution coefficients, K_D, as a function of the ligand concentration L were determined by DEELSTRA[14]. From these results, it appears that

$$\mathrm{d}\log K_D/\mathrm{d}\log L = n \quad (-5.73 < n < -4.88)$$

Tracer quantities of impurities which have not been separated in the group separation or may have been reintroduced after the cation-exchange step can interfere. Therefore, the behaviour of some elements was investigated on Dowex 50W-X8 with α-HIBA as the eluting agent with a view to a further separation from the rare earths. Figure 3 gives distribution coefficients of the rare earths[14] and some other cations (experimentally determined or calculated) as a function of pL. Potassium and sodium activate easily and interfere. The distribution coefficients for sodium were determined experimentally. The values are given in Table I.

In a log–log diagram, a linear relationship is obtained with

$$d \log K_D/d \log L = -1.07$$

The behaviour of sodium cannot be explained by complex formation with α-HIBA, but by elution with the ammonium ions added to adjust the pH and thus the ligand concentration. From the relative affinities of potassium and sodium for the resin[15], expected distribution coefficients can be calculated for potassium.

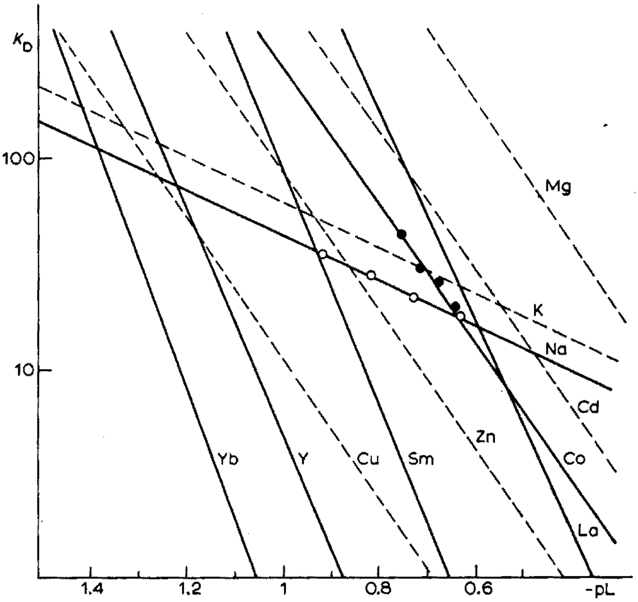

Fig. 3. Calculated and determined distribution constants of elements other than rare earths in the system strong cation exchanger–α-HIBA.

TABLE I

DISTRIBUTION COEFFICIENTS OF SODIUM

Ligand concentration	K_D *(Na)*
0.236	17.5
0.189	21.1
0.155	27.4
0.120	34.9

TABLE II

DISTRIBUTION COEFFICIENTS OF COBALT

Ligand concentration	K_D *(Co)*
0.232	18.9
0.214	24.8
0.195	28.8
0.177	44.5

Since cobalt is added to gadolinium samples to serve as a flux monitor in the determination of trace rare-earth impurities (Part IV of this series), the behaviour of cobalt(II) was investigated to examine the possibility of a Tb–Gd–Eu–Sm–Co separation directly on a cation exchanger with α-HIBA. The behaviour of cobalt may be thought representative for the divalent metals. Table II summarises the experimentally obtained distribution constants for cobalt.

From the distribution coefficients, it is clear (Fig. 3) that cobalt can be separated from the elements terbium to samarium. The value of d log K_D/d log $L = -2.87$ indicates that the predominant complex in solution is CoL_2. From the stability constants determined by VERBEEK[16] and GUNS[17] and the relative affinity constants determined by BONNER AND SMITH[15] one can predict the relative distribution coefficients

$$\beta_B^A(K_D) = \beta_B^A \text{ (stab. const.)} \cdot \beta_A^B \text{ (aff. const.)}$$

where indexes A and B represent two dipositive elements and β is the ratio of the values for these elements of the constants mentioned between brackets. The predicted distribution coefficients relative to $K_D(\text{Co}) = 1$ are represented in Table III (see also Fig. 3).

TABLE III

RELATIVE DISTRIBUTION COEFFICIENTS

Element	K_D	*Element*	K_D
UO_2^{2+}	0.027	Cd^{2+}	2.22
Cu^{2+}	0.04	Mg^{2+}	13
Zn^{2+}	0.32	Ca^{2+}	23
Ni^{2+}	0.52	Sr^{2+}	140
Pb^{2+}	0.59	Ba^{2+}	416
Co^{2+}	1		

The validity of the predictions is partly demonstrated by the fact that the calculated distribution coefficients of the alkali-earth metals are larger than the distribution coefficient for lanthanum, which has been experimentally demonstrated by WISH[18]. Furthermore, in an elution experiment, cobalt and zinc were completely separated and a value of 0.33 was found for the relative distribution coefficient of zinc (compared to a predicted value of 0.32).

Iron(III) is always eluted just before and partially overlapping with lutetium-(III) (range of distribution coefficients of Lu: 2 to 40). Some other elements such as tantalum, protactinium and neptunium form very strong complexes and are eluted before the rare earths. This is important since the only elements that completely follow the rare earths in the group separations described above are thorium and uranium. These elements give rise, upon activation, to radioactive isotopes of protactinium and neptunium, respectively.

It can thus be concluded that:

(1) some possible interfering elements such as the anions, alkaline earth metals, Sb, As, Np and Pa can be separated directly by elution with α-hydroxyisobutyric acid.

(2) cobalt can be used as flux monitor and separated directly in determinations not involving Pm or lighter rare earths.

(3) Na, K, Cu, Co, Zn and Fe can interfere. In practice only ^{24}Na and ^{42}K interfere in the analyses discussed in Parts II and III of this series.

The authors thank Prof. PICCIOTTO and LIC. BOUDIN for the gift of a gadolinite sample and Mr. TOMBU from Métallurgie Hoboken for the gift of the tantalocolumbite sample. One of the authors (D.L.M.) thanks the I.I.K.W. for financial assistance.

SUMMARY

A scheme for the separation of rare-earth elements from gadolinite and tantalocolumbite minerals is discussed. The possibility of interference from traces of non-separated elements in the subsequent separation of rare-earth elements from each other by cation exchange with α-hydroxyisobutyrate as the eluting agent is investigated.

RÉSUMÉ

Un schéma de séparation des éléments de terres rares dans des minerais tels que gadolinite ou tantalocolumbite est examiné. On envisage la possibilité d'interférence de traces d'éléments non-séparés dans la séparation subséquente des éléments de terres rares les uns des autres par échangeur de cation et α-hydroxyisobutyrate comme éluant.

ZUSAMMENFASSUNG

Es wird ein Schema zur Abtrennung der Seltenen Erden aus Gadolinit und Columbit diskutiert. Mögliche Störungen von Spuren nicht abgetrennter Elémente bei der darauffolgenden Trennung der Seltenen Erden von einander mit einem Kationenaustauscher und α-Hydroxiisobutyrat als Eluierungsmittel werden untersucht.

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ACTIVATION ANALYSIS OF RARE EARTHS

PART II. DETERMINATION OF LUTETIUM IN GADOLINITE

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Lutetium-176 is a naturally occurring long-lived isotope with a half-life of $3 \cdot 10^{10}$ years. Hence, it can be used for age determinations of rock formations[1]. This paper describes the determination in rocks by neutron activation analysis. The methods were tested on gadolinite mineral.

As discussed in Part I[2], the rare earths are separated as a group from the rest of the mineral before irradiation. ^{153}Gd is added as chemical yield monitor. After irradiation, lutetium is separated from the other rare earths, by cation exchange with α-hydroxyisobutyrate as the eluting agent. Since lutetium is the heaviest of all rare-earth elements, it leaves the column before all the others. The only possible contaminating rare-earth element is ytterbium.

According to whether the analyst possesses the instrumentation for γ-spectrometry or not, two methods are applicable:

(*a*) lutetium and ytterbium are counted integrally as they come from the column and corrections are made for the overlap of the two fractions;

(*b*) a more rapid separation with a larger ytterbium contamination is carried out. Lutetium and part of the ytterbium are collected and differentiated by γ-spectrometry.

NUCLEAR DATA

The nuclear data of lutetium and ytterbium isotopes are given in Table I. The γ-energies cited comprise also X-rays and sum peaks. Lutetium-175 yields on neutron activation also ^{176}Lu, but owing to its very long half-life, the activity of this isotope is entirely negligible. Ytterbium-177 decays to ^{177}Lu and will interfere with the determination of lutetium.

From these data it is apparent that differentiation by half-life of ^{177}Lu from ^{175}Yb is barely possible and furthermore would necessitate measurements during at least 3 weeks. However, since the biggest activity of ytterbium is due to ^{175}Yb, ytterbium will interfere with the 208-keV peak of ^{177}Lu only to a small extent and it is possible to use this γ-peak for the determination of lutetium.

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TABLE I

NUCLEAR DATA

Mother isotope	θ	σ	*Daughter isotope*	$T_{\frac{1}{2}}$	*γ-energies (keV)*
^{168}Yb	0.135	11,000	^{169}Yb	32 days	21, 50, 110, 131, 177, 199, 240, 261
^{174}Yb	31.84	60	^{175}Yb	4.2 days	53, 114, 137, 145, 283, 396
^{176}Yb	12.73	5.9	^{177}Yb	1.9 hours	Not measured
^{175}Lu	97.41	35	^{176m}Lu	3.7 hours	Not measured
^{176}Lu	2.59	4,000	^{177}Lu	6.8 days	55, 113, 208, 263, 321

EXPERIMENTAL

Sample and standard preparation

The 6 *M* hydrochloric acid solution eluted from the cation-exchange column (see Part I[2]) was evaporated at a temperature not exceeding 70°. The residue was redissolved in 1 ml of 0.1 *M* nitric acid. The yield was determined by counting the ^{153}Gd in a well-type crystal.

The standard solution was prepared by dissolving 5 mg of lutetium (as Lu_2O_3 spec pure, Johnson and Matthey) in strong nitric acid which had been purified by double distillation in a silica apparatus. The solution was evaporated to dryness at a temperature not exceeding 70°. The lutetium nitrate was redissolved in 10 ml of slightly acidified twice-distilled water.

Aliquots (100 μl) of both the sample and the standard solution were pipetted into small silica ampoules. These were sealed and irradiated in the BR-1 reactor of the S.C.K. in Mol for 2 h (flux $4 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot sec^{-1}$). A maximum of 5 samples was activated in one irradiation.

Separation of lutetium from ytterbium and other rare earths

This separation was carried out by means of cation exchange with α-hydroxyisobutyrate as the eluting agent. A column of 14 cm × 0.4 cm^2 was used. The analytical concentration of the complex-forming agent was 0.5 *M*, and the free ligand concen-

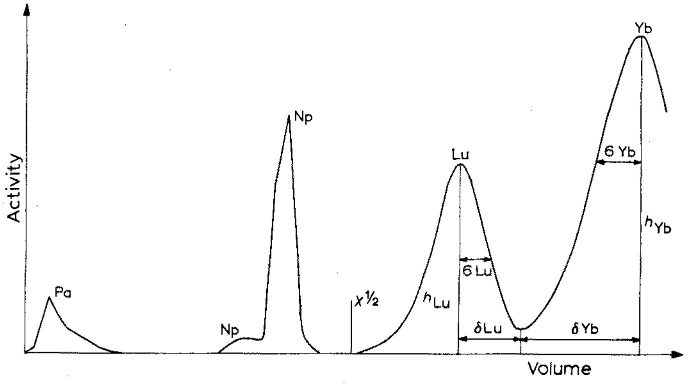

Fig. 1. Separation of Lu and Yb. Determination by integral counting.

tration was 0.05 M. The eluate was collected in fractions of 2 ml. A typical separation is shown in Fig. 1. The ^{239}Np peak stems from ^{238}U and the ^{233}Pa peak from ^{232}Th.

Both isotopes were identified by γ-spectrometry and half-life determination. The presence of thorium and uranium is not surprising since both elements are very often associated with the rare earths in minerals. These elements accompany the rare earths in the group separation.

The separation of lutetium from ytterbium was nearly complete. The cross-contamination never exceeded 5%. For the γ-spectrometric determination, the separations were carried out with a ligand concentration of up to 0.075 M. In this case, the distribution coefficients were too small to obtain a good separation of lutetium from ytterbium. However, lutetium was completely separated from other rare earths.

Analysis by integral counting

The sample was adsorbed quantitatively on the column and eluted. The eluate was collected, the fractions counted in a well-type scintillation counter and the activities plotted as a function of volume. The collected lutetium fraction was corrected for the activity lost under the ytterbium peak and the ytterbium activity present under the lutetium peak according to eqns. (1) and (2) (see SAID[3]).

$$\lambda_{\mathrm{Lu}} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\delta_{\mathrm{Lu}}/\sigma_{\mathrm{Lu}}} \exp(-x^2/2)\mathrm{d}x = A\left(\frac{\delta_{\mathrm{Lu}}}{\sigma_{\mathrm{Lu}}}\right) \tag{1}$$

$$\nu_{\mathrm{Yb}} = \frac{m[1-A(\delta_{\mathrm{Lu}}/\sigma_{\mathrm{Lu}})]}{\lambda_{\mathrm{Lu}}} \tag{2}$$

where $A(x)$ = area under the normal curve of error for argument x

$m = m_{\mathrm{Yb}}/m_{\mathrm{Lu}} = h_{\mathrm{Yb}}/h_{\mathrm{Lu}}$

h_{Yb}, h_{Lu}, σ_{Lu}, σ_{Yb}, δ_{Lu}, δ_{Yb}: see Fig. 1

λ_{Lu} = fractional Lu recovery

ν_{Yb} = fractional Yb contamination

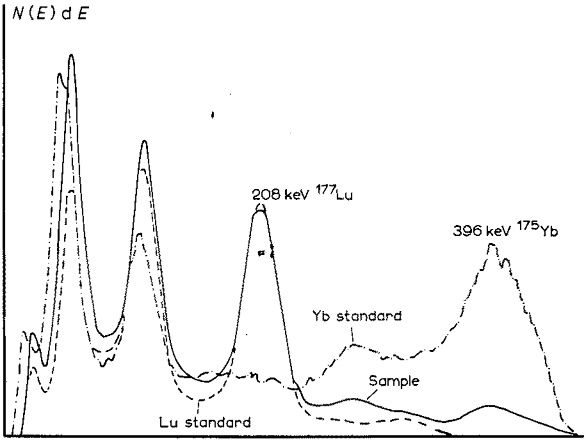

Fig. 2. γ-spectra of Lu, Yb and a collected Lu fraction for γ-spectrometric differentiation.

Analysis by γ-spectrometry

This method required an ytterbium standard as well as a lutetium standard. After cation exchange, the lutetium activity was collected along with the first quarter of the ytterbium fractions. This ensured a 100% recovery of the lutetium activity. The sample and the standards were measured in 50-ml calibrated flasks with a 400-channel γ-spectrometer.

From the activities in the 208-keV and the 396-keV energy regions (Fig. 2), two equations were obtained, which were solved for the ^{177}Lu activity under the 208-keV peak.

RESULTS

The experimental results are summarised in Table II. The first group of 3 results was obtained by integral counting, the second by γ-spectrometry and the third by the method used for analysis of all the rare earths described in Part III. Three possible sources of error were investigated (the blank, neutron shadowing and (n,γ; β⁻) errors) and corrections have to be made for two of these. These corrections are included in the results of Table II.

TABLE II

CONCENTRATION OF LUTETIUM IN GADOLINITE (IN % OF THE MINERAL)

Method of analysis	*Results*	*Mean values*
Integral counting	0.205^{3} 0.206^{3} 0.210^{0}	0.207^{2} $s = 0.002^{5}$
γ-spectrometry	0.203^{3} 0.199^{3} 0.195^{3}	0.199^{3} $s = 0.004^{0}$
Single comparator	0.200^{4} 0.192^{0} 0.208^{6}	0.200^{3} $s = 0.008^{3}$
	Average = 0.202±0.003%	

Blank

A group separation was simulated following the method described in Part I[2] but without addition of the rare-earth mineral. Iron (15 mg) was added to carry down possible rare earths during the hydroxide precipitation step. The iron was purified before the addition by anion exchange in hydrochloric acid. The rare-earth fraction was activated and a separation of lutetium from ytterbium was carried out. Since no activity was found where lutetium and ytterbium should have been eluted, no correction had to be made.

Neutron shadowing

The presence of gadolinium in the separated rare-earth fractions causes neutron shadowing and thus a negative error. This error was estimated by the addition of 500 μg of cobalt to the rare-earth fraction. Cobalt was separated, after irradiation, from the rare earths by anion exchange in hydrochloric acid medium and its activity compared with the activity of a cobalt standard (500 μg Co in 200 μl solution) irradiated under the same condition. A mean value of 3.4% for 2.55 mg of gadolinite in a 100-μl aliquot of solution was obtained. Accordingly, a correction of +1.35%/mg mineral in 100 μl of solution was applied.

(n,γ; β⁻) correction

The formation of ^{177}Lu from ^{177}Yb by the reaction $^{176}\text{Yb}(n,\gamma)^{177}\text{Yb}(\beta^-)^{177}\text{Lu}$ causes a positive error. This error was calculated by means of a general program permitting calculation of all types of secondary order interferences, programmed in SPS-language and performed on an IBM-1620 computer. For equal quantities of ytterbium and lutetium and a 2-h irradiation, an error of 0.12% was found. Since the ytterbium concentration was 12 times higher (see Part III) than the lutetium concentration, the total error was 1.5%. When the ytterbium concentration is not known, one can consider that as a general rule it is equal to 5–20 times the lutetium concentration.

To portions of 50 mg of the mineral, known amounts of lutetium solution were added and the lutetium activity was determined by the integral counting method. The lutetium content of the mineral was determined by least squares extrapolation (Fig. 3). A value of 0.132%±0.019 was found. The specific activity per μg addition was 8297 counts, and the specific activity of the standard was 8601 counts, *i.e.* a difference of 5%, which is within the limits of experimental error. One can thus conclude that the results given in Table II are accurate.

The precision of the different methods is high if one takes into account that the variation in the results is due not only to chemical processing and counting statistics but also to inhomogeneities in the mineral sample, which almost certainly occur.

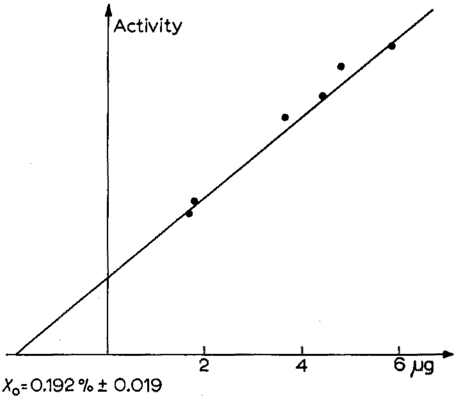

Fig. 3. Standard addition method for the analysis of Lu.

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SUMMARY

Two precise and accurate methods for the determination of lutetium in the presence of other rare earths and after separation from a mineral, gadolinite, are described. Both methods require separation of lutetium and ytterbium from the other rare earths. A complete separation of Lu and Yb is necessary when integral counting is used. The other method differentiates between the two elements by γ-spectrometry.

RÉSUMÉ

On décrit deux méthodes précises et réproductibles pour le dosage du lutétium en présence d'autres terres rares et après séparation d'un minerai, de la gadolinite par exemple. Les deux procédés nécessitent une séparation du lutétium et de l'ytterbium d'avec d'autres terres rares. Une séparation totale de Lu et Yb est nécessaire avec le comptage intégral. L'autre méthode distingue les deux éléments par spectrométrie-γ.

ZUSAMMENFASSUNG

Zwei reproduzierbare und zuverläsliche Methoden zur Bestimmung von Luthetium in Gegenwart anderer Seltener Erden und nach Abtrennung dieser aus dem Gadolinit werden beschrieben. Beide Methoden erfordern die Trennung des Luthetiums und Ytterbiums von den anderen Seltenen Erden. Eine vollständige Abtrennung des Lu und Yb ist notwendig, wenn eine integrale Zählweise angewendet wird. Die andere Methode unterscheidet mit Hilfe der γ-Spektrometrie zwischen den beiden Elementen.

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ACTIVATION ANALYSIS OF RARE EARTHS

PART III. THE DETERMINATION OF RARE EARTHS IN MINERALS BY THE SINGLE COMPARATOR TECHNIQUE

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The determination of the rare-earth elements in rocks, meteorites, minerals and similar materials has been described by several authors[1–5]. The present paper deals with the application of the so-called single comparator technique to the determination of rare earths in minerals, in this case gadolinite and a tantalocolumbite. The single comparator technique was proposed by GIRARDI[6] who discussed its merits and its application for the determination of chromium in iron, chloride in water, and gallium and copper in aluminium. In our laboratory, the technique has been used by ISSELEE[7] for the determination of As, Sb, Cu and Au in lead. The technique consists essentially in standardising the activity of the rare-earth standards obtained after irradiation in a fixed position and during a constant period against the activity of a flux monitor. The principal advantage of this method is in its applicability to routine analysis since ideally the 16 rare-earth standards can be replaced by a single measurement of the comparator. In fact only 12 were standardised according to this procedure for various reasons.

As flux monitor cobalt was chosen, because it is activated easily ($\sigma = 36$ barn) to the ^{60}Co isotope which has a long lifetime ($T_{\frac{1}{2}} = 5.3$ years) and possesses characteristic γ-emitting energies (1.17 and 1.33 MeV). The single comparator method requires that for identical irradiation times, always the same ratio between the activities of cobalt and the different rare earths will be obtained. Since the excitation functions (*i.e.*, the activation cross-section as a function of neutron energy) of the rare earths and cobalt are not identical, this can only be the case if the neutron spectrum is constant over the whole series of irradiations.

The errors induced by shifts in the neutron spectrum depend on the fraction of total activation due to epithermal activation of flux monitor and standard. The ratio of the specific activities of the rare earths and cobalt depends on the ratio of the effective activation cross-sections, σ_{act}, defined as:

$$\sigma_{\text{act.}} = \sigma_{\text{th}}(1 - f_{\text{r}}) + \sigma_{\text{r}} f_{\text{r}}$$

where r stands for resonance and th for thermal.

$$f_{\text{r}} = \varphi_{\text{r}}/(\varphi_{\text{th}} + \varphi_{\text{r}}) \quad (\varphi = \text{flux})$$

or

$$\sigma_{\text{act.}}/\sigma_{\text{r}} = (\sigma_{\text{th}}/\sigma_{\text{r}})(1 - f_{\text{r}}) + f_{\text{r}}$$

and since $(\sigma_{\text{r}})_{\text{R.E.}}/(\sigma_{\text{r}})_{\text{Co}}$ is a constant

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$$(\sigma_{\text{act.}})_{\text{R.E.}}/(\sigma_{\text{act.}})_{\text{Co}} = \left[\frac{(\sigma_{\text{th}}/\sigma_{\text{r}})_{\text{R.E.}}\ (1-f_{\text{r}})+f_{\text{r}}}{(\sigma_{\text{th}}/\sigma_{\text{r}})_{\text{Co}}\ (1-f_{\text{r}})+f_{\text{r}}}\right] \times \text{constant}$$

From the cadmium ratio of cobalt and the values of the resonance integral and the thermal activation cross-section, one can calculate f_r. For the irradiations in BR-1 a value of 0.128 was found. From the cadmium ratios of the rare earths, one can determine σ_{th}/σ_r, if f_r is known. With σ_{th}/σ_r the value of $(\sigma_{act})_{\text{R.E.}}/(\sigma_{act})_{\text{Co}}$ was calculated for $f_r = 0.118$ and $f_r = 0.138$. The percentage difference between these values is given in Table I (Δ% calc.).

TABLE I

STANDARDISATION OF RARE EARTHS

Element	*Cd-ratio*	*Counts/min*	*Counts/µg/min*	*Extreme values Δ% over 4 detns.*	*Δ% calc.*
Lu	8.62	38269	1000	5.9	0.15
Tm	2.38	779	21.7	8.0	6
Er	3.25	82343	1984	4.6	2
Ho	2.08	5970	131	6.8	7
Tb	1.80	5306	116	17.8	8
Gd	1.23	6488	119	14.0	13
Eu	21.5	872977	207850	4.8	1
Sm	1.78	516509	12663	7.5	8
Nd	5.00	344	0.85	7.8	0
Pr	11.14	3046	82.2	5.6	0.1
Ce	11.08	761	27.9	11.0	0.1
La	11.7	25578	598	5.9	0.2
Co	6.1	7305		5.3	0

TABLE II

THE γ-ENERGIES SELECTED

Isotope	*Half-life*	*Selected energy*	*Isotope*	*Half-life*	*Selected energy*
^{177}Lu	6.8 d	208 keV	^{152m}Eu	9.2 h	837 + 961 keV
^{170}Tm	130 d	84 keV	^{153}Sm	47 h	70 + 102 keV
^{171}Er	7.8 h	296 + 308 keV	^{143}Pr	19.2 h	1.57 MeV
^{166}Ho	27.3 h	1.36 MeV	^{143}Ce	33 h	294 keV
^{160}Tb	72 d	880 + 970 keV	^{140}La	40.2 h	1.60 MeV
^{159}Gd	18 h	364 keV	^{60}Co	5.3 y	1.17 + 1.33 MeV

γ-Spectrometric measurements were carried out with a multichannel analyser. For each rare earth a characteristic γ-energy was selected and the counts under the corresponding peak were summed. Sometimes the sum of more than one peak was used. Table II summarises the selected γ-energies and the half-lives of the measured isotopes. The choice of the isotopes for Lu, Tm, Er, Ho, Tb, Eu, Sm, Pr, La and Co is obvious, no other isotopes of the element being formed with a sufficient activity.

Gadolinium yields 3 measurable isotopes: ^{153}Gd and ^{159}Gd by (n,γ) reactions and ^{161}Tb by an (n,γ; β^-) reaction. ^{153}Gd could not be used since it was added as chemical yield monitor (see Part I of this series[8]). ^{160}Tb formed by the (n,γ) reaction on terbium interferes with the measurement of ^{161}Tb as the former gives rise to higher γ-energy. Thus ^{159}Gd was chosen for the determination of gadolinium.

Cerium gives rise to one isotope besides the already mentioned ^{143}Ce. This isotope, ^{141}Ce, has a half-life of 33 days. ^{143}Ce was chosen because there is no interference with its γ-energy of 294 keV by ^{141}Ce (highest γ-energy 145 keV). ^{141}Ce can be used but its standardisation must be carried out after complete decay of ^{143}Ce. There is an interference with the spectrum of ^{175}Yb by the longer-lived ^{169}Yb, hence ytterbium was determined in the mineral by direct comparison with an ytterbium standard. ^{151}Pm and ^{149}Pm formed by (n,γ; β^-) reactions interfere with ^{147}Nd, hence neodymium was separated from promethium on a cation exchanger with α-hydroxyisobutyrate (α-HIBA) as eluant. The neodymium was collected in a 50-ml flask and measured under the same conditions as the other rare earths. The 533-keV peak was selected. The dysprosium isotopes are too short-lived to be measured since between the end of irradiation and the beginning of the measurements there is a time lapse of 20 h. ^{90}Y is a pure β-emitter and is not included in the single comparator technique.

Table I gives the results of the standardisation as well as the measured cadmium ratios. As can be expected, the range on the results is highest for the lower cadmium ratios (Tm, Ce and Nd are not active enough to be compared with the others).

Separations

The rare earths were separated as a group before irradiation and after addition of ^{153}Gd, which has a high specific activity, as a chemical yield monitor (see Part I[8]). After irradiation, the rare earths were separated by cation exchange with 0.5 M α-HIBA as the eluting agent. The speed with which the elution was achieved, was mainly determined by the short half-lives of ^{171}Er and ^{152m}Eu. Different procedures were tested always at a flow-rate of 1 ml/min·cm^2.

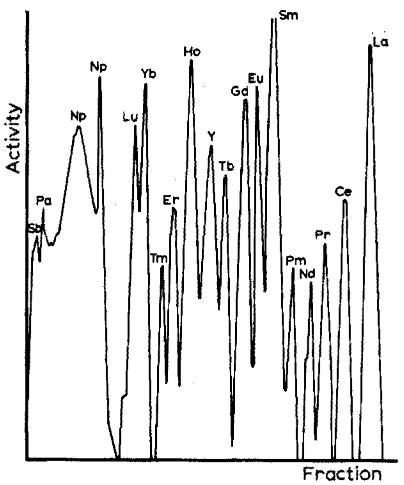
(*1*) A linear gradient was used with the volume of the two communicating vessels $V_t = 500$ ml, an initial ligand concentration $c_0 = 0.03$ M and a ligand concentration in the reservoir $c_L = 0.33$ M. With this gradient one can collect the following fractions: Np+Lu+Yb+part of the Tm activity; part of the Tm activity+Er; Ho. Subsequently the lighter rare earths were separated quantitatively. In the second fraction Tm does not interfere with the measurement of ^{171}Er. After the decay of ^{171}Er, ^{170}Tm can be counted without any interference. In the first fraction, ^{177}Lu and ^{175}Yb can be determined easily, but interfere with ^{170}Tm, as their half-lives are too long. If required, a subsequent complete separation of Lu–Yb–Tm can be applied on another column.

(*2*) Elution of lutetium and ytterbium at constant ligand concentration was followed by a linear gradient to separate the other rare earths. A quantitative separation was obtained but the procedure was too long to allow determinations of erbium and europium because 20 h were lost during transportation.

(*3*) A linear gradient was tested with $V_t = 500$ ml, $c_0 = 0.03$ M, $c_L = 0.165$ M. This gradient permitted the collection of the following fractions: Np; Lu+Yb; Tm; Er followed by the other individual rare earths. This gradient was not as steep as the first but still permitted the determination of erbium. After the elution of yttrium, the concentration c_L in the reservoir was increased to 0.33 M. This procedure was finally adopted for the separation of the rare-earth fraction of gadolinite (Fig. 1) and tantalocolumbite (Fig. 2).

Measurements of separated rare-earth fractions

Lutetium and ytterbium were determined by the γ-spectrometric procedure described in Part II[9]. The other rare earths were measured under the same conditions as described for standardisation. Some corrections had to be made, however, for interferences from other isotopes. In the analysis of gadolinite, holmium and terbium have sometimes to be corrected for Bremsstrahlung of ^{90}Y. Since terbium was measured in the 800–1000 keV range and holmium in the 1.4-MeV range, these corrections were small and never exceeded 5%.



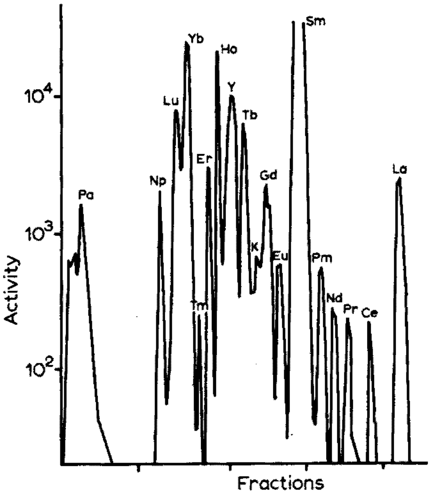


Fig. 1. Gradient elution of rare-earth fraction of gadolinite.

Fig. 2. Gradient elution of rare-earth fraction of tantalocolumbite.

Gadolinium and europium had to be corrected in some cases for ^{24}Na and ^{42}K. Since these isotopes have γ-energies of 2.75 MeV and 1.52 MeV, respectively, and since these energies are higher than any γ-energy of ^{152m}Eu, ^{153}Gd or ^{159}Gd, they can be easily stripped from the spectrum. A control was made by measuring the mixed spectra at different times and using the difference in half-life between the alkali impurities and the rare earths. ^{90}Y was measured by G.M. counting after evaporation of the eluted fraction on a filter paper disk. The reproducibility of the method depended on a careful standardisation of the procedure. The different factors that had to be held constant were: (*1*) the concentration of the α-HIBA (a double α-HIBA concentration decreased the counting rate by 10%); (*2*) the absorbing qualities of the filter paper; and (*3*) the rate of evaporation: since α-HIBA can sublimate, it is necessary to evaporate standards and samples at the same temperature and during the same time.

RESULTS AND DISCUSSION

The calculated results were corrected for neutron self-shielding (see Part II[9]). The corrections were +1.35%/mg of gadolinite irradiated in 100 μl of solution and 0.08%/mg of tantalocolumbite irradiated in 100 μl of solution. Corrections for (n,γ;

β^-), (n,γ; β^-; n,γ) and (n,γ; n,γ; β^-) reactions were calculated. In all cases, these corrections were negligible except for the ^{176}Yb(n,γ; β^-)^{177}Lu reaction which has already been discussed in Part II[9].

An important correction was required by the reactivation of ^{153}Gd used as chemical yield monitor because it was not carrier-free. This error was determined by reactivating ^{153}Gd samples of known activity and counting the resultant ^{159}Gd. The correction never exceeded 25%. The presence of ^{239}Np activity indicated the presence of uranium in the irradiated sample. By fission this could give rise to positive errors in the lanthanum and cerium determinations. Therefore, a determination was carried out on a rare-earth fraction of gadolinite from which uranium had been eliminated before irradiation.

The separation of uranium was achieved by paper chromatography with 5% nitric acid in ether as eluant. This method has already been described for the elimination of uranium on cellulose columns[10]; uranium migrates close to the front and the rare earths remain on the starting line. After activation of the isolated rare-earth fraction and a similarly treated blank, lanthanum was determined. The result was 0.13^2%, which indicates that there was no positive error caused by the fission of uranium.

The results obtained for gadolinite by the normal standard procedure and the single comparator method are summarised in Table III. The results obtained by the single comparator method for tantalocolumbite are summarised in Table IV.

TABLE III

THE PERCENTAGE AMOUNTS OF RARE EARTHS IN GADOLINITE BY THE NORMAL STANDARD AND SINGLE COMPARATOR METHODS

Element	*Single comparator*	*Standard deviation (%)*	*Direct comparison*	*Standard deviation (%)*
Lu	0.20^2	3	0.20^0	4
Yb	Not detd.	—	1.33	4.5
Tm	0.19^7	2	0.19^8	3
Er	1.75	5	1.78	—
Ho	0.53^7	0.5	0.56	5.5
Y	Not detd.	—	39	—
Tb	0.53	4	0.55	2
Gd	2.06	8.5	2.01	13.5
Eu	0.0013^5	—	0.0013^0	—
Sm	1.29^5	4	1.46	7
Pr	0.17^9	5	0.18^9	6.5
Ce	0.59	5	0.59	—
La	0.13^5	3	0.13^8	3.5

Accuracy of the results

The sum of the rare earths found by activation analysis was 52.4 (as the oxides) whereas gravimetry gave 50.05% for gadolinite. For tantalocolumbite rare-earth contents of 5.27% (activation analysis) and 4.50% (gravimetric method[11]) were found. The error was +4.8% for gadolinite and +13.7% for tantalocolumbite. The gravimetric method for the determination of rare earths, however, employs a homogeneous precipitation technique for which a loss of 7% can be predicted (Part I[8]).

TABLE IV

THE AMOUNTS OF RARE EARTHS IN TANTALOCOLUMBITE BY THE SINGLE COMPARATOR METHOD

	Detn. 1[a]	*Detn. 2*[a]	*Mean*	*p.p.m. in the mineral*
Lu	0.59	0.57	0.58	260
Yb[b]	4.19	4.13	4.16	1870
Tm	0.71	0.67	0.69	310
Er	4.32	4.26	4.29	1930
Ho	1.52	1.71	1.61	720
Y[b]	47.2	49.4	48.3	2.4%
Tb	0.91	0.84	0.88	400
Gd	3.04	2.99	3.02	1360
Eu	0.10	0.10	0.10	45
Sm	2.08	1.96	2.02	910
Nd	8.29	7.79	8.04	3620
Pr	1.31	1.27	1.29	580
Ce	9.91	9.91	9.91	4460
La	6.07	5.93	6.00	2700

[a] Expressed as a percentage of the rare-earth fraction.
[b] By direct comparison.

This reduces the error for tantalocolumbite to +7%. To obtain the totals in question the concentration of dysprosium was assumed to be equal to the concentration of erbium.

In two experiments samarium and holmium were added in amounts about 2 and 12 times the quantity present in the mineral. The yields were respectively 106.4% and 102.0% for samarium and 99.6% and 99.8% for holmium. It may thus be concluded that the described method is accurate and relatively precise.

EXPERIMENTAL

Rare-earth standards

Standard solutions of rare earths were made by dissolving *ca.* 5 mg of rare-earth oxides (Specpure, Johnson & Matthey) in nitric acid which had been purified by double distillation in a silica apparatus. Evaporate the solution to dryness under an infrared lamp at a temperature not exceeding 70°. Redissolve the nitrates in 10 ml of twice-distilled water to which a drop of nitric acid had been added. For neodymium, dissolve *ca.* 40 mg of the oxide and for europium *ca.* 0.5 mg. For the cobalt solution dissolve approximately 50 mg of cobalt nitrate hexahydrate in 10 ml of slightly acidified water.

Samples of rare earths

Proceed with the group separation as described in Part I[8]. Evaporate the 6 *M* hydrochloric acid eluate of the cation-exchange column at a temperature not exceeding 70°. Redissolve the residue in *ca.* 1 ml of 0.1 *M* hydrochloric acid. Determine the chemical yield by counting the ^{153}Gd in a well-type crystal.

Irradiations

For the standardisation, weigh 100-mg quantities of the 12 rare-earth standards and 2 cobalt standards in silica ampoules. Seal and pack in 2 aluminium capsules, each one containing at least one cobalt monitor. For the activation analysis, weigh the sample solution, transfer about 100 μl to a silica ampoule and weigh again. Seal the ampoule and irradiate together with two cobalt monitors, one ytterbium standard and one yttrium standard.

All irradiations took place in BR-1 at Mol (2 h at a flux of $4 \cdot 10^{11}$ n$\cdot$cm$^{-2}\cdot$sec^{-1}).

Standardisation measurements

After irradiation, break the ampoules and transfer the contents to 50-ml graduated flasks. Do not fill to the calibration mark, but to the beginning of the neck to obtain a more reproducible geometry.

All measurements were carried out on a 3×3″ flat NaI(Tl) crystal coupled to a 400-channel analyser.

Sample separation

After irradiation break the ampoules and wash the contents with 0.1 N hydrochloric acid into a column of Dowex 50W-X8 (200–400 mesh) of size 14 cm × 0.4 cm^2. Elute with a 0.5 M α-HIBA solution with a ligand gradient ($V_t = 500$ ml; $c_0 = 0.03$ M; $c_L = 0.165$ M) and follow the elution by counting the eluted fractions (2 ml) in a well-type crystal. After the elution of yttrium, increase the ligand concentration in the reservoir to 0.33 M by addition of concentrated ammonia. Collect *ca.* 200 fractions for the complete elution of the rare earths. The elution peaks are identified by γ-spectrometry.

Activation analysis measurements

Collect the individual separated rare earths in 50-ml graduated flasks and also transfer the standards to 50-ml graduated flasks with 0.1 M hydrochloric acid. For yttrium add first a quantity of α-HIBA equal to the quantity in the eluted yttrium fraction. Make the measurements under the same conditions as described for the standardisation and for ytterbium as described in Part II[9].

The measurement of yttrium is done by G. M. counting. Pipette from both the standard and the eluted yttrium fraction three 1-ml portions onto aluminium cups fitted with a filter-paper disk. Place the cups in a ring at equal distances from an infrared lamp, evaporate and count.

Separation of uranium

After the precipitation step with ammonia in the group separation (see Part I[8]), dissolve the precipitate in a minimal quantity of hydrochloric acid and spot on three Whatman 3MM papers (30 × 15 cm) in a 12-cm long and 2-cm wide band. After elution (front 20 cm), cut out the starting line, ash, ignite and redissolve in hot 12 N hydrochloric acid. Dilute to 2 N hydrochloric acid and proceed as described in Part I[8] with the cation-exchange step.

SUMMARY

The determination of rare earths in minerals by activation analysis is described. The rare earths are separated as a group from the bulk of the material before irradiation. After irradiation the rare earths are separated from each other by gradient elution with ammonium α-hydroxyisobutyrate on a cation-exchange column. The elements are determined by the single comparator technique. This method permits a practical application of activation analysis to the routine determination of rare earths in complex matrices.

RÉSUMÉ

On décrit un dosage de terres rares dans des minerais. Les terres rares sont séparées en un groupe avant irradiation. Après irradiation les terres rares sont séparées les unes des autres par élution sélective à l'aide d'α-hydroxyisobutyrate d'ammonium sur une colonne d'échange de cations. Chaque élément est ensuite dosé au moyen de la technique du "comparateur simple". Ce procédé permet une application pratique de l'analyse par activation au dosage de routine des terres rares dans des matrices complexes.

ZUSAMMENFASSUNG

Die Bestimmung der Seltenen Erden in Mineralien mit der Aktivierungsanalyse wird beschrieben. Die Seltenen Erden werden als Gruppe vor der Bestrahlung aus dem Material abgetrennt. Nach der Bestrahlung werden sie mit einem Kationenaustauscher getrennt und mit der sogenannten Single-Komperator-Technik bestimmt. Die Methode erlaubt eine praktische Anwendung der Aktivierungsanalyse bei der Routinebestimmung Seltener Erden in komplexen Matrices.

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ATOMIC-FLUORESCENCE SPECTROSCOPY OF MAGNESIUM WITH A HIGH-INTENSITY HOLLOW-CATHODE LAMP AS LINE SOURCE

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As a trace technique for the analysis of metals, atomic-fluorescence spectroscopy, AFS, possesses all the merits of atomic-absorption spectroscopy, AAS, but usually at a sensitivity at least one order of magnitude better than the established technique[1]. It can be operated with continuous sources[2,3] more readily than AAS[4,5], and frequently shows calibration curves which extend almost linearly over a thousand-fold concentration range, whereas the absorption method usually extends only over a decade of concentration. Several AFS procedures have been described recently in communications from this laboratory[3,6,7] and elsewhere[2,8,9]. In most cases spectral discharge atomic vapour lamps have been used to excite fluorescence[3,6,8,9] or, more effectively, microwave-excited electrodeless discharge tubes[6,7].

Source intensity is of prime importance to the sensitivity of AFS since the fluorescence signal varies linearly with the energy flux in a given atomic line from the source, provided that the quantum efficiency remains constant and that the atomic population of the atom-reservoir is insufficiently dense to produce self-absorption. The evolution of the high-intensity hollow-cathode lamp by SULLIVAN AND WALSH[10] furnishes an intensely bright line source well worthy of examination for AFS.

In a recent investigation of the high-intensity silver hollow-cathode lamp, it has been shown[11] that this source may be used to determine silver in the range 0.01–10 p.p.m. with detection limits of 1.7 ng/ml for aqueous solutions of silver, or, following extraction, 0.5 ng/ml. ARMENTROUT[12], however, was only able to obtain a detection limit of 0.1 p.p.m. for nickel in aqueous solution using a similar source. In the present study, magnesium was selected for further investigation with this type of source, since its spectral characteristics are rather different from those of the other two elements which have been examined up to the present time, and because it is an element which can be determined very sensitively by AAS. It was, therefore, of interest to study the determination of this element by both techniques using the same source and spectrometer, and to report for the first time on the atomic-fluorescence characteristics of magnesium using a magnesium line source. In this work, atomic fluorescence in a nitrous oxide–acetylene flame was investigated for the first time, a specially designed water-cooled emission head being used. The atomic absorption of magnesium with the same source and equipment and all 3 flame media is also briefly discussed.

EXPERIMENTAL

Apparatus

A Techtron AA4 atomic-absorption spectrophotometer fitted with an ASL high-intensity magnesium hollow-cathode lamp was used. An EEL emission head was employed for the air–propane flame, and a Techtron emission head for the air–acetylene flame. The lamp and detector were modulated at 285 Hz.

Instrumental settings. The instrumental settings were: primary current, 20 mA; slit, 300 μ; booster current, 400 mA; wavelength, 285.21 nm; air-pressure, 15 p.s.i. and fuel gas pressure at the maximum consistent with a stable, oxidising flame.

Reagents

A stock magnesium solution (100 p.p.m. in 0.1 F hydrochloric acid) was prepared by dissolving 0.1657 g of magnesium oxide in 10 ml of 10 F hydrochloric acid and diluting to 1 l. More dilute solutions were prepared as required; these should not be kept for long periods because of adsorption of magnesium on the glass surface.

Construction of calibration curves, etc.

Switch on the AA4 units with the lamp in the warm-up position and allow to stand for about 1 h to attain maximum stability of source and electronics. Peak the monochromator on the signal from the lamp at 285.21 nm. Situate the lamp at right angles to the optical bar of the instrument and, with the focussing lens and saddle removed, move the burner as close as possible to the slit, and place the end-window of the hollow-cathode lamp at about one inch distance from the flame. Spray a magnesium solution into the flame and adjust the height and position of the burner head and lamp so that the maximum fluorescence signal is obtained.

Concentrations up to 100 p.p.m. of magnesium were determined. For the range 0.002–0.1 p.p.m., scale expansion was used. Maximum amplifier gain and slit width were used for the range 0.01–0.5 p.p.m. Above this concentration the amplifier gain was reduced to bring the maximum signal expected to approximately 100% galvanometer deflection. The calibration curves were constructed in the usual way[11].

SPECTRAL CHARACTERISTICS OF ATOMIC MAGNESIUM

The sensitivity of AAS is virtually independent of the absolute strength of the line emitted by the spectral line source since the analytical signal is a logarithmic ratio of incident and emergent light signals in the flame. It is, within limits, also independent of the spectral response characteristics of the detector for the same reason. The sensitivity of AFS on the other hand, depends on the absolute emission signal from the line source and on the sensitivity of the detector against wavelength. Thus it does not necessarily follow that the most sensitive line in absorption, usually the principal resonance line, will be the best choice for AFS. This is well illustrated by the different behaviour observed for silver using a 150-W high-pressure Xenon arc lamp[3] or a high-intensity hollow-cathode lamp[11]. For this reason, it was necessary to examine the spectral characteristics of magnesium in atomic fluorescence.

In AAS, the 285.21 nm line, corresponding to the 3s $'S_0 \rightarrow 'P_1$ transition appears to be the most sensitive, but the 202.58 nm ground-state line and an ionic line at

279.55 nm have also been employed. ELWELL AND GIDLEY[13] quote detection limits of 0.01, 2 and 5 p.p.m. Mg respectively for these lines and give the corresponding ranges of determination as 0.2–2, 50–500 and 100–1000 p.p.m.

In the present study, the ground-state lines of magnesium were examined, *viz.*, those at 202.58, 285.21 and 457.11 nm. Lines emanating from states higher than the ground state were not examined, though they might prove useful in high-temperature flames or at higher concentrations of magnesium where self absorption becomes a limiting factor. Fluorescence of the 285.21 nm line was very marked, but no detectable signals were obtained for the other magnesium lines in air-supported propane and acetylene flames. This simplicity of the fluorescence emission spectrum of atomic magnesium is extremely attractive from the viewpoint of analytical utility, since wide slits may be used with advantage except where flame background is high. No scatter signals were observed in any of these experiments.

VARIATION OF EXPERIMENTAL PARAMETERS

Intensity of source

In the high-intensity hollow-cathode lamp the photoemission is controlled by the (primary) cathode current and by the (secondary or booster) current flowing between the two auxiliary electrodes which discharge across the cloud of atomic vapour at the exit of the cathode. It was found that the intensity of fluorescence at 285.21 nm for a given solution of magnesium increased markedly with increasing primary current. Increasing the secondary current from 0 to 100 mA gave an increase of fluorescence signal of more than 10-fold, but further increase from 100 to 400 mA enhanced the signal by only 2.5%. To increase the life of the lamp, the work subsequently described here was done at a secondary current of 100 mA. (Increasing the secondary current to 500 mA increased the signal by 7%, but this is above the maximum recommended running current of the lamp.)

Positioning of excitation source and flame

As in all previously reported studies of AFS, the line source was situated so as to subtend a right angle with the monochromator slit at the centre of the flame. The flame was positioned as close as practicable to the slit with the end-window of the lamp as close to the flame as possible to ensure minimal light loss. With the focussing lenses available, no benefit was gained by placing these between the source and the flame, or between the flame and the monochromator, but collection of light by an ellipsoid mirror [14] might be beneficial.

Flame conditions

The cylindrical flame-emission burner heads mentioned above were used in conjunction with several fuel gases and different fuel/support-gas ratios. In all instances, the best fluorescence signals were obtained from the region immediately above the primary reaction zone in the centre of the flame with a slightly fuel-rich flame burning below the level of C_2 luminosity. Since the signal/noise ratio is one of the features which is important in defining the sensitivity of atomic fluorescence it was found best, in the absence of interfering elements, to use an air–propane rather than an air–acetylene flame since there is sufficient energy in the former to ensure efficient atomisation of most magnesium salts. Moreover, it was found easily possible to use scale-expansion with the air–propane flame, but not with the noisier air–acetylene flame.

Because of interference effects noted subsequently in the air–propane and air–acetylene flames, the atomic fluorescence of magnesium in a nitrous oxide–acetylene flame was examined. For this purpose, a specially designed nitrous oxide–acetylene emission burner head (Fig. 1) was constructed, based on a previous unit constructed in this laboratory[15]. In this instance, a close-fitting water cooling tank surrounded the burner head to cool it and prevent the formation of hard carbon deposits on the burner head; the deposits formed on the present burner were soft and easily swept aside. The flame used in this way was too noisy to be used with full amplifier gain (noise ± 5% scale deflection at gain 20) but at a gain setting of 14 the noise level was reduced to ± 0.5% scale deflection and linear calibration curves could be obtained from 0.5–25 p.p.m., whilst at a gain setting of 12 (*i.e. ca.* half full sensitivity) the calibration curves were linear over the range 0.5–100 p.p.m. Above 200 p.p.m. Mg, the fluorescence signal decreased with increase of magnesium concentration. The nitrous oxide–acetylene flame is not suitable for the determination of small amounts of magnesium because of its high background radiation at the wavelength used for measurement of magnesium. However, as will be seen later, the magnesium determination is free from interference in this flame and the upper range for magnesium is

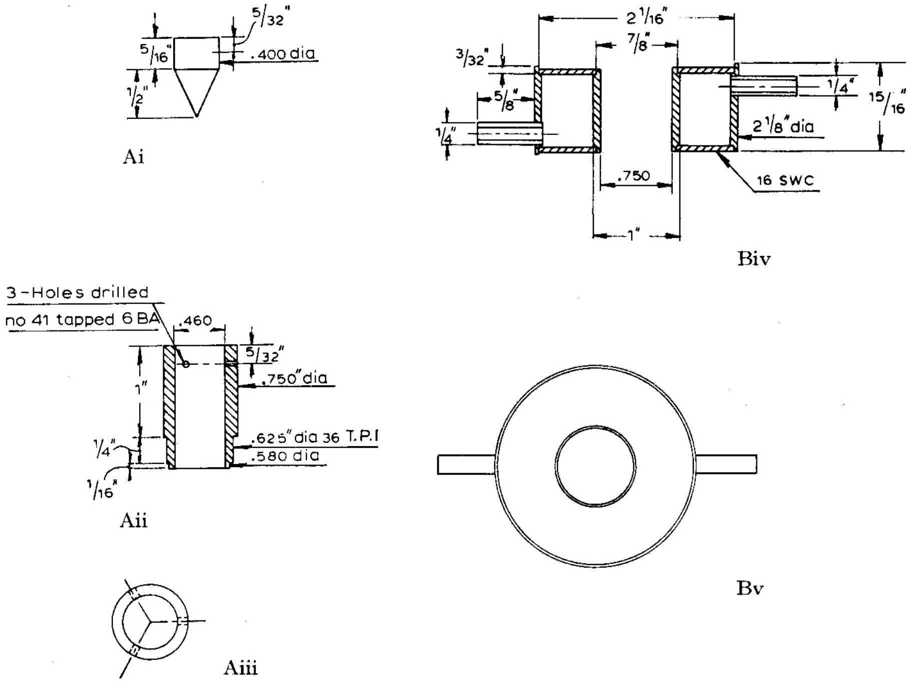

Fig. 1. Emission burner head for N_2O–C_2H_2 flame. (A) Exploded view of burner head. (i) Central cone. (ii) Stem of burner head to fit Techtron unit. (iii) Plan view of assembled unit. (B) Cooling tank to surround burner head. (iv) Sectional view. (v) Plan view.

increased up to 100 p.p.m. (5 p.p.m. in other two flames), so that the flame serves two useful functions.

Amplifier gain and slit-width

Because the principal resonance line for magnesium at 285.21 nm was the most sensitive and was the only one to be emitted in the flame with reasonable sensitivity, it was practicable to use the maximum light-gathering power of the instrument at maximum slit-width. Maximum amplifier gain was also used except where solutions more concentrated than 0.5 p.p.m. Mg were employed. In these instances the gain was reduced to obtain *ca.* full-scale deflection on the transmission scale for the strongest magnesium solution in the series.

Range of determination of magnesium by AFS and detection limits

The lowest concentration of magnesium determined in these studies was 0.01 p.p.m. The maximum concentration of magnesium that could be determined in the propane or acetylene flame, whilst retaining a linear dependence of fluorescence signal to concentration, was 5 p.p.m. Above 20 p.p.m. the fluorescence signal decreased with increasing concentration of magnesium owing to re-absorption of the fluorescence signal by the surrounding dense population of ground-state magnesium atoms, collisional quenching, etc. This behaviour appears to be characteristic of all AFS systems. The lowest amount of magnesium determined was twenty times less than that quoted for AAS and the upper limit is *ca.* twice as high. The detection limit in the air–propane flame, corresponding to 1% scale deflection at maximum gain (signal/noise ratio of *ca.* 1 : 1), was 1 ng Mg/ml. Without scale expansion, a detection limit of 4.7 ng Mg/ml at a signal to noise ratio of 1 : 0.75 was obtained and 5 ng Mg/ml in the air–acetylene flame. These results are summarised in Table I.

TABLE I

AFS DETECTION LIMITS FOR MAGNESIUM AT 285.21 nm

(Primary cathode current 20 mA; secondary current 100 mA; slit 300 μ; support gas pressure 15 p.s.i.; amplifier gain at maximum (20) except for N_2O–C_2H_2[10])

Flame	*Scale expansion*	*Detection limit*[a] *(ng/ml)*
Air–propane	None	4.75
Air–propane	×5	1
Air–acetylene	None	5
Air–acetylene	×5	1
N_2O–acetylene	None	50

[a] Signal: noise = 1 : 0.75, except for N_2O–C_2H_2 where S : N = 1 : 0.5.

The analytically useful range of 0.01–5 p.p.m. of Mg is a considerable improvement on the AAS procedure and as in previously described methods for other elements, the lowest amount which may be determined is more than ten-fold less than that obtainable with AAS[13]. Efficient light collection could further improve this limit.

