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Provisional Publication Schedule for 1969

In the interests of rapid publication it has been found necessary to schedule 5 volumes for appearance in 1969. Since monthly publication will be maintained, this implies that 2 of the volumes will each consist of three issues, while 3 of the volumes will each consist of only 2 issues. The following provisional schedule applies:

Vol. **44,** No. **1**	January 1969	
Vol. **44,** No. **2**	February 1969	**(completing Vol. 44)**
Vol. **45,** No. **1**	March 1969	
Vol. **45,** No. **2**	April 1969	
Vol. **45,** No. **3**	May 1969	**(completing Vol. 45)**
Vol. **46,** No. **1**	June 1969	
Vol. **46,** No. **2**	July 1969	**(completing Vol. 46)**
Vol. **47,** No. **1**	August 1969	
Vol. **47,** No. **2**	September 1969	
Vol. **47,** No. **3**	October 1969	**(completing Vol. 47)**
Vol. **48,** No. **1**	November 1969	
Vol. **48,** No. **2**	December 1969	**(completing Vol. 48)**

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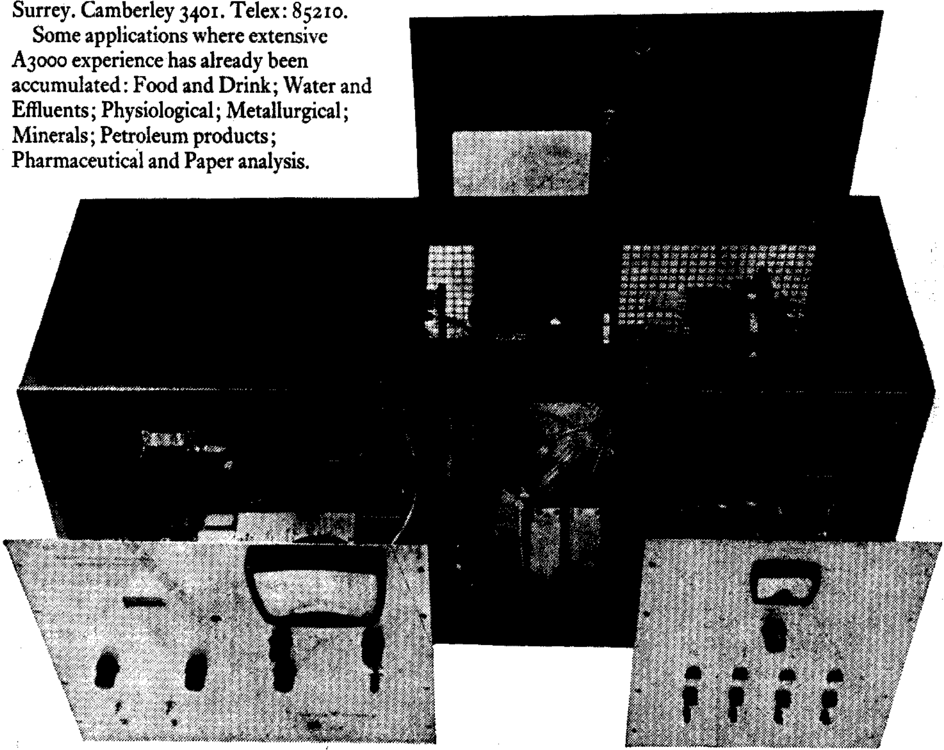

SOUTHERN ANALYTICAL


ARIST

SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 47, No. 2, September 1969

DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

PART III. DETERMINATION OF VANADIUM AND ALUMINUM IN TITANUM AND TITANIA BY PRESEPARATION

The determination of vanadium and aluminum by activation analysis was applied to titanium and titania samples. Three preseparation procedures, precipitation of titanium hydroxide, anion-exchange separation and scavenging with lead fluoride, were examined on different samples. The sensitivity of these methods is higher than for a non-destructive determination.

R. NEIRINCKX, F. ADAMS AND J. HOSTE,
Anal. Chim. Acta, 47 (1969) 173–182

THE DETERMINATION OF SULPHUR IN FLUOROCARBON POLYMERS BY NEUTRON ACTIVATION

Sulphur can be determined in fluorocarbon polymers and other fluorine compounds by neutron irradiation to convert sulphur-32 to phosphorus-32 by the (n, p) reaction. The phosphorus produced is determined by a substoichiometric extraction of vanadomolybdophosphoric acid, followed by measurement of β-emission. The method is satisfactory for sub-milligram quantities of sulphur irradiated for only 8 h.

R. B. HESLOP AND S. K. TAY,
Anal. Chim. Acta, 47 (1969) 183–188

DETERMINATION OF TRACES OF SILVER IN WATERS BY ANION EXCHANGE AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

A method has been developed for the accurate determination of 0.1–1 μg of silver per liter of water. The method permits stabilization of silver in water without loss to container walls. Optimum conditions have been established for the complete recovery of silver from water with an anion-exchange column, for quantitative elution of silver from the resin, and for measurement of silver by atomic absorption spectrophotometry after chelation with ammonium pyrrolidine dithiocarbamate and extraction of the chelate with MIBK. Silver in the 1–10 μg/l range can be determined by extraction without pre-concentration on an ion-exchange resin.

T. T. CHAO, M. J. FISHMAN AND J. W. BALL,
Anal. Chim. Acta, 47 (1969