Interferences in the AFS determination of magnesium

Interference effects in AFS have been studied extensively for elements such as cadmium[6] and zinc[3]. In the present instance, only a selected range of elements was studied, *e.g.* aluminium, molybdenum and titanium, which are prone to cause serious matrix effects, iron as a line-rich element likely to cause spectral interference and strontium as a typical alkaline earth.

Aluminium, molybdenum and titanium all caused a depressive interference as expected; the effects were more marked in the cooler air–propane flame than in air–acetylene owing to less efficient break-down of their refractory oxide particles. In the range up to 800 p.p.m. of aluminium, for example, the signal for 1 p.p.m. of magnesium decreased with increase of aluminium concentration, but remained constant thereafter. Similar effects are listed for the other elements which form refractory oxides (Table II). Iron markedly depresses the magnesium signal in air–propane, but shows no interference whatsoever in air–acetylene, *cf.* Table II. Strontium showed no interference in either flame even at a 1000 p.p.m. level. It will be seen from Table II that magnesium can be determined reliably at reduced sensitivity in the presence of any of the refractory oxide formers without variation in signal above a minimum specified concentration of the element. In the presence of 1000 p.p.m. of Al, for example, magnesium may be determined in the range 0.1–2 p.p.m. (upper and lower limits not explored) in an air–propane flame with only a four fold loss in sensitivity. In air–acetylene the loss of sensitivity is two fold.

TABLE II

CONCENTRATION OF ELEMENTS ABOVE WHICH NO FURTHER INTERFERENCE IS OBSERVED IN THE AFS DETERMINATION OF 1 μg OF Mg IN VARIOUS FLAME MEDIA

Element	*Air–propane (μg/ml)*	*Air–acetylene (μg/ml)*	*N_2O–acetylene (μg/ml)*
Al	800	800	No interference$^+$
Fe	1500	No interference$^+$	No interference$^+$
Mo	2000	800	No interference$^+$
Ti	800	500	No interference$^+$
Ca, Sr, Cu, La, Mn, Na, Zn	No interference$^+$	No interference$^+$	No interference$^+$

$^+$ 1000 μg/ml level.

In the nitrous oxide–acetylene flame none of these elements interfered at the 1000 p.p.m. level in any way with the AFS determination of magnesium, nor did calcium, copper, manganese, sodium or zinc. This is undoubtedly due partly to the slightly higher temperature of the flame, but more particularly to the induced dissociation of the refractory oxides

$$MO_n \rightleftharpoons M + n[O]$$

brought about by the removal of atomic oxygen by cyanogen radicals in the red secondary zone of the nitrous oxide–acetylene flame[16].

Atomic absorption of magnesium

To enable a reliable comparison of AFS and AAS to be made, the same line source was used in conjunction with the same spectrophotometer in its AAS mode. A 10-cm slot burner was used for air–propane and air–acetylene and a 5-cm path for nitrous oxide–acetylene. In this instance, the air–acetylene flame yielded the lowest detection limits for magnesium (Table III).

The greatest sensitivity in AAS was obtained with a primary cathode current of 2 mA and no secondary current. Since use of the latter showed no benefit in AAS it may be concluded that self-absorption does not occur in the lamp used. The detection limit at 285.21 nm under these conditions was 0.017 p.p.m. Mg without, and 0.003 p.p.m. with, × 5 scale expansion. In this instance, however, the nitrous oxide–acetylene flame was less sensitive than air–propane, although it has the advantage that the number of interfering elements is greatly reduced[17].

TABLE III

AAS DETECTION LIMITS FOR MAGNESIUM AT 285.21 nm

(Primary cathode current 2 mA; secondary current 0; slit 300 μ; support gas pressure 15 p.s.i.; amplifier gain at 4 (max = 20))

Flame	*Detection limit*[a] *(ng/ml)*
Air–propane	26
Air–acetylene	17
N_2O–acetylene	7

[a] Detection limit = 1% absorption.
10-cm flames except for N_2O–C_2H_2 (5 cm).

The smallest amounts of magnesium which could be determined by AAS in these studies were 0.4 p.p.m., 0.5 p.p.m. and 1.5 p.p.m. in air–acetylene, air–propane and nitrous oxide–acetylene flames respectively. These figures are comparable to the values quoted in the literature[13] but the × 5 scale expansion facility allowed magnesium to be determined by AAS down to 0.1 p.p.m.

DISCUSSION

The atomic fluorescence of magnesium when a high-intensity hollow-cathode magnesium lamp is used, provides a means of determining magnesium in the range 0.01–5 p.p.m. The air–propane flame gives the best signal: noise ratio, but where interfering elements are present, an air–acetylene flame is better. None of the refractory oxide-forming elements interfered with the determination of magnesium by AFS when a nitrous oxide–acetylene flame was used and the upper limit of determination was raised to 100 p.p.m. However, because of the background noise of this flame, solutions more dilute than 0.5 p.p.m. are not easily determined with precision, though separation of the nitrous oxide–acetylene[15] flame offers the possibility of considerable suppression of the noise level.

As in previous cases, it has been shown that AFS is at least one order of magnitude more sensitive than AAS, and in this instance even for the element which can be determined more sensitively than most others by the absorption technique. No scatter problems were encountered using the Techtron nebulizer–burner system and the range of freedom from interference was shown flame by flame to be similar to that previously reported for AAS. Amongst the elements examined no interference was found during AFS in the nitrous oxide–acetylene flame.

We are grateful to the Science Research Council for a grant in aid of this work, and record our thanks to Mr. H. G. COBLEY for his construction of the nitrous oxide–acetylene emission burner head.

SUMMARY

Atomic fluorescence of magnesium is possible in air–propane or air–acetylene flames at 285.21 nm, using a high-intensity hollow-cathode magnesium lamp for excitation. The technique permits determinations of magnesium in the range 0.01–5 p.p.m., *i.e.* with more than 10 times the sensitivity of the atomic absorption method even for this most sensitive element. The detection limit in either flame is 1 ng/ml (signal: noise ratio 1 : 0.75). In a nitrous oxide–acetylene flame, atomic fluorescence may be carried out with linear signal/concentration dependence up to 100 p.p.m. without interference even from metals such as aluminium, titanium, etc. at a 1000-fold excess ratio to magnesium. A brief comparison is made with atomic absorption using the same source and equipment.

RÉSUMÉ

La fluorescence atomique du magnésium est possible dans des flammes air–propane ou air–acétylène à 285.21 nm, en utilisant une lampe à cathode creuse de magnésium, à haute intensité, pour l'excitation. Cette technique permet des dosages de magnésium de 0.01 à 5 p.p.m. avec une sensibilité plus que 10 fois supérieure à celle de la méthode par absorption atomique. La limite de détection dans les deux flammes est de 1 ng/ml. Dans une flamme oxyde nitreux–acétylène, la fluorescence atomique peut être mesurée jusqu'à 100 p.p.m. sans interférence même en présence de métaux tels que aluminium, titane, etc., en proportion métal/magnésium de 1000 : 1. Une brève comparaison est faite avec l'absorption atomique utilisant la même source et le même équipement.

ZUSAMMENFASSUNG

Die Bestimmung von Magnesium mit der Atomfluoreszenzspektroskopie ist mit Luft–Propan- oder Luft–Acetylen-Flammen bei 285.21 nm möglich, wenn zur Anregung eine intensitätsstarke Magnesium-Hohlkathodenlampe benutzt wird. Die Technik erlaubt die Bestimmung des Magnesiums im Bereich von 0.01–5 p.p.m., d.h. sie ist mehr als 10 mal empfindlicher als die Atomabsorptionsmethode. Die Nachweisgrenze liegt in jeder der beiden Flammen bei 1 ng/ml (Signal: Untergrund = 1:0.75). In einer Stickstoffoxid–Acetylen-Flamme kann die Atomfluoreszenz bei linearer Signal/Konzentrations-Abhängigkeit bis hinauf zu 100 p.p.m. durchgeführt werden. Dabei stören selbst solche Metalle wie Aluminium, Titan usw. im 1000-fachen Überschuss nicht. Die Methode wird mit der Atomabsorption unter Verwendung der selben Quelle und Apparatur kurz verglichen.

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ANALYSE DU CHROME PAR SPECTROMETRIE-GAMMA APRES SEPARATION DES RADIOELEMENTS SUR RESINES ECHANGEUSES D'IONS*

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(Reçu le 12 janvier, 1968)

La présente étude revêt essentiellement un caractère d'application, dans la mesure où la technique de séparation des radioéléments sur résines échangeuses d'ions telle que nous l'utilisons (schéma de AUBOUIN ET LAVERLOCHERE[1]) a déjà fait l'objet d'un certain nombre de publications, notamment à propos du niobium[2] et du béryllium[3]. A l'aide d'une méthode tout à fait analogue, GIRARDI ET PIETRA[4] ont analysé l'aluminium et ont pu séparer un certain nombre d'impuretés. Cependant ces trois matrices constituent, en analyse par activation, des cas favorables du fait qu'elles présentent, au moment des séparations, des activités nulles ou faibles, ce qui simplifie à la fois le problème de protection et de séparation. Le cas du tantale, également analysé par cette méthode[2], nécessite des manipulations en sorbonne blindée, ce qui limite considérablement les possibilités d'utilisation.

Des études sur la ductilité du chrome ont amené à utiliser l'activation aux neutrons pour l'analyse de quelques échantillons. A cette occasion, il est apparu que la littérature contenait fort peu de références se rapportant à cette matrice; d'autre part, il est intéressant de constater qu'un élément comme le chrome, dont l'activité après irradiation est élevée (70 mC/g pour 140 h à $2 \cdot 10^{12}$ $n \cdot cm^{-2} \cdot sec^{-1}$) peut être très efficacement séparé des autres éléments de façon à ce que cette activité ne masque pas celle des impuretés et permette leur dosage par spectrométrie-γ. En outre, grâce au fait que l'émission-γ du chrome se situe à 0.325 MeV, il est possible d'effectuer les manipulations en laboratoire froid.

Le but de cette étude étant de comparer entre eux des échantillons de compositions a priori assez voisines, nous n'avons pas cherché à doser le plus grand nombre d'éléments, mais à obtenir pour les éléments dosés le maximum d'efficacité dans les séparations, afin d'aboutir à des résultats aussi exacts que possible.

Après une seule irradiation, on a pu doser sur le même échantillon les impuretés suivantes: Fe, Co, Ni, Cu, Ga, Zn, W, Mo, Ta.

La sensibilité est élevée, mais en travail de routine la nécessité de limiter la durée des comptages l'abaisse très sensiblement.

La reproductibilité est de l'ordre de 10%.

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IRRADIATION

Caractéristiques nucléaires du chrome (Tableau I)

Bien qu'il existe 4 isotopes naturels du chrome, seul ^{50}Cr donne naissance, en pile, à un isotope de période longue; la section efficace de la réaction mise en jeu est suffisamment élevée pour que le dosage du chrome soit très sensible (0.01 μg environ). Mais cette qualité devient un défaut majeur lorsqu'il s'agit de doser des impuretés dans le chrome lui-même. Les inconvénients qui résultent de cette activation sont de deux ordres:

Protection. D'après les caractéristiques données dans le Tableau I, on calcule qu'après 140 h d'irradiation dans un flux de $2 \cdot 10^{12}$ n·cm^{-2}·sec^{-1} le chrome présente une activité de 70 mC par g. La dose de rayonnement reçue est donc de 10 Rh à 1 cm. Ceci implique une distance minimum de 70 cm entre l'échantillon et l'opérateur pour

TABLEAU I

CARACTÉRISTIQUE NUCLÉAIRE DU CHROME POUR LES NEUTRONS THERMIQUES

Isotopes naturels:
^{50}Cr(4.31%) ^{52}Cr(83.76%) ^{53}Cr(9.55%) ^{54}Cr(2.38%)
Seul ^{50}Cr donne en pile un isotope à période longue d'après la réaction:
^{50}Cr(n, γ)^{51}Cr.

Sections efficaces de ^{50}Cr:
Absorption: $17 \times 0.043 = 0.73$ barn
Activation : $13.5 \times 0.043 = 0.58$ barn

Caractéristiques de ^{51}Cr:
Période : 27.8 jours
Décroissance: capture électronique (100%) ⟶ ^{51}V stable
Emissions : pas de β;
γ à 0.325 MeV (8%)
Activité spécifique: 70 mC/g de Cr pour $2 \cdot 10^{12}$ n·cm^{-2}·sec^{-1} pendant 140 h
Energie spécifique : 0.15 Rh par mC à 1 cm.

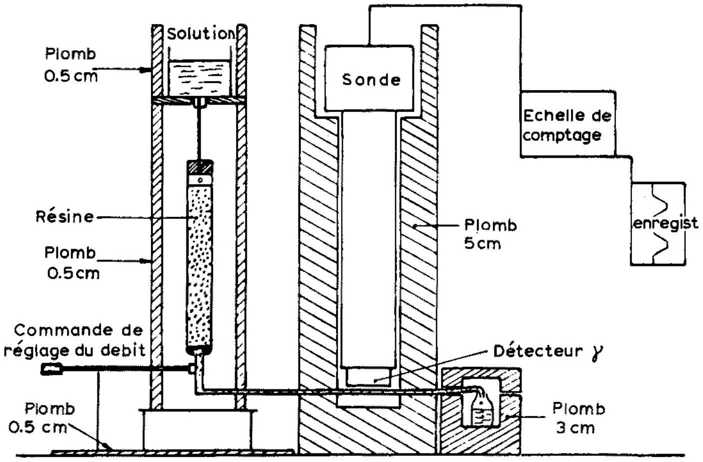


Fig. 1. Schéma d'appareillage pour séparation sur résine des impuretés du chrome.

ne pas dépasser la dose admissible (2.5 mRh). Cependant, du fait de la faible énergie du rayonnement-γ émis par ^{51}Cr (0.325 MeV), nous avons jugé préférable d'adopter le dispositif représenté sur la Fig. 1. En effet, un écran de plomb de 5 mm d'épaisseur atténue la dose, à cette énergie, d'un facteur 15; on peut donc de ce fait travailler à distance normale de l'échantillon sans craindre une irradiation prolongée.

Contamination. Le problème de la protection se trouvant assez facilement résolu, il reste à trouver une méthode de séparation suffisamment efficace pour que l'activité d'une impureté ne soit pas masquée, dans sa fraction, par l'activité résiduelle du chrome.

Au moment des séparations chimiques, on peut estimer à 10^8 impulsions/min le taux de comptage de l'échantillon en solution. Par contre, dans les fractions d'élution on a relevé les activités suivantes pour ^{51}Cr:

Fraction Cu: $2 \cdot 10^4$ impulsions/min. Cette activité relativement élevée provient du fait qu'une élimination plus poussée du chrome risquait d'entraîner ^{64}Cu. La Fig. 8 montre qu'il n'en résulte aucune interférence et que le rendement de séparation est donc de 99.98%.

Dans les fractions tungstène et molybdène, l'activité résiduelle de ^{51}Cr n'est plus que de 10^3 et 10^2 impulsions/min respectivement, d'où un rendement moyen de séparation de 99.9995%.

Il apparaît également que, seules, les résines sont susceptibles d'aboutir à des rendements aussi élevés, à cause sans doute du grand nombre de fois où le phénomène de séparation se trouve répété au cours du passage de la solution sur la résine.

Réactions parasites. Du fait que l'irradiation a lieu en pile piscine (refroidie à l'eau légère), le flux de neutrons rapide provoque des réactions parasites du type (n, p) et (n, α) qui rendent généralement impossible la détermination d'éléments dont le nombre atomique est immédiatement inférieur à celui de l'élément matrice (c'est le cas de Mn dans Fe, Mg dans Al, Na dans Al).

Pour le chrome, on note les réactions:

$$^{52}\text{Cr(n, p)}^{52}\text{V} \qquad T = 3.8 \text{ min}$$

$$^{50}\text{Cr(n, 2n)}^{49}\text{Cr}$$

Il n'y a donc pas d'interférence entre la matrice et les impuretés dosées puisque aussi bien la détermination du vanadium, du fait de sa période, n'est pas à notre portée.

TABLEAU II

CARACTÉRISTIQUES NUCLÉAIRES DES IMPURETÉS DOSÉES

Réaction nucléaire utilisée	*Section efficace (barn) × θ%*	*Période du radioisotope*	*Energie utilisée (MeV)*
^{58}Fe (n, γ) ^{59}Fe	0.98 · 0.31	45 j	1.10 –1.29
^{58}Ni (n, p) ^{58}Co	0.16 · 67.8	71 j	0.511–0.810
^{64}Zn (n, γ) ^{65}Zn	0.44 · 48.9	245 j	1.12
^{59}Co (n, γ) ^{60}Co	36.4 ·100	5 a	1.17 –1.33
^{181}Ta (n, γ) ^{182}Ta	19 ·100	115 j	0.068–1.2
^{68}Zn (n, γ) ^{69m}Zn	0.1 · 18.6	13.8 h	0.440
^{98}Mo (n, γ) ^{99}Mo $\xrightarrow{\beta^-}$ ^{99m}Tc	0.45 · 23.8	67 h	0.140–0.74
^{186}W (n, γ) ^{187}W	34 · 28.4	24 h	0.686
^{71}Ga (n, γ) ^{72}Ga	4.0 · 39.8	14.1 h	0.835
^{63}Cu (n, γ) ^{64}Cu	4.3 · 69.1	12.8 h	0.511

Caractéristiques nucléaires des impuretés dosées

Les réactions mises en jeu sont données dans le Tableau II. Le Tableau III donne les principales réactions susceptibles de se produire en pile piscine, ainsi que l'évaluation de l'erreur (par excès) susceptible d'en résulter. Les teneurs trouvées dans nos échantillons pour les éléments dosés montrent que ces interférences peuvent être considérées comme négligeables.

TABLEAU III

INTERFÉRENCES POSSIBLES DU FAIT DE LA PRÉSENCE DE NEUTRONS RAPIDES DANS LE FLUX D'IRRADIATION

Isotope utilisé	*Réaction parasite possible*	*Erreur relative par excès pour des quantités égales d'éléments (%)*
^{64}Cu	^{64}Zn (n, p) ^{64}Cu	0.07
^{69}Zn	^{69}Ga (n, p) ^{69}Zn	0.8
^{72}Ga	^{72}As (n, α) ^{72}Ga	0.05
	^{72}Ge (n, p) ^{72}Ga	0.1
^{59}Fe	^{59}Co (n, p) ^{59}Fe	2
	^{62}Ni (n, α) ^{59}Fe	0.05
^{60}Co	^{63}Cu (n, α) ^{60}Co	0.01
	^{60}Ni (n, p) ^{60}Co	0.01

SÉPARATIONS CHIMIQUES

L'activité du chrome à la sortie de pile et sa période de décroissance (27 jours) ne permettent pas d'envisager une analyse en non destructif. Par ailleurs, nous avons vu que le choix de la méthode de séparation est très fortement limité par le coefficient de séparation très élevé qu'il est indispensable d'atteindre.

Schéma de séparations sur résines échangeuses d'ions

Principe. On utilise la formation de complexes anioniques des métaux en milieu chlorures ou fluorures à diverses concentrations[5–7]. Bien que l'on sache peu de choses sur les complexes et les degrés d'oxydation du chrome pour des valeurs du $pH < 0$, on a toutes raisons de croire qu'à la fin de l'attaque du métal par HCl–HF (voir mode opératoire) le chrome se trouve au degré d'oxydation III. C'est ce qui ressort de l'examen des courbes de potentiel apparent données par CHARLOT[8]. La coloration verte de la solution est par ailleurs caractéristique des ions Cr(III). En ce qui concerne les complexes Cl^- et F^- du chrome(III) en milieu acide concentré, on sait seulement, d'après KRAUS ET NELSON[9], que le chrome(III) n'est que très légèrement fixé, quelle que soit la concentration en acide chlorhydrique (le chrome(VI) serait par contre fortement retenu); par ailleurs, en acide fluorhydrique 2 *M*, le coefficient de partage du chrome(III) est voisin de zéro[6] et celui du chrome(VI) à peine plus élevé (inférieur à 1). Ces caractéristiques sont favorables à la séparation des éléments qui seront fixés sur la résine anionique d'avec la matrice chrome.

Nous avons vérifié expérimentalement que le chrome n'était pas retenu sur la résine, quel que soit le milieu choisi pour la fixation des impuretés.

Le schéma (Fig. 2) utilisé est le suivant: Sur la colonne no. 1, un premier groupe d'éléments est retenu sous forme de complexes fluorhydriques ou chlorhydriques: Ta, Nb, W, Mo, Th, Sc, Zr, Ag, Hg. L'éluat de cette colonne, concentré et repris par l'acide chlorhydrique, permet la fixation sur la colonne no. 2 d'un second groupe d'éléments sous forme de complexes chlorhydriques: Fe, Co, Zn, Cu, Ga. Sur chacune de ces colonnes, les élutions successives des éléments sont obtenues par variation des concentrations en F^- et Cl^- de telle sorte que, pour éluer un élément, on se place dans des conditions où le complexe correspondant à cet élément, s'il existe, ait un coefficient de partage voisin de zéro. Il faut, en outre, que le milieu propre à l'élution d'un élément ne favorise pas celle d'un autre élément encore fixé.

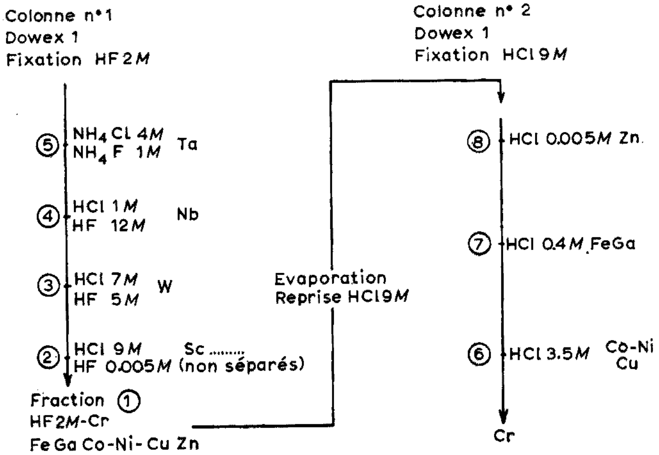


Fig. 2. Schéma de séparation sur résines utilisé dans l'analyse du chrome.

Les aspects théoriques de la formation des complexes et de leur comportement n'entrent pas dans le cadre de ce travail. Des hypothèses ont été avancées dans des articles spécialisés[10-15] auxquels on pourra utilement se référer.

Application. Dans un premier stade, on a vérifié que la présence de chrome en grande quantité (0.2 g) ne perturbait pas la fixation des éléments sur chacune des deux colonnes. A cet effet, la séparation a été réalisée à partir d'un mélange de

TABLEAU IV

ACTIVITÉ, EN NOMBRE D'IMPULSIONS, DES FRACTIONS SÉPARÉES AVEC OU SANS CHROME

(Les différences ne dépassent pas 2% en valeur relative)

Eléments dosés	*Eléments étalons seuls*	*Eléments étalons + 0.2 g chrome*
Fe	9.993	9.990
Zn	99.960	99.880
Ni	9.620	9.360
Co	9.790	9.860
Cu	49.440	49.200
Ga	99.826	99.713
W	15.000	15.200
Mo	96.230	96.820
Ta	98.900	97.000

traceurs et d'une matrice chrome inactive. Les courbes d'élutions sont identiques à celles que l'on obtient avec les traceurs seuls et le Tableau IV montre que les séparations, en présence de chrome, sont parfaitement quantitatives. En présence de chrome actif, c'est-à-dire après irradiation d'un échantillon, on vérifie que l'activité du chrome dans chaque fraction est suffisamment faible pour ne pas masquer les pics dûs aux impuretés.

Les Figs. 3 et 4 montrent les courbes d'élutions obtenues sur échantillons en plaçant, à la sortie de la colonne de résine, une sonde γ reliée à un intégrateur. Les activités à la sortie sont enregistrées sur une échelle logarithmique et permettent de vérifier l'élimination du chrome.

Nota. Après évaporation et reprise par l'acide chlorhydrique 0.1 M de la

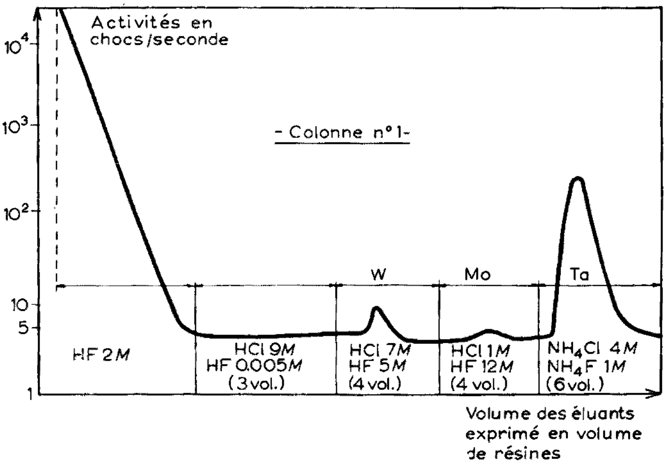


Fig. 3. Séparation W, Mo, Ta sur résine Dowex 1 X8, 100–200 mesh. Matrice: chrome; fixation: HF 2M; colonne en plexiglass: diamètre 7 mm, hauteur résine 10 cm, volume résine 4 ml, débit éluants 0.2 ml/min.

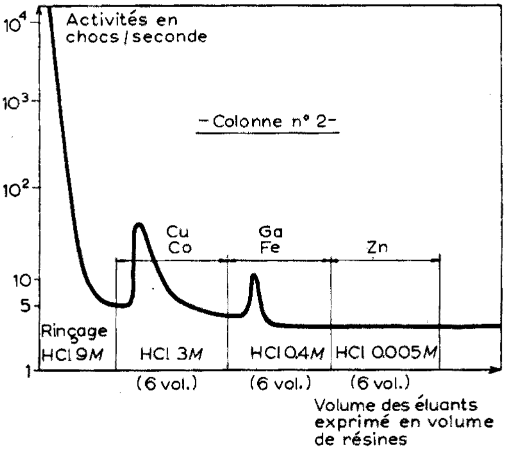


Fig. 4. Séparation Cu-Co/Ga-Fe/Zn sur résine Dowex 1 X8, 100–200 mesh. Matrice: chrome; fixation: HCl 9 M; colonne en verre: diamètre 7 mm, hauteur résine 15 cm, volume résine $\simeq$ 6 ml, débit éluants 0.2 ml/min.

fraction no. 2 de la première colonne, il est possible d'effectuer de nouvelles séparations sur résines cationiques (Sc, Pa, Ag, Zr, Hf). Toutefois, dans le cas de la matrice chrome, les essais auxquels nous avons procédé nous ont montré que ces séparations n'étaient pas suffisamment sûres pour être utilisées en routine. Les difficultés proviennent à notre avis du fait: que le chrome s'élimine plus difficilement sur Dowex 50 (cationique) et que de très faibles traces d'ions F^- résiduels modifient le comportement de Sc, Pa, Zr.

C'est pour cette raison qu'il n'est pas fait état de ces séparations au cours de cette étude.

MODE OPÉRATOIRE

Irradiation

En raison de l'activité due au chrome, on ne traite qu'un échantillon à la fois. D'autre part, afin d'éviter dans la mesure du possible les gradients de flux que l'on sait être importants en pile piscine, on dispose les étalons symétriquement autour de l'échantillon suivant le dispositif représenté sur la Fig. 5.

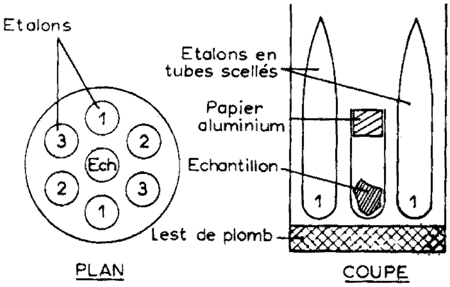


Fig. 5. Schéma de la cartouche d'irradiation. Le tube central contient des fragments de métal superposés. Les étalons sont disposés autour, symétriquement.

L'échantillon est constitué par des fragments de métal de dimensions telles qu'ils puissent être introduits dans le tube de quartz central (diamètre intérieur 3 à 4 mm).

Les étalons, préparés à partir de métaux purs (3 à 5 *N*), sont contenus dans des tubes de quartz où ils ont été introduits sous forme de 50 µl de solution HCl 9 *M* ou HCl 9 *M*–HF 0.5 *M*. Après lente évaporation les tubes sont scellés.

La composition des étalons est la suivante:

Etalon 1 *HCl 9 M*	*Etalon 2* *HCl 9 M*	*Etalon 3* *HCl 9 M–HF 0.5 M*
Fe (500 µg)	Cu (10 µg)	Ta (10 µg)
Ni (500 µg)	Ga (10 µg)	W (10 µg)
Zn (100 µg)		Mo (500 µg)
Co (10 µg)		

Pour ne pas augmenter exagérément l'activité du chrome, la cartouche contenant échantillon et étalons est irradiée dans un flux de $2 \cdot 10^{12}$ n·cm^{-2} sec^{-1}, pendant 100 à 120 h. Les dosages portant sur des périodes longues et moyennes, il convient de procéder aux séparations peu de temps après la sortie de pile. Dans le cas de réacteurs fonctionnant en continu, on procède de telle façon que l'irradiation se termine en début de semaine.

Certains réacteurs (tel Mélusine à Grenoble) s'arrêtent deux jours par semaine. On procède alors de la façon suivante: irradiation 120 h du lundi soir au samedi soir; irradiation 15 h du lundi soir suivant au mardi matin. Ainsi, on ne perd pas d'activité sur les périodes moyennes.

Séparations chimiques

Toutes les manipulations se font à l'aide de pinces de 40 à 50 cm de longueur et en plaçant une plaque de plomb de 5 mm d'épaisseur devant l'échantillon. Les opérations de mise en solution et évaporation sont surveillées à l'aide de miroirs convenablement disposés.

Mise en solution. Echantillon. La mise en solution se fait très rapidement et à froid en HCl 6 *M*–HF 1 *M*. Le bécher (en téflon) doit être couvert afin d'éviter les projections de gouttelettes entraînées par le dégagement d'hydrogène. On procède ensuite aux opérations suivantes:

Evaporation jusqu'à consistance pâteuse et teinte vert très foncé de la solution.

Reprise par 2 ml HF concentré et évaporation comme précédemment.

Addition de 2 ml HF concentré, remise en solution, addition de 20 ml de l'eau de façon à obtenir une solution environ HF 2 *M*. Il convient à ce moment d'ajouter quelques gouttes d'une solution de $KMnO_4$ afin d'oxyder Fe et W tout en laissant le chrome sous forme de chrome(III).

Etalons. Les étalons 1 et 2 mis en solution HCl 9 *M* sont passés sur des colonnes identiques à la colonne no. 2. L'étalon 3 est repris en HF 2 *M* et les éléments sont séparés sur une colonne identique à la colonne no. 1 à l'aide des éluants appropriés (voir plus loin les conditions d'élution des éléments contenus dans l'échantillon).

Passage sur résines (voir Figs. 3 et 4: caractéristiques des colonnes). La solution est transvasée dans le réservoir en polythène de la colonne no. 1, et l'ensemble réservoir–colonne est entouré de plomb (voir Fig. 1). Le débit est fixé à 0.2 ml/min environ. Lorsque toute la solution est passée sur la résine, le rinçage s'effectue à l'aide de l'acide fluorhydrique 2 *M*. Environ 20 ml sont nécessaires à l'élution du chrome; cette élution peut être suivie grâce à la disparition de la couleur verte dans la résine et à la diminution de l'activité de l'effluent à la sortie de la colonne (Fig. 1); la solution d'attaque et le volume de rinçage constituent la fraction 1 qui contient Cr, Fe, Cu, Co, Ni, Ga, Zn.

Les autres éléments sont alors élués dans les conditions suivantes:

3 vol (12 ml) HCl 9 *M*–HF 0.005 *M* (Zr, Hf, Sc, etc.)	(fraction 2)
4 vol (16 ml) HCl 7 *M*–HF 5 *M* (élution du tungstène)	(fraction 3)
4 vol (16 ml) HCl 1 *M*–HF 12 *M* (élution du molybdène)	(fraction 4)
6 vol (25 ml) NH_4Cl 4 *M*–NH_4F 1 *M* (élution du tantale)	(fraction 5)

La fraction 1, aussitôt recueillie, est évaporée sur bain de sable jusqu'à un volume de 2 ml environ. Elle est alors reprise par 15 ml d'acide chlorhydrique 12 *M* (+ 1 ml d'eau de chlore) et passée sur la colonne no. 2. Le rinçage s'effectue avec 6 volumes d'acide chlorhydrique 9 *M* (+ eau de chlore).

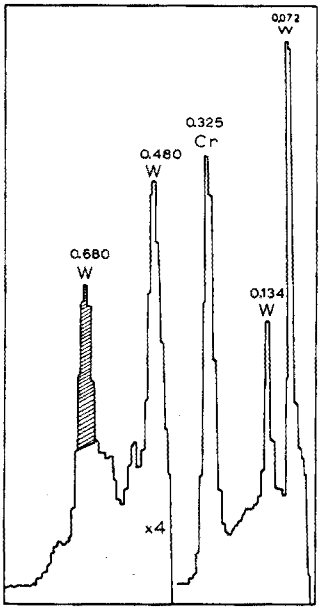
Les autres éléments sont élués comme suit:

6 vol (40 ml) HCl 3.5 M (+ eau de chlore)	(cobalt, cuivre)
6 vol (40 ml) HCl 0.4 M	(fer, gallium)
6 vol (40 ml) HCl 0.005 M	(zinc)

Les Figs. 3 et 4 montrent les courbes d'élution obtenues en mesurant directement l'activité à la sortie des colonnes.

Comptages

Ils sont effectués directement dans les cruchons de polythène de 30 ou 60 ml dans lesquels sont recueillis les effluents à la sortie des colonnes de résine. Les étalons correspondant à chaque élément sont comptés dans les mêmes conditions.



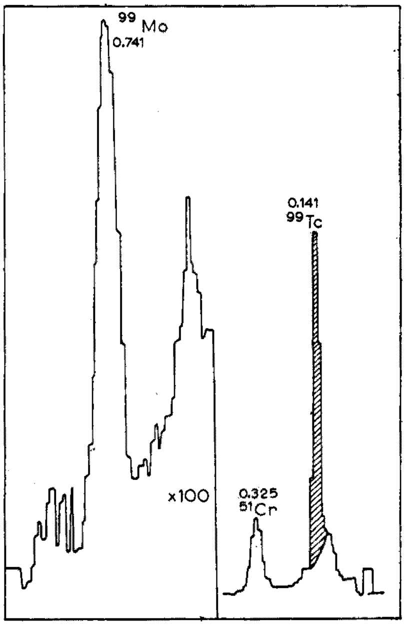


Fig. 6. Spectre de ^{187}W. Le comptage s'effectue sur le pic de 0.680 MeV.

Fig. 7. Spectre de ^{99}Mo et de son descendant ^{99}Tc sur le pic duquel s'effectue le comptage.

Eléments de période moyenne. Ils sont comptés aussitôt après séparation: *Tungstène (Fig. 6).* Le calcul se fait sur le pic de 0.680 MeV.

Molybdène (Fig. 7). Dans le cas de teneurs supérieures à 5 p.p.m., le calcul peut se faire sur le pic de ^{99}Mo (T=66 h); E_γ=0.740 MeV. Pour des teneurs plus faibles, il est préférable d'attendre environ 48 h que soit atteint l'équilibre de filiation

$$^{99}\text{Mo} \xrightarrow{\beta^-} {}^{99}\text{Tc}\ (T = 6.6\ \text{h});\ E_\gamma = 0.140\ \text{MeV}.$$

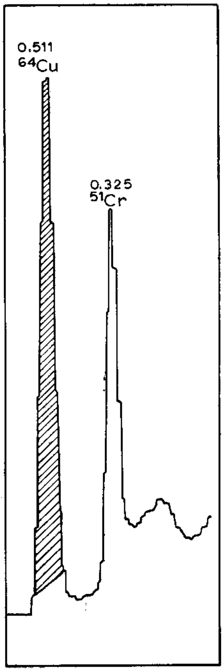
On peut alors doser molybdène jusqu'à des teneurs $\leqslant$ 0.1 p.p.m.

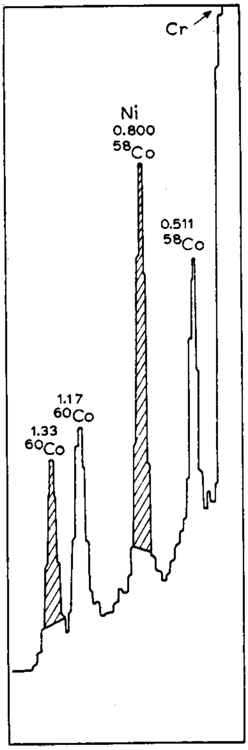
Cuivre (Fig. 8). Sur la colonne no. 2, le cuivre sort en milieu HCl 3.5 M en même temps que les isotopes du cobalt: ^{60}Co et ^{58}Co; on trouve donc sur le spectre de cette fraction des pics à 0.511 MeV (^{60}Co et ^{58}Co), 0.810 MeV (^{58}Co), et 1.17 et 1.33 MeV (^{60}Co).

Le dosage de ^{64}Cu à 0.511 MeV présente donc une interférence d'émetteurs β^+. Toutefois, cette interférence est généralement facile à éliminer du fait:

d'une différence importante de période entre ces deux radioéléments (12.8 h et 71 j)

de la grande sensibilité de ^{64}Cu par rapport à celle de ^{58}Co. Dans nos conditions de travail, 1 μg Cu correspond à 1200 impulsions/min, et 1 μg Ni correspond à 5 impulsions/min.





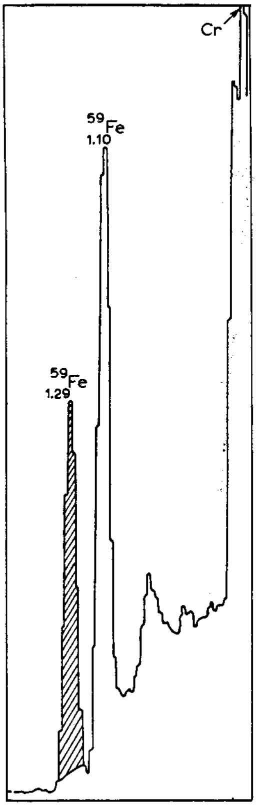


Fig. 8. Spectre de ^{64}Cu.

Fig. 9. Spectre de ^{58}Co et ^{60}Co (dosage Ni et Co sur pics hachurés).

Fig. 10. Spectre de ^{59}Fe.

A teneurs égales l'erreur due à ^{58}Co ne serait donc que de 0.5%. De toutes façons, l'interférence de ^{58}Co peut être éliminée, par correction graphique, en traçant une courbe de décroissance sur le pic de 0.511 MeV.

Gallium. Bien que cet élément soit facilement dosable par cette technique, son spectre n'est jamais apparu sur la fraction correspondant à son élution, ce qui laisse supposer une teneur nettement inférieure à 0.1 p.p.m. Le fer présent dans cette fraction ne gêne pas le dosage du gallium.

Eléments de périodes longues. Ils doivent être comptés après décroissance des éléments de périodes moyennes lorsque la fraction en contient; le dosage y gagne toujours en exactitude. Les spectres de cobalt, nickel (Fig. 9) et celui du fer (Fig. 10) ne présentent pas de particularités. La présence de traces de chrome à 0.325 MeV ne gêne pas. Le spectre de ^{65}Zn n'est pas apparu dans sa fraction d'élution, ce qui laisse supposer une teneur inférieure à 0.1 p.p.m.

LIMITES DE DOSAGE

Dans le cas de l'analyse du chrome, les limites de dosage des éléments déterminés sont très fortement relevées du fait de l'activité notable de la matrice, qui oblige à une irradiation dans un flux relativement faible, ainsi qu'à une prise d'échantillon peu importante (0.2 g). Le Tableau V montre, dans les conditions opératoires fixées, quelles ont été les activités mesurées pour chaque élément à l'aide d'un cristal INa 7.5 cm × 7.5 cm. D'après les teneurs trouvées, on en déduit la masse d'élément nécessaire pour que la précision sur le comptage reste de 5% environ (2500 impulsions sur le pic photoélectrique).

D'autre part, sauf pour le fer et le nickel, nous avons volontairement fixé les temps de comptage à 10 ou 100 min, limites compatibles avec le travail de routine.

TABLEAU V

LIMITE INFÉRIEURE DU DOSAGE POUR 2500 IMPULSIONS SUR LA SURFACE DU PIC PHOTOÉLECTRIQUE, D'APRÈS LES RÉSULTATS OBTENUS SUR DES ÉCHANTILLONS DE 0.2 g DE MÉTAL

Elément	*Impulsions/min pour un des éch. analysés*	*Teneur trouvée (p.p.m.)*	*Limite de dosage (p.p.m.)*	*Temps de comptage maximum (min)*
Fe	250	300	3	1000
Ni (^{58}Co)	200	40	0.5	1000
Mo (Tc)	1000	6	0.2	10
Cu	25000	20	0.2	10
W	250	0.15	0.1	10
Co	100	0.3	0.1	100
Ta	10000	20	0.07	100

RÉSUMÉ

En analyse par activation, les matrices telles que l'aluminium, le béryllium ou le niobium peuvent être considérées comme inactives quelques heures après la sortie de pile. Il n'en est pas de même pour le chrome, qui est très facilement activable puisque sa limite inférieure de dosage est de l'ordre de 0.01 μg. On décrit dans cette étude une mode opératoire permettant le dosage de 9 éléments dans cette matrice. Après irradiation aux neutrons de pile, on peut effectuer toutes les séparations au laboratoire, et, dans les conditions expérimentales que nous avons définies, doser: Fe, Co, Ni, Cu, Zn, W, Mo, Ga, Ta. La limite inférieure de dosage est inférieure à 1 p.p.m. sauf pour Fe. La reproductibilité est de 10%.

SUMMARY

In activation analysis, matrices such as Al, Be or Nb are essentially inactive a few hours after irradiation. This is not the case for chromium which is very easily activated, the lower limit of determination being *ca.* 0.01 μg. A procedure is given for the determination of 9 elements in this matrix. After neutron irradiation, all separations, on Dowex 1 resin with chloride or fluoride–chloride eluants, can be done in a "cold" laboratory. Fe, Co, Ni, Cu, Zn, W, Mo, Ga and Ta can be determined. The lower limit of determination is *ca.* 1 p.p.m., except for Fe. The reproducibility is about 10%.

ZUSAMMENFASSUNG

Während bei der Aktivierungsanalyse Matrices wie Al, Be oder Nb einige Stunden nach der Bestrahlung im wesentlichen inaktiv sind, ist dies beim Chrom, welches sehr leicht aktiviert wird, nicht der Fall. Zur Bestimmung von 9 Elementen in dieser Matrix wird ein Verfahren angegeben, bei dem nach der Bestrahlung diese Elemente mit einem Dowex-1-Austauscher und durch Elution mit Chlorid oder Fluorid die Elemente in einem "kalten" Laboratorium abgetrennt werden können. Ausser für Eisen beträgt die Nachweisgrenze etwa 1 p.p.m. für die Elemente Co, Ni, Cu, Zn, W, Mo, Ga und Ta. Die Reproduzierbarkeit liegt bei ca. 10%.

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ON THE SEPARATION MECHANISM OF GEL PERMEATION CHROMATOGRAPHY

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Gel permeation chromatography (GPC) is a comparatively new technique which separates substances according to their molecular size, larger molecules being eluted from a column earlier than smaller molecules[1]. It is used widely to determine the molecular weight distribution of polymers[2,3], and as an excellent separation tool[4,5].

Several attempts have been made to explain the separation mechanism of GPC but the results are inconclusive. Among the hypotheses proposed are effects due to exclusion of molecules from gel particles[6], restrictive migration[7], adsorption[8], and diffusion[9], etc. Most of the GPC work has been carried out in dynamic systems. The hypotheses proposed were based on results after separations were completed, since no information was available about what occurs inside the GPC column. Too many factors are involved in the results of such systems for a proper judgment to be made.

It is felt that under static conditions, some of these factors may be eliminated, *e.g.*, restricted migration and diffusion effects. An investigation can be carried out with a much simpler system. The present study was made to confirm some of the separation mechanisms.

It is not intended, however, to discount the importance of major factors which do not exist in static systems.

EXPERIMENTAL

Chemicals and apparatus

Bio-bead S-X8 cross-linked nonionic polystyrene gel was obtained from Bio-rad Laboratories.

Sephadex LH-20 cross-linked polydextran gel was obtained from Pharmacia Fine Chemicals.

All other chemicals were acquired from Eastman Kodak Inc.

The gas chromatographic unit employed was a Perkin Elmer Model 880 (Perkin Elmer Inc.) with a 6-ft. silicon grease-coated column packed with Celite diatomaceous earth (Johns–Manville Corp.).

Procedures

Unless otherwise stated, the procedures used were the following.

Dried gel particles (5 g) were weighed out and placed in a 50-ml flask. Tetrahydrofuran (THF) (25 ml) containing a known concentration of the solute being studied was added. The flask was tightly covered and the mixed solution was gently shaken for 48 h to reach equilibrium. The gel particles were allowed to settle. An aliquot (10 ml) of supernatant solution was taken and the solute concentration was determined by appropriate methods. The acid concentrations were determined by titration[10] with sodium hydroxide after adding the sample to 50 ml of alcohol. Polystyrene, *n*-eicosane ($C_{20}H_{42}$), and *n*-hexadecane ($C_{16}H_{34}$) were determined gravimetrically after the solvent was evaporated; *n*-decane ($C_{10}H_{22}$) and *n*-heptane (C_7H_{16}) were determined by gas chromatography.

THEORY

Among the hypotheses proposed for the separation mechanism of GPC, those of PORATH[6] and ACKERS[7] are most prominent.

On the assumption that the gel pores are conical in shape, PORATH derived a theoretical formula for the exclusion process,

$$K_d = k(1 - a/r)^3 \qquad (1)$$

where r is the average radius of the pore, k is a constant and K_d and a are the distribution coefficient and the radius of the solute molecule, respectively.

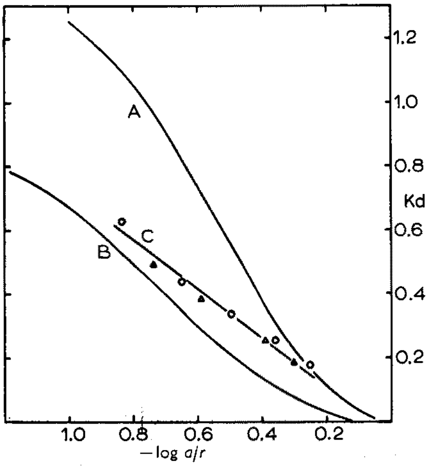

Fig. 1. Distribution coefficient *versus* logarithm of a/r. (A) from PORATH's hypothesis; (B) from ACKERS' hypothesis; (C) from experimental results.

An alternative approach was used by ACKERS. By applying RENKIN's equation[11] to the diffusional restriction encountered by a molecule during migration through a restrictive barrier of effective radius, ACKERS wrote the relation between K_d and a/r as

$$K_d = (1 - a/r)^2(1 - 2.104a/r + 2.09(a/r)^3 - 0.95(a/r)^5) \qquad (2)$$

These two equations were used by ANDERSON AND STODDART[12] to replot K_d *versus* the logarithm of a/r. A wide range of linearity was obtained for both equations as shown in Fig. 1. These linear portions may be reduced to a general form of

$$K_d = k_1 \log a/r + k_2 \tag{3}$$

with k_1 and k_2 as empirical constants.

Under static conditions the system should reach equilibrium, if enough time were allowed. The restrictive migration is no longer a major concern. The effects of diffusion are also eliminated. If adsorption effects can be ignored the only major factor remaining is the physical exclusion of solute molecules from the gel particle.

The following processes are considered to exist in the static experiments. The solvent molecules are engaged in the swelling of the gel particles; thus, they permeate farthest into gel particles. The solute molecules migrate freely in solvent outside the gel particle and into part of the gel particle. Restricted by their molecular size, however, they are excluded from the center core of the gel particle. Since a portion of the solvent becomes unavailable to the solute due to this exclusion effect, an increase of solute concentration is expected. This relation can be expressed as

$$c_1 V = c_2(V - \alpha \Delta V) \tag{4}$$

or

$$\Delta V = (c_2 - c_1) V/\alpha c_2 \tag{5}$$

where ΔV is the volume of solvent unavailable to solute due to the exclusion effect, and also the volume within the gel particle excluded to solute (ml/g of gel particle); V is the volume of solvent added to α grams of gel particle; c_1 and c_2 are the initial and final concentrations of the solute in the solution.

If the separation is based on the molecular size as was proposed, the excluded volume should be proportional to the molecular size of the solute.

RESULTS AND DISCUSSIONS

Several straight-chain acids and hydrocarbons were studied by the procedures described in the experimental section. The gel substance was a cross-linked nonionic polystyrene gel. The increase of solute concentration due to the exclusion effect was determined. The exclusion volumes, ΔV, listed in Table I, were calculated from eqn. (5) and plotted against the logarithm of molecular size. The molecular size was expressed in effective carbon chain length units, # C, as proposed by HENDRICKSON AND MOORE[13]. A correction of 3.0 # C unit was made for the hydrogen bonding between acids and the solvent, tetrahydrofuran[14]. A linear relation was obtained as can be seen from Fig. 2. This is in agreement with the results of the dynamic GPC system described in our previous work[14]. The fact that the acid and hydrocarbon curves coincide indicates that the absorption effect is minimal with this gel substance.

It is interesting to compare these experimental results with PORATH's theoretical treatment. The excluded volume of polystyrene was 1.04 ml/g. This value was taken as the inner volume of the gel substance. The distribution coefficient of a solute can be calculated from

$$K_d = (\Delta V_p - \Delta V_i)/\Delta V_p \tag{6}$$

where ΔV_p and ΔV_i are the excluded volumes of polystyrene and solute i, respectively. When ΔV_p was projected into the extrapolation of the curve in Fig. 2, the observed

TABLE I

EXPERIMENTAL RESULTS USING BIO-BEAD S-X8 GEL (25 ml of solution used)

Solute	*Solute concentration*		*ΔV (ml/g)*	*Gel used (g)*
	Added	*Recovered*		
$C_{20}H_{42}$	2.00%	2.39%	0.81	5.00
$C_{16}H_{34}$	2.00	2.36	0.76	5.00
$C_{10}H_{22}$	2.00	2.29	0.63	5.00
C_7H_{16}	2.00	2.23	0.52	5.00
Polystyrene	5.00	6.39	1.09	5.00
Polystyrene	2.00	2.52	1.04	5.00
Polystyrene	1.00	1.26	1.04	5.00
$C_{17}H_{35}COOH$	0.505 *N*	0.610 *N*	0.85	5.00
$C_{17}H_{35}COOH$	0.101	0.122	0.86	5.00
$C_{17}H_{35}COOH$	0.0505	0.0620	0.92	5.00
$C_{17}H_{35}COOH$	0.0202	0.0245	0.88	5.00
$C_{13}H_{27}COOH$	0.102	0.142	0.71	10.00
$C_{13}H_{27}COOH$	0.102	0.131	0.73	7.50
$C_{13}H_{27}COOH$	0.102	0.120	0.74	5.00
$C_{13}H_{27}COOH$	0.102	0.110	0.73	2.50
$C_8H_{17}COOH$	0.102	0.118	0.68	5.00
C_4H_9COOH	0.101	0.114	0.57	5.00
CH_3COOH	0.505	0.543	0.35	5.00
CH_3COOH	0.101	0.109	0.36	5.00
CH_3COOH	0.0505	0.0545	0.37	5.00
CH_3COOH	0.0202	0.0218	0.37	5.00
CH_3COOH	1.74 (10%)	1.87	0.34	5.00
CH_3COOH	3.49 (20%)	3.74	0.33	5.00
CH_3COOH	8.71 (50%)	8.97	0.15	5.00

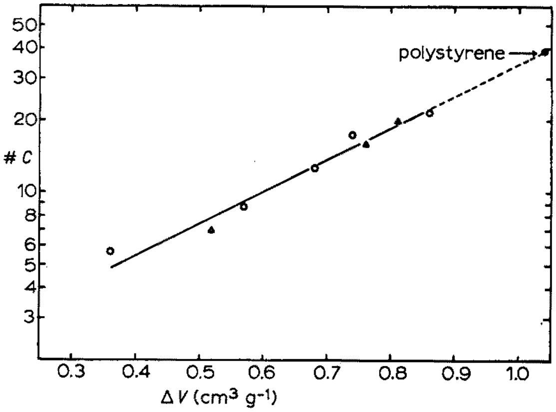

Fig. 2. Excluded volume *versus* molecular size using Bio-bead S-X8 gel.

chain length was 39.0 # C. This value was taken as the pore size of gel substance. Therefore,

$$a/r = \#C_i/\#C_p \tag{7}$$

with $\#C_i$ and $\#C_p$ as the effective carbon chain lengths of solute *i* and polystyrene, respectively.

The logarithm of a/r was then plotted against the K_d determined for acids and hydrocarbons. A linear relation was obtained as curve C in Fig. 1. It also followed the general form of eqn. (3). The empirical constants were $k_1=0.77$ and $k_2=-0.04$ compared with $k_1=1.75$ and $k_2=-0.30$ for curve A. However, after a proper correction for these two empirical constants, the experimental curve can be superimposed on PORATH's curve.

Some of the solvent molecules absorbed by gel particles possibly are engaged in the swelling of the gel particles. They may not be considered as part of inner volume. Nevertheless, this error requires only a correction of k_2 value but does not jeopardize the linear relationship between K_d and log a/r.

If the excluded volume, ΔV, is determined by the size of solute molecule, ΔV is expected to be independent of solute concentration. The effect of solute concentration on ΔV was therefore investigated. The solutes studied were polystyrene, stearic acid ($C_{17}H_{35}COOH$) and acetic acid (CH_3COOH). The results are listed in Table I. It was found that ΔV remained almost unchanged for all solute concentrations studied. Acetic acid was studied at higher concentrations. No obvious change of ΔV was noticed up to 20%, or 3.6 N, acetic acid. The only exception was a drastic drop in ΔV when the acetic acid concentration was 50%, or 9 N. However, at such a high concentration, acetic acid should be considered as part of the mixed solvent rather than a solute. The ΔV is expected to decrease to zero as the acetic acid concentration increases toward 100%.

Another study was performed by adding various amounts of gel particles to a set volume of 0.1 N myristic acid ($C_{13}H_{27}COOH$). The specific excluded volume remained unchanged (Table I).

From the results obtained from these experiments, it is obvious that an exclusion of solute molecule from gel particle takes place, thus validating eqn. (4) proposed in the theoretical section. The degree of the exclusion is based on the size of molecule, as was suggested. PORATH's hypothesis may be too simple in nature, yet the exclusion effect is undoubtedly a major separation mechanism of gel permeation chromatography.

It was suggested by PECSOK AND SAUNDERS[8] that absorption effects be considered as a major factor of separation mechanism. It was also frequently noticed in practice that when polydextran gel was used as a column substrate in GPC, acids were either retained in the column or eluted much later than hydrocarbons of comparable size.

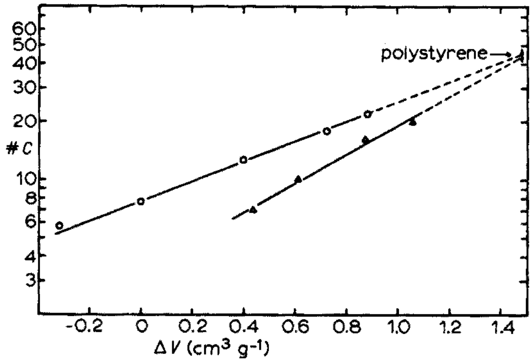

Fig. 3. Excluded volume *versus* molecular size using Sephadex LH-20 gel. (A) from acids; (B) from hydrocarbons.

A static experiment was performed by using polydextran gel as substrate. The procedures were identical to those previously described. The obtained results are shown in Table II. The ΔV was plotted against the #C as shown in Fig. 3. Curve A was obtained from hydrocarbons and curve B from acids. It can be seen that the acid has a smaller excluded volume than the hydrocarbon of comparable molecular size. The most reasonable explanation is an absorption effect. In the case of acetic acid, the acid concentration in the supernatant solution decreased rather than increased. The absorption effect obviously overshadowed the exclusion effect. The presence of absorption effects is certainly unquestionable. However, if one recalls that no absorption was observed with polystyrene gel, one may either consider the absorption effect as a separation mechanism, or merely as a characteristic of gel substance.

TABLE II.

EXPERIMENTAL RESULTS USING SEPHADEX LH-20 GEL (25 ml of solution used)

Solute	*Solute concentration*		*ΔV (ml/g)*	*Gel used (g)*
	Added	*Recovered*		
Polystyrene	2.00%	2.83%	1.48	5.00
$C_{20}H_{42}$	2.00	2.54	1.06	5.00
$C_{16}H_{34}$	2.00	2.42	0.87	5.00
$C_{10}H_{22}$	2.00	2.28	0.61	5.00
C_7H_{16}	2.00	2.19	0.43	5.00
$C_{17}H_{35}COOH$	0.101 *N*	0.123 *N*	0.88	5.00
$C_{13}H_{27}COOH$	0.102	0.119	0.72	5.00
$C_8H_{17}COOH$	0.102	0.111	0.40	5.00
C_4H_9COOH	0.101	0.101	0	5.00
CH_3COOH	0.101	0.095	−0.32	5.00

It certainly is advantageous to have absorption effects for separation purposes, even though it is troublesome to polymer chemists interested in the determination of molecular weight distribution. The range of separation is not limited by the inner volume. An absorbed substance may possess a distribution coefficient far greater than unity. The separable range is widely expanded. Selection of gel substances with a proper absorption effect for better separation is a possibility which analytical chemists should not overlook.

The excluded volume of polystyrene, ΔV_p, was 1.48 ml/g with polydextran gel. This value was projected into the extrapolations of curve A and curve B of Fig. 3. It is interesting to note that both curves yield an effective carbon chain length of 45 #C for polystyrene. This value was taken as the pore size of the gel particle in the previous discussion. Since the length of one carbon unit is 1.25 Å as defined by HENDRICKSON AND MOORE[13], the pore size of the gel is approximately 56 Å. By the same method, the pore size of the polystyrene gel is calculated to be approximately 50 Å. Unfortunately, there are no data readily available to compare these results with the true values.

SUMMARY

The separation mechanism of gel permeation chromatography was investigated by static experiments. It was found that the solute molecule is excluded from part of the inner space of the gel particle, which is entirely available to the solvent molecule. The excluded volume, ΔV, increases with increase of molecular size of the solute. A linear relationship was observed between the ΔV and the logarithm of molecular size. Excluded volume was found to be independent of solute concentration as was expected. Absorption effect was negligible with polystyrene gel. However, a strong effect was observed between acids and polydextran gel. The possibility of using absorption effects to increase the separability of GPC is suggested.

RÉSUMÉ

Une étude est effectuée sur le mécanisme de séparation de gel en chromatographie. On constate que la molécule de soluté est exclue de l'espace intérieur de la particule de gel, qui est entièrement disponible à la molécule du solvant. Le volume exclu ΔV augmente avec la dimension des molécules du soluté. Une relation linéaire est observée entre ΔV et le logarithme de la grandeur moléculaire. Le volume exclu est indépendant de la concentration du soluté. L'effet d'absorption est négligeable avec un gel de polystyrène, contrairement à celui observé entre acides et gel polydextran. On envisage la possibilité d'utiliser les influences de l'absorption pour augmenter la séparabilité de GPC.

ZUSAMMENFASSUNG

Durch statische Versuche wurde der Trennungsmechanismus bei der Gelchromatographie untersucht. Es ergab sich, dass das gelöste Molekül aus dem Teil des inneren Raums des Gel-Teilchens ausgeschlossen wird, welcher völlig für das Lösungsmittelmolekül zur Verfügung steht. Dieses Volumen ΔV wächst mit steigender Molekülgrösse des Lösungsmittels. Es wurde eine lineare Beziehung zwischen ΔV und dem Logarithmus der Molekülgrösse beobachtet. ΔV ist unabhängig von der Konzentration des Gelösten. Beim Polystyrolgel waren Absorptionseffekte vernachlässigbar. Dieser Einfluss war jedoch stark zwischen Säuren und Polydextringelen. Es wird vermutet, dass die Absorptionseffekte eine Verbesserung der Trennung herbeiführen.

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THE CHROMATOGRAPHIC PROPERTIES OF TRANSITION METAL COMPLEXES OF PYRIDINE-2-ALDEHYDE-2-QUINOLYLHYDRAZONE

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Pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) has been applied successfully as a spraying reagent for cobalt, nickel and copper after separation of these ions on thin-layer chromatograms[1]. In previous work it has also been shown that PAQH complexes can be extracted easily from aqueous solutions with solvents such as benzene, chloroform, etc.[2,3].

In the present study, PAQH has been used as a semiquantitative scavenging agent and the metal chelates chromatographically separated. This approach to metal trace analysis has several advantages over the method previously proposed[1]. The extracted chelates can be applied directly to the chromatogram without prior sample preparation; the sensitivity is increased through evaporation of the organic solution of extracted chelates to the small volume required for chromatographic separation; and adsorbent impurities do not interfere. In addition, faster and clearer separation of the metal chelates can usually be achieved in comparison to separation of free metal ions, because less polar solvents can be used for the separation process on highly polar adsorbents such as alumina and silica gel; since the chelates have an intense color themselves, no spraying reagent is needed for the detection of the metals and variables such as background coloration, irregular color development, etc., can be eliminated.

EXPERIMENTAL

Reagents

The stock solutions of the metals Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, and Mn^{2+} were prepared from reagent-grade chemicals. PAQH was prepared as previously described[4] and dissolved in 95% ethanol. Doubly distilled water was used throughout. Thin-layer chromatographic grade alumina G from Merck Darmstadt with about 15% plaster of paris as a binder was employed. Prefabricated alumina chromatogram sheets (#6062, Eastman Kodak Company) were also investigated. The solvents used for chromatographic separation and for the extraction were reagent grade.

Apparatus

The diffuse reflectance spectra were measured with an automatic recording Spectronic 505 spectrophotometer equipped with a standard reflectance attachment for the ultraviolet and visible region. The chromatoplates were coated with a Desaga thin-layer chromatography applicator with the layer thickness adjusted to 0.25 mm. For development of the chromatogram sheets, the sandwich-type chromatogram apparatus from Eastman Kodak was used.

Procedure

The 20 × 5 cm chromatoplates, after coating with alumina G, were heated at 110° for 3 h and then stored in a dry cabinet over silica gel. The plates were exposed to atmospheric conditions for 1 h before use. Stock solutions of the metals (1 g/l) were prepared. The reagent solution consisted of a 0.03% (w/v) solution in 95% ethanol. The complexes were formed in a solution adjusted by an ammonia–ammonium chloride buffer to about pH 10 and extracted with chloroform. To ensure complete recovery of cobalt, a second extraction with amyl alcohol was carried out. The extracts were evaporated to a volume of 200 μl, and sample spots were applied by means of a 10-μl Hamilton syringe in 2.5-μl increments. After drying for 5 min at 110°, the plates were cooled to room temperature and chromatographed by the ascending technique in a chromatography chamber which had been preconditioned for 12 h. No preconditioning was required with the sandwich-type developing apparatus.

For reflectance measurements the spots were removed from the plates, mixed homogeneously and packed in a reflectance cell as described elsewhere[5]. When chromatogram sheets were used, the spots were simply cut out and placed in the same cell. The reference standards used consisted of adsorbent from the plate or sheet under investigation. For an investigation of the temperature stability of the adsorbed complexes, the samples were packed between two microscope slides which could withstand higher temperatures than the cardboard or plastic material of the regular cells.

RESULTS

Extraction of the complexes

Based on an approximate knowledge of total ion concentration in the solution a sufficient excess of reagent[2] was added. If insufficient amounts of reagent were present, it was observed, when only iron, nickel, copper and cobalt were present, that reagent was preferentially used up in the order Co^{2+}, $Cu^{2+} \rightarrow Ni^{2+} \rightarrow Fe^{3+}$. The iron(III) complex was always the last one to form, even in presence of the other ions.

Chromatographic separation

The separation of iron, nickel, copper and cobalt was of major interest since previous work had shown that their PAQH complexes are most suitable for analytical purposes. Best separation was achieved on alumina layers with chloroform used as chromatographic solvent.

The R_F values for the Fe^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} complexes were determined from 6 separate runs (Table I). The other metal complexes had their R_F values all in the range of 0.03 to 0.06 on alumina plates and slightly higher on alumina sheets. Their separation from the copper, the iron(III) and sometimes the cobalt complex was therefore possible only by resorting to two-dimensional chromatography (Fig. 1).

The same order of separation was observed on alumina plates and alumina sheets but the actual R_F values, particularly for iron(III) and copper, differed considerably (Table I). The separation on alumina sheets was actually found to be somewhat more efficient.

A light yellow spot resulting from an excess of reagent extracted along with the complexes, usually appeared between the copper and nickel spots, completely separated from the other components. The development time for the complete separation of the iron(III), nickel, copper, cobalt and reagent spot ranged between 20 and 40 min.

TABLE I

R_F VALUES FOR PAQH COMPLEXES SEPARATED ON ALUMINA PLATES AND SHEETS

Metal	*Alumina plates*			*Alumina sheets*		
	Range	*Average*	*%rel.st.dev.*	*Range*	*Average*	*%rel.st.dev.*
Fe^{3+}	0.76–0.86	0.82	3.1	0.52–0.60	0.56	4.3
Ni^{2+}	0.31–0.38	0.35	5.5	0.36–0.39	0.37	3.5
Cu^{2+}	0.06–0.08	0.07	7.1	0.26–0.28	0.27	5.7
Fe^{2+}	0.05–0.06	0.05	7.0	0.08–0.10	0.09	5.2
Co^{2+}	0.00	0.00	0	0.00	0.00	0

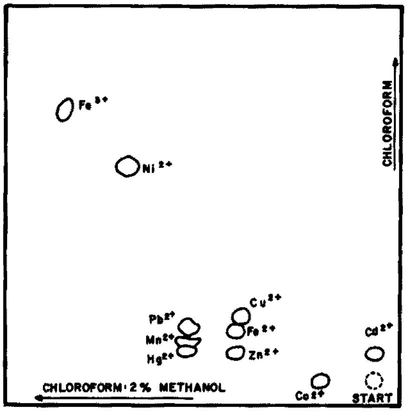

Fig. 1. Two-dimensional chromatogram for the separation of 10 PAQH complexes of the marked metals on alumina G.

Interferences

From the list of R_F values it is apparent that Fe^{2+}, Mn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Zn^{2+} do interfere with the copper spot and, if tailing occurs, also with cobalt. However, except for iron(II), equimolar concentrations can be tolerated; the color intensities for the Hg^{2+}, Pb^{2+} and Mn^{2+} complexes are considerably lower and the visual appearance of the Zn^{2+} and Cd^{2+} complexes (yellow-orange and yellow-green respectively) offers little interference with the red copper and cobalt spots.

The interference from iron(II) can be eliminated by oxidizing iron(II) to iron(III) before complexation and extraction; hydrogen peroxide or sodium nitrite at pH *ca.* 5 proved satisfactory as oxidizing agents. If more than equimolar concentrations of the interfering ions are present, then development of the chromatogram in a second dimension (Fig. 1) is recommended. This was investigated for up to tenfold molar excesses. Similar observations were made on alumina sheets.

Limits of detection

The visual limits of detection were found to be 0.01 μg per spot for iron(II), iron(III), nickel and copper, and 0.0007 μg per spot for cobalt. The lower detection limit for cobalt may be simply because it does not move at all on the chromatogram and therefore no diffusion of the spot occurs. The detection limits for the other chelates are between one and two orders of magnitude higher.

Reflectance spectroscopic investigation

Reflectance spectra of the iron(III), nickel, copper and cobalt complexes adsorbed on alumina plates and on alumina sheets were recorded (Table II and Fig. 2). The maxima given in Table II are average values obtained from 4 spectra recorded separately from different spots and at different days. The values are significant to ± 3 nm. The iron(III) complex, which appears greenish to the eye, has actually two maxima. Investigation of a dilution series of iron revealed that the absorption maximum at 490 nm is the more suitable one for analytical purpose.

TABLE II

ABSORPTION MAXIMA (nm) OF THE CHELATES ON ALUMINA PLATES AND SHEETS

Metal	*Alumina plates*	*Alumina sheets*
Fe^{3+}	490	491
Ni^{2+}	496	495
Cu^{2+}	502	492
Co^{2+}	522	513
Reagent	357	—

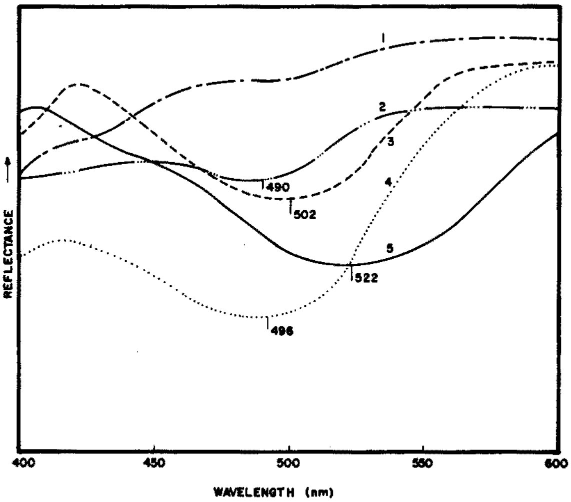

Fig. 2. Reflectance spectra of PAQH and its metal chelates adsorbed on alumina G. (1) Reagent (2) iron(III); (3), copper; (4) nickel; (5) cobalt complex.

The effect of heat on these adsorbed complexes was investigated by reflectance spectroscopy. Increases in color intensity were observed for all chelates upon heating the samples at 110° for periods of 5 and 30 min. These observations are in agreement with an earlier temperature study of PAQH complexes adsorbed on silica gel[1] and are the result of an increased removal of coadsorbed water from the alumina surface; a stronger adsorbent–chelate interaction therefore occurs and a more intense color is observed. A small bathochromic shift is also observed upon prolonged heating[1], but no considerable increase in intensity occurs, if the system is heated at 110° for periods longer than 30 min.

The stability of these chelates toward higher temperatures was also investigated. Complete decomposition of the adsorbed metal chelates was observed at the temperatures and times indicated in Table III. The decomposition appeared as a progressive fading of the spots until they could no longer be distinguished from the background. The color did not reappear after cooling.

TABLE III

DECOMPOSITION STUDY OF THE CHELATES

Metal	*Decomposition*	
	Temperature (°)	*Time (h)*
Fe^{3+}	180	1.5
Ni^{2+}	180	2
Cu^{2+}	180	2
Co^{2+}	200	4

DISCUSSION

In the reflectance spectroscopic investigation of the metal chelates it is interesting to observe the relationship between absorption maxima of the adsorbed complexes (Fig. 2 and Table II), their R_F values (Table I) and temperature stability (Table III).

The cobalt complex, for example, is the only complex stable in acidic medium[2] and shows the highest temperature stability. Its absorption maxima appear at the longest wavelength (522 nm) observed for the 4 chelates. On the chromatogram it does not move at all.

The iron(III) complex decomposes most readily and has an absorption maximum shifted furthest to the ultraviolet side of the spectrum (490 nm). On the chromatogram it moves close to the solvent front. The data for copper and nickel lie between the two extremes, following the actual order of separation.

Since pure chloroform was used as chromatographic solvent, the separation mechanism is based primarily on adsorption rather than partition chromatography. The greater the polarity of the chelate therefore, the more strongly it will be held by alumina and hence the polarity and the degree of interaction with the adsorbent decreases in the order of separation (cobalt→copper→nickel→iron(III) complex) as documented by the R_F values.

Previous work[4] has shown that cobalt(II) is oxidized to cobalt(III) on reaction with PAQH and that a diamagnetic bis-chelate is formed. Copper and nickel form paramagnetic bis-complexes and remain in the +2 oxidation state. The complexes obtained from iron(II) and iron(III) solutions at pH 5–6 in 80% ethanol have identical spectra ($\lambda_{max}=425$ nm)[6]. Magnetic measurements carried out in 1:1 water–dimethyl sulphoxide show that diamagnetic chelates are formed for both iron(II) and iron(III) and suggest (when coupled with absorption spectroscopic results) that the two complexes are the same, with iron(III) being reduced to iron(II) by one molecule of complexing agent. (Mole ratio plot showed 3 moles of reagent involved in the reaction with iron(III).)

The complexes extracted from aqueous iron(II) and iron(III) solutions, at pH 10, differ; a red iron(II) and a green iron(III) complex are obtained. Further investigation of the iron(III) complex is necessary. The phenomena of bathochromic shift for adsorbed compounds as a result of enhanced adsorbent–adsorbate interaction have been reported in several reflectance studies[7].

From the analytical point of view it is possible with this approach to cut the separation time of metals on alumina layers from 6–8 h[8] to 20–40 min, and to achieve cleaner separation. Iron, nickel, copper and cobalt can be determined efficiently even if up to tenfold excesses of interfering ions are present. Since the metal chelates have an intense color, no chromogenic spraying reagents are needed, which simplifies the experimental procedure considerably. Background coloration and other irregularities inherent with the spraying procedure[1,8] are eliminated. The evaporation of the chloroform fraction, after extraction of the chelates, permits the sensitivity to be increased by a factor of 100 or more.

The total iron content of a solution can be determined by oxidizing all the iron(II) to the iron(III) state. On the other hand an elegant method is provided to determine Fe^{2+} and Fe^{3+} simultaneously since both form stable and intensely colored chelates. Their R_F values are indeed so different (0.05 and 0.82) that if no interfering ions are present, they can be separated within a few minutes. Identification of the metals can be made on the basis of color and R_F values.

The use of the prefabricated alumina sheets in connection with the simple and rugged sandwich-type chromatogram apparatus which does not require preconditioning, renders this method particularly suitable for field work. The reproducibility of reflectance values was also briefly investigated by simultaneously analysing samples of the same concentration. The results were encouraging and suggest the use of this method also for semiquantitative or quantitative determination of these metals. The technique is currently under further investigation for later application to polluted water supplies and algae.

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SUMMARY

A scheme has been devised whereby PAQH complexes of iron, nickel, copper and cobalt can be separated chromatographically and determined semiquantitatively in presence of up to tenfold excesses of interfering metal ions. The visual detection limits for iron, nickel and copper were found to be 0.01 μg and for cobalt 0.007 μg per spot. Interesting relationships were observed between R_F values, decomposition temperatures and position of the absorption maxima of the adsorbed complexes.

RÉSUMÉ

Un schéma est donné permettant de séparer chromatographiquement les complexes pyridine-2-aldéhyde-2-quinolylhydrazone de fer, nickel, cuivre et cobalt et de les doser semiquantitativement en présence d'un excès d'ions métalliques gênants (jusqu'à 10 fois). Les limites de détection visuelle sont 0.01 μg par tache pour fer, nickel et cuivre et 0.007 μg pour cobalt. Des relations intéressantes sont observées entre valeurs de R_F, températures de décomposition et position des maxima d'absorption des complexes adsorbés.

ZUSAMMENFASSUNG

Es wurden die chromatographischen Eigenschaften der Übergangsmetallkomplexe von Eisen, Nickel, Kupfer und Kobalt mit Pyridin-2-aldehyd-2-chinolylhydrazon untersucht und ein Schema entwickelt, das es gestattet, diese Elemente halbquantitativ zu bestimmen und zwar in Gegenwart eines 10-fachen Überschusses von störenden Ionen. Die visuellen Nachweisgrenzen von Eisen, Nickel und Kupfer betragen 0.01 μg und von Kobalt 0.007 μg. Zwischen den R_F-Werten, den Zersetzungstemperaturen und der Lage der Absorptionsmaxima der adsorbierten Komplexe wurden interessante Beziehungen beobachtet.

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DISTRIBUTION COEFFICIENTS FOR TWELVE ELEMENTS IN OXALIC ACID MEDIUM ON A STRONG ANION-EXCHANGE RESIN

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Systematic surveys of the behaviour of elements on a strong base anion-exchange resin have been reported for hydrochloric[1], nitric[2], hydrofluoric[3], phosphoric[4], sulfuric acid[5], and hydrochloric–hydrofluoric[6,7], nitric–hydrofluoric[8,9] and sulfuric–hydrofluoric acid mixtures[9]. The adsorption characteristics in the above-mentioned mineral acids are now always applicable to separation techniques, as stated by SPEECKE[10], who used a chloro-oxalate medium for the separation of niobium and tantalum. Since oxalic acid is a good complexing agent, it would be of interest to investigate the adsorption of some elements from pure oxalic acid solutions as has already been published for zinc(II)[11].

In this study, the distribution coefficients for twelve elements on Dowex 1-X8, 100–200 mesh, were determined in oxalic acid medium. The elements investigated were arsenic, cerium, chromium, cobalt, copper, indium, lutetium, manganese, mercury, molybdenum, scandium and zinc. The concentration range of the oxalic acid was chosen from 10^{-3} to 0.98 M (saturation). The K_D values allowed the separation of five elements from each other, namely As(III), Mn(II), Co(II), Zn(II) and Cu(II).

DETERMINATION OF THE DISTRIBUTION CONSTANTS

The adsorbabilities are expressed as weight distribution coefficients, K_D (amount per g dry resin/amount per ml of solution). They can be determined by batch[12] or column methods. When column techniques are used, either the elution chromatographic or the break-through method[13,14] can be applied. Furthermore, for the determination of large distribution coefficients, use can be made of the pre-loaded column technique[14,15].

In this study, small K_D values were calculated from the corrected peak elution volume, V_{max}, *i.e.* the volume of eluant required to elute the maximum of the elution band, by the following expression[16,12]

$$\varrho \cdot (V_{max}/V - i) = K_D \qquad (1)$$

where V = total volume of the column (height × cross-sectional area), ϱ = specific volume of the exchanger, and i = void fraction of the column.

Small aliquots of 50–100 μl of the tracer solution containing the ion under

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investigation, were adsorbed on the top of the column, after the resin had been pretreated with the appropriate oxalic acid solution.

Columns of cross-sections ranging from 0.14 to 0.39 cm^2 and of varying heights (5–12 cm) were used. The elution rate was kept between 0.5 and 0.8 ml/cm^2 min. Depending on the K_D value, the eluates were collected in fractions ranging from 4 to 64 drops with an automatic transistorized fraction collector. The "dead" volume, the volume of the column and the volume per drop of eluate were determined by weighing.

To determine the specific volume, ϱ, of the exchanger in oxalic acid medium, a column of 10 ml was packed in a graduated tube and washed successively with 0.75 M oxalic acid and water. The resin was extruded, air-dried at 50–60°, and finally dried in vacuum in the presence of anhydrone to constant weight. ϱ was found to be 2.01.

The void fraction i of the column was determined as described by KRAUS *et al.*[14] from V_{max} of the non-adsorbable ^{137}Cs cation. A column distribution coefficient D of 0.39 was obtained. However, batch experiments with ^{137}Cs revealed a K_D value for the Cs$^+$ cation of 0.36. According to the relation $K_D = \varrho D$, D for cesium(I) should thus be 0.18. As $i = 1/E - D$, where $E = V/V_{max}$, the void fraction of the column determined as mentioned above was corrected for this D value and evaluated as being 0.21.

A visual method for the determination of the void fraction of the column was also used. A green-coloured solution of dithizone in chloroform was passed through a column conditioned with water. After the green band of the organic liquid had reached the lowermost layer of the resin, the i value was calculated by simple weighing of the expelled water. The void fraction thus determined was independent of the cross-sectional area of the column and was found to be 0.23.

For measurements of large distribution coefficients, batch equilibration techniques were used. Weighed amounts (g_r mg) of the resin were shaken with known volumes (V ml) of solution until equilibrium was reached. An aliquot of 4 ml was pipetted into a counting vial and the activity A_x compared with the total introduced activity A_s. The K_D value was computed from the following equation:

$$K_D = \frac{(A_s - \frac{1}{4}VA_x)\cdot 1000}{\frac{1}{4}A_x \cdot g_r} \tag{2}$$

where A_s = activity in counts per minute of the standard; A_x = activity in counts per minute of the 4-ml aliquot; g_r = weight of dry resin used (mg); and V = volume of the solution.

The anion exchanger was treated as described by SPEECKE[10]. The resin was washed 3 times for 1 h with 0.5 M oxalic acid solution. Each time the colloidal particles were removed together with the washing liquid, and the resin was washed several times with distilled water. The oxalate form of the resin thus obtained was first air-dried at 50–60°, and next dried under vacuum over anhydrone to constant weight.

About 100 mg of dried resin was mixed with 25 ml of oxalic acid solution of different concentration, containing the metal ions under investigation. After the resin particles had been removed by filtering, 4 ml of the aqueous phase was pipetted into a counting tube and the activity measured against a standard activity.

For all elements, except chromium, equilibrium was reached rapidly as shown in Fig. 1. For practical reasons the stirring was carried out overnight for at least 17 h. All experiments were performed at 25°.

The distribution coefficients were determined at metal concentrations sufficiently low that the loading of the resin was less than 1%. This means that the metal concentrations were sufficiently low not to exceed the solubility product of the metal oxalates.

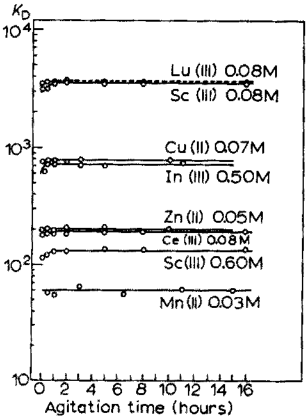


Fig. 1. Attainment of equilibrium.

Radioactive tracers and counting techniques

For the experiments, the following tracers were used: ^{22}Na, ^{46}Sc, ^{51}Cr, ^{54}Mn, ^{60}Co, ^{64}Cu, ^{65}Zn, ^{76}As, ^{99}Mo, ^{99m}Tc, ^{114m}In, ^{137}Cs, ^{144}Ce–^{144}Pr, ^{177}Lu, ^{203}Hg.

Most of the tracers were obtained by neutron irradiation of appropriate target materials in the BR-1 and BR-2 reactors in Mol, operating at fluxes of $4 \cdot 10^{11}$ and 10^{14} n/cm^2 sec respectively.

The tracers ^{54}Mn, ^{22}Na, ^{137}Cs and ^{144}Ce were obtained from U.K.A.E.A. (Amersham).

All tracers were of sufficient radiochemical purity to be used directly.

Since all of the radioisotopes used were γ-emitters, the counting of the samples was performed in a well-type NaI(Tl) scintillation counter by integral measurements.

Where separations were carried out, the purity of the eluates was checked by means of a 400-channel γ-spectrometer.

RESULTS

Determination of K_D values

Arsenic. Batch experiments showed K_D values much smaller than 10 over the whole molarity range investigated. The values obtained by column experiments are summarized in Table I.

Manganese. Batch experiments showed strong adsorption at 10^{-3} M oxalic acid, the adsorption decreasing rapidly with increasing molarity, and no appreciable adsorption was found for oxalic acid concentrations higher than 0.1 M. For oxalic acid concentrations higher than 0.01 M, the experimental conditions were changed, *i.e.* the ratio of the volume of the oxalic acid solution to the weight of dry resin was reduced as indicated in Table II.

The adsorbability of manganese(II) thus found, was checked by column experiments over the entire molarity range investigated. Good agreement was found between the K_D values obtained by both techniques. The results, together with the geometrical column volumes and the V_{max} values, are shown in Table III.

TABLE I

K_D VALUES FOR ARSENIC(III) FROM COLUMN EXPERIMENTS

Oxalic acid concentration (M)	*K_D value*	*Oxalic acid concentration (M)*	*K_D value*
0.001	1.70	0.100	1.35
0.003	1.65	0.300	1.10
0.010	1.70	0.750	0.90
0.030	1.45		

TABLE II

K_D VALUES FOR MANGANESE(II) FROM BATCH EXPERIMENTS

Oxalic acid concentration (M)	*Experimental conditions*		*K_D values*
	Volume acid (ml)	*Weight resin (mg)*	
0.00096	25	100	100
0.0019	25	100	85
0.0048	25	100	44
0.0096	25	100	22
0.0240	25	100	7
0.0091	10	250	22
0.0230	10	250	6
0.0450	10	250	1.5
0.0910	10	250	1.0
0.1800	10	250	0.2

TABLE III

K_D VALUES FOR MANGANESE(II) FROM COLUMN EXPERIMENTS

Oxalic acid concentration (M)	*Column volume V (ml)*	*V_{max} (ml)*	*K_D values*
0.002	0.64	32.6	100
0.010	0.75	6.35	17
0.010	0.75	7.15	19
0.025	2.65	6.85	4.8
0.025	2.65	6.09	4.7
0.050	2.67	2.32	1.4
0.050	0.71	0.74	1.7
0.100	0.71	0.29	0.4
0.200	0.70	0.29	0.4
0.500	0.70	0.29	0.4

Cobalt, mercury, zinc and copper. A portion (1 ml) of the respective tracer solution was added to 25 ml of the different oxalic acid solutions and shaken for at least 17 h together with 100 mg of dry resin. The results obtained from these experiments are summarized in Tables IV and V.

TABLE IV

K_D VALUES FOR COBALT(II) AND ZINC(II) FROM BATCH EXPERIMENTS

Oxalic acid concentration (M)	*K_D values*		*Oxalic acid concentration (M)*	*K_D values*	
	Co(II)	*Zn(II)*		*Co(II)*	*Zn(II)*
0.00096	1540	14400	0.072	17	100
0.0019	1270	9700	0.096	15	54
0.0048	770	6340	0.140	13	23
0.0096	420	3610	0.190	5	12
0.024	126	810	0.240	4	9
0.048	41	230	0.290	3	6

TABLE V

K_D VALUES FOR MERCURY(II) AND COPPER(II) FROM BATCH EXPERIMENTS

Oxalic acid concentration (M)	*K_D values*		*Oxalic acid concentration (M)*	*K_D values*	
	Cu(II)	*Hg(II)*		*Cu(II)*	*Hg(II)*
0.00093	33100	4990	0.2300	130	57
0.0018	21800	3990	0.2800	110	45
0.0046	13800	2890	0.3200	80	37
0.0042	9400	2080	0.3700	61	—
0.0230	3130	1000	0.4200	59	—
0.0460	1250	500	0.4600	45	—
0.0690	790	330	0.4800	38	—
0.0930	530	260	0.7200	26	—
0.1400	280	136	0.9400	19	—
0.1900	140	87			

At low oxalic acid concentrations, the K_D values increase in the sequence Co(II) < Hg(II) < Zn(II) < Cu(II). At 0.02 M, the adsorption functions for zinc(II) and mercury(II) intersect. The copper(II) and mercury(II) curves approach each other at higher molarity.

Consequently, the separation of copper and mercury will not be rapid and efficient, as is desirable in activation analysis.

From column experiments, carried out at molarities ranging from 0.075 to 0.75 M oxalic acid, K_D values were obtained in good agreement with those obtained from batch experiments. The results are presented in Table VI.

Indium and molybdenum. From batch experiments (Table VII) it was found that indium(III) shows a strong adsorbability. Though indium(III) might be removed quantitatively with oxalic acid solution of high molarity from an anion-exchange column, this medium is not suited for practical elutions of this element.

The K_D values for molybdenum(VI) were estimated as being higher than 10^5

over the whole molarity range. After agitation for 17 h, the tubes were removed from the agitation bath and allowed to stand for 2 days. This time interval was necessary for either the establishment of the ^{99}Mo–^{99m}Tc equilibrium or the decay of the ^{99m}Tc daughter. After this time, aliquots were pipetted and counted. For the whole concentration range, the activities measured fell within the standard deviation σ of the background. By taking 2σ as the upper limit of activity, a minimum K_D value of 10^5 was calculated.

TABLE VI

K_D VALUES FOR Co(II), Zn(II), Hg(II) AND Cu(II) FROM COLUMN EXPERIMENTS

Oxalic acid concentration (M)	*K_D values*			
	Co(II)	*Zn(II)*	*Hg(II)*	*Cu(II)*
0.0625	34	—	—	—
0.125	11	30	—	—
0.150	—	—	120	—
0.250	3.9	7.6	—	—
0.300	—	—	49	—
0.500	1.7	4.6	28	—
0.750	1.4	2.5	22	25

TABLE VII

K_D VALUES FOR INDIUM(III) FROM BATCH EXPERIMENTS

Oxalic acid concentration (M)	*K_D values*	*Oxalic acid concentration (M)*	*K_D values*
0.0096	76450	0.290	2910
0.024	60000	0.340	1980
0.048	46400	0.380	1550
0.072	41900	0.430	1200
0.096	20870	0.480	930
0.140	11740	0.720	430
0.190	5750	0.940	340
0.240	3990		

Chromium. Batch experiments showed that the K_D values increase with increasing stirring time. Even after 144 h no constant values were obtained as shown in Fig. 2. The dotted curve was obtained at 0.75 *M* oxalic acid and represents the K_D values as a function of time. The full lines result from experiments over the whole molarity scale with shaking times of 6, 17 and 144 h.

In column experiments, freshly prepared oxalic acid solutions of chromium(III) were added to small columns of Dowex 1-X8 resin. On elution with the appropriate acid molarity, large amounts (60–80%) of chromium(III) immediately passed through the columns, while the remainder was strongly adsorbed. A plausible explanation of these results may be given by assuming that in the original chromium(III) solution weakly adsorbed chromium-chloro and chromium-chloro-aquo complexes are present. Upon shaking with oxalic acid solutions, the latter may be converted slowly into strongly adsorbed oxalato complexes.

Scandium. Results from batch experiments are presented in Table VIII. No values are given for molarities lower than 0.019 as the K_D values are too high and the specific activity of the ^{46}Sc tracer too low for accurate results.

Column experiments gave results (Table IX) in good agreement with the results obtained from batch experiments.

Cerium and lutetium. The results of batch and column experiments are given in Table X.

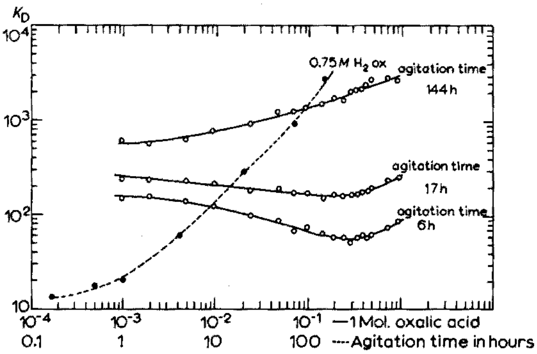


Fig. 2. K_D values for chromium(III) as a function of oxalic acid concentration and of time.

TABLE VIII

K_D VALUES FOR SCANDIUM(III) FROM BATCH EXPERIMENTS

Oxalic acid concentration (M)	*K_D value*	*Oxalic acid concentration (M)*	*K_D value*
0.0192	28600	0.2885	355
0.0384	11800	0.4327	170
0.0577	6220	0.5769	108
0.0772	3510	0.7209	80
0.1923	680	0.9423	50
0.2404	460		

TABLE IX

K_D VALUES FOR SCANDIUM(III) FROM COLUMN EXPERIMENTS

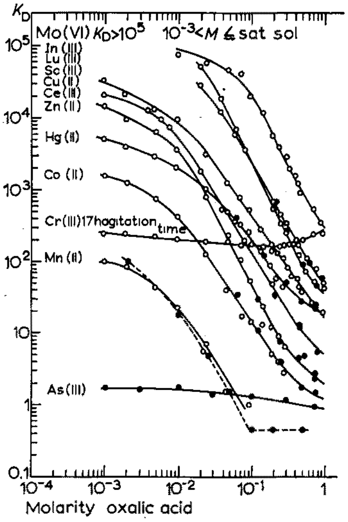
Oxalic acid (M)	*Amount of Sc adsorbed (µg)*	*Column volume (cm³)*	*V_{max} (µg/ml)*	*K_D value*
0.200	0.011	0.483	156	679
0.600	0.060	0.483	23.5	99.3
0.900	0.016	0.483	14.0	61

From Fig. 3, a β-value (ratio of the two K_D values) of 8 was calculated for an oxalic acid concentration of 0.5 M. From this it may be concluded that cerium and lutetium can be separated in this medium (see below). Furthermore, it may be expected that the rare earths can be separated into groups each including three successive elements.

TABLE X

K_D VALUES FOR CERIUM(III) AND LUTETIUM(III) FROM BATCH AND COLUMN EXPERIMENTS

Oxalic acid concentration (M)	*K_D values*		*Oxalic acid concentration (M)*	*K_D values*	
	Ce(III)	*Lu(III)*		*Ce(III)*	*Lu(III)*
Batch					
0.00096	20600	—	0.0770	185	3550
0.0019	15600	—	0.1923	50	544
0.0038	12900	—	0.2404	29	342
0.0058	9230	—	0.2885	26	248
0.0077	7110	—	0.4327	13	121
0.0192	1840	52500	0.5769	11	74
0.0384	522	18800	0.7209	10	52
0.0576	380	6740	0.9423	—	44
Column					
0.060	405	—	0.450	12	—
0.200	36	558	0.500	—	94
0.300	—	260	0.750	5.6	48



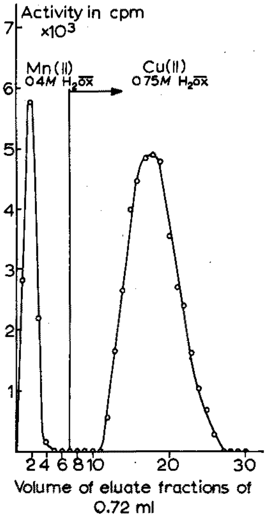


Fig. 3. K_D values as a function of oxalic acid concentration. ● column experiments, ○ batch experiments.

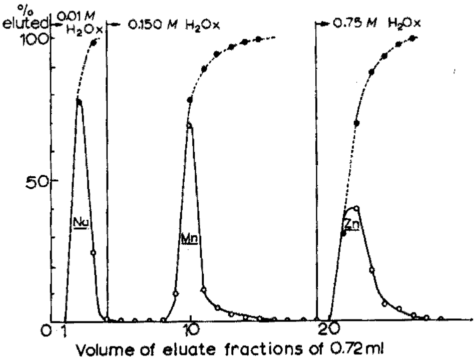
Fig. 4. Separation of manganese(II) from copper(II). Column height 4.4 cm, cross-section 0.136 cm².

Separations

When ion-exchange separations are applied to practical determinations of trace elements in neutron activation analysis, it is desirable that: (*a*) the element under investigation should be recovered quantitatively in the eluate; (*b*) the volume of eluate should be small (20 ml) so that a high counting efficiency can be achieved; (*c*) the cross-contamination of the eluted bands must be negligible; and (*d*) a short separation time is required for the determination of elements giving rise to short-living isotopes.

In the separation of manganese(II) from copper(II) (Fig. 4), the yield was 100% for both elements, while the elution volumes were 5 ml for manganese(II) and about 15 ml for copper(II). The elution of copper(II) may also be performed with a mixture of 0.75 *M* oxalic acid and 5% thiourea; under these conditions the elution band of copper(II) becomes sharper. Checking both eluates by means of the multichannel analyser revealed absolute purity of both fractions. The separation was accomplished in about 2.5 h.

In Fig. 5, the quantitative separation of sodium, manganese and zinc is represented. The volume in which the tracers were originally present, was 300 μl. Sodium was eluted with 6 ml of 0.01 *M* oxalic acid. The volume in which the total ^{54}Mn activity was present amounted to about 12 ml of 0.150 *M* oxalic acid. Finally, zinc was recovered quantitatively in 15 ml of 0.75 *M* oxalic acid. The total separation was carried out in about 3 h but the manganese fraction was recovered in about 1.5 h which represents less than one half-life of the ^{56}Mn isotope obtained by the (n,γ) reaction, on irradiating the only natural isotope of manganese.



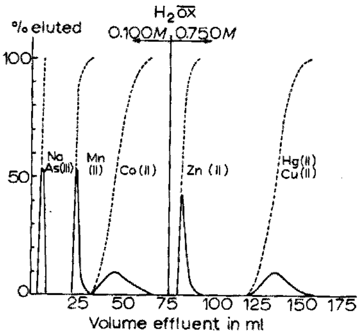


Fig. 5. Separation of sodium(I), manganese(II) and zinc(II). ● total percentage eluted. Column height 11.0 cm, cross-section 0.15 cm^2.

Fig. 6. Separation of As(III)[+Na(I)], Mn(II), Co(II), Zn(II) and Cu(II)[+Hg(II)]. Column pretreated with 0.005 *M* oxalic acid. — percentage eluted per fraction; ---- total percentage eluted. Column height 12.9 cm, diameter 0.704 cm.

The separation of five elements, As(III), Mn(II), Co(II), Zn(II) and Cu(II), in pure oxalic acid is shown in Fig. 6. From the adsorption curves shown in Fig. 3, it is obvious that sodium might be eluted together with arsenic(III) in the first fraction, while mercury(II) will be present in the copper(II) eluate. The experimental conditions are summarized in Table XI. The geometrical column volume for these experiments was equal to 5.02 ml. The resin was pretreated with 0.005 *M* oxalic acid. The tracers were added in fractions of 100 μl of 0.005 *M* acid and adsorbed at a rate of 1 drop per min (0.0505 ml/min). The elution was performed at a flow rate of 0.30 ml/min (=0.77 ml/min cm^2). The column sizes are critical for the separation of manganese(II) from cobalt(II).

For practical purposes (determination of short-lived isotopes by short irradiation at high neutron fluxes), the elution of cobalt(II) may be omitted, while thiourea may be added to the 0.75 *M* oxalic acid solution after zinc(II) has been eluted. Mercury and copper may then be counted by simple pulse-height discrimination.

For the separation of cerium(III) and lutetium(III), a mixture of these elements was adsorbed in 0.50 *M* oxalic acid on a column of 0.92 ml; cerium(III) was eluted first with 20 ml of 0.50 *M* oxalic acid, whereafter lutetium(III) was removed with about the same volume of 0.75 *M* oxalic acid. The elution curves are shown in Fig .7.

TABLE XI

EXPERIMENTAL CONDITIONS FOR THE SEPARATION OF As(III), Mn(II), Co(II), Zn(II) AND Cu(II) WITH OXALIC ACID AS ELUANT

Element	*Carrier amount (μg)*	*Oxalic acid concentration (M)*	*Volume for quantitative recovery (ml)*
As(III)	7	0.10	8.1
Mn(II)	2	0.10	13.0
Co(II)	5	0.10	40.5
Zn(II)	5	0.75	17.8
Cu(II)	20	0.75	40.5

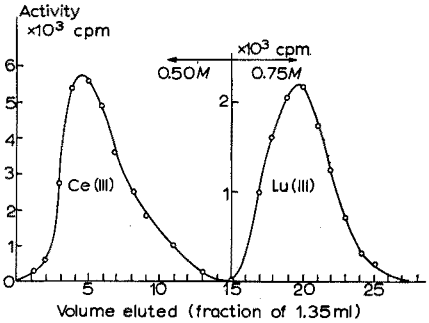


Fig. 7. Separation of cerium(III) from lutetium(III). Column volume 0.92 cm³.

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SUMMARY

The distribution coefficients were determined for twelve elements, namely As(III), Ce(III), Cr(III), Co(II), Cu(II), In(III), Lu(III), Mn(II), Hg(II), Mo(VI), Sc(III) and Zn(II), on a strong base anion exchanger in pure oxalic acid solutions. The K_D curves are given. A scheme was developed for the chromatographic separation of five elements, namely As(III), Mn(II), Co(II), Zn(II) and Cu(II). Ce(III) can be separated from Lu(III).

RÉSUMÉ

On a déterminé les coefficients de partage pour 12 éléments, notamment As(III), Ce(III), Cr(III), Co(II), Cu(II), In(III), Lu(III), Mn(II), Hg(II), Mo(VI), Sc(III) et Zn(II), sur un échangeur d'anions fortement basique, en milieu acide oxalique pur. Les courbes K_D sont données. Un schéma est proposé pour la séparation chromatographique de cinq éléments, notamment As(III), Mn(II), Co(II), Zn(II) et Cu(II). Le cérium(III) peut être séparé d'avec le lutécium(III).

ZUSAMMENFASSUNG

Die Verteilungskoeffizienten folgender 12 Elemente an einem stark basischen Anionenaustauscher in reinen Oxalsäure-Lösungen wurden bestimmt: As(III), Ce(III), Cr(III), Co(II), Cu(II), In(III), Lu(III), Mn(II), Hg(II), Mo(VI), Sc(III) und Zn(II). Die K_D-Kurven werden angegeben. Es wurde ein Schema zur chromatographischen Trennung von As(III), Mn(II), Co(II), Zn(II) und Cu(II) entwickelt. Ce(III) kann von Lu(III) getrennt werden.

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THE EXTRACTION OF COPPER(II) FROM HYDROCHLORIC ACID BY SOLUTIONS OF TETRA-*n*-HEXYLAMMONIUM CHLORIDE IN ETHYLENE DICHLORIDE

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In an earlier paper[1] it was shown that copper(I) was extracted very efficiently from chloride media by means of solutions of the liquid anion exchanger tetra-*n*-hexylammonium chloride in ethylene dichloride. The extraction equilibria could be represented by the equation

$$(NR_4^+Cl^-)_{org.} + CuCl_2^- \rightleftharpoons (NR_4^+CuCl_2^-)_{org.} + Cl^- \qquad (1)$$

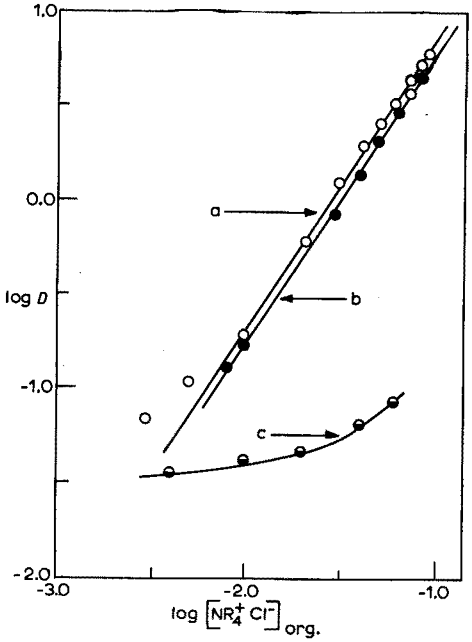
(where the subscript *org.* distinguishes species in the organic phase and $R = n$-hexyl) for which the equilibrium constant was found to be $10^{5.9}$. Copper(I) is a class (b) metal and forms strong halogen complexes whose stability increases in the order $F^- \ll Cl^- < Br^- < I^-$ [2,3]. Copper(II), on the other hand, is a typical class (a) metal which forms weaker complexes whose stability decreases in the order $F^- \gg Cl^- > Br^-$. Its behaviour towards a liquid ion exchanger would thus be expected to differ markedly from that of the metal in the lower oxidation state. NAKAGAWA[4] reported that the extraction of copper(II) reached a maximum of 35% only from 7 *M* hydrochloric acid when the secondary amine Amberlite LA1 [N-dodecenyl(trialkylmethyl)-amine] was used as the anion exchanger. Although quaternary ammonium salts should be more effective, the present paper appears to be the first attempt to examine the extraction of copper(II) and to attempt to elucidate the distribution equilibria.

Distribution ratios defined by

$$D = \frac{\text{Total concentration of copper in the organic phase}}{\text{Total concentration of copper in the aqueous phase}}$$

were determined in the usual manner after equilibrations had been carried out at room temperature. Copper was determined spectrophotometrically in aliquot portions of both phases by the oxalyldihydrazide method[5], the metal being first "stripped" from the organic phase by shaking with 0.1 *M* sodium perchlorate. Satisfactory mass-balances were obtained.

Extractions from aqueous phases of constant acidity by excess of the liquid anion exchanger at different concentrations gave the results shown in Fig. 1. The results for 0.8 *M* hydrochloric acid are effectively the same for both 10^{-4} *M* and $5 \cdot 10^{-5}$ *M* copper (blackened and open circles, respectively) and the plot of log *D* against log $[NR_4^+Cl^-]_{org.}$ conforms to a straight line of slope 1.5. This implies that, independent of the concentration of copper in the aqueous phase, the extracted complex contains 1.5 mole of quaternary ammonium ion per atom of copper. This would be consistent with the extraction of a single species $(NR_4^+)_3(Cu_2Cl_7^{3-})$, or an aggregate of $(NR_4^+)Cl^-$ with two molecules of $(NR_4^+)(CuCl_3^-)$, if it is assumed that changes in the degree of dissociation of the complex anion are negligible over the rather small range of copper concentrations involved. On the other hand, these results are equally consistent with the simultaneous extraction of the species $(NR_4^+)(CuCl_3^-)$ and $(NR_4^+)_2(CuCl_4^{2-})$.



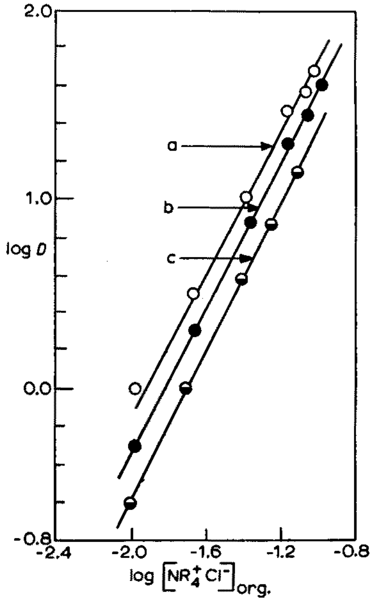
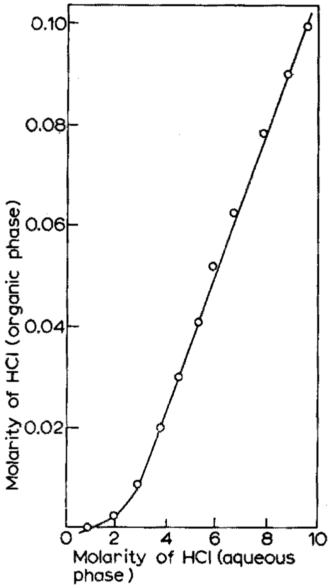


Fig. 1. The extraction of copper(II) from hydrochloric acid by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride. Curve (a) (open circles): $[HCl] = 0.8\ M$, $[Cu^{2+}]_{initial} = 5 \cdot 10^{-5}\ M$. Curve (b) (blackened circles): $[HCl] = 0.8\ M$, $[Cu^{2+}]_{initial} = 10^{-4}\ M$. Curve (c) (half-blackened circles): $[HCl] = 0.1\ M$, $[Cu^{2+}]_{initial} = 10^{-4}\ M$.

Fig. 2. The effect of changes in acidity on the extraction of copper(II), $[Cu^{2+}]_{initial} = 10^{-4}\ M$ from a medium of constant chloride content $[Cl^-] = 0.80\ M$ by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride. Curve (a) $[H^+] = 0.01\ M$. Curve (b) $[H^+] = 0.40\ M$. Curve (c) $[H^+] = 0.60\ M$.

When the acid concentration was reduced from 0.8 to 0.1 *M* hydrochloric acid the distribution ratio decreased some thirty-fold (Fig. 1, half-filled circles) but this effect could not be attributed uniquely to the decrease in chloride ion concentration as there was a simultaneous decrease in hydrogen-ion concentration. Changes in chloride concentration will certainly have a profound effect on the nature of the chloro-complexes in the aqueous phase. The possible effect of pH changes will be discussed later but the reality of the effect is further illustrated in Fig. 2 which shows the results of extraction from mixtures of sodium chloride and hydrochloric acid such that $[H^+] = 0.01$, 0.40 and 0.60 *M* with a constant $[Cl^-] = 0.800\ M$. Figure 2 shows how the extraction decreases as the concentration of hydrogen ion is increased. The linear slopes for the two stronger acid concentrations are exactly 1.0 and although the points for 0.01 *M* acid show a greater scatter they do not deviate significantly from this. This would seem to indicate that a complex is being extracted that contains two molecules of quaternary ammonium cation per copper atom. These results provide further evidence that a 1:1 species such as $NR_4^+CuCl_3^-$ cannot be wholly responsible for the observed extraction. The effect of hydrogen ions in reducing the value of *D* from that in *e.g.* 0.8 *M* hydrochloric acid may be due to the more favourable extraction of the species $HCuCl_4^-$ compared to that of the higher charged complex $CuCl_4^{2-}$ [6]. On the other hand, the decrease in the activity of water consequent upon the massive increase in hydrogen-ion concentration is a more plausible explanation if the four-coordinate solvated ion $CuCl_3(H_2O)^-$ is the actual uni-negative ion involved in the extraction. At the same time, it must be emphasised that the adverse effect of hydrogen ions is quite a minor effect in comparison to that produced by changes in chloride concentration.

GOOD *et al.*[7] have shown that solutions of tricaprylammonium chloride in toluene can extract the species HCl_2^-, the existence of which is well-established from its infrared spectra. Figure 3 shows that a solution of tetrahexylammonium chloride in ethylene chloride can extract increasing amounts of hydrochloric acid as the concentration in the aqueous phase increases. But at the maximum acidity (0.8 *M* in hydrochloric acid) used in the studies of our copper extraction, the amount of HCl_2^-



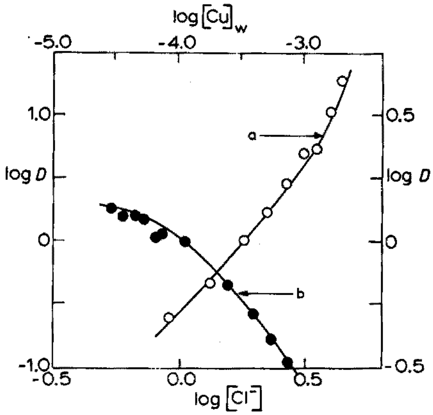


Fig. 3. The extraction of hydrochloric acid by equilibration with an equal volume of a solution of tetra-*n*-hexylammonium chloride in ethylene dichloride.

Fig. 4. The extraction of copper(II) by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride to show the effect of varying (a) the concentration of chloride ions and (b) that of the total metal. Curve (a) (open circles and lower abscissae): $[Cu^{2+}]_{initial} = 10^{-4}$ *M*; $[H^+] = 10^{-2}$ *M*; $[NR_4^+Cl^-]_{org.} = 9.5 \cdot 10^{-3}$ *M*. Curve (b) (blackened circles and upper abscissae): $[H^+] = 10^{-2}$ *M*; $[Cl^-] = 0.80$ *M*; $[NR_4^+Cl^-]_{org.} = 1.1773 \cdot 10^{-3}$ *M*.

extracted would clearly be negligible and this species can confidently be disregarded when discussing the problem of the metal distribution ratios.

Figure 4 (curve a) shows the effects of varying the chloride-ion concentration whilst keeping that of the liquid exchanger constant at $[NR_4^+Cl^-] = 9.5 \cdot 10^{-3}\ M$. The plot of log D against log $[Cl^-]$ (where $[Cl^-] \gg [Cu(II)]$ for a constant total excess amount of anion exchanger ($[NR_4^+Cl^-] = 9.3 \cdot 10^{-3}\ M$) gives a steeply rising curve with a positive slope increasing from 2.5 to 4.0. Clearly the distribution ratio depends on a high power of the chloride-ion concentration and since D increases with $[Cl^-]$ with no signs of a maximum being reached, this indicates that the complexes involved are of low stability.

A final complication is the observation that when the concentrations of extractant, of chloride ions and of hydrogen ions are all kept constant, the distribution ratio depends on the amount of copper(II) in the system. Explicitly, the distribution ratio D, is found to *decrease* with increasing copper concentration in the aqueous phase (Fig. 4, curve b).

Although the system is very complicated the foregoing results can be interpreted qualitatively at least, if it is assumed that a polymeric chloro–copper complex exists in equilibrium with mononuclear complexes in the aqueous phase, but that only mixtures of mononuclear complexes are extracted into the organic phase. The composition of the species existing in aqueous solutions of high chloride content has still been insufficiently studied, for among the 35 papers listed in the monograph on *Stability Constants*[8] few measurements extend above $\mu = 1$ ($HClO_4$ or $NaClO_4$). There is abundant evidence for the existence of $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$ in aqueous solution and in certain organic solvents. $Cu_2Cl_6^{2-}$ has been shown to occur in solid $KCuCl_3$ and in $Li_2Cu_2Cl_6H_2O$ ($LiCl$, $CuCl_2$, 0.5 H_2O).

Consider an aqueous phase containing the mononuclear species Cu^{2+}, $CuCl^+$, $CuCl_2$, $CuCl_3^-$ (as $CuCl_3(H_2O)^-$) and $CuCl_4^{2-}$ in equilibrium with the binuclear species $Cu_2Cl_6^{2-}$ and $Cu_2Cl_7^{3-}$ formed by the reactions,

$$2\ CuCl_3^- \rightleftharpoons Cu_2Cl_6^{2-} \tag{2}$$

$$CuCl_3^- + CuCl_4^{2-} \rightleftharpoons Cu_2Cl_7^{3-} \tag{3}$$

If we make the reasonable assumption that anionic species of formal charge greater than -2 do not extract appreciably in comparison to those of lower negative charge, the main extraction processes will be

$$CuCl_3^- + (Q^+Cl^-)_{org.} \overset{K_3}{\rightleftharpoons} (Q^+CuCl_3^-)_{org.} + Cl^- \tag{4}$$

$$CuCl_4^{2-} + 2\ (Q^+Cl^-)_{org.} \overset{K_4}{\rightleftharpoons} (Q^+_2CuCl_4^{2-})_{org.} + 2\ Cl^- \tag{5}$$

where $Q^+ = N(n\text{-hexyl})_4^+$.

The distribution ratio will be given by

$$D = \frac{[Q^+CuCl_3^-]_{org.} + [Q^+_2CuCl_4^{2-}]_{org.}}{[Cu^{2+}] + \ldots + [CuCl_4^{2-}] + 2[Cu_2Cl_6^{2-}] + 2[Cu_2Cl_7^{3-}]}$$

which reduces to

$$D = \frac{\{K_3\beta_3[Q^+Cl^-]_{org.} + K_4\beta_4[Q^+Cl^-]^2_{org.}\}[Cl^-]^2}{\sum_0^4 \beta_j[Cl^-]^j + 2\ [Cu^{2+}]\{\beta_{2,6}[Cl^-]^6 + \beta_{2,7}[Cl^-]^7\}} \tag{6}$$

on introducing the distribution constants K_3 and K_4 defined by eqns. (4) and (5) and the overall formation constants for the mononuclear and binuclear complexes defined by

$$\beta_j = [\mathrm{CuCl}_j]/[\mathrm{Cu}][\mathrm{Cl}]^j$$

and $\beta_{x,y} = [\mathrm{Cu}_x\mathrm{Cl}_y]/[\mathrm{Cu}]^x[\mathrm{Cl}]^y$

where charges have been omitted to simplify the typesetting.

Since the total copper content of the aqueous phase $[\mathrm{Cu}]_w$ is an experimentally measurable quantity we can write

$$\begin{aligned}[\mathrm{Cu}]_w &= [\mathrm{Cu}^{2+}] + [\mathrm{CuCl}^+] + \ldots + [\mathrm{CuCl}_4{}^{2-}] + 2[\mathrm{Cu}_2\mathrm{Cl}_6{}^{2-}] + 2[\mathrm{Cu}_2\mathrm{Cl}_7{}^{3-}]\\ &= [\mathrm{Cu}^{2+}]\cdot\sum_0^4 \beta_j[\mathrm{Cl}^-]^j + 2[\mathrm{Cu}^{2+}]^2 \sum_6^7 \beta_{2,y}[\mathrm{Cl}^-]^y \qquad (7)\end{aligned}$$

which can be rearranged as a quadratic in $[\mathrm{Cu}^{2+}]$ and solved to give

$$[\mathrm{Cu}^{2+}] = \frac{-\sum_0^4 \beta_j[\mathrm{Cl}^-]^j + \left\{\left(\sum_0^4 \beta_j[\mathrm{Cl}^-]^j\right)^2 + 8[\mathrm{Cu}]_w \sum_6^7 \beta_{2,y}[\mathrm{Cl}^-]^y\right\}^{\frac{1}{2}}}{4\sum_6^7 \beta_{2,y}[\mathrm{Cl}^-]^y}$$

If this value for $[\mathrm{Cu}^{2+}]$ is substituted in eqn. (5), we obtain

$$D = \frac{2\{K_3\beta_3[\mathrm{Q}^+\mathrm{Cl}^-]_{org.} + K_4\beta_4[\mathrm{Q}^+\mathrm{Cl}^-]^2_{org.}\}[\mathrm{Cl}^-]^2}{\sum_0^4 \beta_j[\mathrm{Cl}^-]^j + \left\{\left(\sum_0^4 \beta_j[\mathrm{Cl}^-]^j\right)^2 + 8[\mathrm{Cu}]_w \sum_6^7 \beta_{2,y}[\mathrm{Cl}^-]^y\right\}^{\frac{1}{2}}} \qquad (8)$$

Consider now the case where $[\mathrm{Cl}^-]$ and $[\mathrm{Q}^+\mathrm{Cl}]_{org.}$ are kept constant. It can easily be shown that eqn. (8) can now be written in the form

$$D^{-1} = \mathrm{A}\{1 + (1 + \mathrm{B}[\mathrm{Cu}]_w)^{\frac{1}{2}}\} \qquad (9)$$

where A is a composite constant and

$$\mathrm{B} = 8\sum_6^7 \beta_{2,y}[\mathrm{Cl}^-]^y \Big/ \sum_0^4 \beta_j[\mathrm{Cl}^-]^j$$

Taking into account the hypothesis that the reactions leading to the formation of the binuclear species $\mathrm{Cu_2Cl_6}^{2-}$ and $\mathrm{Cu_2Cl_7}^{3-}$ (eqns. (2) and (3)) lie to the right, we must have

$$\beta_{2,6} > (\beta_3)^2 \quad \text{and} \quad \beta_{2,7} > \beta_3 \times \beta_4$$

and since $[\mathrm{Cu}]_w \ll 1$, it follows that the product $\mathrm{B}[\mathrm{Cu}]_w \ll 1$ under the conditions of these experiments, so that eqn. (9) can be rewritten in the form

$D^{-1} = \mathrm{A}\{1 + (1 + 0.5\mathrm{B}[\mathrm{Cu}]_w)\} = K_1 + K_2[\mathrm{Cu}]_w$, where K_1 and K_2 are constants.

A plot of $1/D$ against $[\mathrm{Cu}]_w$ should thus be linear. This is shown to be the case in Fig. 5.

Equation (6) also provides an interpretation of the other experimental observations on the effect of varying such parameters as $[\mathrm{Cl}^-]$ and $[\mathrm{NR}_4{}^+\mathrm{Cl}^-]_{org.}$.

No quantitative explanation of the very complex situation can profitably be attempted at this juncture in view of the large number of equilibrium constants involved whose magnitudes are unknown; in the first instance, some at least of these should be determined by methods independent of the present liquid–liquid extraction studies.

The extractability of copper(II) by tetrahexylammonium chloride is seen to be more effective than that by the secondary amine Amberlite LA1 reported by NAKAGAWA[4]; this could have been anticipated. On the other hand, the present results appear at first sight to be in complete disagreement with those reported by MAEK *et al.*[9], who carried out a screening survey of the extraction of most of the metals in the Periodic System by solutions of a quaternary iodide, $NR_4^+I^-$ (R = *n*-propyl, butyl or hexyl) from aqueous phases containing *(inter alia)* hydrochloric acid. Their graphs show the extraction of copper(II) by solutions of hexylammonium iodide in methyl isobutyl ketone as being *ca.* 100% over the range 1–5 *M* hydrochloric acid. Clearly the metal has been reduced to copper(I) by the excess of iodide ions and their graph really reports data for the extraction of copper(I) which agrees satisfactorily with the results reported by us in an earlier paper[1]. In the same survey[9], MAEK *et al.* show the maximum extraction of iron (from iron(III)) as *ca.* 100% between 2 and 3 *N* hydrochloric acid and they attribute this to reduction to iron(II). In view of the low stability of the complexes $FeCl_3^-$ and $FeCl_4^{2-}$ of iron(II) compared with the much higher stability of $FeCl_4^-$ (from iron(III)), and the much lower stability (as yet not measured) expected for the iodo-complexes FeI_3^- and FeI_4^{2-}—since iron(II) is a typical class (a) metal—this explanation is surprising and probably untenable.

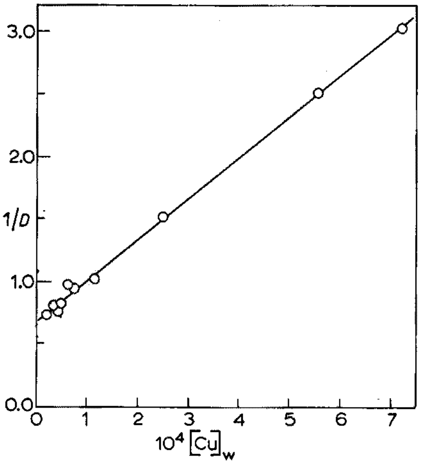


Fig. 5. The reciprocal of the distribution ratio plotted against the total concentration of copper in the aqueous phase after equilibration. Conditions as in Fig. 2, curve (b).

EXPERIMENTAL

Solutions of *n*-hexylammonium chloride in ethylene dichloride were prepared, and their concentrations determined, as described in the previous paper[1]. Equilibrations with known initial concentrations of copper(II) were carried out by vigorously shaking equal volumes (5 ml) of the two phases in stoppered centrifuge tubes at room temperature. Known concentrations of hydrochloric acid and of sodium chloride were included in the aqueous phase. After equilibration and centrifugation to separate the phases completely, aliquot portions of each were removed for determination of their copper content spectrophotometrically by the oxalyldihydrazide method[5]. Copper was stripped from the organic phase by a 0.1 *M* solution of sodium perchlorate as previously described[1]. The mass-balance of copper was always checked against the known total amount taken and results were discarded if discrepancies were found.

The partition of hydrochloric acid between an aqueous solution and a $9.50 \cdot 10^{-2}$ *M* solution of tetrahexylammonium chloride in ethylene dichloride was studied by shaking equal volumes of the two phases in stoppered centrifuge tubes. After equilibration their contents were centrifuged, the phases were separated, and the concentration of hydrochloric acid in the organic phase was determined by stripping with an equal volume of water followed by titration with standard alkali. The following results were obtained.

[HCl], aqueous phase	0.968	1.936	2.904	3.872	4.647
10^3[HCl], organic phase	0.880	2.97	8.80	20.3	30.1
[HCl], aqueous phase	5.809	6.583	7.745	8.907	9.681
10^3[HCl], organic phase	52.4	63.6	79.2	90.7	100

SUMMARY

In marked contrast to the behaviour of copper(I), the extraction of copper(II) by solutions of tetra-*n*-hexylammonium chloride in ethylene dichloride is very small from 1.0 *M* chloride and although it increases with concentration it does not reach 90% until the chloride concentration exceeds 4 *M*. By varying such parameters as $[Cl^-]$, $[NR_4^+Cl^-]_{org.}$ and the total amount of copper in the system, it was shown that the distribution equilibria could best be explained by postulating the presence of binuclear complexes $Cu_2Cl_6^{2-}$ and $Cu_2Cl_7^{3-}$ in addition to mononuclear complexes in the aqueous phase, while only mononuclear species such as $NR_4^+CuCl_3^-$ and $(NR_4^+)_2CuCl_4^{2-}$ are extracted. A linear relationship is predicted between the reciprocal of the distribution ratio and the total amount of copper present at equilibrium in the aqueous phase and confirmed by the experimental results.

RÉSUMÉ

Contrairement au cuivre(I), l'extraction du cuivre(II) à l'aide de solutions de chlorure de tétra-*n*-hexylammonium dans le dichlorure d'éthylène est très faible à partir de chlorure 1.0 *M*; bien qu'elle augmente avec la concentration elle n'atteint pas 90% jusqu'à des concentrations en chlorure dépassant 4 *M*. En faisant varier des paramètres tels que $[Cl^-]$, $[NR_4^+Cl^-]_{org.}$ et la concentration totale du cuivre dans le système, on peut admettre la présence de $Cu_2Cl_6^{2-}$ et $Cu_2Cl_7^{3-}$ à côté de complexes mononucléaires dans la phase aqueuse, tandis que seules les formes $NR_4^+CuCl_3^-$ et $(NR_4^+)_2CuCl_4^{2-}$ sont extraites. Une relation linéaire peut être prévue entre le coefficient de partage et la concentration totale en cuivre présent à l'équilibre en phase aqueuse; elle est confirmée par des résultats expérimentaux.

ZUSAMMENFASSUNG

Im deutlichen Gegensatz zu dem Verhalten von Kupfer(I) ist die Extraktion von Kupfer(II) mit Tetra-*n*-hexylammoniumchlorid in Äthylendichlorid aus 1.0 *M* Chloridlösung sehr viel kleiner. Obwohl sie mit der Konzentration steigt, erreicht sie nicht 90%, bis die Chloridkonzentration 4 *M* übersteigt. Durch Veränderung solcher Parameter wie die Konzentrationen von Cl^-, $NR_4^+Cl^-$ und dem Gesamtgehalt an Kupfer im System kann gezeigt werden, dass das Verteilungsgleichgewicht am besten unter den Annahme erklärt wird, dass zusätzlich zu mononuklearen Komplexen in der wässrigen Phase auch binukleare Komplexe ($Cu_2Cl_6^{2-}$, $Cu_2Cl_7^{3-}$) vorliegen, während nur mononukleare Spezies ($NR_4^+CuCl_3^-$, $(NR_4^+)_2CuCl_4^{2-}$) extrahiert werden.

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SOLVENT EXTRACTION SEPARATIONS WITH BPHA. APPLICATIONS TO THE MICROANALYSIS OF NIOBIUM AND ZIRCONIUM IN URANIUM*

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N-Benzoyl-N-phenylhydroxylamine (BPHA), a cupferron analog, is used extensively as an organic precipitant[1] and solvent extractant[2] since it reacts with several metals to form stable chelates that are soluble in organic solvents. BPHA, however, is superior to cupferron because it exhibits good thermal and chemical stability, and it forms chelates with several metals in concentrated acids. In strong acids, BPHA becomes more selective and reacts only with some transition elements. Consequently, the solvent extraction from uranium of 52 elements with BPHA–chloroform–hydrochloric acid was thoroughly investigated; particular emphasis was devoted to extraction of easily hydrolyzed transition metals.

ALIMARIN AND PETRUKHIN[3] investigated the extraction of the benzoylphenylhydroxaminates of niobium, tantalum, titanium, vanadium, and zirconium from strong sulfuric acid. NABIVANETS[4] found that extraction of easily hydrolyzed elements at pH >0 is often suppressed by formation of polymeric or colloidal particles; therefore, extraction from concentrated acids is desirable. LYLE AND SHENDRIKAR[5] investigated extraction of antimony and tin from strong hydrochloric acid or perchloric acid with BPHA. RYAN[6] extracted vanadium from strong hydrochloric acid with BPHA.

During the development of colorimetric procedures for vanadium and titanium in uranium[7], it was found that the extraction of their BPHA chelates from hydrochloric acid was superior to sulfuric acid. Studies of the extraction characteristics of niobium, tantalum, and zirconium with the BPHA–chloroform–hydrochloric acid system[8], therefore, were extended to include a total of 52 elements. From these studies, a method was developed for the quantitative separation of hafnium, niobium, tantalum, titanium, vanadium, and zirconium from uranium. After the elements have been separated, they can be determined by chemical or instrumental methods.

EXPERIMENTAL

A preliminary survey was made of extraction characteristics of elements in Groups I through VIII, the rare earths, and the actinides with the BPHA–chloroform–hydrochloric acid system. Extraction efficiencies of the elements, grouped into 3 categories, are shown in Fig. 1.

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For the extraction studies, a sulfate residue of 0.5 or 1 mg of each element was dissolved in 25 ml of hydrochloric acid of the desired normality, and the solution was transferred to a separatory funnel. Twenty-five ml of 0.5% BPHA in chloroform was added to the funnel, and the two solutions were contacted for 15 min. After a 5-min phase separation, the organic extract and aqueous raffinate were drained into separate platinum dishes and evaporated to dryness. The residues were digested with nitric and sulfuric acids, and fumed to dryness. The residues were ignited at 500° for 20 min, and the oxides were analyzed for their metal contents by atomic absorption, colorimetric, or radiometric methods. Whenever possible, raffinates or extracts were analyzed directly. Matrix effects of raffinates analyzed directly by atomic absorption procedures[9] were controlled by analyzing portions of the standard solutions along with the reacted solutions. Colorimetry was used extensively for analyses of oxides dissolved in acids or fused with potassium pyrosulfate. For the chloroform extracts of titanium and vanadium, the evaporation step was omitted and the colors were measured directly[8]. Radiometric methods were applied for the actinides, ruthenium, tantalum and technetium. Both organic extracts and aqueous raffinates were analyzed directly after appropriate treatment.

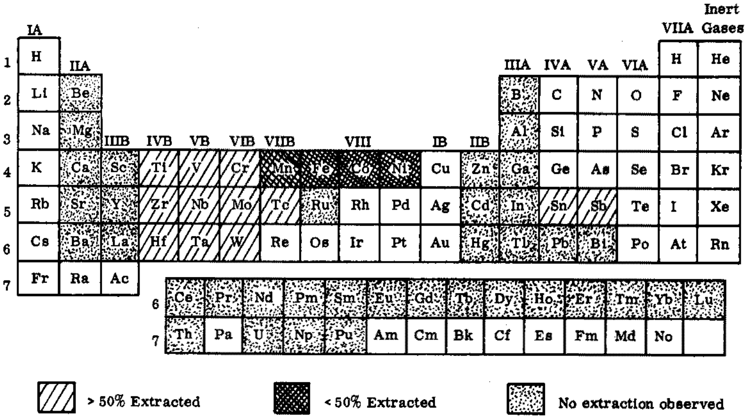


Fig. 1. Solvent extraction of elements with BPHA–chloroform–hydrochloric acid.

EXTRACTION STUDIES

Extraction time

Contact time affects extraction of many metals, especially those that hydrolyze easily. Nearly all the elements that could be extracted reached equilibrium after a 5-min contact period. Nb and Ta were exceptions and required a 10-min contact period to reach equilibrium. For this study, however, test solutions were contacted for 15 min to insure that equilibrium conditions had been reached.

Solution age

Solution age adversely affects extractions of several elements because some hydrolyze to form chemically inert polymeric or colloidal species and others change valence. When freshly prepared 10 N hydrochloric acid solutions of niobium or tantalum were allowed to stand for 48 h, extraction efficiency decreased markedly from 99% to 93% for niobium and to 84% for tantalum. Chromium and vanadium are partially reduced in strong hydrochloric acid; consequently, they are extracted incompletely from aged solutions. Other elements studied were not affected by solution age because of their stability in strong hydrochloric acid. However, all aliquots of stock solutions were fumed with sulfuric acid immediately before the extraction procedure. That this treatment was sufficient to produce chemically active species was verified by extraction studies with niobium and tantalum. Effects of solution age also were observed in color development of easily hydrolyzed metal ions with chromogenic reagents, and the sulfuric acid pretreatment was used before colorimetric analyses for these elements.

Valence state

Valence state affects the extraction characteristics of some elements with BPHA–chloroform–hydrochloric acid system. In general, BPHA reacts with elements only in their highest valence state to form extractable chelates, but only those elements which yield stable ions of more than one valence in hydrochloric acid were studied. In most cases, oxidation–reduction potentials of BPHA controlled the valence state of the element. BPHA reduces strong oxidizing ions such as chromate and permanganate, and oxidizes others like Fe^{2+}. The effects of valence were studied for the extraction of antimony, chromium, iron, manganese, molybdenum, neptunium, plutonium, technetium, tin, vanadium, and uranium. Only antimony was extracted at more than one valence, and its extraction characteristics are shown in Fig. 7.

Distribution of BPHA

The distribution of BPHA between chloroform and hydrochloric acid phases is shown in Fig. 2. The solubility of the reagent in the aqueous phase increases as the hydrochloric acid concentration is increased. This higher concentration of the BPHA in the aqueous phase favors chelate formation and stabilizes the metal ions in the hydrochloric acid. Stabilization could explain the higher extraction efficiencies observed for the transition metals of Groups IV, V, and VI-B.

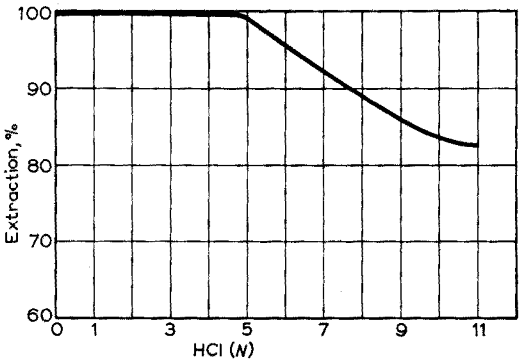


Fig. 2. Distribution of BPHA between chloroform and HCl phases.

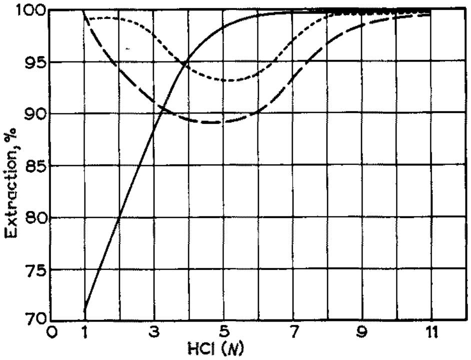
Hydrochloric acid concentration

The effect of hydrochloric acid concentration on the extraction of metals with the BPHA–chloroform system was evaluated for concentrations of hydrochloric acid ranging from 1 to 11 *N*. A single 15-min contact was used.

Extraction characteristics of Group IV-B elements (titanium, zirconium, and hafnium) are shown in Fig. 3. Chloro-complex formation could explain the observed minima for hafnium and zirconium extraction at 5 *N* hydrochloric acid.

Extraction characteristics for Group V-B elements (vanadium, niobium, and tantalum) are illustrated in Fig. 4. Vanadium(IV) is not extracted from hydrochloric acid at any concentration; thus vanadium must be oxidized to vanadium(V) immediately before extraction to ensure complete separation. At the tantalum extraction minima, precipitates developed at lower acid concentrations and were observed at the phase interface. Formation of stable chloro-complexes in 3 *N* and 7 *N* hydrochloric acid could account for the observed extraction minima.

Figure 5 shows the extraction characteristics of Group VI-B elements (chromium, molybdenum, and tungsten). Chromium(III) is not extracted from 1 to 11 *N* hydrochloric acid, and reduction of Cr(VI) to Cr(III) in strong hydrochloric acid causes



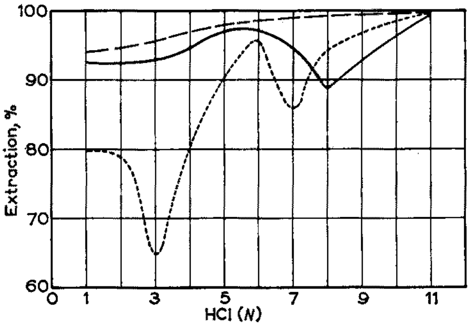
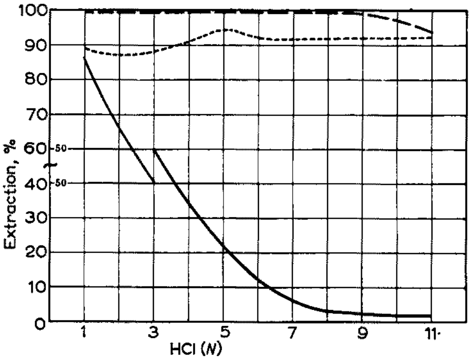


Fig. 3. Extraction of group IV-B elements. Titanium —; hafnium — —; zirconium - -.

Fig. 4. Extraction of group V-B elements. Vanadium —; niobium — —; tantalum - -; vanadium(IV): no extraction.



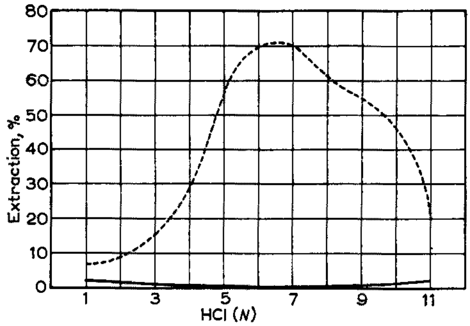


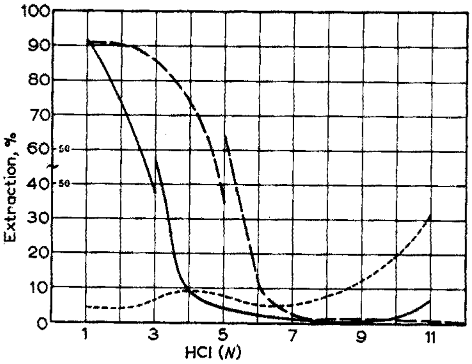
Fig. 5. Extraction of Group VI-B elements. Chromium(VI) —; molybdenum(VI) — —; tungsten - -; chromium(III): no extraction.

Fig. 6. Extraction of group VII-B elements. Mn —; Tc - -.

the sharp decrease in Cr(VI) extraction efficiency with increasing hydrochloric acid concentration. For tungsten, a slight extraction peak is observed at 5 *N* hydrochloric acid. In milligram quantities, tungsten partially precipitated in the extraction system if the hydrochloric acid concentration was below 7 *N*.

Extraction of the Group VII-B elements (manganese and technetium) is shown in Fig. 6. Manganese(II) extraction is negligible from 1 through 11 *N* hydrochloric acid with only 1 to 2% extracted. Manganese(VII) as permanganate was quickly reduced in the BPHA–chloroform–HCl extraction system; consequently, no extraction was observed. For technetium, a peak extraction efficiency of 70% was observed from 6.5 *N* hydrochloric acid. The valency state of technetium during the extraction was not determined although technetium(VII) was initially introduced into the extraction system. Technetium probably is extracted in a reduced form, but a reason for the vast differences between the extraction of manganese and technetium is not evident.

Figure 7 shows the extraction of the Group IV-A and V-A elements (antimony and tin). About 90% of antimony(III) is extracted from 1 *N* hydrochloric acid, but extraction efficiencies decrease as the acid concentration increases. A complex formation between antimony and BPHA apparently does not occur in strong hydrochloric acid. Tin(IV) extraction (~93% from 1 *N* HCl) is similar to that of antimony(III). The extraction efficiency decreased sharply to negligible values in 7 through 11 *N* hydrochloric acid.



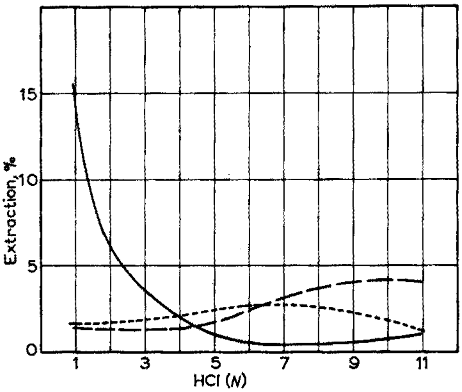


Fig. 7. Extraction of group IV-A and V-A elements. Sb(III) —; Sb(V) – –; Sn(IV) —— —; Bi and Pb: no extraction.

Fig. 8. Extraction of group VIII elements. Fe —; Co —— —; Ni – –.

Extraction of the Group VIII elements (iron, cobalt, and nickel) is shown in Fig. 8. Only iron(III) is significantly extracted, and its extraction occurs only at low concentrations of acid.

The actinides (thorium, uranium, neptunium, and plutonium) in any valence state, are not extracted into BPHA–chloroform from 1 through 11 *N* hydrochloric acid. Distribution ratios were approximately 10^{-6} for uranium and 10^{-4} for neptunium and plutonium for a single extraction. These values represent significant decontamination factors, and the extraction system probably can be used for radiochemical separations.

By means of this extraction system, it was possible to develop a procedure for separating niobium, tantalum, titanium, and zirconium from uranium[8]. Two established colorimetric procedures for niobium[10,11] and zirconium[12] were evaluated and applied to the microanalysis of these separated elements. Interferences in both colorimetric methods include only those elements which are extracted along with niobium and zirconium. Tantalum interferes more seriously than reported, but a ratio of 1:3 (tantalum to niobium) can be tolerated. Hafnium interferes with the analysis of zirconium, but a ratio of 1:5 (hafnium to zirconium) can be tolerated.

Apparatus

Beckman Model DU spectrophotometer or equivalent, complete with 1- and 5-cm cells.

Reagents

All chemicals were reagent grade.

Benzoylphenylhydroxylamine, 0.5% (w/v) (Eastman Organic Chemicals No. 7297). Dissolve 5 g of BPHA in 1.0 l of chloroform.

Arsenazo III, 0.1% (w/v) (J. T. Baker Chemical Company No. B-577). Dissolve 100 mg in 100 ml of water, made basic with 0.5 ml of 5% sodium carbonate.

4-(2-Pyridylazo)resorcinol, 0.1% (w/v) (Eastman Organic Chemicals No. 8706). Dissolve 100 mg in 100 ml of methanol.

Procedure

Dissolve 1.0–5.0 g of uranium sample with 8 *N* nitric acid in a 200-ml platinum dish. Add 10 ml of concentrated sulfuric acid and 10 ml of concentrated hydrofluoric acid, and thoroughly mix the contents. Fume to dryness to expel nitrate and fluoride ions. Dissolve the residue with 30 ml of 10 *N* hydrochloric acid, and transfer the solution to a separatory funnel using 10 *N* hydrochloric acid as a rinse. Add 20 ml of 0.5% BPHA–chloroform solution to the separatory funnel. Stopper the funnel and shake it for 10 min. Allow the phases to separate for 5 min, and drain the chloroform layer into a second 125-ml separatory funnel. Repeat the extraction with 15 ml of BPHA solution, shaking the funnel for 5 min, and combine the two extracts. Wash the extract twice for 30 sec with 25 ml of 10 *N* hydrochloric acid. Drain the extract into a platinum crucible and evaporate to dryness. Add 2 ml of 5 *N* nitric acid to the residue, and evaporate it to dryness over a water bath. Repeat the nitric acid step twice with concentrated nitric acid. Ignite the residue at 600° for 15 min.

Niobium. Dissolve the residue with 1 ml of concentrated hydrofluoric acid and 1 ml of conc. sulfuric acid. Add 80 mg of potassium pyrosulfate to the solution, and fume to dryness. Dissolve the residue with 10 ml of 0.05 *M* ammonium tartrate, and transfer the solution to a 50-ml volumetric flask. Rinse the dish with 38.5 ml of 1 *N* hydrochloric acid, and add the rinsings to the flask. Add 0.5 ml of 0.025 *M* EDTA to the solution, and mix the contents of the flask. Add 1 ml of 0.1% 4-(2-pyridylazo)resorcinol solution to the flask, dilute to volume with water, stopper, and shake. After 1 h, measure the optical density of the solution in 5-cm cells at 540 nm against a blank prepared with the same reagents. Determine the niobium content from a calibration curve established with uranium standards.

Zirconium. Dissolve the residue with 1 ml of concentrated hydrofluoric acid and 2 ml of concentrated sulfuric acid. Fume to approximately 0.1 ml. Dilute the solution with 10 ml of concentrated hydrochloric acid, and transfer it to a 50-ml volumetric flask. Rinse the dish with 10 *N* hydrochloric acid, and after adding the rinsings to the flask, dilute the solution to about 45 ml with 10 *N* hydrochloric acid and 4 ml of 0.1% arsenazo III. Dilute to volume with 10 *N* hydrochloric acid, stopper, and shake. Measure the optical density of the solution in 1-cm cells at 665 nm against a blank prepared with the same reagents. Determine the zirconium content from a calibration curve established with uranium standards.

Analysis of uranium standards

Uranium oxides spiked with niobium and zirconium at two levels (2.0 μg and 100 μg) were analyzed by the procedure. At the 2.0-μg level, analyses were made on separate extracts, and at the 100-μg level, both niobium and zirconium were analyzed on the same extract. Results of standard analyses are shown in Table I.

TABLE I

ANALYSES FOR NIOBIUM AND ZIRCONIUM IN URANIUM

2.0 μg niobium Found	*2.0 μg zirconium Found*	*100 μg niobium Found*	*100 μg zirconium Found*
1.9	1.8	93.3	98.7
2.0	2.1	104	97.5
2.1	2.0	93.3	99.9
2.1	1.7	96.0	99.3
1.8	—	99.5	97.6
L.E./det 18%	L.E./det 30%	100	93.3
Bias 1.0±1.8%	Bias 5.0±14.5%	98.5	98.8
		101	99.6
		L.E./det±9.0%	L.E./det±5.1%
		Bias −1.8±3.1%	Bias −1.9±1.8%

SUMMARY

A detailed study of the benzoylphenylhydroxylamine (BPHA)–chloroform–hydrochloric acid solvent extraction system with 52 elements is described with emphasis placed on extraction of the easily hydrolyzed transition metals from strong hydrochloric acid. From this study, a separation procedure for hafnium, niobium, tantalum, titanium, vanadium, and zirconium from uranium was developed, and procedures are given for the microanalysis of niobium and zirconium in uranium. Niobium and zirconium are separated from uranium by extraction into BPHA–chloroform from 10 *N* HCl. The separated elements are then measured colorimetrically as the niobium–4-(2-pyridylazo)resorcinol and zirconium–arsenazo III complexes. The limit of detection is 1 μg/g U.

RÉSUMÉ

Une étude détaillée est effectuée sur l'extraction dans un solvant du système benzoylphénylhydroxylamine (BPHA)–chloroforme–acide chlorhydrique avec 52 éléments, spécialement sur l'extraction de métaux de transition facilement hydrolysables en milieu acide chlorhydrique concentré. On propose une séparation de l'hafnium, du niobium, du tantale, du titane, du vanadium et du zirconium d'avec l'uranium, et un microdosage du niobium et du zirconium dans l'uranium. Niobium et zirconium sont séparés d'avec l'uranium par extraction au moyen du mélange BPHA–chloroforme en milieu HCl 10 *N*. Les éléments séparés sont ensuite dosés colorimétriquement sous forme de complexes niobium–4-(2-pyridylazo) résorcinol et zirconium–arsenazo III. La limite de détection est de 1 μg/g U.

ZUSAMMENFASSUNG

Es wird für 52 Elemente die Flüssigextraktion mit Benzoylphenylhydroxylamin (BPHA) in Chloroform aus salzsauren Lösungen untersucht; dabei wird die Extraktion der leicht hydrolisierbaren Übergangsmetalle aus starker Salzsäure besonders berücksichtigt. Aus diesen Untersuchungen wurde ein Verfahren zur Abtrennung von Hafnium, Niob, Tantal, Titan, Vanadin und Zirkonium von Uran entwickelt. Daneben wird eine Methode für die Mikroanalyse von Niob und Zirkonium in Uran angegeben. Dazu werden Niob und Zirkonium mit BPHA aus 10 *N* HCl vom Uran abgetrennt und anschliessend das Niob mit 2-Pyridylazoresorcinol und das Zirkonium mit Arsenazo III kolorimetrisch bestimmt. Die Nachweisgrenze beträgt 1 μg/g U.

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EINE NEUE PHOTOMETRISCHE BESTIMMUNGSMETHODE VON 1,1-DIALKYLHYDRAZINEN

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(Eingegangen den 23. Dezember, 1967)

Die verbreitete Verwendung von 1,1-Dimethylhydrazin und anderen unsymmetrischen Dialkylhydrazinen, besonders als Raketentreibstoffe, hat zahlreiche biochemische, pharmakologische und toxikologische Untersuchungen dieser Stoffklasse veranlasst[1]. 1,1-Dimethylhydrazin ist nach eigenen Untersuchungen an Ratten nur sehr schwach carcinogen[2]. An Mäusen bewirkt es eine signifikante Zunahme der Lungenadenomrate[3].

Für weitere Untersuchungen sind empfindliche analytische Nachweismethoden für diese Stoffklasse notwendig. NEURATH *et al.*[4] bestimmen qualitativ 1,1-Dialkylhydrazine als 5-Nitro-2-hydroxy-benzal-Derivate. 1,1-Dimethylhydrazin wird nach BAILEY UND MEDWICK[5] als Salicylaldehyd-Hydrazon photometrisch, titrimetrisch[6] bzw. polarographisch[7] bestimmt. SUTTON[8] beschreibt die oxydative Abspaltung von Formaldehyd aus 1,1-Dimethylhydrazin als Grundlage einer colorimetrischen Bestimmungsmethode. Diese Methode ist langwierig und umständlich. Im Anschluss an unsere Arbeiten zur Analytik von Azoalkanen und 1,2-Dialkylhydrazinen fanden wir[9], dass die für symmetrische Dialkylhydrazine ausgearbeitete Methode auch auf unsymmetrische Dialkylhydrazine ausgedehnt werden kann. Sie beruht auf der oxydativen Abspaltung eines Alkylrestes als Aldehyd durch Quecksilber(II)-Sulfat in schwefelsaurer Lösung und colorimetrischen Bestimmung des freigesetzten Aldehyds.

EXPERIMENTELLES

1,1-Dimethylhydrazin war Handelsprodukt (Fluka) und wurde vor Gebrauch frisch destilliert. Die anderen 1,1-Dialkylhydrazine stellten wir aus den entsprechenden Nitrosaminen durch Reduktion mit Lithium-Aluminiumhydrid her[10]. Trimethyl- und Tetramethylhydrazin[11], Tetramethyltetrazen[12] und 1-Methyl-1-formylhydrazin[13] wurden nach Literaturvorschriften synthetisiert.

Die anderen Reagentien entsprachen p.a.-Qualität oder wurden durch Kristallisation gereinigt.

Für die photometrischen Untersuchungen verwandten wir das "Beckman-DB"-Spektralphotometer.

Analysenmethode

Eine wässrige Lösung von 0.2 bis 2 μMol des zu bestimmenden unsymmetrischen Hydrazins als freie Base, Hydrochlorid oder Sulfat wird mit 4 ml einer 0.1%igen Quecksilber(II)-Sulfat-Lösung in 10%iger Schwefelsäure versetzt und nach Verdünnen auf 25 ml in einen 50-ml Destillationskolben gegeben. Der Kolben wird an eine Mikrodestillations-Apparatur angeschlossen. Für die Formaldehyd-Bestimmung destilliert man 15 ml und zur Bestimmung der übrigen Aldehyde 10 ml in eine graduierte, mit Eiswasser gekühlte Vorlage. Aliquote Anteile des Destillats werden pipettiert und die Aldehyd-Konzentration colorimetrisch bestimmt.

Formaldehyd-Bestimmung erfolgt nach der Chromotropsäure-Methode nach MACFADYEN[14], Acetaldehyd wird mit 4-Hydroxy-diphenyl nach STOTZ[15] und Propion- bzw. Butyraldehyd mit 3-Methyl-2-benzthiazolonhydrazon nach SAWICKI *et al.*[16] gemessen. Für genauere Durchführungsangaben vergl. PREUSSMANN *et al.*[9].

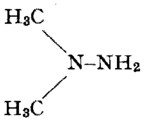
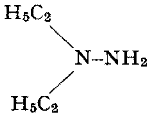
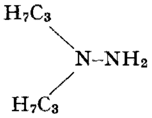
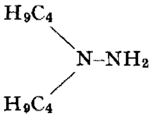
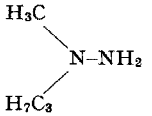
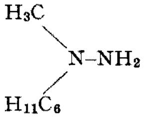
ERGEBNISSE UND DISKUSSION

Die Untersuchungen ergaben, dass unter den angegebenen Reaktionsbedin-

TABELLE I

BILDUNG VON OXOVERBINDUNGEN AUS 1,1-DIALKYLHYDRAZINEN NACH OXYDATION MIT $HgSO_4$ IN SCHWEFELSAURER LÖSUNG

(Ausbeuten beziehen sich auf die Freisetzung *einer* Alkylgruppe (= 100%))

1,1-Dialkylhydrazin	*Formel*	*Gebildeter Aldehyd*	*Ausbeute (%)*
Dimethylhydrazin	 $\substack{H_3C\\ H_3C}{>}N{-}NH_2$	Formaldehyd	100±2
Diäthylhydrazin	 $\substack{H_5C_2\\ H_5C_2}{>}N{-}NH_2$	Acetaldehyd	100±2
Dipropylhydrazin	 $\substack{H_7C_3\\ H_7C_3}{>}N{-}NH_2$	Propionaldehyd	100±3
Dibutylhydrazin	 $\substack{H_9C_4\\ H_9C_4}{>}N{-}NH_2$	Butyraldehyd	100±3
Methylpropylhydrazin	 $\substack{H_3C\\ H_7C_3}{>}N{-}NH_2$	Formaldehyd Propionaldehyd	39±2 61±3
Methylcyclohexylhydrazin	 $\substack{H_3C\\ H_{11}C_6}{>}N{-}NH_2$	Formaldehyd	81±2

gungen quantitativ I Äquivalent Aldehyd pro Mol I,I-Dialkylhydrazin abgespalten wird. Die Ergebnisse sind in Tabelle I zusammengefasst. Bei I-Methyl-I-propylhydrazin werden Propionaldehyd und Formaldehyd nebeneinander erhalten, die Summe beider Konzentrationen ergibt 100% = I Äquivalent Gesamtaldehyd. Bei Methylcyclohexylhydrazin werden reproduzierbar 81% der theoretisch erwarteten Formaldehydmenge gefunden.

Die Höhe der erhaltenen Extinktionen steht in direkter Korrelation mit der Menge des eingesetzten Hydrazins, wie an drei Beispielen in Tabelle II dargestellt ist. Das Lambert–Beer'sche Gesetz ist somit erfüllt, es werden für Dialkylhydrazin-Konzentrationen von 0.2 bis 2 μMol lineare Eichkurven erhalten, die die quantitative Bestimmung der Stoffklasse erlauben.

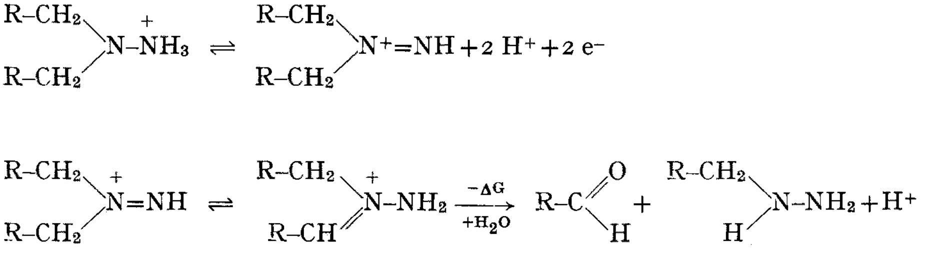
TABELLE II

EXTINKTIONEN IN ABHÄNGIGKEIT VON DER KONZENTRATION AN I,I-DIALKYLHYDRAZINEN

I,I-Dimethylhydrazin		*I,I-Diäthylhydrazin*		*I,I-Dibutylhydrazin*	
Einwaage (μMol)	*Ext.*	*Einwaage (μMol)*	*Ext.*	*Einwaage (μMol)*	*Ext.*
0.2	0.075	0.1	0.060	0.2	0.065
0.4	0.150	0.2	0.125	0.4	0.125
0.8	0.300	0.4	0.255	0.8	0.250
1.6	0.595	0.8	0.515	1.6	0.495

Die untere Nachweisgrenze liegt bei 0.1–0.2 μMol I,I-Dialkylhydrazin und kann, falls notwendig, durch Anwendung empfindlicherer Aldehyd-Bestimmungsmethoden verbessert werden.

Für den Mechanismus der oxydativen Dealkylierung kommt wohl der von McBride[12] beschriebene Mechanismus der Oxydation von Hydrazinen in saurem Medium in Frage:



$$(R\text{–}CH_2)_2\overset{+}{N}\text{–}NH_3 \rightleftharpoons (R\text{–}CH_2)_2N^+\text{=}NH + 2\,H^+ + 2\,e^-$$

$$(R\text{–}CH_2)_2\overset{+}{N}\text{=}NH \rightleftharpoons (R\text{–}CH_2)(R\text{–}CH\text{=})\overset{+}{N}\text{–}NH_2 \xrightarrow[+H_2O]{-\Delta G} R\text{–}C\overset{O}{\underset{H}{\lessgtr}} + (R\text{–}CH_2)(H)N\text{–}NH_2 + H^+$$

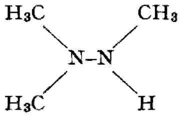
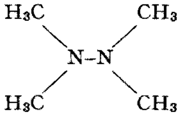
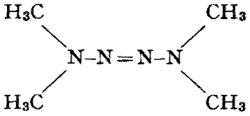
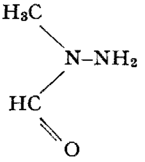
Eine weitere Stütze für den vorgeschlagenen Mechanismus ist neben der quantitativen Bildung des Aldehyds auch der Nachweis des entstandenen Monoalkylhydrazins als *p*-Nitrobenzaldehydhydrazon. Es konnte durch Schmelzpunkt und IR-Spektrum identifiziert werden.

Die Oxydation verläuft nicht über Tetraalkyltetrazene als Zwischenprodukte. Wie gezeigt, spalten I,I-Dialkylhydrazine einen Alkylrest als Aldehyd ab, Tetramethyltetrazen jedoch ebenfalls nur 1 Methyl-Rest als Formaldehyd, wie in Tabelle III gezeigt. Der saure Zerfall von Tetraalkyltetrazenen ist bekannt[17]. Dabei entstehen jedoch Dialkylamin, Monoalkylamin, Aldehyd und Stickstoff, während in vorliegendem Fall stets Aldehyd und Monoalkylhydrazin gebildet werden.

Die Untersuchung der Spezifität der Reaktion ergab, dass dabei auch höher alkylierte Hydrazine oxydativ gespalten werden. Wie aus Tabelle III ersichtlich, gibt Trimethylhydrazin 2 Äquivalente Formaldehyd ab. Die Reaktion ist reproduzierbar und daher zur quantitativen Bestimmung von Trialkylhydrazinen geeignet. Tetramethylhydrazin ergibt schwankende Formaldehydabspaltungen, die aber nur zwischen 0.1 und 0.3 Äquivalenten liegen. 1-Formyl-1-methylhydrazin ist unter den Versuchsbedingungen nicht spaltbar.

TABELLE III

BILDUNG VON FORMALDEHYD AUS METHYLHYDRAZIN-DERIVATEN NACH OXYDATION MIT $HgSO_4$ IN SCHWEFELSAURER LÖSUNG

Name	*Formel*	*Gebildeter Aldehyd*	*Ausbeute (%)*
Trimethylhydrazin		Formaldehyd	200 (2 Mol)
Tetramethylhydrazin		Formaldehyd	30 (0.3 Mol)
Tetramethyltetrazen		Formaldehyd	100 (1 Mol)
1-Formyl-1-methyl-hydrazin		Formaldehyd	0

Aldehyd-Abspaltungen, die die Spezifität der analytischen Reaktion stören, ergeben aliphatische Azo- und Hydrazo-Verbindungen[9] sowie Aldehyd-Derivate wie Acetale, Aminale, Hydrazone, Schiff'sche und Mannich-Basen usw. Eine Unterscheidung zwischen 1,1- und 1,2-Dialkylhydrazinen ist leicht möglich durch die Fähigkeit der unsymmetrischen Dialkylhydrazine zur Hydrazon-Bildung, z.B. nach BAILEY UND MEDWICK[5] mit Salicylaldehyd. 1,2-Dialkylhydrazine reagieren hier nicht.

Versuche, die beschriebene Reaktion auf die Analyse von organischen N-Nitroso-Verbindungen, die potente Carcinogene sind[2], nach geeigneter quantitativer Reduktion auszudehnen, sind geplant.

ZUSAMMENFASSUNG

1,1-Dialkylhydrazine spalten nach Oxydation mit Quecksilber(II)-Sulfat in schwefelsaurem Medium einen Alkylrest als Aldehyd ab und können durch photometrische Bestimmung des freigesetzten Aldehyds quantitativ erfasst werden. Die untere Nachweisgrenze liegt bei 0.1 bis 0.2 μMol 1,1-Dialkylhydrazin pro Ansatz. Anwendbarkeit und Störfaktoren werden diskutiert.

SUMMARY

1,1-Dialkylhydrazines after oxidation with mercury(II) sulfate in aqueous sulfuric acid split off one alkyl group as aldehyde and this reaction can be utilized for quantitative determination of 1,1-dialkylhydrazines by photometric estimation of the released aldehyde. The lower detection limit is 0.1–0.2 μmoles 1,1-dialkylhydrazine. The applicability and specificity of the analytical method are discussed.

RÉSUMÉ

Les 1,1-dialkylhydrazines après oxydation à l'aide de sulfate de mercure(II) en milieu acide sulfurique libèrent un groupe alkyle sous forme d'aldéhyde. Cette réaction peut être utilisée pour le dosage quantitatif des 1,1-dialkylhydrazines par photométrie de l'aldéhyde libérée. La limite inférieure est de 0.1–0.2 μmoles 1,1-dialkylhydrazine. Les possibilités d'application et la spécificité de la méthode sont examinées.

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DETERMINATION OF URANIUM IN PLUTONIUM BY DIFFERENTIAL LINEAR SWEEP OSCILLOGRAPHIC POLAROGRAPHY*

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(Received December 21st, 1967)

A polarographic method for the determination of uranium in the presence of plutonium was required to supplement the method recently developed in this laboratory whose lower limit of detection was 225 p.p.m.[1].

The polarography of uranium was first reported by HERASYMENKO[2]. STRUBL[3] used hydroxylamine hydrochloride which served not only as the supporting electrolyte but also as a reducing and holding reductant. Several other electrolytes have also been suggested[4–6] for the polarographic determination of uranium. This report describes a method that uses differential oscillographic polarography in a hydroxylamine hydrochloride medium.

EXPERIMENTAL

Apparatus

A Davis Differential Cathode Ray Polarotrace, Type A-1660 (Southern Analytical Ltd., Camberley, England) equipped with an electrode stand and constant temperature water bath, was used. This instrument has a voltage sweep rate of 0.25 V per sec, a sweep time of 2 sec, and a delay period of 5 sec. All polarographic measurements were made at 25.0 ± 0.1°. A polarographic cell employing a mercury pool anode was used throughout the investigation. The differential mode of operation was used with the second cell containing a reagent blank.

Dual 15-cm long capillaries were used to obtain all measurements. The $m^{2/3}t^{1/6}$ value, obtained at zero voltage in 2.0 M hydroxylamine hydrochloride, was 2.02.

Reagents

Stock solutions of uranyl chloride were prepared from U_3O_8 standard sample 950a (U.S. National Bureau of Standards).

All other reagents were analytical grade and were prepared in the normal manner.

Safety precautions

Extreme care must be exercised in the handling of plutonium because of its toxicity. All work with plutonium metal was performed in a glove box. The solutions containing plutonium were analyzed polarographically in a well-ventilated hood.

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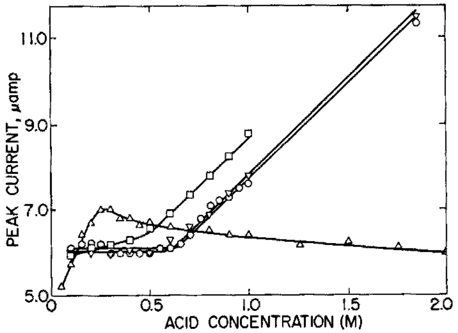
* Work performed under U. S. Atomic Energy Commission contract AT(29-1)-1106.

STUDY OF VARIABLES

Effect of various acids

Polarograms were obtained in hydrochloric, nitric, perchloric, and sulfuric acids to determine the effect of each of the acids on the peak currents of uranium. The solutions used for the investigation were $1.00 \cdot 10^{-3}$ *M* in uranium(VI), 2.0 *M* in hydroxylamine hydrochloride and had varying concentrations of the acids. Hydrochloric and perchloric acids had no effect on the peak currents until the acid concentrations exceeded 0.6 *M*. Above 0.6 *M* the peak currents increased as the acid concentrations increased (Fig. 1). This increase in peak currents indicated an increase in the rate of disproportionation of uranium(V)[7,8] formed at the electrode during reduction.

As the nitric acid concentration is increased, the peak current also increases (Fig. 1). Below a concentration of 0.4 *M*, the peak current increases gradually, but above this acid concentration, the peak current increases quite rapidly. The increase in the peak current is again an indication that the rate of disproportionation of uranium(V) has increased.



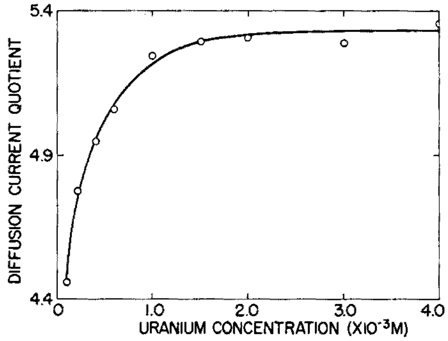


Fig. 1. Effect of acid concentration on the uranium peak current. $1.00 \cdot 10^{-3}$ *M* uranium and 2.0 *M* $NH_2OH \cdot HCl$. (○) HCl; (□) HNO_3; (△) H_2SO_4; (▽) $HClO_4$.

Fig. 2. Effect of sulfuric acid on the uranium diffusion current quotient. 2.0 *M* $NH_2OH \cdot HCl$ and 0.2 *M* H_2SO_4.

Figure 1 also shows the variation of the peak current with the change in sulfuric acid concentration. In the concentration range 0.25–0.30 *M*, the peak current is constant. In the acid concentration range 0.05–0.25 *M*, however, the peak current increases with an increase of acid concentration. This increase in peak current can be explained as an increase in the rate of disproportionation of uranium(V).

Above an acid concentration of 0.30 *M*, the peak current decreases with the increase of acid concentration. To determine what effect a constant concentration of sulfuric acid may have on the diffusion current quotient[9], solutions containing 0.2 *M* sulfuric acid, 2.0 *M* hydroxylamine hydrochloride, and varying concentrations of uranium were prepared and polarographed. At a uranium concentration of $1.00 \cdot 10^{-3}$ *M* and above, the diffusion current quotient was constant, but below this uranium concentration the diffusion current quotient decreased with a decrease of the uranium concentration

(Fig. 2). This indicates that this system does not obey Ilkovic's equation[10]; that is, below a uranium concentration of $1.00 \cdot 10^{-3}$ *M*, the peak current is not proportional to the uranium concentration. The effect of varying the sulfuric acid concentration with a constant uranium(VI) concentration, and of varying the uranium(VI) concentration with a constant sulfuric acid concentration is shown in Table I. It can be seen that when the ratio of the sulfuric acid concentration to the uranium(VI) concentration exceeds 300, the peak current began to decrease. This would indicate the possible formation of other uranyl sulfate ion complexes.

TABLE I

SULFURIC ACID CONCENTRATION–URANIUM CONCENTRATION RATIO

1.00 · 10⁻³ M uranium		*Peak current*	*0.20 M sulfuric acid*		*Peak current*
H_2SO_4 concn. (moles/l)	*$H_2SO_4/U(VI)$ (moles/l/moles/l) concn.*		*UO_2^{2+} concn. (moles/l)*	*$H_2SO_4/U(VI)$ (moles/l/moles/l) concn.*	
0.05	50	Increasing	$4.0 \cdot 10^{-3}$	50	Constant
0.10	100	Increasing	$2.0 \cdot 10^{-3}$	100	Constant
0.15	150	Increasing	$1.0 \cdot 10^{-3}$	200	Constant
0.20	200	Increasing	$6.0 \cdot 10^{-4}$	333	Decreasing
0.25	250	Constant	$4.0 \cdot 10^{-4}$	500	Decreasing
0.30	300	Constant	$2.0 \cdot 10^{-4}$	1000	Decreasing
0.35	350	Decreasing	$1.0 \cdot 10^{-4}$	2000	Decreasing
0.40	400	Decreasing			
0.45	450	Decreasing			
0.50	500	Decreasing			

Effect of various salts

Since the addition of hydrochloric, perchloric, nitric, and sulfuric acids had an adverse effect on the uranium peak current at some concentrations of the acids, it was desirable to know what effect the addition of the salts of these acids would have on the uranium peak current. Polarograms were traced of solutions which were $1.00 \cdot 10^{-3}$ *M* in uranium, 2.0 *M* in hydroxylamine hydrochloride and contained various concentrations of the salts ranging from 0.05 to 2.0 *M*. The salts were added as the sodium salts. The chloride and perchlorate salts had no effect on peak currents of uranium, whereas the nitrate and sulfate salts caused low results. The average recoveries were 90.5% and 95.5%, respectively.

Reversibility

Solutions containing $1.00 \cdot 10^{-3}$ *M* uranium and 2.0 *M* hydroxylamine hydrochloride were prepared and polarographed to determine if the uranium reduction is reversible. Excellent peaks were obtained in the forward and reverse sweeps of the Polarotrace by using the recommended procedure for testing for reversibility[11]. To test further the uranium reduction for reversibility, a cyclic scan was made which produce peaks with the same potential. These results indicate that the electrode reduction is reversible.

DETERMINATION OF URANIUM IN PLUTONIUM

It was shown above that the presence of hydrochloric or perchloric acids will not affect the uranium(VI) peak current if the acid concentration is 0.6 *M* or less. The presence of nitric or sulfuric acids, however, could cause a variation in the peak current if the acid concentration were not controlled closely. It was also shown that the presence of nitrate and/or sulfate salts would be detrimental to the determination of uranium. These factors were considered for the following procedure.

Sample preparation

The plutonium metal sample (2 g) is weighed directly into a tared 10-ml volumetric flask, and dissolved by cautiously adding 5 ml of 6 *M* hydrochloric acid. In the methods usually used for dissolving plutonium metal, uranium is not oxidized to uranium(VI), the oxidation state required for polarographic analysis. Nitric acid (3 ml) is therefore added to oxidize the uranium[1]. The solution is evaporated to dryness in a water bath. Hydrochloric acid (2–3 ml of 1 *M*) is then added to the volumetric flask, and the solution is again evaporated to dryness. To the still warm crystals, 4 ml of 5 *M* hydroxylamine hydrochloride solution are added, and the solution is warmed on a hot plate for 10 min. The plutonium solution is cooled, diluted to volume with water, and a portion is transferred to the polarographic cell where the oxygen is removed by bubbling nitrogen through the solution for at least 10 min.

Calibration procedure

A calibration curve for uranium was prepared by pipetting aliquots of a standard stock solution into 10-ml volumetric flasks. Sufficient 5 *M* hydroxylamine hydrochloride solution was added to each volumetric flask to make the final concentration 2 *M*, and the solution was diluted to volume with water. A portion was transferred to the electrolysis cell, and oxygen was removed by purging the solution with purified nitrogen for approximately 5 min. Four each of 10 different concentrations of uranium were polarographed. The data are shown in Table II. It can be seen that the peak current is proportional to the uranium concentration. The relative standard deviation of the diffusion current quotient[9] for all 40 traces is 2.29 %.

TABLE II

PEAK CURRENT AS A FUNCTION OF THE URANIUM CONCENTRATION

UO_2^{2+} *concn. (C)* *(moles/l)*	i_p *(μA)*	i_p/C *(μA/mmoles/l)*	*R.S.D.*
$1.00 \cdot 10^{-5}$	0.061	6.10	1.38
$2.00 \cdot 10^{-5}$	0.118	5.90	1.22
$4.00 \cdot 10^{-5}$	0.242	6.05	0.99
$5.00 \cdot 10^{-5}$	0.306	6.12	0.75
$1.00 \cdot 10^{-4}$	0.612	6.12	1.56
$2.00 \cdot 10^{-4}$	1.22	6.10	2.54
$4.00 \cdot 10^{-4}$	2.46	6.15	1.76
$5.00 \cdot 10^{-4}$	3.08	6.16	1.57
$1.00 \cdot 10^{-3}$	6.10	6.10	0.92
$2.00 \cdot 10^{-3}$	12.24	6.12	0.98

Reliability of the method

The reliability of the method was determined by analyzing standard uranium solutions, by investigating the effect of impurities, and by analyzing plutonium solutions containing known amounts of uranium.

Analyses of standard uranium solutions. Nine standard uranium solutions covering the range 4.8–953 µg UO_2^{2+}/ml were analyzed as described above. The average percentage recovery for these nine solutions was 100.7% with a standard deviation of ± 0.02%.

Investigation of impurities. Twenty-two impurities that are common in plutonium metal were investigated in the maximum concentrations at which they are usually found to determine their effect on the uranium determination. The results are shown in Table III. It was found that antimony, copper, molybdenum, and titanium interfered. The interference from molybdenum was eliminated by heating the solutions in the presence of hydroxylamine. Heating did not reduce or eliminate the interferences from the antimony, copper, or titanium.

TABLE III

INVESTIGATION OF IMPURITIES

Ion added	*Weight ratio ion/U*	*Recovery of UO_2^{2+}(%)*	*Ion added*	*Weight ratio ion/U*	*Recovery of UO_2^{2+}(%)*
Ag	0.068	[a]	Mn	0.42	[a]
Al	5.1	[a]	Mo	0.42	[a,c]
B	0.22	[a]	Ni	10.4	[a]
Ba	0.21	[a]	Pb	2.2	[a]
Ca	0.42	[a]	Sb	0.11	107
Cd	0.12	[a]		0.006	[a]
Cr	8.4	[a]	Si	0.11	[a]
Cu	0.54	317	Sn	0.11	[a]
	0.028	128	Sr	0.11	[a]
Fe	8.4	[a,b]	Ti	1.1	Ill-defined peak
Ga	1.7	[a]		0.11	Ill-defined peak
K	0.25	[a]	Zn	1.1	[a]
Mg	2.0	[a]			

[a] Error < ±3%.
[b] Fe interfered until the starting potential was changed from 0.00 to −0.05 V *vs.* Hg pool.
[c] Interference was eliminated by heating.

The copper was removed by mercury cathode electrolysis, but the antimony was only partially removed. The ratio of antimony to uranium could be sufficiently lowered, however, to eliminate its interference. A semi-micro electrolysis cell[12] proved to be convenient for removing the interfering metal impurities.

Uranium can be separated from titanium by the use of Dowex-1, 200–300 mesh, anion-exchange resin[13,14]; uranium remains on the column while titanium passes through.

Recovery of uranium in the presence of plutonium. The effect of plutonium on the polarographic determination of uranium was determined by spiking plutonium solutions with standard uranium solutions. The concentration of uranium in plutonium solutions ranged from 1.9 to 237 µg/ml, and the plutonium concentration was 2.0 g/10 ml. These solutions were analyzed according to the sample preparation procedure.

The average percentage recovery was 99.9% with the recovery ranging from 93.2 to 106.6%.

SUMMARY

The polarographic behavior of uranium in hydroxylamine hydrochloride was investigated by differential oscillographic polarography. A procedure is presented for the determination of uranium in plutonium for concentrations of uranium greater than 10 p.p.m. Analyses of solutions containing 22 common impurities found in plutonium metal revealed that antimony, copper, and titanium cause significant interference. A reversible peak corresponding to a one-electron reduction was obtained with a peak potential of −0.167 V *vs.* Hg pool electrode. The diffusion coefficient is $0.51 \cdot 10^{-5}$ cm^2/sec and the diffusion current constant is 1.59 with an average relative standard deviation of 2.28%. The peak current of uranium can be affected by hydrochloric, nitric, perchloric, and sulfuric acids, depending on the acid concentration.

RÉSUMÉ

Une étude polarographique du comportement de l'uranium en présence de chlorhydrate d'hydroxylamine est effectuée par polarographie oscillographique différentielle. Un procédé est proposé pour le dosage de l'uranium dans le plutonium pour des concentrations supérieures à 10 p.p.m. Des analyses de solutions contenant 22 impuretés courantes dans le plutonium montrent que l'antimoine, le cuivre et le titane gênent. Un pic réversible correspondant à une réduction d'un électron est obtenu à −0.167 V vs. Hg. Le coefficient de diffusion est de 0.51×10^{-5} cm^2/sec et la constante du courant de diffusion de 1.59 avec une déviation standard relative de 2.28%. Le pic de l'uranium peut être affecté par les acides chlorhydrique, nitrique, perchlorique et sulfurique, suivant leur concentration.

ZUSAMMENFASSUNG

Das polarographische Verhalten von Uran in Hydroxylaminhydrochlorid wurde mit der differenziellen oscillographischen Polarographie untersucht. Es wird ein Verfahren zur Bestimmung von Uran in Plutonium für Urankonzentrationen von mehr als 10 p.p.m. angegeben. Von 22 der üblichen Verunreinigungen im Plutonium verursachen Antimon, Kupfer und Titan ernsthafte Störungen. Ein reversibler Peak, der zu einer Einelektronenreduktion gehört, wurde bei einem Potential von −0.167 V gegen Quecksilber erhalten. Der Diffusionskoeffizient beträgt $0.51 \cdot 10^{-5}$ cm^2/sec und die Diffusionsstromkonstante 1.59 mit einer mittleren relativen Standardabweichung von 2.28%. Der Peak-Strom des Urans wird durch Salz-, Salpeter-, Perchlor- und Schwefelsäure und deren Säurekonzentration beeinflusst.

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RADIATION RESEARCH

RADIATION RESEARCH
REVIEWS

EDITORS: G.O. PHILLIPS (Salford)
R.B. CUNDALL (Nottingham)
CONSULTANT EDITOR: F.S. DAINTON, F.R.S. (Nottingham)

While there is adequate review coverage of the effect of ionizing radiation from the biological point of view, there is no publication which allows the regular appearance of authoritative and critical review articles dealing with the physical and physico-chemical aspects of radiation research. In recent years this field has grown rapidly, and the subject would be considerably benefited by the regular publication of comprehensive review articles written by active researchers.

Radiation research extends beyond the normal boundaries of any particular discipline and the vast increase in the amount of publication makes review articles essential sources of information. At present, papers and reviews relevant to this subject are widely distributed throughout the literature of chemistry, physics and biology.

The objective of the new publication will be to secure from leading workers throughout the world review papers giving broad coverage of important topics on the physical and chemical aspects of radiation research. The main emphasis will be on experimental studies, but relevant theoretical subjects will also be included.

In addition to specific reviews which come clearly within the scope of radiation chemistry, articles on subjects which help to elucidate the nature of processes which control chemical changes will receive attention.

Tabulated data helpful to workers in the field will also be published. An example of this is the extensive table of absorption spectra of radical and ionic intermediates which can be formed during radiolysis and photolysis, which appears in the second issue.

Suggestions for review articles should be sent to

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SOME ARTICLES FROM EARLY ISSUES

1. The radiolysis of aliphatic and alicyclic hydrocarbons (Gordon R. Freeman, Edmonton, Canada).
2. Methods of production of solvated electrons and their chemical and physical properties (J.K. Thomas, Argonne, Ill., U.S.A.).
3. Absorption spectra of intermediates formed during radiolysis and photolysis (A. Habersbergerová, I. Janovský, J. Teplý, Rez u. Prahy, Czechoslovakia).
4. Gas phase photolysis of hydrocarbons in the photoionization region (P. Ausloos, S.G. Lias, Washington D.C., U.S.A.).
5. Fundamental processes of inert gas sensitisation (D. Brocklehurst, Sheffield, England).
6. Primary radical and molecular yields in aqueous solutions; the effect of pH and solute concentration (G.V. Buxton, Leeds, England).

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THE OSCILLOPOLAROGRAPHIC DETERMINATION OF URANIUM AND THORIUM IN SUPPORTING ELECTROLYTES CONTAINING CUPFERRON

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The polarographic behaviour of cupferron and systems formed by cupferron with various cations has been studied by several authors. Two cupferron polarographic waves have been described; the first corresponds to the reduction from the acid form to phenylhydrazine and involves 6 electrons; the second, involving the transfer of 4 electrons, corresponds to the anion reduction. The latter only occurs at pH values above 6.6 [1–3].

Studies of systems formed by a cation and cupferron have shown the influence of chelation on the cupferron wave in acidic media, and various amperometric methods for the determination of cations have been developed [4–9]. The uranyl–cupferron system has received special attention [10–12]. RULFS AND ELVING[11] demonstrated that the formation of a uranium(IV)–cupferrate film on the surface of the dropping mercury prevents the uranyl ions from approaching the electrode.

The oscillopolarographic behaviour of some cations in the presence of cupferron and the development of oscillopolarographic methods in supporting electrolytes containing cupferron have not previously been studied. In the work described below, the oscillopolarographic activity of cupferron in different supporting electrolytes was examined, and sensitive methods which permit the identification and determination of some cations, especially uranium and thorium in the presence of various metals, were developed. On the basis of the polarographic studies quoted above and of the experimental observations obtained in the present work, it was possible to explain the behaviour of uranium and thorium in these supporting electrolytes.

EXPERIMENTAL

Instrumentation and chemicals

A Polaroscope model P 576 (Krizik, Prague) was used.

Supporting electrolyte A. 0.1 *M* perchloric acid, 0.5 *M* ammonium thiocyanate, $5 \cdot 10^{-3}$ *M* cupferron.

Supporting electrolyte B. 0.1 *M* succinic–succinate buffer pH 4, 0.1 *M* sodium chloride, 10^{-3} *M* cupferron, 0.05% gelatine.

The cupferron used was of p.a. quality and was obtained from: Carlo-Erba, AnalaR, Union Chimie Belge, and Mathieson, Coleman and Bell. The results were the same in every case and reproducible results were obtained with solutions stored for up to 15 days protected from light. The work done in inert atmospheres (obtained by the elimination of oxygen with nitrogen) gave results the same as those obtained in the presence of air.

Standard solutions. A 10^{-2} *M* uranium(VI) solution was prepared from AnalaR uranyl acetate dihydrate and a 10^{-2} *M* thorium(IV) solution from AnalaR thorium nitrate hexahydrate. The latter was standardized with EDTA. A uranium(IV) solution was prepared by reduction of the uranyl solution with zinc amalgam.

All the solutions were prepared in twice-distilled water. In the electrolytic cell a dropping mercury electrode was used as cathode with a mercury pool anode.

RESULTS AND DISCUSSION

Oscillopolarographic behaviour of cupferron

The oscillopolarographic behaviour of cupferron was observed in several buffered solutions. At pH values lower than 3, the cupferron gave an irreversible cathodic incision (Q ranged between 0.52 and 0.66). The highest sensitivity was obtained between pH 1 and 3 (Fig. 1). In highly acidic solutions, the indentation was smaller; above pH 3 the oscillopolarogram showed two or more incisions but these were less sensitive than those observed at lower pH values. The potential of the main indentation was –0.8 V at pH 1; this incision should correspond to the reduction from the acid form to phenylhydrazine. The incision observed at higher pH values in the negative potential region ($Q = 0.78$–0.9) should correspond to the anion reduction.

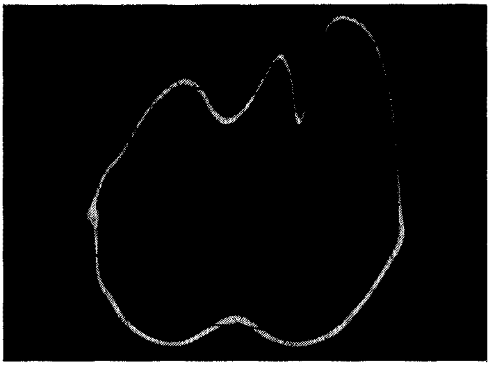


Fig. 1. Oscillopolarogram of $3 \cdot 10^{-5}$ *M* cupferron in 0.1 *M* perchloric acid.

The sensitivity of the cupferron incisions decreased greatly in the presence of surface-active substances as gelatine and with the addition of thiocyanate, iodide and bromide, which caused a shift of the incision to more positive potential values ($Q = 0.56$ in a supporting electrolyte consisting of 1 *M* perchloric acid and 0·5 *M* ammonium thiocyanate).

Oscillopolarographic behaviour of some cations in supporting electrolytes containing cupferron

In order to record the activity of various cations in supporting electrolytes containing cupferron, those supporting electrolytes were chosen in which the cupferron incisions were smallest or completely absent. These supporting electrolytes were denomi-

TABLE I

ACTIVITY OF SOME IONS IN SUPPORTING ELECTROLYTES A AND B

Ion	*Supporting electrolyte A*		*Supporting electrolyte B*	
	Q	*Sensitivity (M)*	*Q*	*Sensitivity (M)*
Tl(I)	—	—	0.30[a,c]	$1 \cdot 10^{-4}$[a,c]
Pb(II)	0.25[a,c]	$3 \cdot 10^{-6}$[c]	0.33[a,c]	$2 \cdot 10^{-5}$[c]
Mn(II)	—	—	0.90[c,id]	$2 \cdot 10^{-4}$
Co(II)	—	—	—	—
Ni(II)	—	—	—	—
Cu(II)	0.41[c]	$1 \cdot 10^{-6}$	0.30[c]	$4 \cdot 10^{-5}$
Zn(II)	0.73[c]	$2 \cdot 10^{-5}$[c]	0.71[c,id]	$2 \cdot 10^{-5}$[c]
	0.51[a]		0.46[a,id]	$3 \cdot 10^{-5}$[a]
Cd(II)	0.36[a,c]	$2 \cdot 10^{-6}$[c]	0.40[a,c]	$6 \cdot 10^{-5}$[c]
Sn(II)	0.33[a,c]	$1 \cdot 10^{-5}$[c]	0.55[c,id]	$3 \cdot 10^{-5}$[c]
Cr(III)	0.28[a]		0.60[c,id]	$2 \cdot 10^{-6}$
	0.55[c]	$3 \cdot 10^{-4}$[c]		
Fe(III)	—	—	—	—
Al(III)	—	—	—	—
Ga(III)	0.63[a,c]	$1 \cdot 10^{-6}$[c]	0.75[c,id]	$1 \cdot 10^{-4}$[c]
			0.43[a]	
In(III)	0.41[c]	$1 \cdot 10^{-6}$	0.47[c]	$1 \cdot 10^{-6}$[c]
As(III)	0.78[c]	$1 \cdot 10^{-5}$	0.76[c,id]	$1 \cdot 10^{-5}$
Sb(III)	—	—	0.45[c]	$2 \cdot 10^{-5}$
Bi(III)	—	—	0.16[c]	$1 \cdot 10^{-5}$[c]
			0.21[c]	$1 \cdot 10^{-5}$[c]
La(III)	—	—	—	—
Th(IV)	0.73[c]	$4 \cdot 10^{-6}$	0.78[c]	$4 \cdot 10^{-7}$
Ti(IV)	0.84[c]	$5 \cdot 10^{-4}$	—	—
Zr(IV)	0.66[c]	$1 \cdot 10^{-4}$	—	—
Sn(IV)	—	—	—	—
V(V)	0.33[a,c]	$3 \cdot 10^{-5}$[a,c]	0.50[c,id]	$1 \cdot 10^{-5}$
As(V)	—	—	—	—
Mo(VI)	—	—	0.50[c,id]	$4 \cdot 10^{-5}$
U(VI and IV)	0.75[c]	$3 \cdot 10^{-7}$	0.73[c]	$3 \cdot 10^{-7}$
W(VI)	—	—	[id]	—
Cr(VI)	—	—	—	—

[a] Anodic incision.
[c] Cathodic incision.
[id] Ill defined.

nated as A and B (see EXPERIMENTAL). Table I shows the position of the incisions on the curve $dE/dt = f(E)$ in Q values and the sensitivity of each incision in terms of molarity.

Supporting electrolyte A. In this medium, indentations were observed for Cu(II), Cd(II), Zn(II), Pb(II), In(III), Ga(III), Ti(IV), Zr(IV), Th(IV), U(VI) and U(IV). The Cu(II), Zn(II), Pb(II) and In(III) incisions also developed in supporting electrolytes which were free of cupferron and therefore were caused by the reduction of the thiocyanate complexes.

The incisions of Ga(III), Ti(IV), Zr(IV), Th(IV), U(IV) and U(VI) occurred only in the presence of cupferron. The incisions of Ti(IV), Zr(IV) and Th(IV) were ill-defined and showed low sensitivity. On the other hand, those of Ga(III) ($Q = 0.63$) and U(IV) and U(VI) ($Q = 0.75$) were very well defined and sensitive (Fig. 2 a, b).

Supporting electrolyte B. In this supporting electrolyte, In(III), Th(IV), U(VI) and U(IV) presented the most sensitive indentations. In some instances, *e.g.* arsenic(III), the presence of cupferron inhibited the characteristic incision of arsenic(III) in weakly acidic media. The incisions of Th(IV), U(IV) and U(VI) only occurred in the presence of cupferron (Fig. 3 a, b, c, d) and the indium(III) incision was much more sensitive in the presence of this reagent.

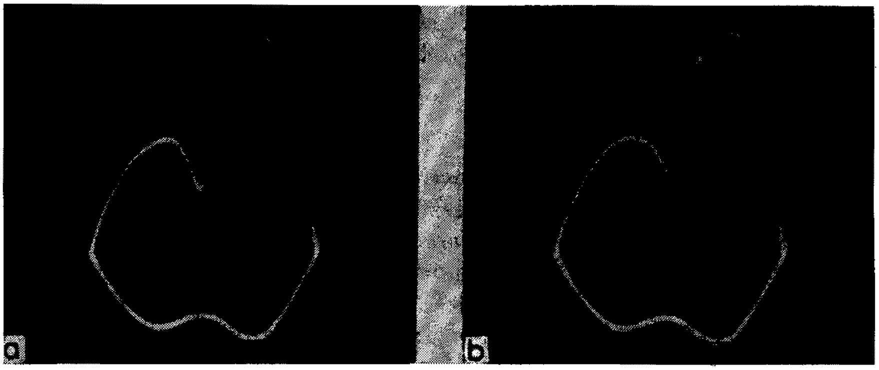


Fig. 2. (a) Oscillopolarogram of supporting electrolyte A. (b) Supporting electrolyte A with $4 \cdot 10^{-6}$ *M* U(VI).

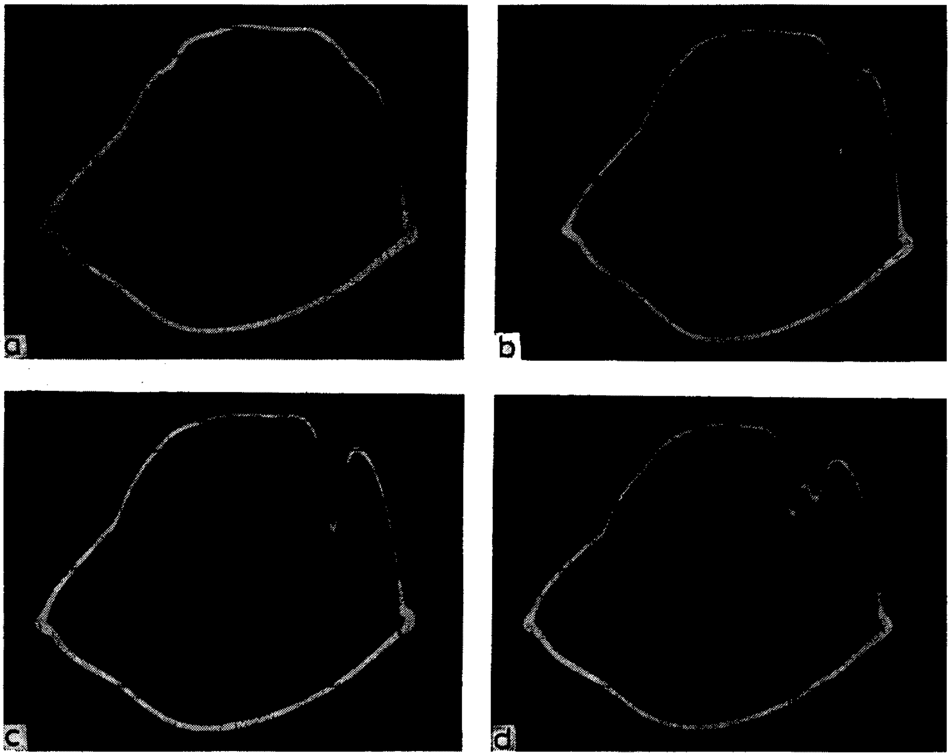


Fig. 3. (a) Oscillopolarogram of supporting electrolyte B. (b) Supporting electrolyte B with $4 \cdot 10^{-6}$ *M* U(VI). (c) Supporting electrolyte B with $4 \cdot 10^{-6}$ *M* Th(IV). (d) Supporting electrolyte B with $4 \cdot 10^{-6}$ *M* U(VI) and $4 \cdot 10^{-6}$ *M* Th(IV).

The behaviour of uranium and thorium

Uranium. The incision of uranium in the A and B supporting electrolytes was also observed in several buffered media between pH 0 and 5 (acetic–acetate, formic–formate, tartaric–tartrate). On the basis of previous studies[10–12], the different reactions of the cupferron with U(VI) and U(IV) and the oscillopolarographic behaviour of cupferron in different media as mentioned above, a number of conclusions were drawn.

The uranium(VI) is reduced to uranium(V) in the region of the most positive potentials. The corresponding incision appears distinctly only if the uranium(VI) concentration is higher than 10^{-3} *M* in the cell. The uranium(V) disproportionates into U(VI) and U(IV); the latter, even in highly acidic media, precipitates as uranium–tetracupferronate, thus shifting the disproportionation equilibrium and favouring the reduction of U(VI) to U(IV). The cupferron is thus changed to a form which is very difficult to reduce and its incision is shifted to the most negative potential region. The incision at –1.3 V in these media is thus the cupferron incision of uranium(IV)–cupferronate.

The following observations support this idea: (*a*) substances like EDTA which form U(IV) complexes, decrease the incision; (*b*) uranium(IV) behaved exactly like uranium(VI) (zinc(II) was present in the U(IV) solution used, but did not interfere because of the low sensitivity of its incision); (*c*) the potential of the characteristic incision of uranium was –1.3 V, while that of cupferron was –0.8 V in an acid medium; (*d*) an increase in temperature had a more marked effect on the cupferron incision in acid medium than on the uranium incision. In supporting electrolyte A, an increase in temperature accelerated the decomposition process of the acid form of cupferron, which at the same time, determined the elimination of the uranium incision. In supporting electrolyte B, on the other hand, an increase in temperature had no noticeable effect on the uranium incision. Further evidence was provided by the fact that above pH 5, the incision of uranium was as ill-defined and insensitive as the cupferron incisions. Cupferron forms a complex with uranium(IV) which is stable even in highly acid media, whereas uranium(VI) only forms a chelate between pH 4 and 7.

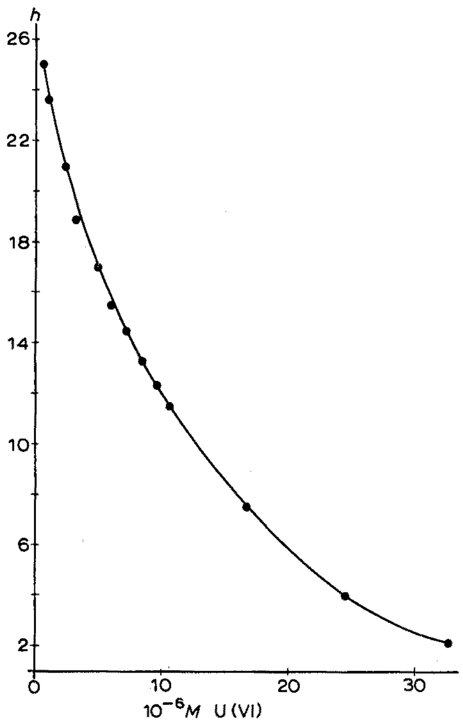
The high sensitivity of the uranium incision, especially at the first curve, is due to the adsorption of the complex at the electrode surface. Gelatine and other surfactants which decrease the cupferron incision, have a smaller effect on uranium.

Thorium. The incision of thorium in supporting electrolytes A and B should correspond, as in the case of uranium, to the reduction of the $Th(cupf)_4$, which is adsorbed on the mercury surface. Its potential is –1.4 V. Substances such as fluoride and EDTA which form complexes with thorium(IV) eliminate the indentation. An increase in temperature and the addition of gelatine have the same effect as in the case of uranium incision.

It cannot be supposed that thorium(IV) could be reduced to the metal, since this would require extremely negative potentials. The fact that uranium and thorium behave similarly reinforces the previous interpretation of the incision.

Detection and determination of uranium

It is possible to detect $3 \cdot 10^{-7}$ *M* of uranium in supporting electrolytes A and B and to determine between $6 \cdot 10^{-7}$ and $2 \cdot 10^{-5}$ *M* of uranium in supporting electrolyte



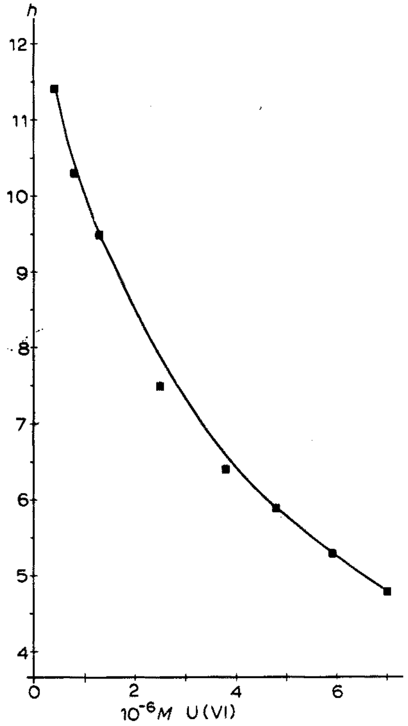


Fig. 4. Calibration curve of U(VI) in supporting electrolyte A.

Fig. 5. Calibration curve of U(VI) in supporting electrolyte B.

A, and $8 \cdot 10^{-7}$–$6 \cdot 10^{-6}$ M of uranium in supporting electrolyte B. These results were obtained by reference to calibration curves drawn by plotting *h*-values *vs.* concentration (*h* represents the distance between the extreme of the incision and the half line of the curve) (Figs. 4 and 5). As shown in Table I, of the 27 ions examined, the following have indentations near that of uranium: for supporting electrolyte A, Zn(II), As(III), Th(IV), Ti(IV) and Zr(IV); for supporting electrolyte B, Zn(II), Sn(II), As(III), Ga(III), Th(IV). All the incisions, except that of thorium, are much less sensitive than that of uranium. Moreover, other ions affect the sensitivity of uranium although they neither cause incisions in the negative potential region nor deform the oscillopolarogram. The limiting ratios for a maximum error of ± 5% are shown in Table II. In supporting electrolyte A, there are fewer interferences than in supporting electrolyte B, because in medium A some cations form thiocyanate complexes which are more stable than the corresponding chelate. Anions such as nitrate, sulfate, chloride and acetate in concentrations up to 0.1 M have no influence in either of the supporting electrolyte.

Elimination and separation of interferences

Arsenic(III), antimony(III) and tin(II) can be previously oxidized with hydrogen peroxide to prevent their interference. It was not possible to eliminate other interferences by the addition of complex-forming agents. EDTA or fluoride could, however, be used to eliminate small quantities of thorium; the incision of

TABLE II

THE INFLUENCE OF SOME IONS ON THE U(VI) AND Th(IV) DETERMINATION

(Limiting ratio for a maximum error of 0%)

Ion	$4\cdot10^{-6}$ *M U(VI)*		$4\cdot10^{-6}$ *M Th(IV)*	*Ion*	$4\cdot10^{-6}$ *M U(VI)*		$4\cdot10^{-6}$ *M Th(IV)*
	Support A Ion/U(VI)	*Support B Ion/U(VI)*	*Support B Ion/Th(IV)*		*Support A Ion/U(VI)*	*Support B Ion/U(VI)*	*Support B Ion/Th(IV)*
Tl(I)	360	80	100	As(III)	3	2	2
Pb(II)	92	58	20	Sb(III)	130	7	7
Mn(II)	112	60	27	Bi(III)	370	5	1
Co(II)	12	30	50	La(III)	615	12	12
Ni(II)	8	30	5	Th(IV)	60	0.6	—
Cu(II)	56	35	25	Ti(IV)	10	2	0.5
Zn(II)	250	10	12	Zr(IV)	60	8	1
Cd(II)	250	127	320	Sn(IV)	116	92	6
Sn(II)	264	10	4	V(V)	40	16	5
Cr(III)	16	10	10	As(V)	100	300	300
Fe(III)	125	0.5	0.2	Mo(VI)	8	1	2
Al(III)	300	300	50	U(VI)	—	—	0.2
Ga(III)	3	0.3	0.3	W(VI)	8	10	2
In(III)	50	7	3	Cr(VI)	10	10	10

thorium is more affected than that of uranium by the addition of small quantities of EDTA or fluoride. If the EDTA or fluoride concentration does not exceed $5\cdot10^{-3}$ *M*, then a uranium concentration of 10^{-6} *M* can be determined in the presence of 10^{-5} *M* thorium in supporting electrolyte B, without interference and with a maximum error of less than ± 5%.

The separation of interfering ions is important when supporting electrolyte B is used, as shown in Table II. In this electrolyte, Fe(III), Ga(III), Th(IV), Ti(IV) and Mo(VI) interfere, when the concentration is less than 5-fold that of uranium. In supporting electrolyte A, only gallium(III) interferes (arsenic(III) is oxidized with hydrogen peroxide). Most of the interfering ions can be precipitated by means of cupferron and extracted together with the excess of cupferron. The precipitation and extraction were done in 0.1 *M* hydrochloric acid solution containing uranium and the interfering ions. Uranium(VI) is not precipitated under these conditions. A 6% cupferron solution was used to precipitate the cupferronates and the extraction was carried out with chloroform. After three successive extractions, aliquots of the aqueous phase were added to supporting electrolyte B to register the uranium indentation. When 1 mg of each of the following ions, Fe(III), Bi(III), Ga(III), Zr(IV), Ti(IV), Mo(VI), In(III) and V(V), was extracted from a hydrochloric solution containing 23 μg of uranium, the uranium could be determined with a maximum error of less than ± 5%. In supporting electrolyte A, the same result was obtained by separating Ga(III), Ti(IV) and Mo(VI) from 23 μg of uranium.

Applications

The characteristics of the methods developed help to solve some important problems in chemical analysis. Uranium can be determined in supporting electrolyte A without previous separation in the presence of large quantities of metals such as Pb, Bi, V, Fe, La, etc., which generally accompany it in natural samples. The determination is also possible in the presence of small quantities of thorium without previous separation. If high concentrations of Ga, Ti and Mo are present, only a simple preliminary extraction is necessary.

In order to test the methods developed, carnotite and coal from California were analysed. These samples contained 15 and 0.08% of uranium respectively.

Carnotite. 0.5 g of carnotite was dissolved in a mixture of nitric and hydrofluoric acids, then the nitric acid was eliminated with sulfuric acid and the solution was evaporated to dryness. The residue was dissolved in 25 ml of 4 *M* hydrochloric acid and the solution was diluted to 250 ml with water. A 10-ml aliquot of this solution was diluted to 100 ml, to obtain a 10^{-4} *M* uranium solution. This solution also contained vanadium in a *ca.* 1 : 1 molar ratio to uranium, but this did not interfere; traces of Fe, Ni, Zn and Cd present also did not interfere. A method of comparative titration was used to determine uranium, titrating with a 10^{-5} *M* uranium(VI) standard solution. Several analyses following methods A or B showed an average error of ± 3%.

Coal from California. 0.5 g of ash obtained after calcination of the sample was dissolved in hydrofluoric–sulfuric acid mixture as described above. The residue was dissolved in 4 *M* hydrochloric acid and the solution was diluted to 50 ml. To 5 ml of this solution, 1 ml of 6% cupferron was added and the cupferronates and the excess of cupferron were extracted with chloroform. The aqueous phase was evaporated to dryness, the residue was dissolved in 0.1 *M* hydrochloric acid and the solution was diluted to 10 ml. Aliquots of this solution were used for oscillopolarographic analysis by the method of comparative titration using supporting electrolytes A and B. Four analyses showed an average error of ± 5%.

Detection and determination of thorium

Supporting electrolyte B is the more suitable for the determination of thorium

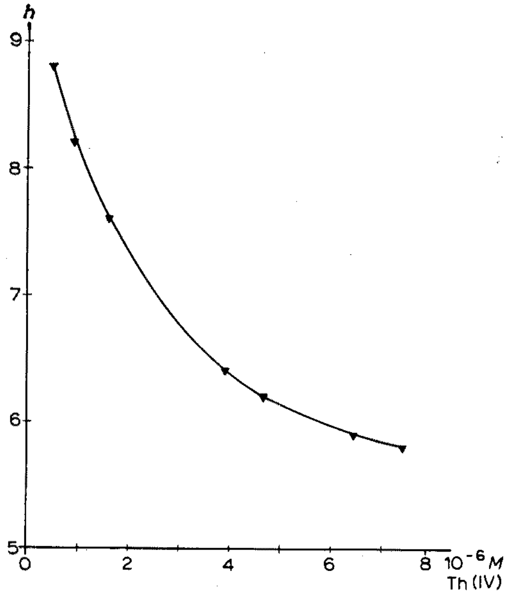


Fig. 6. Calibration curve of Th(IV) in supporting electrolyte B.

because it gives a better ratio of *h*-value *vs.* concentration. With electrolyte B, the limit of detection is $4 \cdot 10^{-7}$ *M* and $8 \cdot 10^{-7}$–$6 \cdot 10^{-6}$ *M* of thorium can be determined (Fig. 6).

The most sensitive incision near that of thorium is the uranium incision ($Q = 0.73$). Those of gallium(III) ($Q = 0.75$) and zinc(II) ($Q = 0.71$) are ill-defined and rather insensitive. Some other ions decrease the sensitivity of the thorium incision. The limiting ratio for a maximum error of 5% is shown in Table II; Fe(III), Ga(III), Ti(IV) and V(V) are the most important interferences. The method permits the determination of thorium in the presence of large amounts of Tl, Pb, V, Bi, Cd, Mn, La, etc.

SUMMARY

Uranium(VI and IV) and thorium(IV) give cathodic indentations in supporting electrolytes prepared from 0.1 *M* perchloric acid, 0.5 *M* ammonium thiocyanate and $5 \cdot 10^{-3}$ *M* cupferron (solution A) or from 0.1 *M* succinic–succinate buffer pH 4, 0.1 *M* sodium chloride, 10^{-3} *M* cupferron and 0.05% gelatine (solution B). The uranium indentation on the $dE/dt = f(E)$ curve ($Q = 0.75$ and 0.73) permits its detection at the $3 \cdot 10^{-7}$ *M* level. The thorium indentation ($Q = 0.78$) permits its detection at the $4 \cdot 10^{-7}$ *M* level in solution B. Methods for the elimination of interfering ions for the uranium determination are described. In the determination of thorium, Ga(III), Fe(III), Ti(IV) and U(VI) interfere.

RÉSUMÉ

L'uranium(VI et IV) et le thorium(IV) donnent une indentation cathodique dans une solution contenant de l'acide perchlorique (0.1 *M*), du thiocyanate d'ammonium (0.5 *M*) et du cupferron ($5 \cdot 10^{-3}$ *M*), (solution A) et avec un tampon succinique (0.1 *M* pH 4), du chlorure de sodium, (0.1 *M*) du cupferron (10^{-3} *M*) et de la gelatine 0.05% (solution B). L'indentation de l'uranium sur la courbe $dE/dt = f(E)$ ($Q = 0.75$ et 0.73 respectivement) est perceptible à partir d'une concentration de $3 \cdot 10^{-7}$ *M*; alors que dans la solution B l'indentation du Th ($Q = 0.78$) peut être percue à partir de $4 \cdot 10^{-7}$ *M*. Les indentations correspondent à la réduction des complexes du cupferron adsorbés sur la goutte de mercure. Des méthodes d'élimination des ions gênants d'uranium sont également décrites. La détermination du thorium est spécialement gênée par Ga(III), Fe(III), Ti(IV) et U(VI).

ZUSAMMENFASSUNG

Die oscillopolarographische Bestimmung von Uran und Thorium ist durch kathodische Anzeige mit einem Elektrolyten möglich, der 0.1 *M* Perchlorsäure, 0.5 *M* Ammoniumthiocyanat und $5 \cdot 10^{-3}$ *M* Cupferron (Lösung A) oder 0.1 *M* Succin–Succinat-Puffer vom pH 4, 0.1 *M* Natriumchlorid, 10^{-3} *M* Cupferron und 0.05% Gelatine (Lösung B) enthält. Uran kann bis $3 \cdot 10^{-7}$ *M*, Thorium mit der Lösung B bis $4 \cdot 10^{-7}$ *M* nachgewiesen werden. Es werden Methoden zur Eliminierung störender Ionen bei der Uranbestimmung beschrieben. Die Bestimmung des Thoriums wird durch Ga(III), Fe(III), Ti(IV) und U(VI) gestört.

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DETERMINATION OF FLUORINE IN SILICATE AND PHOSPHATE ROCKS, MICAS AND STONY METEORITES

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In a recent publication HUANG AND JOHNS[1] described a method for determining fluorine in silicate rocks. The significant feature of the method is that the determination is said to be possible without the separation of fluorine from possible interferences by distillation or pyrohydrolysis. However, the present author has experienced some trouble with this method in some silicate rocks, and also in samples containing high fluorine, *e.g.* phosphate rocks, opal glass and micas. The difficulty has been overcome by introducing modifications, and these modifications have made it possible to extend the method to samples containing large amounts of fluorine.

EXPERIMENTAL

Apparatus

A Beckman model B spectrophotometer with matched 1.0-cm glass cells was used for measuring the absorbances of solutions.

Thermolyne Corporation Type A 1400 electric furnace.

Reagents and solutions

Alizarol cyanine RC (Allied Chemical) (Reagent A). Dissolve 0.9 g in 500 ml water.

Zirconyl chloride (Reagent B). Dissolve 0.133 g pure $ZrOCl_2 \cdot 8H_2O$ (Fisher) in 5 ml water and dilute to 500 ml in a volumetric flask with concentrated hydrochloric acid.

Standard sodium fluoride solution (20 µg/ml). Dry sodium fluoride (Baker analyzed reagent, 100% NaF) in a platinum dish at 150° for 2 h and cool in a desiccator. Weigh out 0.5525 g, dissolve in 1 l of water in a volumetric flask and transfer to a polyethylene bottle. Dilute 20 ml of this stock solution to 250 ml ($F = 20$ µg/ml) and store in a polyethylene bottle.

Standard curve, optimum range and effect of time

When the procedure of HUANG AND JOHNS[1] for the determination of fluorine was used, it was found that the method had the following drawbacks.

(*1*) The standard curve was not reproducible even when duplicate aliquots of the same standard solution were carried through the calibration procedure at the same time with the same batch of reagents (see curves A of Fig. 1). Also, there was a very narrow range of absorbance (0.28–0.06 corresponding to 0–40 µg F) available for the determination. Consequently, a small change of absorbance, particularly when 40–50 μg F is present, may cause a significant error in the determination.

(2) Although a batch of standard solutions prepared by adding 3 ml of the dye (alizarol cyanine RC) and 5 ml of zirconium solution to alkaline solutions of pure sodium fluoride gave stable absorbance for a long period of time, the unknown sample solutions of fluorides (containing aluminium, silicate and phosphate as in the case of phosphate rocks), treated identically, were found to undergo a gradual decline of absorbance values with time. Because of this instability of the colour, the measurement of absorbance even after 1–1.5 hours' standing, as recommended by HUANG AND JOHNS[1], may not be reliable and reproducible. The error thus introduced is particularly serious in analysing samples whose fluorine contents are much higher than the 0.0–0.4% usually found in silicate rocks (*cf.* Table I).

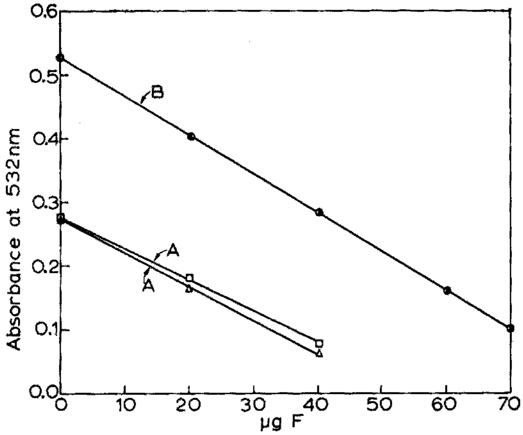

Fig. 1. Standard curve for fluorine. (A) HUANG AND JOHNS[1] method (△ and ⊡ are the duplicate absorbance values); (B) modified method of this paper (⊙ and × are the duplicate absorbance values).

TABLE I

EFFECT OF TIME ON THE DETERMINATION OF FLUORINE IN VARIOUS SAMPLES CONTAINING HIGH FLUORINE BY HUANG AND JOHNS' METHOD

Sample	*Standard value (% F)*	*Found % F[a] after*		
		1 h	*1.5 h*	*3 h*
NBS 56 b	3·4	4·0	4·8	5·2
(Phosphate rock)		3·5	3·5	3·7
NBS 91	5·7	4·9	5·8	6·4
(Opal glass)			5·9	6·0
Mica 1	4·4[b]	4·0	5·2	5·6
(Lithium Muscovite)			4·6	4·9
Mica 2	3·78[b]	2·7	4·8	4·9
(Lepidolite)			4·2	4·4

[a] Duplicate values are from two different aliquots of the same solution.
[b] Distillation value by an independent operator.

The method was, therefore, studied in detail with respect to: (*1*) effect of addition of 3 drops of 6 *N* sodium hydroxide solution according to the method of HUANG AND JOHNS[1], (*2*) effect of the order of addition of the dye and zirconium solutions to the fluorine, (*3*) effect of setting zero absorbance with a bleached colour complex solution formed by the addition of 100 μg of fluoride to the dye and zirconium solution, (*4*) effect of time, and (*5*) effect of addition of more dye solution.

The results of these studies indicated that in order to obtain quantitative and reproducible results the method should be modified as detailed under *Recommended procedure*.

Recommended procedure

Weigh out the finely ground and homogenized sample (500 mg for rocks and stony meteorites containing 0–0.5% F, 100 mg for samples containing 0.5–2.0% F and 50 mg for samples containing 2–8% F) into a 30-ml platinum crucible, add 3 g of sodium carbonate and 0. 6 g of zinc oxide and mix thoroughly with a glass rod. Tap the crucible at the bottom to settle its contents, brush off any adhering particles from the glass rod into the crucible and spread uniformly on the surface an additional 0.5 g of sodium carbonate.

Cover the crucible with the lid and place near the entrance of a hot muffle furnace for 2–3 min, then transfer the crucible to the hot zone of the furnace and heat at 950° for 20 min. Raise the temperature to 1000° and heat for an additional 10 min.

Take out the crucible, cool to room temperature in a desiccator (containing sodium hydroxide pellets), add 10 ml of water and 3 drops of 95% ethanol and heat on a medium hot sand bath while stirring with a Teflon rod. Continue heating and stirring, with occasional addition of 1–2 ml of water to make up evaporation losses, until the solid lump is completely broken into fine particles and a thin slurry is obtained. Allow the solid particles to settle to the bottom of the crucible and filter* the supernatant liquid into a 500-ml polyethylene flask, by suction through a 9-cm Whatman No. 42 filter paper placed on a Fisher Filtrator funnel. Wash the solid particles in the crucible several times with boiled hot water, transferring the supernatant liquid each time into the filter paper. Finally wash the filter paper, particularly at the edge, with hot water (total wash water should not exceed 75 ml).

Disconnect the suction apparatus, add 4.2 ml of concentrated nitric acid to the filtrate, cover with the lid of the platinum crucible and shake well until the reaction ceases. Transfer the solution quantitatively to a 100-ml volumetric flask and make up the volume with water. Immediately transfer to a 100-ml polyethylene bottle.

Pipette 5 ml each of reagents A and B into a 50-ml volumetric flask, add 25–30 ml water and mix well. Add an aliquot of the sample solution containing less than 70 μg F, and make up to volume with water.

Prepare five standard solutions (each in a 50-ml volumetric flask) in the same way, the first containing only reagents A and B and the others containing 20, 40, 60, 70 and 100 μg F, respectively in addition to reagents A and B.

For samples where 500 mg was taken for analysis, wait for 2 h before measuring absorbance. For those where only 50 mg was taken, a 30-min wait is sufficient. In all

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* If the sample cannot be filtered on the day on which it is fused, it should be stored in a sealed container (*e.g.* a desiccator charged with NaOH pellets) to protect it from contamination by HF of HCl fumes in the laboratory atmosphere.

cases, complete measurement in less than 3 h. Set zero absorbance at 532 nm, using the standard containing 100 μg F, and measure the absorbance of each sample. Measure the absorbances of the other standard solutions against the same zero setting and after the same time interval as used with the unknown. Obtain the concentration of fluorine in the unknown sample from the calibration curve (*cf.* line B of Fig. 1).

RESULTS AND DISCUSSION

According to HUANG AND JOHNS[1], the solution obtained by neutralizing the sodium carbonate fusion product with 4.1 ml of concentrated nitric acid was slightly acidic. Actual measurements in this work revealed a pH of 8 in such a solution. HUANG AND JOHNS[1] added 3 drops of 6 *N* sodium hydroxide solution to an aliquot of such a solution, presumably to convert aluminium to AlO_2^- and thus prevent its interference. GLASÖ[2] has pointed out that in order to eliminate interferences from aluminium and phosphate in the determination of fluorine by the zirconium–alizarol cyanine RC method, the final acidity of the solution should be maintained at about 1.3 *N*. The proposed method of HUANG AND JOHNS[1] would bring down the acidity much lower than this because of the presence of the additional 3 drops of 6 *N* sodium hydroxide solution. At this lower acidity, silicate and phosphate (as in the case of phosphate rocks) might possibly remove zirconium from the zirconium–alizarol cyanine RC complex, thereby decreasing the absorbance of the colour complex, and hence showing apparent increase of concentration of fluorine with time (see Table I).

The question of the effect of order of addition of reagent is very important. The method depends on the action of fluoride ions in removing zirconium from the coloured complex. If the dye is added first, two things can cause difficulty: (*a*) the dye may react with other metals (at the lower acidity); and (*b*) the zirconium, when added, must divide itself between reacting with fluoride ions and reacting with dye, in some cases involving removal of dye from complexes with other metals.

Also direct addition of the dye and zirconium solution to the sample solution (resultant acidity about 4.5 *N*) does not favour immediate formation of the zirconium–fluorine complex owing to the high acidity. After dilution to volume, the zirconium–fluorine complex is very slowly formed. This may affect the reproducibility of results where conditions vary slightly from one sample to another (see Table I and Curves A of Fig. 1). If the zirconium and the dye are allowed first to interact, the solution is then diluted to acidity of 1.5 *N*, and the sample solution is added, the possible reactions are then reduced mainly to decomposition of the zirconium–dye complex by the action of fluoride ions.

Therefore, to obtain reliable and reproducible results, HUANG AND JOHNS[1] method was modified by: (*a*) avoiding the use of sodium hydroxide solution; (*b*) adding 5 ml of the dye solution instead of 3 ml; (*c*) first forming the zirconium–alizarol cyanine RC complex, diluting with water to an acidity of about 1.5 *N* and then adding the sample solution containing fluoride; and (*d*) measuring the absorbance against a standard solution containing 100 μg F.

The amount of the dye solution was increased from 3 ml to 5 ml because of the fact that interference was still noticed when the sample solution was added to the zirconium–dye complex formed by using the former amount of the reagent solution.

The advantage of this modified method is that, at the acidity of 1.5 *N*, zirconium readily reacts with fluorine. The explanation for the better results obtained with larger amount of reagent solution may lie in the fact that after the zirconium–fluorine complex is formed, the presence of a large excess of reagent prevents further reaction of zirconium with phosphate and silicate of the solution, thus stabilising the colour. The standard curve covers a broader range of absorbance values for 4–70 μg F and is very reproducible with the same batch of the dye and zirconium solutions (see B of Fig. 1).

Results obtained by this modified method for some National Bureau of Standards standard samples, U.S.G.S. rock standards and some mica and stony meteorites, are given in Tables II–IV. Table II indicates that samples with high fluorine contents (3.4–5.7% F; 50 mg original sample weight) reach stability of colour after standing for 0.5 h, whereas those with low fluorine contents (0.0–0.4% F; 500 mg sample weight)

TABLE II

EFFECT OF TIME ON THE DETERMINATION OF FLUORINE BY THE MODIFIED METHOD

Sample	*Standard value (% F)*	*Found % F after*					
		0.5 h	*1 h*	*1.5 h*	*2 h*	*2.5 h*	*3 h*
NBS 56 b (Phosphate rock)	3.4	3.3	3.3	3.3	3.3	3.3	3.3
NBS 91 (Opal glass)	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Mica 1 (Lithium Muscovite)	4.4[a]	4.4	4.4	4.4	4.4	4.4	4.4
Mica 2 (Lepidolite)	3.8[a]	4.0	4.0	4.0	4.0	4.0	4.0
G-2 (Granite)	0.13[b]	0.09	0.11	0.13	0.13	0.13	0.13
AGV-1 (Andesite)	0.04[b]	0.02	0.03	0.04	0.04	0.04	0.04
BCR-1 (Basalt)	0.05[b]	0.038	0.04	0.05	0.05	0.05	0.05
GSP-1 (Granodiorite)	0.375[b]	0.26	0.32	0.37	0.38	0.38	0.38

[a] Distillation value by an independent operator.
[b] From FLANAGAN[3] and GOLDICH *et al.*[4].

TABLE III

REPRODUCIBILITY OF THE MODIFIED METHOD WITH REGARD TO DIFFERENT ALIQUOTS OF THE SAME AND DUPLICATE SAMPLE SOLUTIONS

Sample	*Standard value (% F)*	*% F found in*			
		Batch 1[a]	*Deviation in two aliquots*	*Batch 2*[a]	*Deviation in two aliquots*
G-2	0.13 (range 0.12–0.14)	0.128 0.120	0.008	0.12 0.12	0.00
AGV-1	0.04	0.036 0.037	0.001	0.032 0.035	0.003
BCR-1	0.05	0.05 0.05	0.00	0.04 0.04	0.00
GSP-1	0.375 (range 0.36–0.39)	0.39 0.38	0.01	0.37 0.37	0.00
NBS 56 b	3.4	3.3 3.3	0.00	3.2 3.2	0.00
NBS 91	5.7	5.7 5.6	0.10	5.6 5.7	0.10

[a] Two values refer to determinations from 2 different aliquots of the same solution.

reach stability after standing for 1.5–2 h. The requirement of longer time in the latter case is presumably due to the presence of a much higher quantity of aluminium. Table III shows that the reproducibility of the method from different aliquots of the same and duplicate sample solutions is satisfactory.

TABLE IV

COMPARISON OF THE FLUORINE RESULTS AS DETERMINED BY THE MODIFIED METHOD WITH OTHER RESULTS IN DIFFERENT SAMPLES (OTHER THAN THOSE INCLUDED IN TABLES II AND III)

Sample	*% F*	
	Other work	*This work*
NBS 120 (Phosphate rock)	3.76	3.8
Mica 3 (Phlogopite)	3.15[a]	3.1
Mica 4 (Manganese Lepidolite)	7.6[a]	7.7
PCC-1 (Peridotite)	0.0[b]	0.0
DTS-1 (Dunite)	0.0[b]	0.0
	Other work (p.p.m. F)	*This work (p.p.m. F)*
Abee (Stony meteorite)	175 (122–280)[c]	250 300
Benton (Stony meteorite)	60[a]	60 66
Farmington (Stony meteorite)	250[c]	300

[a] Distillation value, independent operator.
[b] From Flanagan[3] and Goldich *et al.*[4].
[c] Data from Hey[5].

Fusion of the sample at 900° for 20–25 min, as recommended by Huang and Johns[1] generally produced low results. This may explain why Huang and Johns[1] recovered only about half of the fluorine present in standard granodiorite, GSP-1. The temperature and time of heating were, therefore, increased to 950–1000° and 30 min, respectively, to obtain satisfactory results. No more than four samples should be fused in one batch. The higher temperature has no detrimental effect on the determination of chlorine from the same fusion product. In fact it gives better results for recovering chlorine from stony meteorites which normally require higher temperature for decomposition than terrestrial materials.

In the determination of chlorine by the recommended method of Huang and Johns[1] there was considerable variability in the reagent blank corrections, resulting in corresponding variability in the chlorine found in actual samples. After many experiments it was established that the following points should be strictly adhered to in order to obtain reliable results. (*1*) It is absolutely essential to clean all apparatus by nitric acid to avoid contamination; preferably, separate glassware should be used exclusively for chlorine determination. (*2*) A blank and a standard curve must be run with every batch of samples. (*3*) Chlorine should be determined first from the fusion product, if it is necessary to determine both chlorine and fluorine in it.

SUMMARY

By making certain modifications to a published procedure for fluorine in rocks, it has been possible to improve stability and extend the range of the method. The modified method has been successfully applied to silicate and phosphate rocks, micas, glass and stony meteorites, containing from 60 p.p.m. to 8% fluorine. Some precautions are recommended for reliable determination of chlorine.

RÉSUMÉ

En apportant certaines modifications à un procédé publié pour le dosage du fluor dans les roches, il a été possible d'améliorer la stabilité et étendre le domaine d'application de la méthode. Ce nouveau procédé a pu être appliqué avec succès à l'analyse de silicates, roches phosphatées, micas, verre et météorites pierreux renfermant de 60 p.p.m. à 8% de fluor. Quelques précautions sont recommandées pour le dosage du chlore.

ZUSAMMENFASSUNG

Durch Abänderung eines bekannten Verfahrens zur Bestimmung von Fluor in Gesteinen wurde es möglich die Eignung und den Bereich der Methode zu verbessern. Die modifizierte Methode wurde für Silikat- und Phosphatgesteine, Glimmer, Glas und steinige Meteoriten im Bereich von 60 p.p.m. bis 8% Fluor erfolgreich angewandt. Einige Vorsichtsmassnahmen für die zuverlässige Bestimmung von Chlor werden empfohlen.

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TRACE FLUORIDE DETERMINATION WITH SPECIFIC ION ELECTRODE

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The determination of traces of fluoride in solution is often complicated by the necessity of separating fluoride from interfering ions. However, with development of the fluoride-specific electrode[1], which has a crystal of rare earth fluoride as a sensing membrane, the determination is considerably simplified. LINGANE[2] has used the electrode as an indicator for potentiometric titrations and has accurately determined as low as 10^{-3} M fluoride.

This work extends the range of determination to 10^{-5} M in a variety of solutions without preliminary separation, by taking advantage of the high specificity and sensitivity of the electrode. A standard fluoride curve is constructed within the sample solution, and care is taken to minimize changes in ionic strength, activity coefficients, and junction potentials so that the observed potential changes can be interpreted in terms of concentration, rather than activity, which the electrode actually detects. Also it is shown that total fluoride can be determined in the presence of fluoride-complexing cations by adding sufficient phosphoric acid to complex the cations and release a constant fraction of the total fluoride as undissociated hydrofluoric acid.

PRINCIPLE OF METHOD

The observed cell potential, E, of a solution in contact with a fluoride indicator electrode and a reference electrode is

$$E = E_e - \mathrm{A} \log c_F\gamma_F \tag{1a}$$

$$= E_s - \mathrm{A} \log c_F \tag{1b}$$

where E_e = the potential due to the nature of the electrodes and their contact with the external solution;

$E_s = E_e - \mathrm{A} \log \gamma_F$, where γ_F is the activity coefficient of the fluoride ion;

A = a constant, ideally the Nernst slope of RT/F, which is 59 mV at 25°;

c_F = the concentration of free fluoride ion in solution.

On addition of a small amount of fluoride, x_1, with negligible attendant change in volume or ionic strength, E_s remains unchanged, the new fluoride ion concentration becomes $(c_F + x_1)$, and the new observed potential is

$$E_1 = E_s - \mathrm{A} \log (c_F + x_1) \tag{2}$$

The difference between the observed initial and final potentials eliminates the constant E_s, and

$$\Delta E_1 = E - E_1 = \mathrm{A} \log (c_F + x_1)/c_F \tag{3}$$

from which the unknown concentration c_F can be calculated.

In acid solution, total fluoride (free and complexed) can be determined, provided that the hydrogen ion activity a_H, remains constant, there are no fluoride complexes besides hydrofluoric acid, and enough free fluoride is available for detection. With a high hydrogen-to-fluoride ion ratio, the complex fluoride species is predominantly HF[3]. When a_H and the activity coefficients of fluoride and HF are unaltered by the fluoride additions, the expression for K_a, the association constant of HF, can be rearranged to give another constant, K':

$$K' = K_a(a_H \gamma_F)/\gamma_{HF} = c_{HF}/c_F \tag{4}$$

Since

$$\begin{aligned} c_{F(\text{total})} &= c_F + c_{HF} \\ &= c_F(1 + K') \end{aligned} \tag{5}$$

a constant fraction of total fluoride is always detected, and eqn. (1b) has another constant term, A log $(1 + K')$:

$$E = E_s + \mathrm{A} \log (1 + K') - \mathrm{A} \log c_{F(\text{total})} \tag{6a}$$

$$= E_s' - \mathrm{A} \log c_{F(\text{total})} \tag{6b}$$

When a difference is taken between two readings, as before, E_s and K' are eliminated, giving

$$\Delta E_1 = \mathrm{A} \log (c_{F(\text{total})} + x_1)/c_{F(\text{total})} \tag{7}$$

which is of the same form as eqn. (3).

Total fluoride concentration can thus be calculated from appropriate measurements by solving either eqn. (3) or eqn. (7) for the unknown c_F:

$$c_F = \frac{x_1}{\left(\log^{-1} \dfrac{\Delta E}{\mathrm{A}}\right) - 1} \tag{8}$$

If A is known, c_F can be calculated from a single measurement. Or, c_F and A can be computed by fitting two or more sets of x_i and ΔE_i to eqn. (8).

EXPERIMENTAL

Apparatus

Specific fluoride ion electrode (Model 94-09, Orion Research Incorporated, Cambridge, Mass.) and saturated calomel reference electrode with an expanded-scale pH meter.

Reagents

Reagent-grade phosphoric acid was steam-stripped to remove fluoride, which amounted to about $4 \cdot 10^{-5}$ *M*. Other chemicals were not pretreated to remove fluoride, and blanks were analyzed as required.

Standard 0.1 *M* sodium fluoride was made by dissolving and appropriate dilution of the weighed salt that had been dried at 120°.

Procedure

Measurements were made at about 25°. The potential of a 50-ml sample containing 10^{-4}–10^{-5} M fluoride was determined while the solution was stirred rapidly. Measured 10–100-μl increments of 0.1 M sodium fluoride were added to the stirred solution to attain potential changes of about 10 mV, until the total change was $\geqslant 40$ mV. The potential was recorded after each addition. The total volume of sodium fluoride added did not exceed 1 ml. Response of the electrode was rapid and generally steady within 1 min.

In systems known to contain cations that form complexes with fluoride, phosphoric acid was added to precomplex the cations and thereby free the fluoride for detection. Alkaline systems were acidified to eliminate hydroxyl ions, which interfered with the response of the electrode at concentrations greater than 10^{-5} M. Acid concentrations about 1 M or greater ensured that the principal fluoride complex was HF and that eqn. (7) would be applicable.

RESULTS AND DISCUSSION

Effect of phosphoric acid

The electrode response to sodium fluoride was the same in 1, 5, and 10 M phosphoric acid as it was in water, as shown in Fig. 1. As the concentration of the acid increased, the potential became more positive, indicating that the amount of free fluoride available for detection was diminished by being complexed with hydronium ion. The linear response in acid solution at constant ionic strength agrees with the experience of LINGANE[2], and justifies the use of eqn. (7) for calculating total fluoride in strongly acid solutions.

Figure 1 also shows that the fluoride complexes with aluminum(III), thorium(IV) and uranyl ion are decomposed in 10 M phosphoric acid solution, because the observed potentials and the response to fluoride concentration were essentially unal-

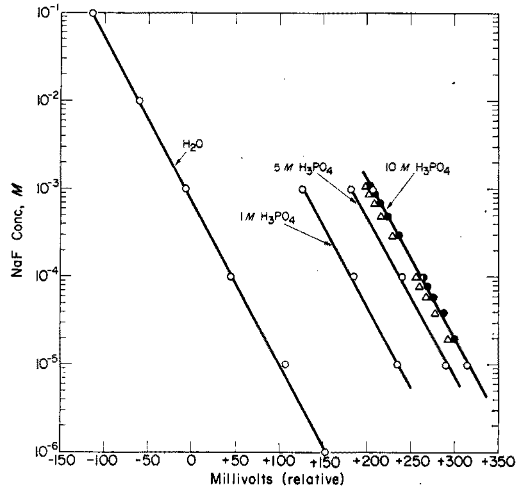

Fig. 1. Response of fluoride-specific electrode to sodium fluoride in water and in phosphoric acid. ○ No added salts; ● 0.015 M Al^{3+}; △ 0.015 M UO_2^{2+} or Th^{4+}.

tered by 0.015 M concentrations of these salts. Table I shows recovery of added fluoride in phosphoric acid in the presence of these salts (as well as information concerning accuracy in this system, as discussed below).

Estimation of accuracy

Exact assessment of the accuracy of the method is hampered by difficulty in obtaining and recognizing fluoride-free solutes, since at about $5 \cdot 10^{-6}$ M fluoride the electrode response may no longer be linear[1]. If the set of known additions conforms to the Nernst equation, however, this should confirm that the calculated c_F is the unknown concentration. In Table I, fluoride concentrations are calculated in two ways:

TABLE I

RECOVERY OF ADDED FLUORIDE

Solution	*Added*	*Fluoride concn. (10^{-5} M) found*		
		By least squares fit (computed A)		*By single increment calculation with A = 59 mV*
0.5 M NaCl	0	0.2	(60)	0.2
	5.0	5.6	(58)	5.9
	10.0	10.7	(58)	11.3
0.5 M NaCl, 1.5 M H_3PO_4	0	0.2	(63)	0.6
	5.0	5.8	(62)	5.2
	10.0	10.7	(63)	10.6
0.5 M $NaNO_3$	0	0.2	(58)	0.2
	5.0	5.6	(57)	5.9
0.5 M $NaNO_3$, 1.5 M H_3PO_4	0	0.5	(62)	0.5
	5.0	5.6	(62)	5.1
0.015 M salt in 10 M H_3PO_4				
$Al(NO_3)_3$	6.0	7.1	(61)	6.5
$UO_2(NO_3)_2$	2.0	2.2	(56)	2.5
$Th(NO_3)_4$	4.0	3.8	(56)	4.3

(*1*) by least squares fit to eqn. (3) or (7) of sets of 5 to 10 data points, with both c_F and A computed, and (2) by calculating c_F from a single point at ΔE equal to about 40 mV, with A equal to 59 mV. The magnitude chosen for ΔE represents a compromise between: remaining in the vicinity of the unknown concentration to reduce possible errors from nonlinearity, providing an accurate value of ΔE, and reducing the sensitivity of the calculation to the choice of A.

Most of the data in Table I suggest that the method may have a positive bias, but with the uncertain blank value, this is not definite. On the basis of Table I, the probable relative error can be safely generalized to 10%. Table I also shows that the single increment values agree satisfactorily with those obtained from the least squares fit, and that use of the theoretical value of 59 mV for A is reasonable.

Precision of measurement

The precision of measurement is better than the accuracy indicated above. For a typical system shown in Table II, the measurement had a relative standard deviation of $< 5\%$. These data also substantiate the relative error presumed above for the single-increment method, since the difference between fluoride ion concentrations of the two solutions ($1.05 \cdot 10^{-4}$) agrees within 5% with the amount of fluoride added (10^{-4} M).

Appraisal of experimental results

A semilog plot of ($c_F + x_n$) *versus* E_n can be used to affirm that the required response has been obtained for a given system. The resultant graph should be a straight line with a slope of about 59 mV. Figure 2 shows normal experimental data before and after inclusion of the calculated c_F. Figure 3 illustrates the interference from iron(III) which forms a fluoride complex, and its elimination by addition of phosphoric acid; no fluoride was detected in this sample solution.

The fluoride electrode was found specific for 10^{-5} M fluoride in the presence of molar quantities of nitrate, chloride, and phosphoric acid. When it does not respond to fluoride additions, (*1*) the fluoride concentration may be too high, and the solution must be diluted; (*2*) the fluoride is being complexed as it is added, and the interfering ion must be eliminated; or (*3*) hydroxyl ion is suppressing the response to fluoride, and the solution must be neutralized.

TABLE II

PRECISION OF MEASUREMENT[a]

(0.6 M LiCl)

	Original solution	*Original solution plus* 10^{-4} M F^-
F^- concentration (10^{-4} M)	0.14	1.19
Relative standard deviation (%)	5	2
No. of measurements	8	5

[a] $\Delta E = 50$ mV; A = 59 mV.

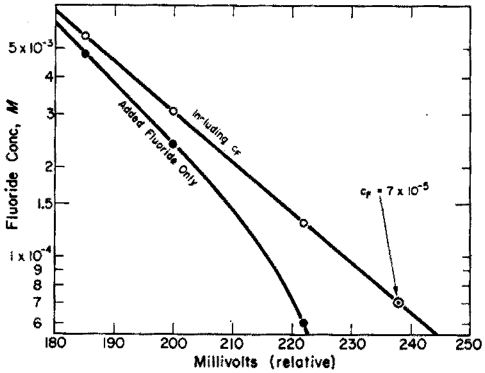

Fig. 2. Typical experimental data. 1 M Sodium silicate neutralized with phosphoric acid.

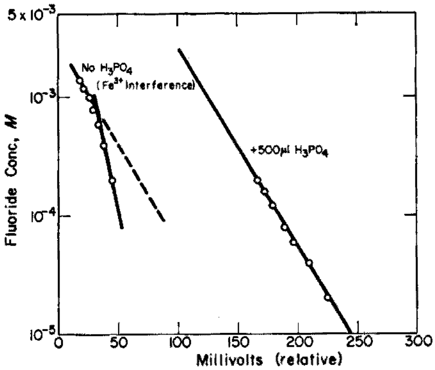

Fig. 3. Interference by iron(III) and elimination of interference. 1.9 M Sodium hydroxide neutralized with nitric acid.

The information contained in this paper was obtained during the course of work under Contract AT(07-2)-1 with the U.S. Atomic Energy Commission.

SUMMARY

A method is described for determining 10^{-5}–10^{-4} M fluoride in a variety of solutions potentiometrically with a fluoride-specific electrode, by a standard addition method. Any change of ionic strength or the nature of the solution that might alter activity coefficients or junction potentials is minimized. The relationship between potential and fluoride *concentration* thus follows the Nernst equation, and the unknown concentration can be calculated. Experimental data are given for solutions of sodium chloride, sodium nitrate, acidified sodium silicate and sodium hydroxide, lithium chloride, and phosphoric acid. Metal ions (*e.g.*, Al^{3+}, UO_2^{2+}, Fe^{3+}, Th^{4+}) that interfere by forming complexes with fluoride can be precomplexed with phosphoric acid. The relative error is estimated at 10%, and the relative standard deviation is less than 5% over the concentration range 10^{-5}–10^{-4} M fluoride.

RÉSUMÉ

On décrit une méthode potentiométrique pour le dosage des fluorures (10^{-5} à 10^{-4} M). On utilise une électrode spécifique au fluorure avec addition de fluorure étalon. Tout changement de force ionique ou de nature de la solution, pouvant modifier les coefficients d'activité ou les potentiels de jonction, est négligeable. La relation entre potentiel et concentration de fluorure suit l'équation de Nernst; la concentration inconnue peut être calculée. Des résultats expérimentaux sont donnés pour des solutions de chlorure de sodium, de nitrate de sodium, de silicate de sodium acidifié et d'hydroxyde de sodium, de chlorure de lithium, et d'acide phosphorique. Des ions métalliques (Al^{3+}, UO_2^{2+}, Fe^{3+}, Th^{4+}) gênant par formation de complexes avec le fluorure peuvent être précomplexés avec l'acide phosphorique. L'erreur relative est estimée à 10%; la déviation standard relative est inférieure à 5% pour des concentrations 10^{-5} à 10^{-4} en fluorure.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur potentiometrischen Bestimmung von 10^{-5} bis 10^{-4} M Fluorid in verschiedenen Lösungen unter Verwendung einer fluoridspezifischen Elektrode und der Zumischmethode. Jegliche Änderung der Ionenstärke oder der Natur der Lösung, die die Aktivitätskoeffizienten oder Potentiale ändern könnten, werden gering gehalten. Dadurch folgt die Beziehung zwischen dem Potential und der Fluoridkonzentration der Nernstschen Gleichung, so dass die unbekannte Konzentration berechnet werden kann. Näher untersucht wurden Lösungen von Natriumchlorid, Natriumnitrat, saurem Natriumsilikat, Natriumhydroxid, Lithiumchlorid und Phosphorsäure. Metallionen, die durch Komplexbildung mit Fluorid stören, können durch Phosphorsäure maskiert werden. Der relative Fehler wird auf 10% geschätzt, die relative Standardabweichung beträgt im Bereich von 10^{-5} bis 10^{-4} M Fluorid weniger als 5%.

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VACUUM-FUSION DETERMINATION OF OXYGEN IN ALUMINIUM AND ALUMINIUM–ALUMINIUM OXIDE COMPOSITES*

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The method commonly used in these laboratories for the determination of the aluminium oxide content of SAP** (Sintered Aluminium Powder) and of other artificially oxidised aluminium-based materials, which have a potential use as canning and structural material for nuclear reactors, involves the hydrochlorination of the sample with dry gaseous hydrochloric acid. The capabilities of the method, which consists of separating the aluminium oxide from the aluminium through volatilization of the matrix as aluminium chloride, and a comparison with other possible chemical methods of aluminium oxide determination, have been fully described[1].

Such methods or their modifications are currently used in chemical laboratories for determining the oxygen content of aluminium[2], but in order to take advantage of their ultimate sensitivity large samples (5–10 g or more) are required and these are not always available. Activation methods, as used at Ispra[3], suffer from the same disadvantage.

The control of the aluminium purity in relation to the preparation of different aluminium–aluminium oxide composites, where it is important to know the oxygen content of the starting aluminium, which may be low, made it necessary to investigate the possibilities of other, more sensitive methods. Accordingly, vacuum-fusion procedures were studied; in these procedures, oxygen in metals is determined as carbon monoxide after reduction of the metallic oxides in a graphite crucible under vacuum. Together with carbon monoxide other gases are evolved from the metal during the vacuum-fusion process: elemental hydrogen, elemental nitrogen, minor amounts of methane through secondary reactions, and carbon dioxide (if the metallic oxides are not sufficiently stable to the carbon reduction) can be produced.

Most of the metals processable by vacuum fusion give oxygen only as carbon monoxide; in the present case, aluminium oxide is one of the most refractory substances and, from thermodynamic considerations, carbon dioxide is not to be expected.

EXPERIMENTAL

Equipment

The instrument used was the commercial vacuum-fusion analyzer Heraeus

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* Work performed within the Orgel project.

**Sintered aluminium–aluminium oxide composite with a variable content of aluminium oxide.

VH 6 (W.C. Heraeus GmbH, Hanau/Main, Germany), which has already been described in full detail[4,5]. The instrument consists of a water-cooled quartz furnace, in which there is a graphite crucible heated by a high-frequency field (300 kc/sec, 10 kVA) coupled to a three-stage mercury diffusion pump–gas burette–Toepler pump for extracting, collecting and measuring the gases; and a gas chromatograph for their separation and analysis. The chromatographic column, 1 m long, is filled with molecular sieve 5A, and the detection system makes use of an argon ionization detector employed for the determination of permanent gases in an argon carrier contaminated with organic substances, as already described by Willis[6] and Lesser[7]. The gas chromatograph is calibrated against known gas mixtures; although the technique is very sensitive for small amounts of gases, the response is not linear, so that calibration curves relating the height of the chromatographic peaks and the amount of the different gases are required. Moreover, calibration curves become flat at certain gas levels; in order to avoid the large errors possible in the flat portion of the calibration curves, the gas levels are best limited to a maximum of about 7 μg hydrogen and 100 μg nitrogen/oxygen (as carbon monoxide). Methane is never a problem as it is evolved from a metal only in small amounts. Carbon dioxide, if any, is not detected because it is totally adsorbed on the molecular sieve at the working temperature of the column (35°). Figure 1, which is self-explanatory, illustrates the equipment used.

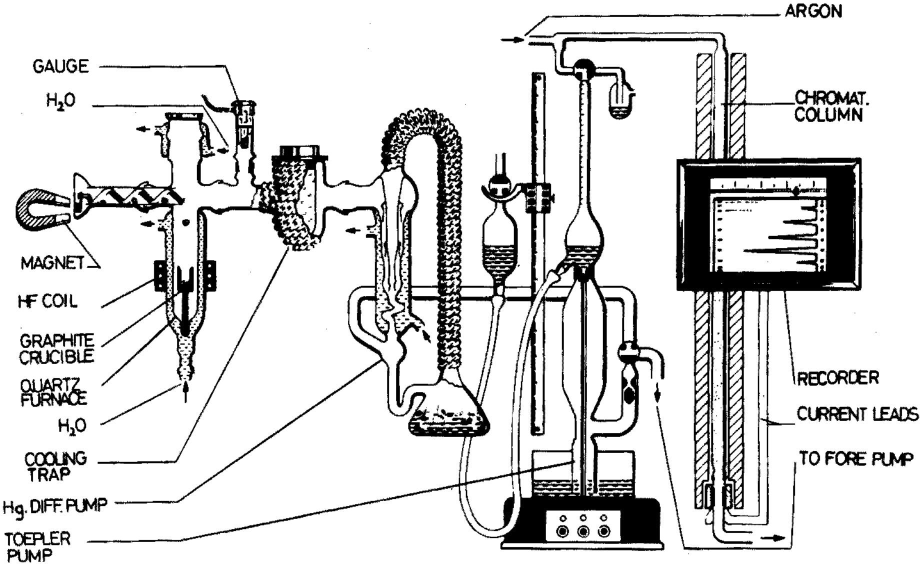

Fig. 1. Equipment used.

Preliminary experiments

No work on the determination of oxygen in aluminium–aluminium oxide composites appears to have been published and only a few papers on the determination of oxygen in aluminium by the vacuum-fusion or by the similar inert gas-fusion method are available. Hatfield and Newell[8], Sloman[9] and Martin[10] report on the successful use of the vacuum fusion–iron bath technique at 1550–1600°. Smiley[11] gives only a couple of results on "service analysis on pure aluminium" by means of the inert gas-fusion–platinum bath technique at 1800°. KOPA[12] reports on unsuccessful results in vacuum degassing of aluminium alone in a graphite crucible 1/3-filled with graphite powder up to a temperature of 1850°, but gives data on the good reliability of the vacuum fusion–iron bath technique. However, he mentions that frequently samples do not dissolve well in the bath, probably because aluminium carbide is formed before the metal is dissolved, thus hindering further analysis. Finally, KOPA discusses the very good results obtained with copper at 1550° instead of iron as bath material.

In the vacuum-fusion process, baths like iron, nickel, cobalt, tin or copper, because of their high vapour pressure require a lid on the crucible to keep the bath evaporation to a minimum at the operating temperature, which usually exceeds 1500°. As equipment available for the present work had no lid for the crucible (Fig. 1), the only metal bath which could be safely used was platinum, which was therefore examined first. Despite the many different operating conditions tried, results were discouraging. Use of platinum baths at temperatures ranging from the melting point of platinum to 1900°; use of platinum flux and tin flux; addition of platinum to the crucible before and after the sample; modifications of the crucible; all these proved to be unsuccessful on samples of pure aluminium, SAP and aluminium oxide.

The next step was to test the behaviour of a copper bath at 1550°. As expected, evaporation was extremely high, and after a short period of time the furnace became covered with a thick layer of copper, so that electrical discharges occurred in the furnace. The normal crucible, the inner dimensions of which are 14 mm diameter and 30 mm height, was then replaced by another crucible of the same height, but with an inner diameter of about 6 mm and fitted with a long graphite chimney. The aim was to use the copper flux technique or to add copper on top of the sample, whilst decreasing the copper evaporation, avoiding the metal condensation on the furnace walls and diminishing the surface exposed to metal vapours. These objectives were achieved and no electrical discharges occurred in the furnace, but another strange effect arose during analysis of pure copper; the first two oxygen determinations seemed to be good, but in subsequent analyses, a high carbon monoxide evolution was noticed, even when only blanks were run. This effect was interpreted as follows: copper condensed on the chimney and as it became thicker, it became hot in the high-frequency field, thus extracting gases from the chimney, which previously had been inadequately degassed, because of the impossibility of moving the induction coil over the surface of the furnace during the initial degassing of the instrument.

To eliminate all these troubles and because of the difficulty of installing a lid, it was finally decided to use graphite capsules, where the aluminium sample and copper flux could be sealed. It is known that graphite is permeable to gases at high temperature: TUROVTSEVA AND KUNIN[13] mention the use of such capsules for the analysis of titanium, but they give little information on their behaviour. The capsules used, together with their covers (Fig. 2), were made from graphite EY X 229*. The normal crucible was replaced with another, the dimensions of which were 28 mm inner diameter and 30 mm height, with a capacity of 6 capsules.

Final procedure

Several (4–6) capsules complete with covers are weighed. Samples of aluminium or aluminium–aluminium oxide composite in pieces of 30–60 mg, are carefully filed,

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* Morgan Crucibles-Morganite Italiana, Via Martini 9, Cinisello Balsamo (Milano), Italy.

washed with ethanol and toluene, dried and weighed. Copper filings are freed from surface oxides with dilute nitric acid, washed with distilled water, ethanol and toluene, dried and weighed. Without touching them by hand, the fluxes and the samples in weight ratios of about 4, are put into the capsules, the covers firmly screwed up, and the filled capsules placed in the sample container of the instrument. The furnace is evacuated, with the capsules at the same vacuum, the crucible is degassed at high temperature, and, when the blank of the instrument is low and constant, analyses are begun.

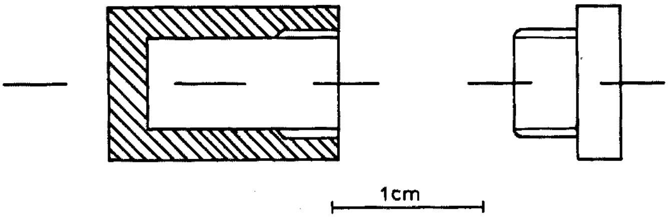

Fig. 2. Graphite capsule.

The first capsule is dropped into the crucible at 1100°* and held at this temperature for 15 min and the extracted gases are discarded (see Discussion). The temperature is then raised to 1600°, which is maintained for 15 min, during which some surges to 1700° lasting a total of 3–5 min are made.

The extracted gases are then analyzed. From the total carbon monoxide evolved, the oxygen of the sample is computed, allowance being made for the carbon monoxide coming from the capsule, flux and blank of the instrument.

All the capsules of the set are analyzed in succession according to the above procedure; the instrumental blanks are in the range of 1–3 μg oxygen (detected as carbon monoxide) and are taken usually at the beginning and after each two capsules for 15 min; the crucible temperature cycle during the blanks is the same as that followed during the second 15 min of gas extraction from the samples.

Degassing can be easily followed on the ionization gauge mounted near the furnace; the prevailing pressure before and after the degassing is in the range of $1–3 \cdot 10^{-5}$ mm Hg.

RESULTS

Table I gives some results on different specimens, compared with those obtained by the hydrochlorination and activation methods. The results are presented as "Direct" and "Indirect". "Direct" means that total carbon monoxide has been computed from its own calibration curve of the gas chromatograph. "Indirect" means that the total carbon monoxide, being beyond the range of its own calibration curve, has been computed from the total extracted gas measured in the burette of the Toepler pump, allowance being made for the hydrogen, methane and nitrogen as computed from their calibration curves. Table I indicates that vacuum fusion gives results in satisfactory agreement with the hydrochlorination and activation methods. The slightly higher vacuum fusion results can be explained by the fact that the present method

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* Temperatures are read using an optical pyrometer.

determines the total oxygen contained in the sample, thus including oxygen from other possible sources[14], whereas hydrochlorination determines only oxygen contained as aluminium oxide[1]. The standard deviations given are inclusive of possible inhomogeneities in the specimens.

TABLE I

OXYGEN DETERMINATION IN Al AND Al–Al_2O_3 COMPOSITES

Specimen	*Vacuum fusion*				*HCl* % *O*[b]	*Activation* % *O*
	% *O* *Direct*	% *O* *Indirect*	*No. of detns.*	*s.d.*[a]		
SAP 1	—	3.51	5	0.079	3.52	3.48
SAP 2	—	1.84	5	0.050	1.79	—
Al artificially oxidized 1	—	0.965	4	0.107	0.945	—
Al artificially oxidized 2	—	0.610	4	0.031	0.540	—
Al artificially oxidized 3	—	0.290	4	0.019	0.260	—
Al artificially oxidized 4	0.175	—	5	0.023	0.140	—
Raffinal[c]	0.0980	—	4	0.006	0.0975	0.1025
Al Merck[d] 99.99% Ribbon	0.0120	—	5	0.0036	—	—

[a] Std. dev. $= \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$

[b] From the found aluminium oxide.

[c] Not filed, as in powder form cold compacted under vacuum. Powders may also be put into the capsules, wrapped in copper foil.

[d] Not filed, as in ribbon form less than 0.5 mm thick.

Analyses were also made with quantitative results on pure aluminium oxide conditioned by heating in air at 1100°. Samples weighing 1.5–2 mg were wrapped in copper foil (200 mg) and put into the capsules together with a piece of pure aluminium (50 mg); complete extraction of gases was achieved in the usual 15 min.

DISCUSSION

Capsules and covers were made on a lathe and weighed together about 2 g. After a strong predegassing at 1700° in the instrument itself in order to reduce their initially large gas content, they were stored until required in a desiccator under rotary pump vacuum. Analyzed empty according to the procedure given above, the capsules showed an apparent oxygen content in the range of 0.3–0.8 p.p.m. with an average value of 0.5 p.p.m. of oxygen.

Although the covers are firmly screwed up after filling, the capsules are not vacuum-tight; thus, any air enclosed in them is evacuated during the initial degassing of the instrument and, as a proof, no nitrogen is detected coming from empty capsules even when dropped in the crucible directly at 1600°.

During the analysis the capsules evolve at 1100°, depending on storage time*, small amounts of carbon monoxide together with larger quantities of hydrogen, me-

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* Our maximum storage time was 3 weeks.

thane and probably carbon dioxide with C_2 hydrocarbons*; this is due to the possible adsorption of vapours from the rotary pump oil and when the desiccator is opened or when they are exposed to air for weighing and filling. Degassing at 1100° helps to keep the hydrogen and methane evolved at 1600–1700° well within the range of their calibration curves and renders the capsules practically independent of their previous history, as far as their oxygen content measured at 1600–1700° is concerned. No danger is expected for the sample, as its degassing only begins at an appreciable rate at 1500–1600°, under the present conditions.

The capsules, empty or filled with the flux alone, when analyzed according to the above procedure, also give at 1600–1700° small amounts of gas undetectable on the gas chromatograph, probably C_2 hydrocarbons and carbon dioxide*, which has seemed to be in quantities independent of the presence of the flux. Such amounts have been computed indirectly, and range from 7 to 14 Nμl/g** capsule, with an average value of 10 Nμl/g. In the "indirect" calculation of carbon monoxide, allowance is made for this "undetectable gas" also. Casual errors which can arise from the use of the "indirect" method with the present equipment, should not be higher in absolute terms than 15 Nμl, *viz.* about 10 μg oxygen. For example, Table II shows the total carbon monoxide computed in the two ways for a specimen of aluminium 99.5% pure.

TABLE II

"DIRECT" AND "INDIRECT" DETERMINATION OF TOTAL CARBON MONOXIDE

Sample weight (mg)	*Nμl CO Direct*	*Nμl CO Indirect*	*Δ CO (Nμl)*
50.1	7.6	0.0	−7.6
66.3	6.7	16.3	+9.6
49.0	7.1	2.9	−4.2
62.1	8.0	5.4	−2.6
61.4	8.3	17.5	+9.2
53.1	8.3	17.6	+9.3

The wide variation of the "indirect" results obviously arises from having used in the calculation the average value of 10 *Nμl*/g instead of the correct variable value pertinent to each capsule. Such a correct value (y) can be computed making use of Table II, and of the equation $\Delta CO + 10 \times 2 = y$, where 2 is the weight in g of each capsule. The average of the y values confirms once more the reported value of 10 Nμl/g.

The oxygen content of the specimen of Table II may be estimated as of the order of some tens of p.p.m.; it is not given exactly as it was below the sensitivity limit, because of the relatively high oxygen content of the flux used.

Once charged in the sample container and before being dropped into the crucible, the capsules are kept at room temperature and must not be subjected to sudden changes of temperature, as they may then evolve gases in an uncontrolled manner.

Copper flux was prepared from electrolytic copper chips with a purity better than 99.8%. In order to lower their possible oxygen content, the chips were placed in

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* The masses 26, 28 (which may include CO and N_2), 30 and 44 have been detected by mass spectrometry.

** 1 Nμl represents 1 μl at 0°, 760 mm Hg.

the crucible of the instrument and melted at 1100° under vacuum until no gas evolution was observed. The ingot was rolled and cut into pieces. Placed in the capsules and analyzed according to the recommended procedure with weights of 100–200 mg, this copper showed an apparent oxygen content (as carbon monoxide) in the range of 3–30 p.p.m. with an average value of 15 p.p.m.

A minimum flux to sample ratio of 3.5 is considered necessary for a quick and complete degassing of the sample. Ratios as high as 7 do not change appreciably the degassing conditions, but if the ratio is increased too much, the gas evolution is retarded especially from samples of very high oxygen content. (For example, for ratios of 10–11, the degassing of SAP 1 of Table I became lengthy, while that of Raffinal was normal; for ratios of 20 the degassing of SAP 1 was not finished after 45 min.) This phenomenon could be explained by the fact that carbon has a very small solubility in liquid copper[15,16]; only when a sufficient quantity of aluminium is present in the melt, because of its great tendency to form a carbide[17], is there sufficient carbon for the reduction of the aluminium oxide. And the higher the oxygen content of the samples, the higher the carbon, *i.e.* the aluminium, concentration needed to complete the reaction. The addition of pure aluminium for the analyses of samples of pure aluminium oxide is explained on this basis: in fact without this addition, the gas extraction was difficult and incomplete even after 45 min. A lack of this knowledge could cause difficulties in applying the classical bath technique, because the first samples, if small, are usually very much diluted in the bath. The problem is not mentioned by KOPA[12], who refers only to copper bath weights of 16–20 g and sample (max. 1800 p.p.m. oxygen) weights of 1.5–2 g. Possibly KOPA chose an acceptable copper to sample ratio by serendipity.

If it is assumed that samples must contain, for a good determination, an amount of oxygen at least equal to the sum of oxygen coming from blank, copper and capsule, the sensitivity of the method as described can be estimated as 100 p.p.m. for samples weighing 50 mg. As the capsules are large enough to accommodate samples weighing 100–130 mg, the sensitivity could be theoretically increased to 15–20 p.p.m., if oxygen-free copper (hydrogen reduced, for instance) were used as flux. Questions on the reliability of the method at such low concentrations may arise. From thermodynamic considerations, it would seem possible that during the degassing at 1100°, some oxygen or oxygen-bearing compound, which is present or develops within the capsule, could oxidize the aluminium, so increasing the amount of carbon monoxide released at the higher temperatures. However, the estimated oxygen content of the specimen of Table II, obtained with capsules not freshly degassed but stored for two weeks, seems to indicate that such an oxidation, if any, is very small.

In order to obtain further information on this point, 100–130 mg samples of the specimen of Table II were analyzed as described in the recommended procedure. The copper flux used had an apparent oxygen content of 2.2 p.p.m. The result obtained was 68 ± 21 p.p.m. oxygen. In order to avoid the "oxidation" step, the specimen was then analyzed using freshly degassed capsules thrown into the crucible directly at 1600–1700°. The apparent oxygen contents of the empty capsules and the copper flux were determined under the same conditions and were respectively of 1 and 2.8 p.p.m. oxygen. The result obtained for the specimen was 35 ± 10 p.p.m. oxygen. The comparison of the two results together with the activation analysis result of 60 p.p.m. on a 25-g sample, seems to confirm that the oxidation at 1100°, if any, was very small. For specimens of low oxygen content, analyses can obviously be performed with less difficulty, by direct introduction of the sample at 1600–1700°.

Despite the fact that the capsules are firmly closed, evaporation occurs at 1600–1700°, and parts of the furnace which are not water-cooled but are exposed to metal vapours, become hot in the high frequency field after being covered with a metal layer. Nevertheless, no getter effects were noticed. The glass joints of the furnace were lubricated with the high-melting grease "Lithelen"*. The furnace, after a working day, is dismantled, washed with aqua regia and distilled water, dried and reinstalled.

The capsules can be recovered, as the alloy within is found only loosely attached to them. They can be used again after a strong predegassing at 1700° in the instrument itself (with capsules open).

CONCLUSION

Because of possible differences in the various commercial instruments, the use of a single established analytical technique may be impossible. In the opinion of the authors, the present method is independent of the equipment available and gives within its limits, readily acceptable results. Many details have been given on the behaviour of graphite capsules, as they could in principle be used for vacuum-fusion determination of other metals.

We thank Mr. LAURENT, Chief of the Analytical and Mineral Chemistry Section, Messrs. COLLIN and SERRINI of the Analytical and Mineral Chemistry Group, for their helpful assistance in supplying the specimens and in discussing the method, and Messrs. GIRARDI and SABBIONI of the Activation Analysis Group for the activation analysis results.

SUMMARY

A copper bath–vacuum fusion method for the determination of oxygen in aluminium was modified because the extensive evaporation of copper at the operating temperature gave trouble in a commercial instrument with unlidded crucibles. The evaporation can be decreased by making use of graphite capsules, where the samples and the copper are sealed before being dropped into the hot crucible. The procedure gives good results for specimens of aluminium and of aluminium–aluminium oxide composites, the oxygen content of which ranged from some tens of p.p.m. to some weight percent. The sensitivity of the method is of the order of 20 p.p.m. for sample weights of 100 mg, if copper of very low oxygen content is used.

RÉSUMÉ

On propose une modification de la méthode par fusion dans le vide, (bain de cuivre) pour le dosage de l'oxygène dans l'aluminium, la forte évaporation du cuivre à la température de l'opération pouvant causer des ennuis dans un appareil commercial avec creusets non couverts. L'évaporation peut être réduite en utilisant des capsules de graphite où les échantillons et le cuivre sont liés avant d'être coulés dans le creuset

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* Leybold-Chima, Milan, Italy.

chaud. Ce procédé donne de bons résultats avec des échantillons types d'aluminium et de composés aluminium–oxyde d'aluminium. La teneur en oxygène va de quelques dizaines de p.p.m. à quelques %. La sensibilité de la méthode est de l'ordre de 20 p.p.m. pour des échantillons de 100 mg, si on utilise un cuivre de faible teneur en oxygène.

ZUSAMMENFASSUNG

Zur Bestimmung von Sauerstoff in Aluminium wurde eine Kupferbad-Vakuum-Schmelzmethode modifiziert, da bei der Verwendung kommerzieller Instrumente mit Tiegeln ohne Deckel die Verdampfung des Kupfers bei der Arbeitstemperatur Schwierigkeiten bereitet.

Die Verdampfung kann durch Verwendung einer Graphitkapsel verringert werden. Das Verfahren ergibt gute Resultate bei Aluminium- und Aluminiumoxidproben, wenn der Sauerstoffgehalt zwischen etwa 10 p.p.m. und einigen Prozenten beträgt. Die Empfindlichkeit der Methode liegt in der Grösse von 20 p.p.m. bei einem Probengewicht von 100 mg, wenn Kupfer mit sehr geringem Sauerstoffgehalt verwendet wird.

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MODULAR SOLID-STATE UNIT FOR ELECTROCHEMICAL STUDIES

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A number of electrochemical instruments based on operational amplifiers have been recently described (*e.g.*, ref. 1–3). These units are generally of limited versatility, although GOOLSBY AND SAWYER[4] have more recently described a versatile solid-state potentiostat–amperostat which could be used for a variety of electrochemical techniques. The latter paper and SMITH's[5] excellent discussion of the technique of alternating current polarography prompted us to design an even more versatile unit than that of GOOLSBY AND SAWYER[4], which could be used as an alternating current polarograph as well as being suitable or adaptable for many other types of electrochemical studies.

The apparatus developed and subsequently described in detail is suitable for conventional constant potential direct current polarography, alternating current polarography, linear scan voltammetry, cyclic triangular scan voltammetry, and coulometry and macroscale electrolysis at controlled potential. The instrument can be adapted to many other uses; particularly useful circuits are described, for example, in references 2–6. The performance of the unit in conjunction with a three-electrode configuration electrochemical cell allows it to be used for electrochemical studies on solutions of high resistance.

Excluding the X-Y recorder, the total cost of the instrument is less than $1000.

INSTRUMENTATION

Instrument arrangement

Each of ten operational amplifiers is so mounted that their functional terminals are connected to identical sets of banana jacks mounted onto the front panel of a suitable cabinet, *e.g.*, a recessed panel mounting chassis; outlets for the +15 and −15 V power supply are also provided within each set of jacks, giving a total of nine jacks per set. The panel layout is shown in Fig. 1; numbers refer to amplifier terminals, which are the same for all the amplifiers used except the P66A current booster amplifier (Unit H) and P6154 voltage booster amplifier, where normally keying terminal 4 replaces terminal 3. A strict color code was employed: red, +15 V; yellow, −15 V; black, ground; green, amplifier inputs; blue, amplifier output; white, all other terminals. Jacks are 0.75-in. center-to-center relative to one another on a diamond spacing in a given set of nine.

The electrical components necessary to program each amplifier to perform

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the required operation are mounted within a 2 × 5.25 × 3 in. aluminum mini-box, which has a set of external banana plugs arranged to fit into the set of 9 banana jacks mentioned. All controls, *i.e.*, switches, potentiometer knobs, etc., are mounted on the front of the mini-boxes (Fig. 2).

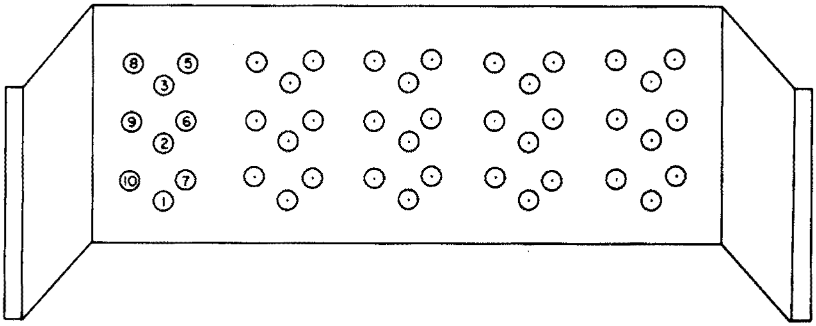

Fig. 1. Arrangement of amplifier terminal jacks on a 7 × 19 in. recessed panel mounting chassis.

Basic circuit design

The basic circuit is essentially that of a simple potentiostat (Fig. 3), with provision for boosting the output of the control amplifier with regard to both current and voltage, and with means for converting the signals into forms that can be readily recorded on an X-Y recorder.

For convenience, the circuit is divided into a series of individual mechanically discrete units, each enclosed within broken lines on the circuit diagram and designated as Unit A through J. Each unit is mounted in a separate mini-box and will be individually described in respect to construction and function.

Power supply

A Philbrick Model Pr300-R solid-state power supply (±15 V d.c. (±0.01%); 0 to 300 mA) was used. When it is necessary to use the P6154 voltage booster amplifier, two such power supplies are used in order to provide the ±30 V power requirements for the amplifier[7].

Sine-wave generator (unit A)

A very stable sine-wave generator was constructed, which utilizes a Philbrick P65AU amplifier (Fig. 4). REILLEY[8] has shown that the frequency of the signal from this circuit is given by:

$$\omega = 2p^{\frac{1}{2}}/(RC)^{\frac{1}{2}} \qquad (1)$$

where p is the proportion of the output fed back into the input of the amplifier, R is the resistance in ohms of R_1 ($R_1 = R_2$), C is the capacitance in microfarads of C_2 ($C_2 = C_3$), and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency in Hz). When ±10% capacitors were used, the useful frequency range of the oscillator was between 50 and 250 Hz. The unit is set to oscillate by means of R_4; the frequency and amplitude are then adjusted by means of R_5 and R_7, respectively.

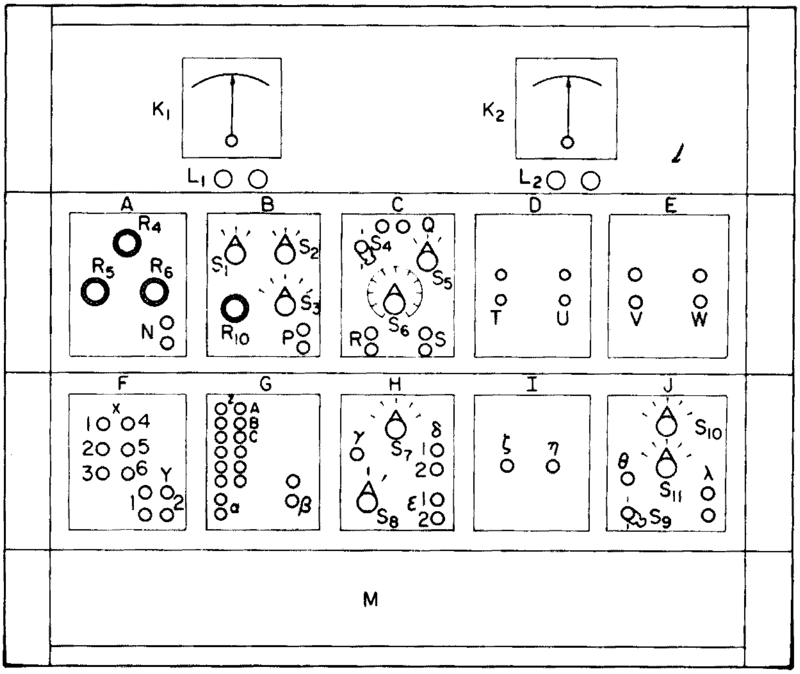

Fig. 2. Arrangement of front of instrument (housed in a 26-in high conventional 19-in cabinet). The units are mounted on three 7-in recessed panel mounting chassis above the power supply M.

(A) Sine-wave generator. R_4, amplifier oscillation adjustment; R_5, frequency adjust; R_6, amplitude adjust; N, signal output.

(B) D.C. voltage level. S_1, polarity set (Off–Negative–Positive); S_2, voltage range set (Off–0 to ±1.0 volt–0 to ±10.0 volt); S_3, damping adjust; R_{10}, voltage adjust; P, output voltage.

(C) Ramp generator. S_4, sweep polarity (Positive–Negative); Q, jacks for 1.0-μF capacitor; S_5, integrator function switch (Sweep–Hold–Reset); S_6, sweep rate set (2 mV/sec to 1.0 V/sec); R_{26}, current trim; R and S, output jacks.

(D and E) Full-wave rectifier. T, input from current amplifier; U, output to unit E; V, input from unit D; W, rectified output signal (to recorder).

(F) Reference electrode follower. X_1, to reference electrode; X_2, to counter electrode; X_3, to working electrode; X_4, from unit H; X_5, output from control amplifier (unit H); X_6, input to current amplifier (unit J); Y_1, output to voltage axis of recorder; Y_2, output to control amplifier (unit G).

(G) Control amplifier. Z, set of 6 identical input jacks; α, output jacks to d.c. voltmeter K_1; β, output jacks to current booster amplifier (unit H).

(H) Current booster amplifier. S_7, booster select (Current Booster–No Booster–Voltage Booster); S_8, Cell In–Cell Out switch; γ, output from control amplifier (unit G); S_1, output to voltage booster (unit I); S_2, input from voltage booster; ε_1, output to reference electrode follower (X_4 jack); ε_2, to counter electrode (X_5 jack, unit F).

(I) Voltage booster amplifier. ζ, input from current booster (jack S_1); η, output to current booster (jack S_2).

(J) Current amplifier. S_{10}, damping adjust; S_{11}, amplification adjust (1 μA = 1 mV–10 mV–100 mV–1 V); θ, input from working electrode (X_6 jack, unit F); S_9, cell In–Out switch; λ, output signal (to recorder or rectifier).

D.C. voltage level (unit B)

The initial potential of a voltammetric scan or the potential for an exhaustive electrolysis can be set anywhere between +10 and −10 V by means of a unit based on a Philbrick P65AU amplifier (Fig. 5). The polarity of the voltage is set with S_1 (note that the output voltage is of opposite sign to the input voltage); the range is

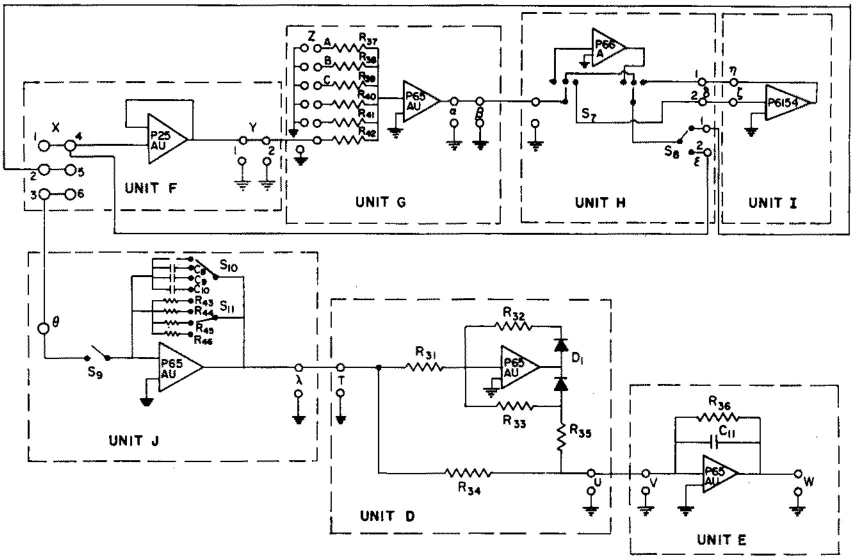

Fig. 3. Basic potential control and measuring circuit of instrument. The components are also identified in Fig. 2, where applicable, to which reference can be made for items not identified in the present figure caption. Dashed lines indicate circuit within each marked unit. Open circles correspond to banana jacks which appear on the front panel of each unit. Solid circles indicate switching points.

S_7, double-pole 3-position shorting; S_8, SPDT shorting; S_9, toggle; S_{10}, S_{11}, single-pole 4-position shorting; R_{31}, R_{32}, R_{33}, R_{34}, R_{36}, 20K; R_{35}, 10K; R_{37-42}, 100K; R_{43}, 1K; R_{44}, 10K; R_{45}, 100K; R_{46}, 1M; C_8, 0.001 μF; C_9, 0.01 μF; C_{10}, 0.1 μF; C_{11}, 100 μF; D_1, Motorola silicon diode, 50 V/V. Except where otherwise stated, resistors are ±1% tolerance and capacitors ±10%; the latter are rated at 600 V d.c.

A, B and C: Inputs from units A (Fig. 4), B (Fig. 5), and C (Fig. 6), respectively.

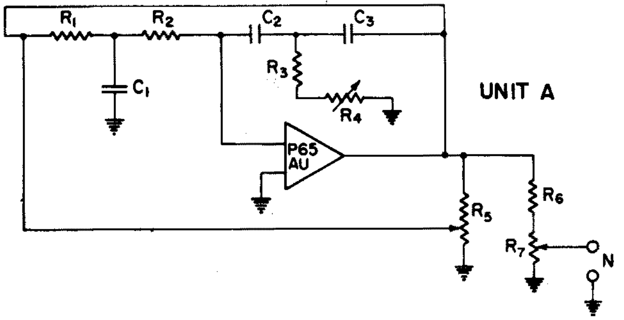

Fig. 4. Sine-wave generator (unit A). R_1,R_2, 20K; R_3, 9K; R_4, 10-turn, 2K potentiometer; R_5, 10-turn, 5K potentiometer; R_6, 100K; R_7, 10-turn, 1K potentiometer.

changed by altering the magnitude of the input resistors R_8 and R_9 to the amplifier by means of switch S_2. Optional dampening of stray noise is provided for by switch S_3 and the associated capacitances.

Ramp generator (unit C)

A suitable ramp generator was built, based on a Philbrick P25AU amplifier

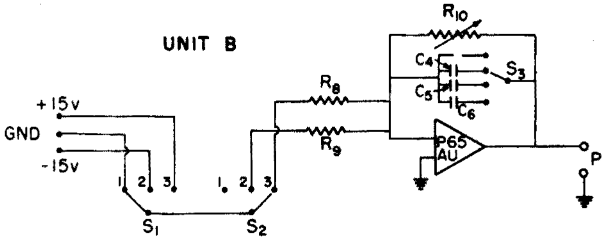

Fig. 5. D.C. voltage level (unit B). S_1, S_2, rotary single-pole 3-position non-shorting; S_3, rotary single-pole 4-position shorting; R_8, 15K; R_9, 150K; R_{10}, 10-turn, 10K potentiometer.

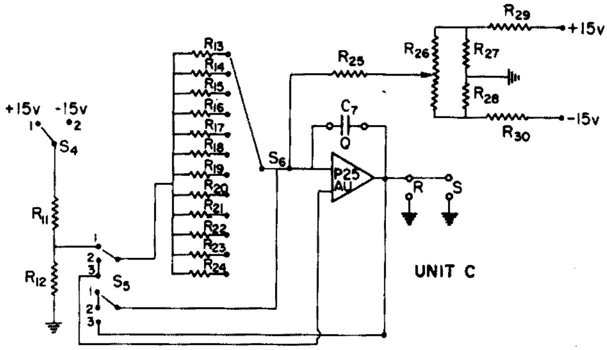

Fig. 6. Ramp generator (unit C). S_5, double-pole 3-position shorting; S_6, single-pole 11-position shorting; R_{13}, 100K; R_{14}, 200K; R_{15}, 500K; R_{16}, 1M; R_{17}, 2M; R_{18}, 5M; R_{19}, 7.5M; R_{20}, 10M; R_{21}, 15M; R_{22}, 20M; R_{23}, 50M; R_{24}, open position for insertion of another suitable resistor; R_{25}, 70K; R_{26}, 25-turn 0.5K trimpot; R_{27}, R_{28}, 22K; R_{29}, R_{30}, 50K; C_7, 1.00 μF ($\pm 1\%$, Southern Electronics, Burbank, Calif., Model PC 105G2APL, 200 V d.c.).

(Fig. 6). By variation of the input resistance with switch S_6, eleven scan rates between 2 and 1000 mV/sec can be generated. A 1.0-mF polystyrene capacitor is used in feedback. The polarity of the output signal is selected by means of a switch S_4. Switch S_3 selects the mode of the integrator to either sweep, hold or reset. The output of the ramp generator is monitored continuously with a (+10)-0-(−10) V d.c. meter (Eberbach Corp. Model 301-57).

The performance of the ramp generator was generally very satisfactory, although the minimum drift attainable, ±0.2 mV/sec, became significant for studies requiring very low scan rates, *e.g.*, 2 or 5 mV/sec. However, when an X-Y recorder is used, slight variations of sweep rate are not important. When the performance of the ramp generator becomes critical, a Philbrick P2 amplifier could be used instead of the P25AU.

Full-wave precision rectifier (units D and E)

A full-wave precision rectifier, based on HOWE's design[9], utilized two Philbrick P65AU amplifiers (Fig. 3). The unit performed well and the output could be fed directly to one axis of an X-Y recorder.

The damping capacitor, C_{11}, tended to cause the output on the recorder to be attenuated by a factor of 1.93, although this was a linear effect over the normal current ranges expected and could easily be corrected. Without the damping capacitor, the current oscillations on the recorder became very large and considerable noise was seen.

Reference electrode follower (unit F)

Because of their high imput impedance and stability, Philbrick P25AU amplifiers were employed in the reference electrode follower, which monitors the potential difference between the reference and working electrodes. The follower was wired in the conventional unity gain, non-inverting mode (Fig. 3).

Control amplifier (unit G)

The control amplifier is based on a Philbrick P65AU amplifier. Five identical sets of input jacks are provided so that several signals can be introduced and summed simultaneously (Fig. 3). The state of control of the output of the control amplifier is monitored by means of a (+10)-0-(−10)-V d.c. meter (Eberbach Corp. Model 301-57).

Current booster (unit H)

The current booster amplifier is a Philbrick P66A amplifier, which has a maximum output of ±20 mA at ±10 V without external resistors and ±100 mA at ±10 V with appropriate externally connected resistors[10].

Voltage booster (unit I)

In order to achieve high voltage outputs in the control amplifier loop, provision is made for the use of a Philbrick P6154 voltage booster amplifier capable of ±10 mA at ±100 V. By means of switch S_7, the current booster or voltage booster can be switched into the circuit or, as is usual, the unit can be used without any booster amplifiers.

In order to prevent the control amplifier from reaching its output limits when the counter and reference electrode leads are disconnected, provision is made by means of switch S_8, for shorting the two electrodes together internally.

Current amplifier (unit J)

A Philbrick P65AU amplifier is used in the inverting mode to convert the current flowing at the working electrode into a proportionate voltage which can be fed to a recorder. By means of the feedback resistor (switch S_{11}), the amplification of the current could be altered to the extent that 1 μA flowing at the working electrode could be converted to 1, 10, 100 or 1000 mV.

In order to eliminate high-frequency noise when the unit is used as an alternating current polarograph, it is necessary to have a small damping capacitance across the amplifier. Generally, a 0.001-mF capacitor was preferred since this did not attenuate the a.c. signals to any appreciable extent.

Operating procedure

Depending upon the operation required, various units are connected together by means of coaxial cable. Thus, for d.c. polarography and voltammetry and for cyclic voltammetry, units B, C, and F to J are used, although booster units H and I are not needed for most purposes.

For controlled potential electrolysis, units B, F, G, and H or I would normally be required.

For alternating current polarography, units A to G are required.

Clearly, by suitable patchcording or, preferably, construction of alternative mini-boxes, many other operations can be performed, *e.g.*, *cf.* references 1–6 and 11.

All voltammograms and polarograms during the testing and subsequent use of the instrument were recorded satisfactorily on either a Moseley Model 135 or Model 7001A X-Y recorder.

INSTRUMENT PERFORMANCE

Inorganic system

The iron(III)/iron(II) system in 0.25 *M* oxalic acid–0.25 *M* potassium oxalate solution (pH 2.65), which is generally considered to be reversible at the dropping mercury electrode, was examined to evaluate the performance of the instrument. Polarography (d.c.) at the dropping mercury electrode (DME) gave the same results as a Sargent Model XXI polarograph. Linear sweep and cyclic voltammetry at the pyrolytic graphite electrode (PGE) and the hanging mercury drop electrode (HMDE) gave results identical to those obtained with a cyclic voltammetry unit based on the original DeFord designs[11], which utilized vacuum-tube operational amplifiers.

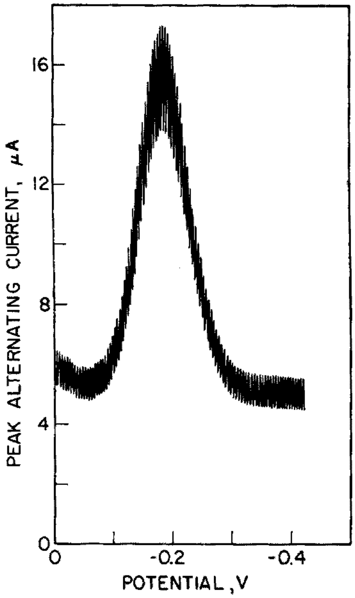

Fig. 7. Alternating current polarogram of 1 m*M* iron(III) in oxalate background (pH 2.65). Frequency: 50 Hz; amplitude: 30 mV peak-to-peak; scan rate: 2 mV/sec. Potential is *vs.* SCE.

Alternating current polarography at the DME was as expected for a reversible system as evidenced by (1) the linear relationship between the peak current and the amplitude of the alternating signal over the range of 4–40 mV peak-to-peak voltage at 50 Hz, (2) the invariance of the peak current with the height of the mercury column, (3) the linear relationship between the peak current and the square root of the applied frequency between 15 and 64 Hz, followed by a region at higher frequencies where the current rapidly decreased with increasing frequency, and (4) the linear peak current–concentration curve at 50 Hz and the 10-mV peak-to-peak amplitude over the concentration range 0.1–1 m*M*. A typical a.c. polarogram is shown in Fig. 7.

The observed alternating current was lower than that predicted theoretically[12], primarily because of the uncompensated capillary resistance of the dropping mercury electrode. By means of recently published circuits[13], it should be possible to reduce substantially the effects of the series resistance.

The unit is capable of performing only fundamental harmonic a.c. polarography, although it would be possible—by increasing the number of operational amplifiers—to extend the unit to perform second and third harmonic a.c. polarography[5].

Organic system

Purine, which gives two 2-electron waves at the dropping mercury electrode

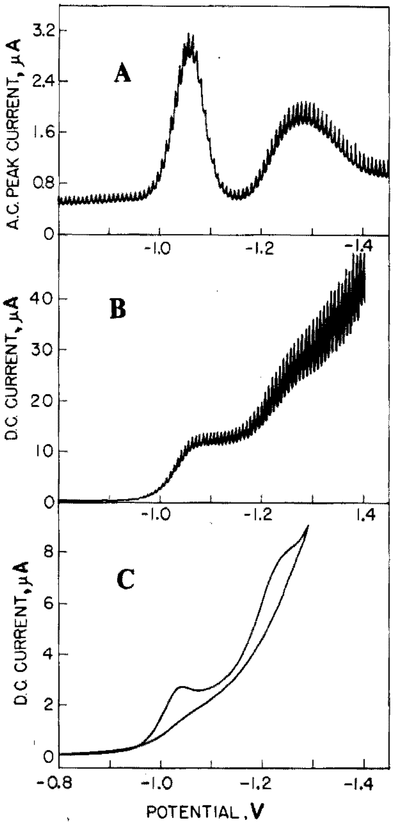

Fig. 8. Response of purine in pH 4.1 aqueous acetate buffer solution (ionic strength: 0.5 *M*). (A) Alternating current polarography at DME; d.c. scan rate, 2 mV/sec; a.c. amplitude, 10 mV peak-to-peak; frequency, 50 Hz; 2 m*M* purine. (B) D.C. polarography at DME; scan or polarization rate, 2 mV/sec; 2 m*M* purine. (C) Cyclic voltammetry at hanging mercury drop electrode; scan rate, 20 mV/sec; 0.5 m*M* purine. Potential is *vs.* SCE.

in acidic solution with some catalytic hydrogen evolution accompanying the second wave[14], was examined in 0.5 *M* acetate buffer solution of pH 4.1. Curves obtained on polarography at the DME, cyclic voltammetry at the hanging mercury drop electrode, and alternating current polarography at the DME are shown in Fig. 8.

The polarographic data agree with those previously reported for a Leeds & Northrup Type E Electro-Chemograph[14]; the cyclic voltammetric and a.c. polarographic data agree with those obtained with separate units based on vacuum-tube operational amplifiers[15].

Of special significance from the analytical viewpoint is the definition of the second purine wave on a.c. polarography as compared to that on d.c. polarography.

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SUMMARY

A relatively inexpensive unit based upon solid-state operational amplifiers is described; its modular design makes it an extremely versatile instrument for many electrochemical techniques, *e.g.*, normal direct current polarography and linear sweep voltammetry, cyclic voltammetry, alternating current polarography, and coulometry and electrolysis at controlled electrode potential. It can be readily adapted to many other functions.

RÉSUMÉ

Une unité modulaire solide relativement peu coûteuse est décrite constituant un instrument extrêmement versatile pour de nombreuses techniques électrochimiques: polarographie à courant direct normal et voltammétrie à balayage linéaire, voltammétrie cyclique, polarographie à courant alternatif, coulométrie et électrolyse à potentiel contrôlé. Cet appareil peut être facilement adapté à plusieurs autres usages.

ZUSAMMENFASSUNG

Es wird eine relativ kleine Verstärkereinheit, welche sich für zahlreiche elektrochemische Techniken wie z.B. die Polarographie, Voltametrie, Coulometrie und für die Elektrolyse eignet, beschrieben. Sie kann ebenso schnell zahlreichen anderen Funktionen angepasst werden.

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THE COULOMETRIC TITRATION OF TETRAPHENYLBORATE ION WITH ELECTROGENERATED SILVER ION AND A BIAMPEROMETRIC END-POINT

APPLICATION TO THE DETERMINATION OF POTASSIUM AND POLYETHYLENEGLYCOLS

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Several investigators have employed an argentimetric titration of redissolved tetraphenylborate ion (TPB) or excess of TPB. Relatively large amounts (up to 25 mg) were determined visually with eosin as an indicator in an acetone solution. The argentimetric titration is based on the large difference in solubility between the potassium and silver tetraphenylborates in an acetone–water solution. A sufficiently high concentration of acetone will dissolve KTPB (and other TPB salts) and yet AgTPB will remain insoluble. RUEDORFF AND ZANNIER[1] recommended that the solution contain 50% acetone at the equivalence point. HAVIR AND KRIVANEK[2] concluded that theoretical results were obtained in a medium of 33% acetone.

FLASCHKA AND BARNARD[3] discussed some discordant findings in the titrimetric procedures with silver nitrate as titrant. Most evidence indicated that the silver TPB precipitate was not stoichiometric. Some investigators have noticed differences in the titer as the concentration of acetone used was changed. PATRIARCHE AND LINGANE[4] suggested some explanations for the conclusions of other investigators. They concluded that silver TPB was stoichiometric. SUZUKI[5] employed a coulometric generation of silver to titrate TPB. His titration medium was 60% acetone acidified with acetic acid. PATRIARCHE AND LINGANE asserted that this medium was extremely unsatisfactory because the amount of acetone was too high and the acidity led to the decomposition of TPB. They recommended a neutral solution of 35–50% acetone.

Potassium has often been determined by precipitation with sodium TPB[3]. Foreign ions may be coprecipitated and this constituted a serious source of error in the gravimetric procedure. Titrimetric methods have been adapted both for the determination of the excess TPB added and for the amount of TPB in the precipitate. By redissolving the precipitate in acetone, the TPB could be determined argentimetrically.

LEVINS AND IKEDA[6] developed a potentiometric titration of polyethyleneglycol (PEG) with sodium TPB in the presence of barium ion. PEG formed an oxonium salt in the presence of barium ion which was instantly precipitated with sodium TPB. Although the complex was not stoichiometric, the ratio of TPB to the number of ethylene oxide units was constant over the range of PEG 600 to 4000. The only exception was PEG 1500 which contained large amounts of PEG 300.

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In the present paper the argentimetric coulometric titration of TPB to a biamperometric end-point is described. This titration is applied to the determination of potassium in standard solutions, in admixture with other ions, and in serum samples. Finally the titration is applied to the indirect determination of PEG.

EXPERIMENTAL

Apparatus

Constant-current coulometric titrations were carried out with a ChrisFeld Microcoulometric Quantalyzer or the equivalent. In later studies, an Aminco-Cotlove Chloride Titrator was employed. The titration cell (a 30- or 50-ml beaker) held the silver generator anode and the auxiliary platinum cathode. The auxiliary cathode was isolated from the bulk of the solution inside a glass tube with a fine glass frit on the end. The titration end-point was detected biamperometrically by impression of 100 mV between two silver wire electrodes with a Sargent Polarograph, Model XV. The amperometric current was recorded on the polarograph[7]. The indicator electrodes were two lengths of silver wire sealed in a glass tube with General Electric RTV silicone cement. A dead-stop technique was employed to mark the end-point as follows: with the indicator electrodes immersed in the solution, the pen of the polarograph (at a sensitivity of 0.01 μA/mm) was set at the 50-mm mark with the displacement knob. The titration was continued until the indicator current (pen) reached the 100-mm deflection point (0.5 μA indicator current). The indicator current remained small until the end-point was reached.

The apparatus used for the filtration of potassium and polyethyleneglycol tetraphenylborate precipitates (Fig. 1) was similar to that previously described[8]. The apparatus was designed around a Millipore filter holder (Millipore Filter Corp., Bedford, Mass.) 1″×6″, with a 25-mm coarse grade frit; 25-mm Whatman fiber glass filters were used to retain the precipitate.

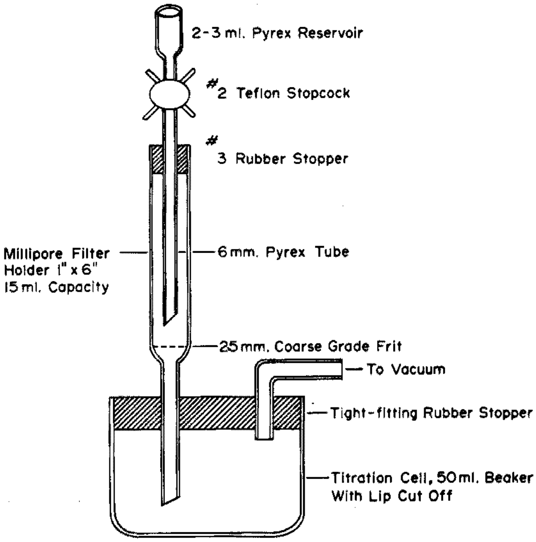

Fig. 1. Precipitation and filtration assembly.

Reagents

All chemicals were of reagent grade unless otherwise specified. Sodium tetraphenylborate (Fisher Scientific Co.) was used without previous drying. Mallinckrodt AR potassium chloride (dried at 110°) was the source of potassium. Versatol serum standards (Warner-Chilcott, Morris Plains, N.J.) were used in the blood studies. The amounts of potassium and other ions assayed in the serum were provided by the manufacturer for each lot. Polyethyleneglycol samples were kindly donated by Carbide and Carbon Chemicals Co.

General electrolyte for the TPB titrations. Add 42.5 g of sodium nitrate and 1.3 ml of glacial acetic acid to 100 ml of water; add 400 ml of acetone and dilute the solution to 1 l with distilled water. This solution remains stable for long periods of time and slight variations in the reagent concentrations do not affect the results.

Precipitating agent for potassium[3]. Prepare fresh aluminum hydroxide by adding dilute ammonia to a solution of aluminum nitrate. Filter and wash 1 g of the precipitate. Dissolve 3 g of NaTPB in 80 ml of water. Add the aluminum hydroxide and 1 drop of a 0.01 *M* potassium nitrate. The precipitate formed scavenges any ammonia impurities and removes colloidal KTPB. Filter the entire solution through retentive filter paper and dilute the filtrate to 100 ml. Adjust to pH 8 with dilute sodium hydroxide. Allow the solution to stand for 1 day before use. Store in a refrigerator, protected from light. If additional precipitate forms, refilter. The solution is stable for long periods of time.

Recommended procedures

Titration of TPB. Add 25–30 ml of the general electrolyte to the titration cell; this electrolyte is also used as the catholyte. Place the freshly cleaned electrodes in the cell. Silver electrodes may be cleaned either with dilute nitric acid (1:3 solution) or with Wright's silver polish. These electrodes are conditioned by the pretitration step; in addition, the cell becomes saturated with AgTPB and the desired level of excess silver ion is achieved. To pretitrate the electrolyte solution add a sample of approximately 4 μeq of NaTPB. Set the polarograph pen at the 50-mm mark (sensitivity 0.01 μA/mm) and with 100 mV between the indicator electrodes, generate silver ion at a rate of 0.1 μeq/sec. During the titration, stir briskly with a magnetic stirring bar. Halt the generation when the polarograph pen reaches the 100-mm mark.

Add the TPB sample to the titration cell and titrate as above. For samples of 1 μeq or more, the generation rate of 0.1 μeq/sec provides usable titration times. For samples less than 1 μeq, a generation rate of 0.01 μeq/sec is used. Reagent and solvent blanks should be determined under the same conditions as the sample.

Determination of potassium. Add the potassium sample to the precipitation apparatus. Add 0.1 ml of 2% acetic acid and 0.25 ml of the 3% NaTPB solution. After stirring, stopper the samples and place in a refrigerator for 15 min. Place the precipitation funnel over the Millipore filter apparatus and open the stopcock. Suck dry under vacuum, and then wash with two 2-ml portions of cold water.

Remove the filter apparatus and place over the titration cell which has been pretitrated. Cautiously apply vacuum and use two 2-ml portions of the generating electrolyte to dissolve the filter cake into the titration cell. Remove the filter apparatus, insert the electrodes, and titrate as above.

Determination of PEG. Place a clean precipitating funnel on the Millipore filter apparatus equipped with a solvent-resistant 0.45 μ Gelman membrane filter. Pipette the sample (dissolved in a barium acetate–acetic acid buffer of pH 4.6) to the funnel with the stopcock closed. Add a known volume of the standardized 3% NaTPB solution and mix. After 10 min, open the funnel stopcock so that the mixture flows onto the filter. Apply vacuum and catch the filtrate in the titration cell (5-ml vial supplied with the Aminco-Cotlove Chloride Titrator). Wash the filter with three 0.5-ml portions of cold water. Dismantle the filter assembly and discard the filter. Wash the glass frit with 1 ml of acetone and add this wash to the filtrate and aqueous washings. Then transfer the contents of the vial containing the total filtrate and washings to a 10-ml volumetric flask with enough acetone to make the total acetone volume 5 ml. Dilute to 10 ml with distilled water. All samples, blank and precipitation reagents are taken through every step of this procedure.

Pipette a 3-ml aliquot of the solution into the titration cell. To each vial add 1 ml of generating electrolyte solution (a solution 2 *M* in sodium nitrate and 0.08 *M* in acetic acid). Titrate at the low generation rate with the shut-off current set at 5 μA (Aminco-Cotlove Chloride Titrator).

Prepare a calibration curve from duplicate determinations on separate samples at each point. Subtract the blank time from all of the titrations, including the sample which is pure NaTPB plus blank. Plot the net sec of titration time against the mg of PEG present in the sample.

Calculations

Calculate the μeq of sodium TPB in the sample by multiplying the titration time in sec (after subtraction of the blank) by the generation rate in μeq/sec.

For the potassium determination (in μeq) multiply the net titration time of the sample by the generation rate.

RESULTS AND DISCUSSION

TPB studies

It has been recommended that gelatin be added for certain precipitation titrations. A stock solution of gelatin was prepared and used to make up electrolyte solutions containing between 1.0 and 0.001% gelatin. Except for the gelatin, all electrolyte solutions were identical. Samples of 0.4 μeq of NaTPB were titrated. At concentrations of 1.0 and 0.1%, no end-point currents were obtained. At lower concentrations, the end-point currents were badly curved. Even with concentrations as low as 0.005%, curvature was noted. Although little curvature was noted at a gelatin concentration of 0.001%, the end-point was sharper in the absence of gelatin.

The range of acetone concentration recommended by PATRIARCHE AND LINGANE[4] (35 to 50%) was found to be satisfactory. Flatter baselines were obtained with lower acetone concentrations. At 50% acetone, the barest trace of a current reversal at the end-point was apparent. Both 45% and 40% acetone displayed current reversals and sharp end-point rises; 35% acetone produced a less prominent current reversal.

At a generation rate of 0.1 μeq/sec, samples of 2–4 μeq of NaTPB were easily determined with a precision of ±0.5% relative (Table I). With a generation rate of 0.01 μeq/sec, a sample of 0.4 μeq could be titrated with a precision of approximately ±1%. The smallest amount of NaTPB which could be reliably determined was 0.1 μeq.

Potassium studies

Table II gives data on the titration of standard potassium solutions. Titrations for duplicate samples were low by about 4% for 2 μeq of potassium, by about 3% for 4 μeq, and by about 7% for 1 μeq. The precision varies from 1–2% for 4 μeq to 5–6% for 1 μeq. The loss of sample occurs during the washing step even though the wash solutions were saturated with KTPB.

TABLE I

TITRATION OF STANDARD SODIUM TPB SOLUTIONS

Sample size (μeq)	*Average titration time[a] (sec)*	*Generation rate (μeq/sec)*	*Polarograph sensitivity (μA/mm)*
4.000	39.2 ± 0.2	0.1	0.010
2.000	19.6 ± 0.03	0.1	0.010
4.000	132.6 ± 0.6	0.03	0.010
2.000	66.3 ± 0.1	0.03	0.010
1.000	32.3 ± 0.5	0.03	0.010
1.000	98.5 ± 0.3	0.01	0.003
0.400	39.2 ± 0.4	0.01	0.003
0.400	131.6 ± 0.5	0.003	0.003
0.100	32.6 ± 0.4	0.003	0.003

[a] Average of 3 determinations.

TABLE II

TITRATION OF POTASSIUM[a]

Standard potassium chloride solutions[b]			*Potassium in special solution[c]*		
Sample size (μeq)	*μeq found*	*Error (%)*	*Sample size (μeq)*	*μeq found*	*Error (%)*
4.000	3.885	−2.8	4.100	3.992	−4.3
2.000	1.938	−3.2	2.050	1.990	−5.9
1.000	0.937	−6.6			

[a] Generation rate 0.03 μeq/sec, sensitivity 0.010 μA/mm.
[b] Data are the average of 4 titrations.
[c] Data are the average of 5 titrations.

Table II also gives data for a potassium sample which contained about 40 times more sodium than potassium and roughly equal amounts of calcium and magnesium. With samples containing 4.1 μeq of potassium, the average value is low by about 4% (the precision is about 2%). The lowest amount of sample which was determined was 2.05 μeq (accuracy 6%, precision 4%).

Versatol standards were assayed with samples of 0.5 ml (*ca.* 2 μeq of potassium). It was possible to obtain results which were approximately correct (*ca.* ±15%). Two methods of preparing protein-free filtrates (P.F.F.) were employed: one method used trichloracetic acid to precipitate the protein[9] and the other employed the barium–zinc sulfate precipitation[8]. One of the major difficulties was in filtering and washing the precipitate. The P.F.F. apparatus tended to clog with membrane filters, making washing very difficult. Various combinations of filters and procedures were tried with no particular success. The P.F.F. was precipitated with 3% solutions of NaTPB. If any proteins were present, the precipitate would clog the filter. With either P.F.F.

procedure followed by NaTPB precipitation and determination of potassium, it was not possible to improve on the 15% accuracy previously mentioned.

PEG studies

The original purpose was to determine the amount of TPB associated with the PEG complex, by redissolving the precipitate and directly determining the TPB content. However, it was impossible to dissolve the precipitates completely in any reasonable volume of acetone–water mixtures. Dimethylformamide (DMF) quickly and completely dissolved the precipitate but large amounts were necessary to prevent reprecipitation in the presence of the generating electrolyte. Furthermore, DMF obscured the end-point by rendering the AgTPB more soluble. Because of these difficulties, the direct titration method was abandoned and the indirect procedure adopted.

The method described above was found to work reasonably well. The titration curves were not good but they were reproducible in spite of the large blank. When determinations were made on more than one aliquot from the same sample, the reproducibility of the titrations was well within 1% relative. A linear calibration curve was obtained from solutions of PEG 600 to 4000. The data are presented in Table III and indicate that in the mid concentration ranges, the error may be held to ±5%.

TABLE III

DETERMINATION OF POLYETHYLENEGLYCOL

mg PEG/ml	*Titration time (sec)*	*Calculated Faradays* $\cdot 10^{-6}$	*% error from calibration curve*
0.000	175.1	2.678	1.4
	174.5	2.668	1.4
0.100	161.2	2.447	4.1
	160.5	2.435	12.3
0.300	128.3	1.901	0.0
	124.3	1.834	3.7
0.500	95.2	1.351	0.0
	97.3	1.386	3.7
0.700	67.8	0.896	2.0
	69.1	0.918	2.0
0.900	37.9	0.400	0.0
	36.5	0.377	10.4

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SUMMARY

Microequivalent amounts of TPB in a 40% acetone generating electrolyte were titrated with coulometrically generated silver ions. With a biamperometric end-point, samples of 0.1–4 μeq of NaTPB were determined with a precision with 1%. The technique was applied to the determination of potassium in potassium chloride alone and in mixtures with other salts. The overall accuracy ranged from −3 to −7% for samples of 4 μeq to 1 μeq of potassium, respectively. Artificial serum samples gave somewhat discordant results, because of difficulty in removing all interfering protein.

A method was developed for the determination of 0.1–1.0 mg of PEG 600 to 4000 with excess TPB in the presence of barium ions. With reasonable care errors may be held to within 5%.

RÉSUMÉ

On décrit une méthode pour le dosage du tétraphénylborate (TPB) en milieu acétone 40%, par titrage coulométrique à l'aide d'ions argent électrogénérés. On peut ainsi, avec point final biampérométrique, analyser des échantillons renfermant 0.1–4 μeq de NaTPB avec une précision de 1%. Cette technique est appliquée au dosage du potassium dans son chlorure et dans des mélanges d'autres sels. L'exactitude est de −3 à −7% pour des échantillons de 4 μeq à 1 μeq respectivement. Des échantillons de sérum artificiel donnent des résultats parfois discordants, en raison de la difficulté d'éliminer toutes les protéines gènantes. Une méthode est proposée pour le dosage de 0.1 à 1.0 mg de PEG 600 à 4000 avec un excès de TPB, en présence d'ions baryum.

ZUSAMMENFASSUNG

Mikromengen von Tetraphenylborat in 40%igem Aceton, welche elektrolytisch erzeugt wurden, wurden mit coulometrisch erzeugten Silber-Ionen titriert. Bei Verwendung eines biamperometrischen Endpunktes konnten Proben mit 0.1–4 μäquiv. von Natriumtetraphenylborat mit einer Genauigkeit von 1% bestimmt werden. Die Technik wurde zur Bestimmung von Kalium in Kaliumchlorid und in Mischungen mit anderen Salzen benutzt. Für Proben mit 4–1 μäquiv. an Kalium betrug die Genauigkeit −3 bzw. −7%. Künstliche Serumproben ergaben etwas uneinheitliche Ergebnisse, da es schwierig war, das gesamte störende Protein zu beseitigen. Es wurde eine Methode zur Bestimmung von 0.1–1.0 mg PEG mit einem Überschuss an TPB in Gegenwart von Barium-Ionen entwickelt. Bei Einhaltung bestimmter Vorsichtsmassnahmen bleiben die Fehler kleiner als 5%.

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SHORT COMMUNICATIONS

Solvent extraction of some actinides and fission products by nitromethane

The possibility of separating plutonium by solvent extraction with nitromethane, nitroethane, nitropropane and nitrobenzene was first reported by SEABORG[1]. However, there appear to be no published data on the extractability of these nitro compounds, or on the conditions under which the separation was carried out. In previous work[2] it was shown that plutonium(IV) and (VI) can be extracted by nitromethane from nitric acid solutions and that the extraction of plutonium increases with increasing nitric acid concentration in the aqueous phase. It was also shown that the extractability of the following nitro compounds with plutonium(IV) decreases in the order: nitromethane > nitroethane > 2-nitropropane > nitrobenzene ≫ nitrooctane.

The present paper deals with the extraction of some other actinides and fission products by nitromethane in order to study the possibilities for the separation of plutonium from these radionuclides.

Experimental

Reagents and radionuclides. All chemicals used were AnalaR grade (BDH). Nitromethane was purified by double distillation before use (b.p. 101.2°, $n_D = 1.3820$) and stored over P_2O_5.

^{239}Np was produced by neutron irradiation of uranium oxide. The separation and purification of ^{239}Np was carried out by precipitation with lanthanum fluoride[3] and ion exchange on Dowex 1-X4 resin[4]. ^{241}Am resulting from β-decay of ^{241}Pu was separated from the aged plutonium solution[5]. ^{234}Th was separated from uranium by the extraction with diethyl ether and ion exchange on Dowex 1-X4 resin[6].

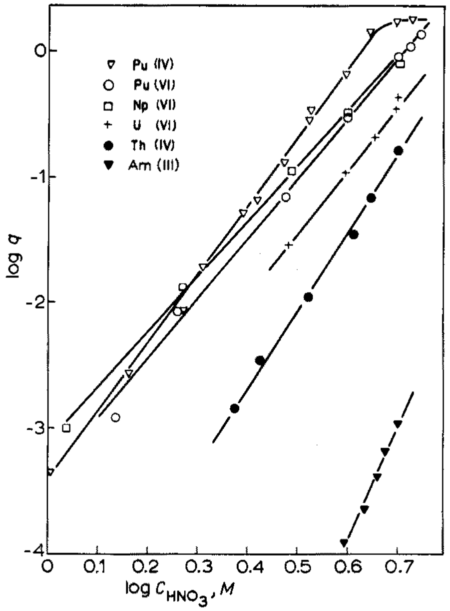
The solutions of uranium were prepared from uranyl nitrate hexahydrate.

Radioisotopes ^{144}Ce, ^{90}Sr–^{90}Y, ^{95}Zr–^{95}Nb, ^{137}Cs and ^{106}Ru (Amersham) were converted, where necessary, to the nitrate form by successive evaporations with concentrated nitric acid.

The amounts of radioisotopes used were at tracer levels.

Procedure. Equal volumes of the aqueous and organic phase were equilibrated by mechanical mixing at constant temperature (25°) for 3–5 min. (The stirring time necessary to reach equilibrium was 3 min[2].) The phases were separated by centrifugation before aliquots were removed for counting.

Determination of radioisotopes. ^{241}Am was measured with a Tracerlab Model P-12 α-scintillation detector. ^{234}Th and ^{90}Sr–^{90}Y were measured on a Nuclear Chicago GM-counter. The activities of ^{239}Np, ^{95}Zr–^{95}Nb, ^{106}Ru, ^{137}Cs and ^{144}Ce were measured on a Nuclear Chicago DS-5 well-type scintillation counter. Uranium was determined spectrophotometrically by the thiocyanate method[7] on a Unicam spectrophotometer, SP-500.



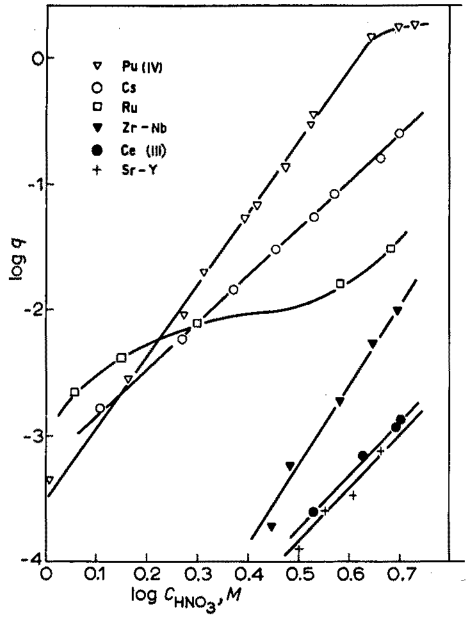


Fig. 1. Extraction of Pu(IV), Pu(VI), Np(VI), U(VI), Th(IV) and Am(III) from nitric acid solution by nitromethane.

Fig. 2. Extraction of Pu(IV), Cs, Ru, Zr–Nb, Ce(III) and Sr–Y from nitric acid solution by nitromethane.

TABLE I

DISTRIBUTION COEFFICIENTS FOR THE EXTRACTION OF SOME ACTINIDES AND FISSION PRODUCTS BY NITROMETHANE FROM 4 *M* NITRIC ACID SOLUTION AND THEIR SEPARATION COEFFICIENTS FROM PLUTONIUM(IV)

Element	*Distribution coefficient*	*Separation coefficient*
Pu(IV)	$7.0 \cdot 10^{-1}$	—
Np(VI)	$3.5 \cdot 10^{-1}$	2.0
Pu(VI)	$2.8 \cdot 10^{-1}$	2.5
U(VI)	$1.2 \cdot 10^{-1}$	5.8
Cs	$1.0 \cdot 10^{-1}$	7.0
Th(IV)	$4.0 \cdot 10^{-2}$	17.5
Ru	$1.8 \cdot 10^{-2}$	39.0
Zr–Nb	$2.0 \cdot 10^{-3}$	350
Ce(III)	$5.0 \cdot 10^{-4}$	1400
Sr–Y	$4.0 \cdot 10^{-4}$	1750
Am(III)	$1.3 \cdot 10^{-4}$	5400

Results and discussion

In order to determine the conditions under which plutonium can be separated by extraction with nitromethane from some other actinides (U(VI), Np(VI), Th(IV), Am(III)) and some fission products (Cs, Ru, Zr–Nb, Sr–Y, Ce(III)), the dependence of the distribution coefficient, *q*, of these elements on nitric acid concentration in the aqueous phase was determined (Figs. 1 and 2). In these Figures, the data for plutonium(IV) and (VI) are taken from previous work[2], for comparison. The data show that the extractability of the mentioned actinides decreases in the following order: Pu(IV) > Np(VI) > Pu(VI) > U(VI) > Th(IV) ≫ Am(III), while the fission products compared with plutonium have the following order: Pu(IV) > Cs > Ru ≫ Zr–Nb, Ce(III), Sr–Y.

Table I shows the distribution coefficients of the elements studied, as well as their separation coefficients from plutonium, for extraction with nitromethane from 4 *M* nitric acid solutions. It is clear that plutonium(IV) could be easily separated from americium(III) and, by multistage extraction, from thorium(IV). The separation of plutonium(IV) from neptunium(VI) and uranium(VI) could be carried out by conversion of plutonium to the tervalent state, the distribution coefficient of which is similar to those for americium(III). Table I also shows that plutonium(IV) could be successfully separated from mixtures with Sr–Y and Ce(III), as well as from Zr–Nb and Ru by multistage extraction. The separation of plutonium(IV) from cesium could be done in the same way as from U(VI) and Np(VI), *i.e.* by its conversion in the tervalent stage.

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Rapid spectrophotometric determination of low-molecular-weight dextran in blood

The use of Rheomacrodex (Pharmacia, Uppsala, Sweden), a low-molecular-weight dextran, as a plasma expander is still in the experimental stage. It has been suggested that dextran-40 could be used in cases of shock, burns, thrombosis, arterial insufficiency, vascular and cardiac surgery, crush injuries and fat embolism[1]. Because each patient and type of disorder requires a different amount of dextran-40 to be kept at a constant level in the system, a fast, reliable method for determining the amount of dextran-40 is needed.

Special emphasis has been given to dextran-40 in cases of shock. It has been used in case studies of shock in man[2] and experimental studies have been made with the use of dextran-40 in cases of experimental cardiogenic shock in dogs[3].

Various methods are now employed in the determination of dextran in blood. WALLENIUS[4] used deproteinization with picric acid while ROE[5] used 5% trichloroacetic acid. HINT AND THORSEN describe a method in which dextran is precipitated by copper sulfate[6] and JACOBSSON AND HANSEN precipitate the dextran with ethanol[7]. These methods all require at least 1 h for completion of the analysis. Since the time element is a critical point in the determination, the method described below is proposed.

Experimental

Apparatus and reagents. All absorbance readings were made with a Bausch and Lomb Spectronic "20" and a Beckman DB-G Ratio Recording Spectrophotometer. Matched silica cells, 1.00 cm, were used for all measurements.

All solutions were prepared with doubly distilled water in order to avoid any possible contamination.

Anthrone solution. Add 1.00 g of reagent-grade anthrone (Eastman Organic Chemicals) and 150 ml of distilled water to a 500-ml three-necked round-bottom flask, and slowly add 350 ml of concentrated sulfuric acid, making sure that the temperature of the solution remains below 20°. The reagent is stable for about one month and should remain in the preparation flask and be stored in a refrigerator at 2–3°. The reagent solution must be at room temperature when used in the determination.

Recommended procedure

Draw 2.00 ml of blood and transfer to a test tube. Immediately add 1.00 ml of aqueous 50% (w/v) trichloroacetic acid solution. Cover with a small square of polyethylene, shake the solution well and centrifuge. Decant the solution into another test tube and centrifuge again to insure an absolutely clear solution. Take a 10.0-μl aliquot of this solution with a 50-μl syringe and place in a clean test tube. Add 7.00 ml of 0.2% anthrone solution and shake well. Place the test tube in a boiling water bath (95°) for exactly 5 min, making sure that no contamination occurs. After heating, immediately remove the test tube from the water bath and place in cold (20–25°) water for 1 min. After cooling, measure the absorbance of the solution in 1.00-cm cells at 625 nm (*vs.* a water blank) with a suitable spectrophotometer within 25 min. The absorbance reading can be compared to a previously prepared calibration curve, and the amount of dextran-40 present in the system determined directly from the curve.

Discussion

In order to determine the amount of trichloroacetic acid required for the reaction, a series of samples containing dextran-40 (0.020 ml of a 10% solution) were treated with from 0.2 to 1.6 ml of 50% trichloroacetic acid solution, by the above procedure. The volume was kept constant by the addition of distilled water to a volume of 1.6 ml. The absorbance of the solution was determined at 625 nm *vs.* a water blank. A plot of the volume of trichloroacetic acid against absorbance showed a plateau at 0.4–1.6 ml, confirming the use of 1.0 ml in the above procedure.

The effect of the amount of anthrone used was studied. The absorbance increased with increasing amounts of anthrone up to 5.0 ml and then remained constant up to at least 9.0 ml, indicating that 7.0 ml is adequate for reproducible measurements.

The effect of heating time was studied to determine the length of time the complex should be heated to develop full color. Samples containing dextran-40 (0.030 ml) were heated in the water bath for times between 1 and 9 min. Each sample was cooled and the absorbance of the solutions determined at 625 nm *vs.* a water blank. The absorbance increased for heating times up to 4 min, remained essentially constant up to 6 min of heating, and then decreased. A heating time of 5 min was optimal.

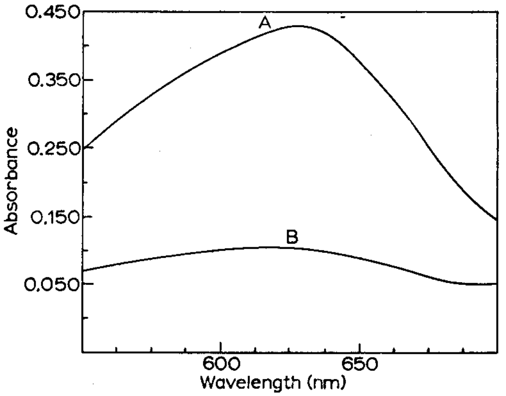
A solution containing a constant amount of dextran-40 (0.020 ml) was prepared by the recommended procedure. The absorbance of the solution was obtained over a 90-min span at 625 nm *vs.* a water blank in order to verify the stability of the complex; it was found to remain constant for 25 min.

TABLE I

EFFECT OF BLOOD TYPE ON COMPLEX FORMATION

	Slope	*% Error*	*Intercept*	*% Error*
Type O[a]	3.935	2.498	0.1485	3.803
	3.670	2.427	0.1486	3.976
	3.640[b]	4.199	0.0788	10.65
Type A	3.955	1.360	0.1445	2.140
	3.805	1.492	0.1470	2.220
	3.775	2.420	0.1455	3.450
	3.625[b]	3.212	0.0872	7.675
Type B	3.665[b]	2.159	0.0808	5.628
	3.540[b]	2.375	0.1004	4.810
	3.405[b]	2.970	0.0985	6.810
Type AB	3.810[b]	2.154	0.0708	7.688
	3.625[b]	2.497	0.1099	3.729
	3.415[b]	2.389	0.0863	6.272

[a] All results calculated by G. E. 225 Time Share Computer System.
[b] Designates new anthrone solution.



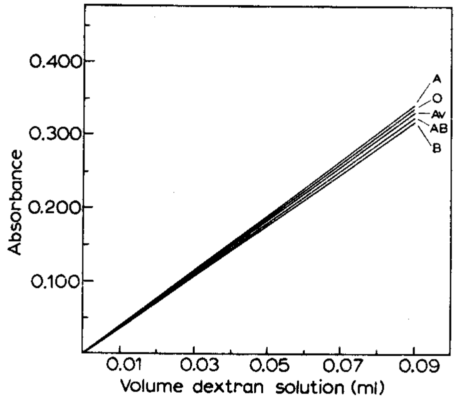


Fig. 1. Visible absorption spectra of the anthrone–dextran complex. (A) Complex; (B) anthrone blank.

Fig. 2. Calibration curves for the 4 blood types studied in comparison to the average.

TABLE II

SUMMARY OF DEXTRAN DETERMINATION

Sample	*Dextran present (ml/2 ml)*	*Dextran found (ml/2 ml)*
S_1	0.020	0.019
S_2	0.030	0.032
S_3	0.040	0.043
S_4	0.070	0.071

The anthrone complex was found to obey Beer's law for all blood types, with no apparent deviation due to Rh factor. Data for the study are presented in Table I. The visible absorption spectrum for the complex compared to that of the anthrone solution (*vs.* a water blank) is shown in Fig. 1. The best value for absorptivity, as determined by least squares, is 3.682 at 635 nm.

The results of the analysis of synthetic samples are presented in Table II. These results show the method to be both accurate and precise.

Figure 2 presents the calibration curves of the 4 blood types in comparison to the average. It is apparent that little difference exists between them. The numerical representation of the slopes and their intercepts (including the relative error) is presented in Table I. The distinct change in the intercept is due to the use of a fresh solution of anthrone with a small difference in concentration. An error analysis of the slopes was conducted and the correlation coefficient found to be 1.0. It is apparent that the deviation of the slopes from the average is not significant.

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Activation analysis of rare earths
Part IV. Determination of traces of rare-earth impurities in Gd_2O_3

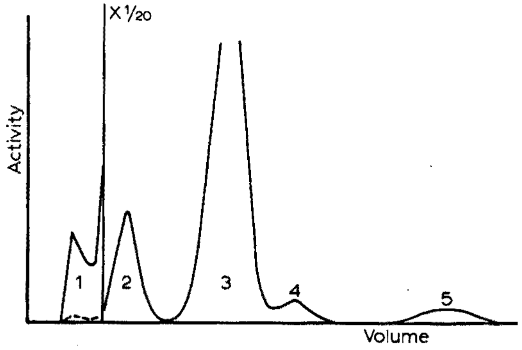
The determination of one or more rare-earth impurities in other rare earths has been described by several authors[1-5]. This communication describes the determination of impurities in a Specpure Gd_2O_3 product.

Semi-quantitative analysis

Figure 1 depicts the chromatographic separation of 50 μl of solution containing 0.7 mg of Gd, irradiated in the BR-1 reactor at Mol for 24 h at a flux of $4 \cdot 10^{11}$ $n \cdot cm^{-2} \cdot sec^{-1}$. The separation was carried out on a 16 cm × 0.36 cm^2 Dowex 50W-X8 (200–400 mesh) column with an exponential ligand concentration gradient. The ligand was α-hydroxyisobutyrate (α-HIBA), the initial concentration being 0.119 *M* in the mixing chamber (constant volume 50 ml) and 0.156 *M* in the reservoir.

Peak 1 is not active enough to identify the isotope with certainty by γ-spectrometry and is presumably due to ^{177}Lu. Peak 2 contains ^{161}Tb formed by the ^{160}Gd(n,γ) ^{161}Gd(β^-)^{161}Tb reaction. A small quantity of ^{160}Tb seems to be also present. Peak 3 contains the gadolinium activity, whereas peaks 4 and 5 are composed of ^{152m}Eu and ^{153}Sm.

To obtain a more positive identification of ^{177}Lu and ^{160}Tb, 0.7 mg of gadolinium in 50 μl of solution were irradiated in the BR-2 reactor for 24 h (flux 10^{14}). Because of the very high ^{159}Gd-activity, the irradiated sample was cooled for 14 days. At that moment, nearly all the ^{159}Gd and all the ^{152m}Eu and ^{153}Sm had decayed. The sample was subjected to cation exchange (linear gradient, column 14 cm × 0.4 cm^2, initial ligand concentration = 0, concentration in the reservoir 0.375 *M*). The elution is represented in Fig. 2. Fraction 2 probably contained the unsorbable anions and was not γ-active except for a small ^{122}Sb γ-peak; it probably consisted of ^{32}P phos-



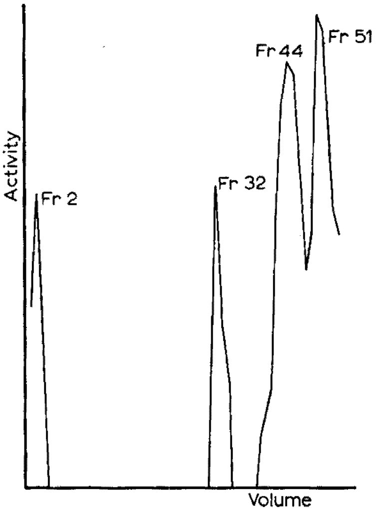


Fig. 1. Gradient elution of activated Gd_2O_3 (irradiated at $4 \cdot 10^{11}$).

Fig. 2. Gradient elution of activated Gd_2O_3 (irradiated at 10^{14}) after 14 days of cooling.

phate. The γ-spectrum of fraction 32 indicated that it consisted mainly of ^{177}Lu; small ^{46}Sc and ^{169}Yb activities were also detected.

Fraction 44 consisted mainly of ^{161}Tb but ^{160}Tb could also be identified in this fraction. Fraction 51 contained ^{153}Gd.

With the aid of lutetium and terbium standards, these elements were estimated by γ-spectrometry using a 400-channel spectrometer and a 3×3″ NaI(Tl) crystal. Lutetium was determined on the 208-keV γ-peak and terbium on the 880+970-keV peaks. The mean of two results for terbium was 290 p.p.m. and for lutetium 310 p.p.m. In these results, an 11.5% correction for neutron self-shielding caused by the gadolinium matrix was incorporated.

Quantitative analysis

The amounts of europium and samarium present were determined with the more easily accessible BR-1 reactor at a lower flux. This determination was studied in more detail.

The nuclear data of the isotopes obtained by (n, γ) reaction are summarised in Table I. ^{161}Tb is formed by (n, γ; β^-) reaction on ^{160}Gd. After decay of ^{152m}Eu a spectrum of ^{152}Eu + ^{154}Eu is obtained ($T_{\frac{1}{2}}$ resp. 12.5 y and 16 y). Because of the short irradiation time, these activities are too small to be useful for a determination of europium. From Table I it is clear that europium can be determined in gadolinium without separation but that samarium can not.

The elementary cross-section for absorption of thermal neutrons for gadolinium is 46,000 barns; self-shielding in the sample was thus to be expected and irradiation in solution was necessary, but even then flux depression occurred. The correction can be made by calculation, but since these corrections are large (15–30%), the average flux was determined experimentally for each irradiated sample, by means of a cobalt flux monitor. The same monitor was also added to the Eu and Sm standards.

The advantages of cobalt as flux monitor have already been discussed[6]; another advantage is that cobalt can be separated without difficulty from the rare earths. The separation was done by anion exchange for the standards and by cation exchange with α-hydroxyisobutyrate (α-HIBA) as eluant for the samples[7]. The α-HIBA technique for the separation of the rare earths was preferred after comparison with the reversed-phase partition chromatographic technique with di(2-ethylhexyl)-phosphoric acid as the stationary phase, as described by CERRAI AND TESTA[8], because less pronounced loading effects were observed with the former technique. ^{60}Co was used not only as flux monitor but also as a chemical-yield monitor. The sample and standards were irradiated in silica ampoules, which were broken after irradiation and the contents transferred to the different ion-exchange columns. This was carried out without trying to obtain a 100% yield, because of the presence of a chemical-yield monitor, which permitted a more rapid start of the separation.

Experimental

Preparation of standards and samples. The Co, Sm and Eu solutions contained respectively 500, 50 and 5 µg/100 ml solution and were prepared as described previously[7,9]. The gadolinium sample solution contained *ca.* 1.4 mg Gd/100 µl. To avoid airborne contamination, the evaporations were carried out in a glass chamber through which filtered air was circulated.

Aliquots of 100 μl of rare-earth solutions and 50 μl of cobalt solution were pipetted into a small crucible. The solutions were mixed and transferred to silica ampoules which were sealed and irradiated.

Irradiations. All irradiations were carried out in the BR-1 reactor. The flux was $4 \cdot 10^{11}$ n·cm^{-2}·sec^{-1} and the irradiation time was 2 h.

Separations. Break the silica ampoules and dilute their contents with a few ml of 0.01 *M* hydrochloric acid for the gadolinium sample and with 9 *M* hydrochloric acid for the standards. Transfer the standards to the top of anion-exchange columns and the samples to the top of cation-exchange columns.

Separate Gd, Eu, Sm and Co on a Dowex 50W-X8, 200–400 mesh, column (15 cm × 0.4 cm^2) by elution with a solution of α-HIBA with an analytical concentration of 0.5 *M*. Adjust the pH with ammonia solution to obtain the desired ligand concentration. Some separations were carried out by the exponential gradient elution technique with a constant solution volume (50 ml) mixing chamber. Collect the eluate either directly in 50-ml graduated flasks or in fractions of approximately 2 ml (64 drops). In the latter case, construct an elution graph and collect the fractions to be measured in 50-ml graduated flasks.

Separate the standards from cobalt by sorption of the latter on a 5 cm × 0.5 cm^2 Dowex 1-X8, 100–200 mesh, anion-exchange column in 9 *M* hydrochloric acid medium. Elute cobalt with 0.5 *N* hydrochloric acid. Collect the Eu and Co fraction in 50-ml flasks. Evaporate the samarium fraction and redissolve in 0.5 *M* α-HIBA to obtain equal self-absorption of the low energy ^{153}Sm radiation by standard and sample.

Measurements. The 2-ml eluate fractions were integral-counted in a well-type scintillation crystal. γ-Spectrometric measurements were carried out on a 3×3″ flat NaI(Tl) crystal with a 400-channel spectrometer. Cobalt was determined by the 1.17 + 1.33-MeV peaks, Eu by its 837 + 961-keV energies and Sm by its 97 + 103-keV energies.

Results

Determination of europium. It is apparent from Table I that europium can be determined without separation from Gd and Sm, but a separation from cobalt is necessary. The only other possible interference would arise from ^{160}Tb (γ-energies of 880 keV and 970 keV), but in the present case, only a very small ^{160}Tb activity was obtained. However, to elaborate a method that could be used if the ^{160}Tb activity were not negligible, two procedures were compared.

TABLE I

NUCLEAR DATA

Active isotopes	*Half-life*	*γ-energies*
^{153}Gd	230 d	70, 97, 103
^{159}Gd	18 h	364
^{161}Gd	3.7 min	
^{161}Tb	7.1 d	26, 49, 75, 103
^{152m}Eu	9.2 h	122, 344, 837, 961, 1327
^{153}Sm	47 h	70, 97, 103
^{60}Co	5.27 y	1170, 1330

(*1*) Separation on a cation-exchange column with α-HIBA of ligand concentration 0.119 *M*. In this way, Tb and Eu were completely separated; the Eu activity was collected from the fraction with maximal Gd activity till no more europium activity could be observed in the eluate. After elution of europium, the ligand concentration was increased to 0.4 *M* and cobalt and samarium were eluted together. When europium and cobalt were measured by γ-spectrometry, gadolinium and samarium did not interfere.

(*2*) Separation on an anion-exchange column with hydrochloric acid. The rare earths were separated as a group from cobalt and both fractions were measured. The results shown in Table II (determinations 1–7) indicate that both methods are equivalent.

TABLE II

CONCENTRATIONS OF EUROPIUM AND SAMARIUM IN A Gd_2O_3 SAMPLE

(in p.p.m.)

Determinations	*Eu*	*Sm*	*Determinations*	*Eu*	*Sm*
1[a]	31.^{0}	—	9	—	331
2[a]	31.^{0}	—	10	—	301
3[a]	30.^{0}	—	11	50.^{9}	314
4[a]	32.^{4}	—	12	34.^{8}	298
5[b]	30.^{0}	—	13	30.^{7}	316
6[b]	33.^{2}	—	14	29.^{9}	328
7[b]	30.^{2}	—	Mean value	31.^{3} ± 1.^{5}	316 ± 15
8	—	325	Standard addition	31.^{6} ± 2.^{8}	307 ± 40

[a] Separation by method 1.
[b] Separation by method 2.

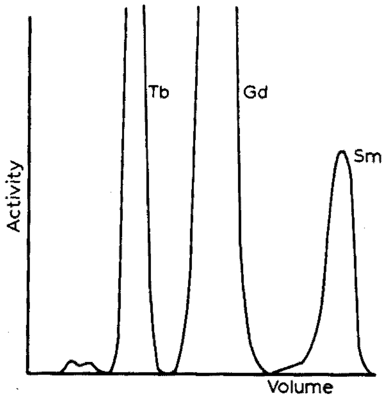


Fig. 3. Gradient elution of activated Gd_2O_3 for the determination of samarium.

Determination of samarium. ^{153}Sm cannot be measured in the presence of ^{152m}Eu. Hence, a separation is necessary. There are two possibilities: a complete separation of Eu from Sm (Fig. 1) or a less complete separation of Sm from Eu (but still complete from Gd) followed by a wait for the decay of ^{152m}Eu. The latter method was preferred. Figure 3 shows a separation achieved by gradient elution with an initial ligand concentration $c_0 = 0.122$ *M* and a ligand concentration in the reservoir of

0.162 *M*. After elution of samarium, cobalt was eluted with a 0.4 *M* ligand concentration. The measurements were carried out 60 h after the irradiation (*i.e.* nearly 7 half-lives of ^{152}Eu and 1.5 half-lives of ^{153}Sm). The results are shown in Table II (determinations 8–10).

Determination of europium and samarium. For this determination a complete Sm–Eu separation must be obtained (Fig. 1). The practical parameters to obtain this separation are described under semi-quantitative analysis. Europium was collected beginning with the fraction with maximal Gd activity. After the elution of samarium, cobalt was desorbed with a 0.4 *M* ligand concentration of α-HIBA. With one automatic fraction collector two complete determinations (irradiation excluded) can be done in one day. The results are summarised in Table II (determinations 11–14). The value of 50.^{9} p.p.m. for europium in determination 11 is clearly due to an experimental error and may be disregarded.

Discussion

From the results it seems that the Gd_2O_3 contained more than 0.1% of other rare-earth metals. The low content of Eu compared to Sm and Tb, is not surprising if one takes into account that in most minerals Eu is present in very small quantities compared to the neighbouring rare earths[6].

In these analyses, there are two possible sources of error. The first is interference by (n, p) activation of ^{152}Gd to ^{152m}Eu. The cross-section has not been determined but has been estimated[10] as 0.14 millibarn. On calculation, the induced activity in this way appears to be negligible compared with the (n, γ) induced activity. Another possible error is due to neutron-flux perturbations. The addition of cobalt eliminates the error due to the thermal neutron self-shielding but not the error caused by the possible overlap of the Gd resonance peaks with those of Eu, Sm or Co. For ^{152m}Eu and ^{60}Co this error cannot be large, since their cadmium ratio under the irradiation conditions used were 21.5 and 6.1 respectively. However, ^{153}Sm has a small cadmium ratio (1.78). The cadmium ratio of the Gd isotopes responsible for the largest part of the neutron capture cannot be determined since the resulting isotopes are not active. From the standard addition experiments (Table II), however, the samarium determination appears to be accurate.

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Interference of perchloric acid with the anthrone reaction for carbohydrates

The anthrone reaction is used widely for the determination of carbohydrates[1-6]. Normally, perchloric acid is the extractant for starch when plant tissues are being analysed[2,3,5]. Results reported here show that perchloric acid itself may modify the anthrone reaction and lead to serious errors in carbohydrate determination.

Procedures

After removing soluble sugars by grinding in distilled water, starch was extracted from *Eucalyptus pauciflora* Sieb. seeds with perchloric acid. Two extractions were made at 0° by means of solutions containing 5 ml of water and 6.5 ml of 52% perchloric acid. The combined extracts were made up to 50 ml in distilled water and filtered. Starch was determined by layering 1 ml of extract on 5 ml of anthrone reagent (0.2 g anthrone in 100 ml of 95% sulfuric acid) in Pyrex tubes in an ice bath. The tubes were shaken vigorously, chilled for a further 5 min, heated in boiling water for 10 min, and finally cooled in water for 5 min. The deep yellow-brown colour developed under these conditions was too dark for accurate readings at 630 nm in a Beckman DU2 spectrophotometer, and samples of the original 50-ml extracts were diluted (1:1) with distilled water. When 1 ml of these diluted extracts was reacted with anthrone, the spectrophotometer value was only 1/5–1/8 of that originally obtained (Table I). When one original extract was serially diluted, results were as shown in Fig. 1.

TABLE I

ABSORBANCE AT 630 nm OF ORIGINAL AND DILUTED (1:1) EXTRACT AFTER REACTING 1 ml WITH 5 ml ANTHRONE REAGENT

Seed extract	*Absorbance*	
	Original	*Diluted (1:1)*
1	1.250	0.226
2	1.120	0.156
3	1.550	0.185

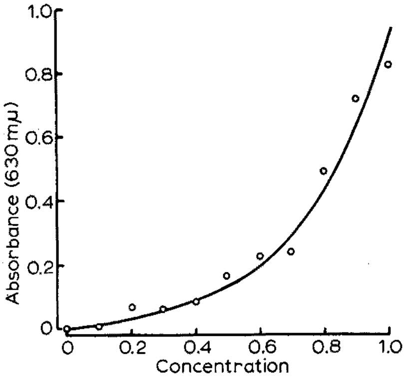
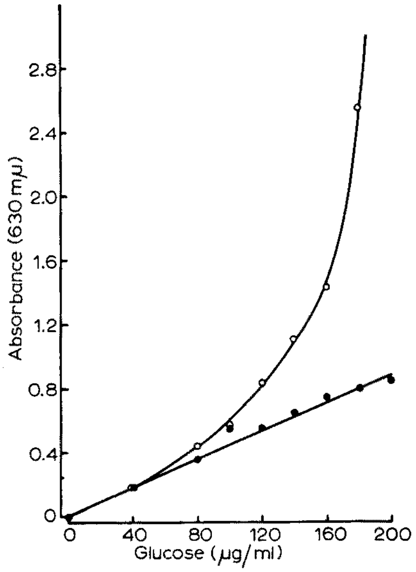


Fig. 1. Absorbance at 630 nm of a serially diluted seed extract after reaction with anthrone reagent.

One obvious difference between the seed extracts, in which linearity between concentration and developed colour was absent, and glucose solutions in water, in which the expected linearity was found, was the presence of perchloric acid in the seed extracts. To test the effect of perchloric acid, glucose was dissolved in perchloric acid (200 μg glucose/ml 27% perchloric acid), and serially diluted. The reactions of these solutions with anthrone reagent are compared with those of glucose in water in Fig. 2. The effects on the anthrone reaction of perchloric acid concentration, in the presence and absence of a constant quantity of glucose, are shown in Fig. 3.

Clearly perchloric acid, at a concentration between 10 and 15%, affects the anthrone reaction to such an extent the effect of sugar is overwhelmed. In the original 50-ml seed extracts, the perchloric acid concentration was 13–14% and is responsible for the effects shown in Table I and Fig. 1.

Although layering 1 ml of solution on 5 ml of anthrone reagent is one method



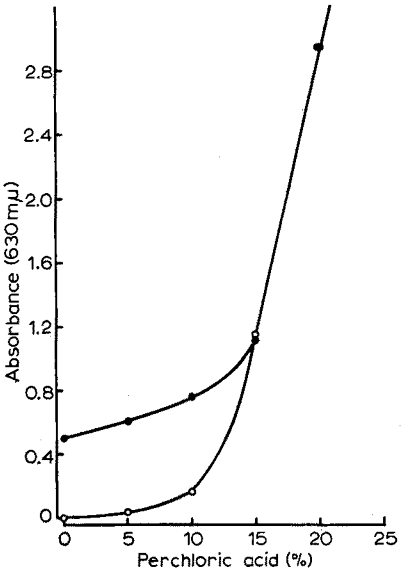


Fig. 2. Absorbance at 630 nm of a serially diluted solution of glucose (200 μg/ml) in 27% perchloric acid (○) and in water (●) after reaction with anthrone reagent.

Fig. 3. Absorbance at 630 nm of perchloric acid alone (○) and with 120 μg/ml glucose (●) after reaction with anthrone reagent.

TABLE II

ABSORBANCE AT 630 nm OF 5 ml SOLUTION AFTER REACTING WITH 10 ml ANTHRONE REAGENT

Perchloric acid (%)	*Absorbance*	
	Blank	*+ Glucose (150 μg/5 ml)*
0	0.000	0.508
13	0.048	0.500
26	0.095	0.426
52	0.190	0.241

described for carrying out this reaction[6], another method commonly used is to place 5 ml of test solution in 10 ml of anthrone reagent[1,2,4]. With this latter method the effect of perchloric acid is much reduced (Table II). Glucose alone gives a clear green colour and with increasing concentrations of perchloric acid the developed colour becomes increasingly red, reducing the absorption of light at 630 nm. This is in complete contrast to the earlier results when perchloric acid increased absorption. When the second method is used, perchloric acid exerts a significant effect only at concentrations above 13%.

These results show that perchloric acid can seriously interfere with the anthrone reaction for carbohydrate estimation, and must be taken into account when perchloric acid is used to extract starch from plant tissues. This is especially important when small amounts of tissue or low starch concentrations are involved.

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Spectrophotometric determination of zirconium and other colour reactions with 3,5,6,7,3′,4′-hexahydroxyflavone

Flavonols occupy a prominent position as sensitive and selective reagents for micro-determination of zirconium. Though they form coloured chelates with other ions, these chelates are largely dissociated at the low pH values at which zirconium is determined. Morin[1], quercetin[2], galangin[3], melanoxetin[4] and more recently robinetin[5] have been used for the purpose. In the present communication, the use of 3,5,6,7,3′,4′-hexahydroxyflavone (quercetagetin) for the spectrophotometric determination of zirconium is described, as well as the complexation with some other ions.

Experimental

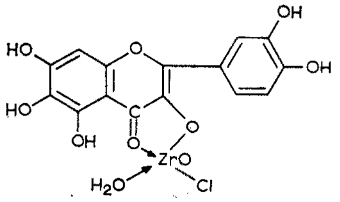
Instruments and reagents. A Unicam SP 600 spectrophotometer, a Perkin-Elmer spectracord and a Metrohm pH-meter E-350 were used. For preparing standard solutions of zirconium, $ZrOCl_2 \cdot 8H_2O$ (E. Merck) in hydrochloric acid (AnalaR) was used. Quercetagetin was isolated from the flowers of *Tagetes erecta*[6] and a standard solution was prepared in ethanol by direct weighing. All other chemicals used were of reagent quality.

Preliminary investigation. Interaction of dilute solution of this hexahydroxyflavone with acidified zirconium results in the development of an intense yellow coloured chelate. The presence of 20% alcohol was found necessary to avoid precipitation of the reagent. To maintain acidic conditions, hydrochloric acid was preferred to other acids because of the greater stability of zirconium in this medium.

Absorption spectra. Solutions were prepared containing the ligand and zirconium solution in different molar ratios and in varying hydrochloric acid concentrations, the total volume being maintained at 10.0 ml in each case. Spectra were plotted with corresponding solutions of the reagent as blanks. In all cases the wavelength of maximum absorbance was found at 415–420 nm, which indicated the presence of only one complex in the system (Fig. 1).

Effect of acidity. The maintenance of a 1 *N* hydrochloric acid concentration for the system was found to be quite appropriate; there was no significant variation in the absorbance of the complex at normalities of 1 ± 0.4. Moreover, the absorbance was maximal in this range, and the absorbance of the reagent blank remained practically constant up to 2 *N* acid concentrations at 415 nm.

Molar composition and physical constants of the complex. The continuous variations and slope-ratio methods showed that the two components were present in equimolar ratio. Consequently, a tentative structure (I) similar to that proposed by GRIMALDI AND WHITE[2] for the quercetin–zirconium complex may be assigned to the complex.



(I)

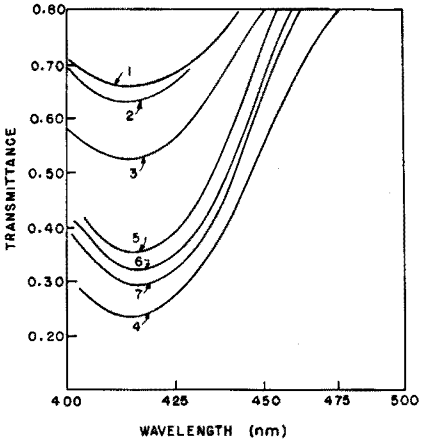
The complex obeys Beer's law up to 2.8 p.p.m. of zirconium concentration and the sensitivity is of the order of 0.0032 μg Zr/cm^2 for log $I_0/I = 0.001$.

Working procedure. To an unknown solution containing up to 2.8 p.p.m. of zirconium, add 1 ml of concentrated hydrochloric acid followed by 2.5 ml of 0.002 *M* quercetagetin in alcohol. Dilute to 10.0 ml with water and measure the absorbance of this solution at 415 nm against a reagent blank. Prepare a standard curve in the same way.

Effect of diverse ions. The effect of various ions in 1 *N* hydrochloric acid medium was examined. When a solution containing 0.92 p.p.m. of zirconium and one of the ions mentioned below was taken through the recommended procedure, there was no interference up to the amounts (in p.p.m.) indicated within brackets: Ba^{2+}(1000), Be^{2+}(15), Cd^{2+}(1200), Ca^{2+}(300), Co^{2+}(120), La^{3+}(230), Mg^{2+}(800), Mn^{2+}(90), Ni^{2+}(120), Pd^{2+}(20), Sr^{2+}(1000), UO_2^{2+}(10), Zn^{2+}(250), CH_3COO^-(1000), $B_4O_7^{2-}$(920), NO_3^-(920), CNS^-(35). However, traces of Cu^{2+}, Fe^{2+}, Ce^{4+}, Ti^{4+}, Th^{4+}, MoO_4^{2-}, I^-, IO_3^-, F^-, $S_2O_3^{2-}$ and PO_4^{3-} were found to interfere.

Reaction with uranyl ion

Reaction of flavonoids with the uranyl ion are well known[7]. The present com-



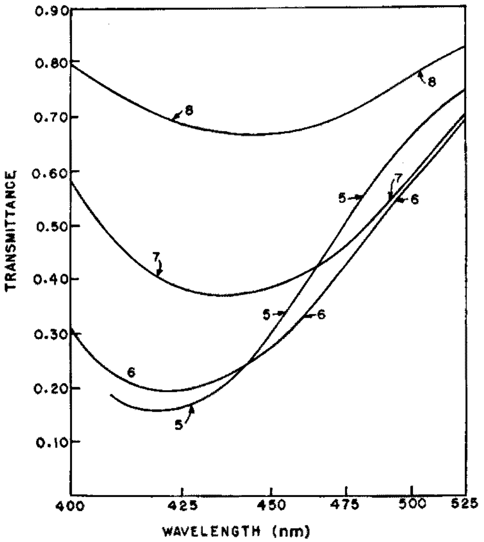


Fig. 1. Absorption spectra of the zirconium–3,5,6,7,3′,4′-hexahydroxyflavone complex. Zr concentration, $2 \cdot 10^{-5}$ M throughout. Reagent concentration. (1) $1 \cdot 10^{-5}$ M in 1 N HCl; (2) $2 \cdot 10^{-5}$ M in 1 N HCl; (3) $4 \cdot 10^{-5}$ M in 1 N HCl; (4) $2 \cdot 10^{-4}$ M in 1 N HCl; (5) $2 \cdot 10^{-4}$ M in 4 N HCl; (6) $2 \cdot 10^{-4}$ M in 3 N HCl; (7) $2 \cdot 10^{-4}$ M in 2 N HCl.

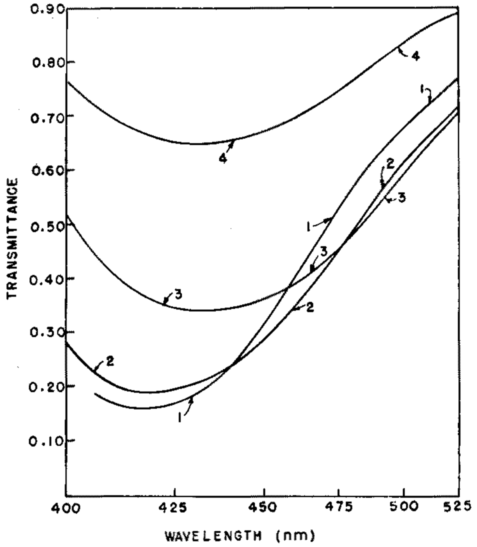
Fig. 2. Absorption spectra of the uranyl–hexahydroxyflavone system at pH 5.0. UO_2^{2+} concentration, $5 \cdot 10^{-5}$ M throughout. Reagent concentration: (1) $2.5 \cdot 10^{-4}$ M; (2) $5 \cdot 10^{-5}$ M; (3) $2.5 \cdot 10^{-5}$ M; (4) $1 \cdot 10^{-5}$ M.

pound gave an orange colour with dilute solutions of uranyl nitrate. The absorbance spectra of the solutions containing uranium and quercetagetin in different molar ratios at different pH values were taken. The wavelength of maximum absorbance was found to shift from 415 nm to 450 nm when the concentration of metal was increased, particularly at higher pH values (Figs. 2 and 3), which indicates the possibility of more than one complex being formed in the system. The continuous variations method showed that two complexes were indeed formed. The 1:1 complex was detected at all wavelengths and at a pH lower than 5, while the 2:1 uranyl–reagent complex was detected at longer wavelengths and at pH values above 5. It is known[7] that in the case of uranyl complexes with 5-hydroxyflavones, chelation takes place by replacement of hydrogen of the 5-hydroxyl group by uranyl and subsequent coordination through the carbonyl oxygen. It seems likely that the 2:1 complex is formed by chelation with the hydroxyl groups at the 3′- and 4′-positions.

Changing the pH value between 3.0 and 6.0 (in presence of excess of reagent) showed that the coloration is pH-dependent so that close pH control is essential for reproducible results; however, the maximum remains unaltered. Below pH 3.0, the coloration is insignificant and above pH 6.0, the reagent starts to decompose. The sensitivity of the reaction at pH 5.0 was found to be 0.0148 μg U/cm² for $\log I_0/I = 0.001$.

Reactions with molybdate and thorium ions

3, 5, 6, 7, 3′, 4′-Hexahydroxyflavone also gives yellow colours with traces of molybdate and thorium(IV). The presence of definite complexes is evident from the



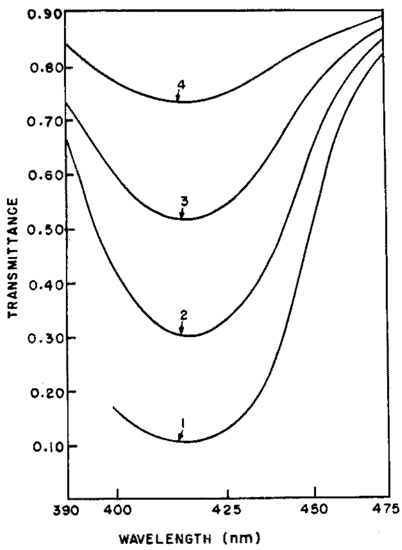


Fig. 3. Absorption spectra of the uranyl–hexahydroxyflavone system at pH 6.5. Lines 5–8 were obtained with the same concentrations as lines 1–4 of Fig. 2.

Fig. 4. Absorption spectra of the molybdenum–3, 5, 6, 7, 3′, 4′-hexahydroxyflavone system at pH 2.0. Mo concentration, $4 \cdot 10^{-5}$ *M* throughout. Reagent concentration: (1) $2 \cdot 10^{-4}$*M*; (2) $4 \cdot 10^{-4}$ *M*; (3) $2 \cdot 10^{-5}$ *M*; (4) $8 \cdot 10^{-6}$ *M*.

maxima obtained (at 420 nm) in both cases (Fig. 4). However, the formation of these complexes cannot be utilized for direct determinations, because the reactions are not selective so that prior separation of accompanying salts is essential.

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Estimation of carboxyl group content of copolymers by the infrared absorbance ratio method

Synthetic rubbers, such as copolymers of butadiene and acrylic acid, contain carboxyl groups which are usually determined by titration methods. In this study, it has been shown that a correlation exists between the carboxyl content and the ratio of certain infrared absorption bands which are characteristic of this type of rubber.

Normally used titration methods involve the dissolution of the rubber sample in an appropriate solvent and subsequent titration of the carboxylic acid groups with standard base. While these are straightforward methods, they are time-consuming in that sample dissolution usually requires a period of about 16 h.

Development of a simple infrared procedure for estimating carboxyl group content is reported. Infrared spectra are easily obtainable from films of these copolymers, and quantitative data may be taken from the recorded curves. The infrared ratio method has been used for other types of rubber samples[1,2] and allows quantitative infrared information to be obtained without the usual preparation of standard solutions and the subsequent use of fixed-thickness cells.

Experimental

Six rubber copolymers of varying butadiene and acrylic acid content were studied by the titrimetric and infrared procedures reported below. The EPHR value (the carboxyl equivalents per 100 g of rubber) of each was determined and compared with the respective infrared absorbance ratios.

Reagents. All chemicals used in this work were ACS grade materials. The nitrogen was dry.

Equipment. Equipment used included flasks fitted with ground glass stoppers, a Burrell wrist-action automatic shaker, a Perkin Elmer Model 21 Infrared Spectrophotometer, and pressed sodium chloride plates.

Procedure for determination of EPHR value. Accurately weigh 0.5 g of the rubber into a 250-ml Erlenmeyer flask. For best results, the rubber sample should be cut into small pieces about 5 mm × 5 mm or less. Direct a stream of nitrogen into the flask to remove air, and add 50 ml of pyridine. Stopper the flask and apply tape in order to obtain a good seal and maintain the nitrogen atmosphere. Place the flask in an automatic shaker for a period of about 16 h. A blank of 50 ml of pyridine should be carried through the procedure. Titrate the solution under a nitrogen atmosphere, with 0.1 N alcoholic potassium hydroxide using thymolphthalein indicator. The final end-point occurs when the blue color of the indicator persists for a period of 5 h, with occasional shaking of the flask.

The EPHR value is calculated from the relationship

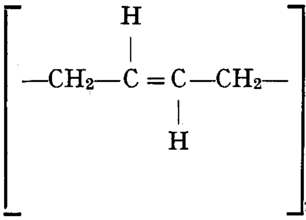
$$\mathrm{EPHR} = (\mathrm{A}-\mathrm{B})\cdot N/10\,\mathrm{W}$$

where A = volume (ml) of KOH used to titrate sample, B = volume (ml) of KOH used to titrate blank, N = normality of KOH, and W = sample weight (g).

Procedure for obtaining the infrared spectra of rubber. The infrared spectra of rubber samples may be obtained by casting films from solution[1], and by pressing the sample into thin films[2]. The samples studied here were of such a nature that films could be stretched by hand over salt plates. Cut the rubber sample roughly to a 10 mm × 10 mm size. Then stretch the piece of rubber with the fingers until a thin transparent film results. Place the film over a salt plate exercising caution to avoid tearing. Cut away excess rubber, assemble the film in the sample holder and record the infrared spectrum from 2.0 to 15 μ. Rubber samples which are too hard to stretch by hand may be softened in hexane prior to obtaining the infrared spectra.

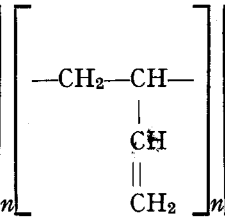
Results and discussion

The infrared spectrum of a polybutadiene–acrylic acid copolymer is relatively simple since the molecules of the polymer consist of units of the two different monomers. This type of polymer consists primarily of the type of units shown by structures I, II, and III.



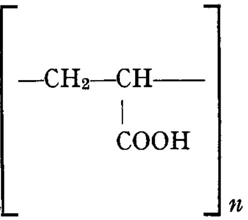
$$\left[-CH_2-\overset{\displaystyle H}{\overset{|}{C}}=\underset{\displaystyle H}{\underset{|}{C}}-CH_2-\right]_n$$

I



$$\left[-CH_2-\underset{\underset{\displaystyle CH_2}{\|}}{\underset{\displaystyle CH}{\underset{|}{CH}}}-\right]_n$$

II



$$\left[-CH_2-\underset{\displaystyle COOH}{\underset{|}{CH}}-\right]_n$$

III

BINDER[3] discusses the estimation of *cis*-1,4-addition product in polybutadienes by noting infrared absorbance at 14.70 μ. This unit was not considered in this study since spectra of the rubber samples showed negligible absorption at 14.70 μ.

The infrared spectra recorded for the 6 rubber samples show 5 major absorption bands to which assignments may be given by consideration of structures I, II, and III as reported in Table I. Of the 6 samples studied, rubbers 5 and 6 required softening prior to obtaining their infrared spectra.

The baseline method[6] was used in obtaining intensity measurements of the infrared absorption bands studied. Measurements were made of P_0 (power of incident radiation) and P (power of transmitted radiation) using a ruler graduated in 0.01 in. Absorbance values (A) were then calculated for each absorption band.

TABLE I

INFRARED SPECTRAL CHARACTERISTICS

Absorption band (μ)	*Assignment*	*Reference*
3.45	C–H asymmetrical stretching of the $-CH_2$ group	4
5.88	C=O stretching of the carboxylic acid group (Structure III)	4
6.93	$-CH_2-$ scissor	4
10.35	C–H out-of-plane deformation of *trans* unit (Structure I)	3–5
10.98	C–H out-of-plane deformation of vinyl unit (Structure II)	3–5

As the acrylic acid monomer content is increased in the copolymer, the EPHR value likewise increases. It would also be expected that the absorbance of the infrared band at 5.88 μ would increase in a proportional manner relative to the absorption bands which correspond to the butadiene structures. To determine this, absorbance ratios were calculated by dividing the 5.88 μ absorbance by the absorbance of the 3.45 μ band, the 10.35 μ band, and the 10.98 μ band, respectively, for each of the 6 samples. Absorbance ratios representing the average of 8 trials are compared in Table II to the EPHR values determined titrimetrically for the 6 rubbers.

TABLE II

INFRARED ABSORBANCE RATIOS AND EPHR VALUES

Rubber	*A at 5.88 μ* / *A at 3.45 μ*	*A at 5.88 μ* / *A at 10.35 μ*	*A at 5.88 μ* / *A at 10.98 μ*	*EPHR value*
1	0.400	0.351	0.827	0.061
2	0.523	0.471	1.213	0.091
3	0.793	0.744	1.885	0.146
4	0.938	0.921	2.437	0.183
5	1.178	1.217	3.338	0.244
6	1.429	1.614	4.637	0.339

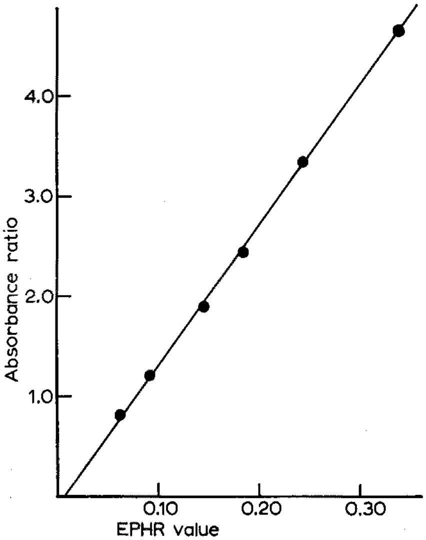


Fig. 1. Least squares evaluation of data for the 5.88 μ/10.98 μ absorbance ratio.

Plots of EPHR values *versus* each of the 3 ratios for which data are listed in Table II, indicated that the calculated absorbance ratios correspond to the chemically determined EPHR values. Figure 1 shows the agreement of the data for the absorbance ratio involving the 10.98 μ absorption band, with a straight line calculated and plotted by the least squares method. This absorbance ratio represents the amount of structure III present in the copolymer compared to the amount of structure II present. Similar plots were obtained for each of the other ratios; however, the extent to which the data involving the 3.45 μ band fit a least squares plot is not as good as that shown in Fig. 1. It is recommended that the 5.88 μ/10.98 μ ratio be used for this method of carboxyl content estimation in rubber copolymers.

While the study was made primarily for the purpose of quickly and easily determining the EPHR value of raw material rubber, it is possible that the method might also be used as an in-process check on the degree of polymerization of this type of copolymer.

The author wishes to express his appreciation to the B. F. Goodrich Chemical Co. for supplying the rubber samples used in this study and to the Olin Mathieson Chemical Corp. for permission to publish this work.

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The determination of trace amounts of phosphorus by a double amplification method

Most methods for the determination of phosphorus are based on indirect amplification reactions in which the amount of molybdenum, associated with phosphate as the 12-molybdophosphoric acid, is measured in some way; because of the favourable 12 : 1 ratio, a 12-fold amplification is obtained in terms of equivalents[1]. It is well-known that when metal–oxine complexes are titrated with potassium bromate, the metal is amplified indirectly and the extent depends on the number of moles of organic reagent combined in the complex; each mole of oxine consumes 4 equivalents of standard bromate solution. With molybdate ion oxine forms an insoluble precipitate of formula $MoO_2(C_9H_6ON)_2$; hence if the heteropoly acid were isolated, molybdenum precipitated with oxine, and the separated complex titrated with bromate, a final 96-fold amplification of phosphorus might be possible.

The most convenient method for selective separation of the heteropoly acid, appeared to be by extraction with iso-butyl acetate[2], which is selective and rapid. The main difficulties were considered to lie with the molybdenum–oxine complex; it is extremely difficult to dissolve the precipitate of molybdenum oxinate in the conventional reagents and also some coprecipitation of oxine molybdophosphate might occur. The oxine compound of molybdenum differs in structure from that formed with most other metals and is said to be a phenolic ester of the metalloacid[3]. The precipitate did not dissolve in 2 *N* sodium hydroxide solution (as sometimes recommended), except immediately after precipitation. However, it readily dissolved in hot concentrated phosphoric acid[4] and did not reprecipitate when the solution was diluted. Under the conditions of precipitation used, there was no evidence for the formation of oxine molybdophosphate.

Procedure

Transfer a sample of solution containing phosphorus in the range 0.5–25 μg and concentration of the order of 5 μg/ml to a 100-ml separatory funnel containing *ca.* 10 ml of a 1% A.R. ammonium molybdate solution. Add enough concentrated hydrochloric acid to make the solution *ca.* 1 *M*. After shaking and standing for 5 min, add 10 ml of iso-butyl acetate and shake for 2 min to transfer the heteropoly acid to the organic phase. Separate the (lower) aqueous layer and wash the organic phase twice with 10-ml portions of 2 *N* hydrochloric acid. Shake the organic phase with 10 ml of *ca.* 4 *N* ammonia in 3–4 ml portions to back-extract the molybdenum, and combine these aqueous extracts.

Heat the ammoniacal molybdenum extract in a covered 25-ml beaker containing a few boiling granules to reduce the volume to 2–3 ml and drive off all the ammonia. When no further ammonia can be detected, add a 3-fold excess of a solution of 0.4% oxine in 50 : 50 ethanol: water to the gently boiling solution. Precipitation of molybdenum oxinate begins after a short induction period; heat the mixture gently for a further 10 min. Maintain the volume at about 3 ml by addition of ethanol to prevent oxine from precipitating. This also ensures a coarser, more tractable precipitate.

Filter on a Pregl No. 4 micro-filter; and use a mounted "snipe feather" to clear the last traces of precipitate from the beaker and the cover glass. Add more ethanol to prevent 'creeping' of the precipitate during filtration. Wash the precipitate with successive portions of ethanol and hot water using suction. Dissolve the precipitate in three 1–2 ml portions of hot syrupy phosphoric acid. Easy dissolution is obtained if the acid is heated to boiling in a small test-tube over a bunsen flame and added to the precipitate immediately on removal from the flame. Draw the solution into the filter flask and wash the filter with about 3 ml of *ca.* 2 *N* hydrochloric acid. Transfer the molybdenum oxinate solution to a 30-ml stoppered bottle, and wash the filtration flask out with two further portions of 2 *N* hydrochloric acid. The total volume of solution and washings should not exceed 15–20 ml.

Titration of the molybdenum oxinate solution. Potassium bromate and sodium thiosulphate solutions of 0.01 *N* concentration are used for amounts of phosphorus greater than 10 μg; for smaller quantities, 0.004 *N* reagents are preferred. Add *ca.* 0.2 g of solid potassium bromide to the oxine solution followed by a drop of methyl orange indicator. Add potassium bromate solution from a burette with constant swirling. The approach of the end-point is shown by the fading of the red solution. When a pale yellow colour is reached, add a further drop of indicator to determine whether premature bleaching has occurred. Add about 1-ml excess of bromate after the end-point, and determine the excess by back-titration with standard sodium thiosulphate solution using 'Thyodene' indicator (1 ml of 0.01 *N* $KBrO_3 \equiv 3.22$ μg P).

P.F.H.S. using 8-acetoxyquinoline

A number of precipitations was carried out employing the hydrolysis of 8-acetoxyquinoline (0.4% in 1 : 1 ethanol–water) to generate 8-hydroxyquinoline. Results obtained were essentially identical to those obtained with ordinary 8-hydroxyquinoline, except that for the smallest quantities of phosphorus, precipitation proceeded after a shorter induction period using P.F.H.S.

TABLE I

DETERMINATION OF PHOSPHORUS BY DOUBLE AMPLIFICATION

P actual (μg)	*P found (μg)*	*No. of results*	*P actual (μg)*	*P found (μg)*	*No. of results*
25.0	24.65 ± 0.48	6	2.0	1.96 ± 0.19	6
10.0	9.93 ± 0.13	6	1.0	0.97 ± 0.090	6
5.0	5.03 ± 0.26	4	0.5	0.503 ± 0.065	2

Results and discussion

It was expected that it would be possible to precipitate molybdenum oxinate at levels below the amounts equivalent to 0.5 μg of phosphorus, but it was found that below this amount complete precipitation became a lengthy process. Oxidation by cerium(IV) perchlorate could have been used to give a 720-fold amplification. Even by the P.F.H.S. method precipitation was not complete. Down to 0.5 μg P, the bromate method gives satisfactory results (Table I) and is more convenient than the ceric perchlorate method, which could, of course, be applied if greater amplification were required. Presumably a spectrophotometric finish could be used, by utilising one of the conventional oxine reactions, but it is doubtful if any advantage would be gained. The titrimetric finish is simple and rapid.

No attempt was made to study interferences, for the first separation with isobutyl acetate is known to be reliable and has been reported on by other investigators[5]. In PAUL's original method, other heteropoly acids can be extracted successively and other elements might be determined by a similar double amplification process.

The accuracy of the method compares favourably with other methods of trace analysis and only simple apparatus is required. The principle could probably be extended to the determination of other elements.

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R. BELCHER
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1 R. BELCHER, *Talanta*, 15 (1968) 357.
2 J. PAUL, *Mikrochim. Acta*, (1965) 830; *Anal. Chim. Acta*, 35 (1966) 200.
3 F. FEIGL, *Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949, p. 185.
4 R. NIERICKER AND W. D. TREADWELL, *Helv. Chim. Acta*, 29 (1946) 1472.
5 G. F. KIRKBRIGHT, A. M. SMITH AND T. S. WEST, *Analyst*, 92 (1967) 411; P. PAKALNS, *Anal. Chim. Acta*, 40 (1968) 1.

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BOOK REVIEWS

F. D. SNELL AND C. T. SNELL, *Colorimetric Methods of Analysis, including Photometric Methods*, 3rd Edn., Vol. IV A, 1967, Van Nostrand, Princeton, N. J., ix + 645 pp., 140/—.

This is the most recent volume of this well known series on colorimetric methods of analysis. The first edition consisted of two volumes but the subject is still growing so rapidly that the total number of volumes which will ultimately be required is difficult to foresee. The authors bring existing volumes up to date by publishing supplementary volumes, II A and III A having already appeared. This volume IV A presents the literature of the past 12 years on organic compounds of non-cyclic and cyclic nitrogen, the subject matter of the first seven chapters of volume IV. The remainder of volume IV will be dealt with in a subsequent volume IV A.A.

There are six chapters dealing with nitrites, nitrates and nitrogen compounds; aliphatic amines and amides; amino acids; proteins; aromatic primary, secondary and tertiary amines and amides; and azo-compounds, nitrogen-containing cycles etc.

This new volume is fully up to the high standard of previous volumes and will be of particular value to those concerned with compounds of biological origin.

R. GADDIE (Birmingham)

G. TÖLG, *Chemische Elementaranalyse mit kleinsten Proben*, Verlag Chemie, Weinheim/Bergstr., 1967, viii+228 pp., price DM 32,— (Kunststoffeinband).

This book deals with the methods available for the elemental analysis of very small (5–250 μg) samples of organic materials. The procedures described are almost entirely those developed by the schools of KIRSTEN, BELCHER and TÖLG himself, the size of sample taken for analysis decreasing roughly in that order. In most cases, practical detail is given for the various procedures for the determination of C,H,N,O,F,Cl, Br,I,S,P, and As, so that recourse to the original literature is unnecessary.

The reviewer would disagree with Dr. TÖLG only in the stress laid on dust-free atmospheres and in the impression given in the figure on p. 17 that quartz-fibre balances can safely be used on trolleys. All the reviewer's experience has indicated that the stability of the balance bench is as vital for these balances as for conventional microbalances. Normal dust is of far less importance though other atmospheric pollutions can have unexpected effects.

This is, nevertheless, an excellent book which gives a very fair picture of the relative virtues of the different methods available for analysing small samples. It is surprising that organic and biological chemists have so far remained largely indifferent to the value of these small-scale methods and it is to be hoped that Dr. TÖLG's book will stimulate wider interest in their application.

A. M. G. MACDONALD (Birmingham)

Trace Characterization: Chemical and Physical, Edited by W. W. MEINKE AND B. F. SCRIBNER, National Bureau of Standards Monograph 100, U.S. Government Printing Office, Washington, D.C., 1967, viii+580 pp., price $4.50.

This volume contains the texts of invited lectures and summaries of contributed papers given at the 1st Materials Research Symposium held at the National Bureau of Standards from October 3rd–7th, 1966. The symposium commenced with a short introductory address by one of the Editors of this volume. Eleven plenary sessions followed, covering chemical and physical techniques for trace characterization grouped under the following headings (names of invited lecturers in parentheses): *Trace characterization and properties of materials* (N. B. HANNAY); *Electrical measurements* (L. R. WEISBERG); *Electrochemical methods* (H. A. LAITINEN); *Optical and x-ray spectroscopy* (N. W. H. ADDINK); *X-ray diffraction* (J. CHIKAWA AND J. B. NEWKIRK); *Physical optical methods* (H. FREDERISKE); *Chemical spectrophotometry* (T. S. WEST); *Nuclear methods* (A. A. SMALES); *Mass spectroscopy* (A. J. AHEARN); *Preconcentration, sampling and reagents* (J. MINCZEWSKI); *Electron and optical microscopy* (S. AMELINCKX).

The standard of the contributions is extremely high, and it is a matter for regret that for reasons of space it was necessary to restrict the reports of the contributed papers to abstracts. Although analytical chemists may find a few of the chapters to be only of limited value, there is much to interest them in the rest of the book. Most of the lectures are in the form of surveys, and the subject matter is, in general, presented in a sufficiently simple manner to be readily understood by the non-specialist. Particularly outstanding in this excellent book are the treatments of electrochemical methods by H. A. LAITINEN and of spectrophotometric methods by T. S. WEST. At its very modest price of $4.50 this monograph should be in the library of every laboratory in which trace element analyses are carried out.

J. P. RILEY (Liverpool)

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Particle Size Analysis, Proceedings of a Conference. The Society for Analytical Chemistry, London, 1967, viii + 368 pp., price 147 s.

Particle size analysis is of importance in a vast range of modern technologies from photographic emulsion and paint manufacture to metallurgy and ore dressing. In recent years developments in the field of automatic particle sizing have been impressive and such methods are now rapidly replacing the time-honoured and time-consuming procedures of sedimentation and sieving in many fields. The present volume contains the Proceedings of a Conference on Particle Size Analysis convened by the Society for Analytical Chemistry and held in Loughborough from September 14th–16th, 1966. The papers presented covered a wide range of techniques from the more classical techniques to sophisticated procedures, including a number which are still in the development stage. After most papers there were lively and informative discussions. The Society for Analytical Chemistry is to be congratulated for publishing this book which will be of great value to those wishing to know about recent developments in this field.

J. P. RILEY (Liverpool)

Advances in Electrochemistry and Electrochemical Engineering. Vol. 6. Electrochemistry, Edited by P. DELAHAY, Interscience Publishers–J. Wiley and Son, Inc., New York, 1967, xi+482 pp., price 155 s.

This Volume contains contributions on the Theory of Charge Effects in the Electrolyte Compact Double Layer by C. A. BARLOW, JR. AND J. ROSS MACDONALD; on the Oxygen Electrode on Noble Metals by J. P. HOARE; on the Electrochemical Kinetics of Metal Complexes by J. KORYTA; on the Electrochemical Responses of Porous and Rough Electrodes by R. DE LEVIE; and on Insulator Electrode Reactions by W. MEHL AND J. M. HALE.

With the exception of the first paper, which is purely theoretical, all the contributions offer some type of information of importance to electroanalytical chemists. The reviews were completed in 1966 and are well documented.

P. ZUMAN (Prague)

Treatise on Analytical Chemistry, édité par I. M. KOLTHOFF ET P. J. ELVING avec la collaboration de E. B. SANDELL, 1ère partie, Vol. 7, Edition Interscience–J. Wiley et Fils Inc., 1967, xviii+621 pp., prix 160 s.

Ce volume, placé sous le signe de la mesure, est consacré à toutes sortes de détermination—celle de la masse, de volume de liquide et de gaz, de pression, de tension de vapeur, de pression osmotique, de sédimentation, de densité, de surface et de tension interfaciale, de viscosité et de stabilité. Il a été fait appel à 13 spécialistes de haute compétence, provenant des Universités et des grandes industries américaines.

La mesure de la masse comprend 5 chapitres qui ont pour objet l'étude des diverses balances et systèmes de pesée, la définition de la masse standard et des équations de base concernant la détermination de ces masses, la précision et divers facteurs de correction, le tout est agrémenté de quelques schémas judicieusement choisis. La determination des volumes de liquide et de gaz est traiteé en quelque 61 pages et renferme une foule de renseignements intéressants: par ex. la calibration des instruments de mesure, la graduation des pipettes, le rôle de la température, le calcul des volumes apparents etc. Le chapitre de la mesure des tensions de vapeur est très développé et renferme entre autres un paragraphe réservé aux applications analytiques. En ce qui concerne la pression osmotique, après la description des principaux osmomètres et des membranes, l'auteur indique comment il faut interpréter les résultats.

Signalons encore la mesure de la solubilité des solides, des liquides et des gaz, et les appareils utilisés, illustrés d'un grand nombre de figures et qui se termine par des applications pratiques: détermination de pureté, identification et analyse, séparation. A la fin de chaque chapitre, une liste de références bibliographiques.

On peut se demander si certains des sujets traités ont leur place dans un traité de chimie analytique. Tout cela dépend évidemment du sens qu'on donne à ce mot.

Il n'en reste pas moins que ce volume apporte bien des précisions sur les mesures physiques et sur la façon de les exécuter.

D. MONNIER (Genève)

N. J. HARRICK, *Internal Reflection Spectroscopy*, Interscience Publishers–J. Wiley and Sons, Inc., New York, 1967, xiv+327 pp., price 132 s.

Internal reflectance spectroscopy is based on the phenomenon of total internal reflection first described by NEWTON in "Opticks" in 1717, in studying the passage of a light beam from glass into a vacuum at an oblique angle. The commonest example is perhaps the completely silvered appearance of the far side of a glass of water when the latter is observed obliquely through the surface. In a more scientific sphere the technique of total attenuated reflectance (TAR), used for the study of thin films by infrared spectroscopy, is now a fairly familiar example.

This monograph is the first to survey the whole area and it incorporates a complete bibliography of all publications relating to internal reflection spectroscopy up to the year ending in 1966. Following an introductory chapter, the author deals with the principles governing the production and control of internal reflection phenomena and this is succeeded by a treatment of the effects of dispersion in the refractive index upon absorption and reflection. Chapter 4 deals with experimental elements for the production of internal reflection, and chapter 5 with optical cavities for the enhancement of absorption. Chapter 6 is devoted to instrumentation and in chapter 7 the information of most immediate interest to analytical chemists appears, *i.e.*, the applications of the technique. Applications to thin films are obvious, but the potentialities of application to liquids, solids and pastes, anisotropic materials and monomolecular layers on electrodes, catalysts and other surfaces where adsorption is critical, are of very considerable interest and show the unique contributions which may be made by this technique. Miscellaneous applications to breath analysis, air pollution, diffusion rate measurements, suspended particulates, biology and medicine are listed, *inter alia*. Finally, the book ends with a brief account of the limitations of internal reflection spectroscopy. These latter are chiefly associated with the fact that it may, on occasion, be dangerous to assume that data obtained for a very thin surface area may be representative of a bulk sample. This, however, should be obvious to the careful experimenter.

Undoubtedly, internal reflection spectroscopy has much to offer analytical chemists, and this book, particularly chapter 7 in the first instance, is one which may well stimulate considerable activity in the near future. We are greatly indebted to the author for a clear and expert guide to a fascinating and largely unexplored area of spectroscopy.

T. S. WEST (London)

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Chemical Analysis for Ironfoundries, Selected Methods, recommended by the BCIRA Methods of Analysis Sub-Committee, The British Cast Iron Research Association, George Allen & Unwin Ltd, London, 1967, 215 pp., price 42 s.

Die BCIRA veröffentlichte erstmals 1959 eine Zusammenstellung ausgewählter chemischer Analysenmethoden zur Untersuchung von Roh- und Gusseisen. Das vorliegende Buch erfuhr eine wertvolle Erweiterung durch die Aufnahme und Ergänzung von Verfahren für die Untersuchung von Ferrolegierungen, Giessereischlacken und legiertem Guss. Übersichtlich gegliedert wird der Stoff in 3 Hauptteilen klar und

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verständlich dargeboten. Als Vorstufe der Analyse behandelt das Buch eingehend die Arten und Durchführung der Probenahme sowohl aus der Schmelze (Barrenprobe, Rotationsprobenahmegerät, Finger- und Saugprobe) als auch von Roh- und Gusseisen und die Herstellung der Proben für die Kohlenstoffbestimmung von grauem Eisen. Ebenfalls wird auf die Probenahme der Ferrolegierungen und Schlacken eingegangen.

Bei den für die Betriebsanalyse empfohlenen Arbeitsvorschriften handelt es sich um gewichtsanalytische, massanalytische und photometrische Verfahren, wobei mehrfach britische Standardmethoden herangezogen wurden. Ferner finden die Komplexometrie und Lösungsmittelextraktion Anwendung sowie die atomare Absorption zur Magnesiumbestimmung in Gusseisen mit Kugelgraphit. Eine kurz gefasste Grundlage mit Anwendungsbereich ist den Vorschriften vorangestellt, die durch Anmerkungen zur sicheren Durchführung ergänzt werden. Zu bedauern ist, dass für die Ermittlung des Gesamtkohlenstoffgehaltes kein volumetrisches oder elektrochemisches Schnellverfahren angegeben wurde. Wünschenswert wäre bei einer Neuauflage auch die Angabe des Zeitbedarfs der einzelnen Bestimmungen und der Fehlergrenzen. Interessant sind die zeitsparenden Untersuchungsverfahren der Verbundanalyse für die Elemente Mn, Cr, Ni, Cu, Mo, Ti und V und ihre Anwendung bei der Ermittlung der Schlackenzusammensetzung.

Der Anhang enthält zweckmässige Angaben zur Geräteausstattung, über die Reagenzien, die Arbeitstechnik und Hinweise auf mögliche Gefahrenquellen im Laboratorium. Für die analytische Arbeit im Giessereilaboratorium ist das gut ausgestattete Buch eine zuverlässige Hilfe.

K. P. ROEDER (Duisburg)

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Annual Surveys of Organometallic Chemistry, Vol. 3, Edited by D. SEYFERTH AND R. B. KING, Elsevier Publishing Company, Amsterdam, 1967, xii+456 pp., price DFl. 77,50.

The present volume is produced in conformity with the earlier ones in this series. Its material is divided into two sections, main group metals and transition metals; boron and silicon are, as before, included in the surveys.

In recognition of the continuing upsurge in the publications in this field, the original editors have enlisted the help of six others. As with all volumes of this nature, speed of production is of paramount importance. Since some of the new editors are in countries outside the U.S.A., this condition cannot be comfortably fulfilled with the present hard-backed volumes. Accordingly, in future years, the series will be produced as Section B of the existing periodical *Organometallic Chemistry Reviews*.

It is a pleasure to record that the standard of this volume is up to that of its predecessors. Diagrams are good and the references are as numerous as would be expected from such a rapidly expanding field. This is clearly an established series and it is good to see that the original editors have taken the necessary steps to ensure its continuity.

E. J. FORBES (Birmingham)

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PUBLICATIONS RECEIVED

ANALAR Standards for Laboratory Chemicals, 6th Edn., Analar Standards, Ltd., London, 1967, x +633 pp., price 43 s (obtainable from Hopkin and Williams, Ltd., or British Drug Houses, Ltd.).

This 6th edition is much larger than the last one, which appeared in 1957. Many additional tests are included and some impurity limits have been made more stringent. Standards for 16 chemicals appear for the first time.

L. LANG, *Absorption Spectra in the Ultraviolet and Visible Region*, Akademiai Kiado, Budapest, 1967.
Vol. VII: 412 pp. +index, price 115 s.
Vol. VIII: 412 pp. +index, price 115 s.
Vol IX: 416 pp. +index, price 135 s.

Each of these volumes contains spectra and relevant data for about 200 compounds. The format is the same as that of previous volumes.

Conference on the Chemistry and Chemical Processing of Petroleum and Natural Gas, Edited by M. FREUND AND W. SZIRMAI, Akademiai Kiado, Budapest, 1968, 980 pp., price 270 s.

This volume contains the proceedings of the international conference held in Budapest in September, 1965. The 108 papers included are in English, French, German and Russian.

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ANNOUNCEMENT

TWELFTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY, GATLINBURG, TENN.

The Twelfth Conference on Analytical Chemistry in Nuclear Technology will be held in Gatlinburg, Tenn., on October 8, 9 and 10, 1968, under the sponsorship of the Analytical Chemistry Division, Oak Ridge National Laboratory. Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

All sessions of the Conference will be held in the Mountain View Hotel.

Technical program

The theme of the Conference this year is "The Role of the Analytical Chemist: (1) in Research on the Production and Chemical Properties of the Actinide Elements, and (2) in the Elucidation and Solution of Problems in the Field of Environmental Pollution and Related Areas." Papers that describe original, unpublished work on the following topics will be given.

Analytical chemistry of the actinide elements

1. Ionic Methods of Analysis; 2. Radiochemical Methods of Analysis; 3. New Methods or techniques potentially useful to the analytical chemist–improved nuclear measurements, methods of separation, and other useful processes; 4. Special facilities and equipment that have been developed and tested in actual operations.

Environmental Pollution and Related Areas

1. Identification of Environmental Hazards in Water; 2. Identification of Environmental Hazards in the Atmosphere; 3. Criteria and Standards for Environmental Quality and Control.

There will be an exhibition of modern analytical instruments and laboratory equipment.

Inquiries concerning the Conference, including requests for programs, should be directed to the Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37830, Attention: L. J. BRADY, Chairman.

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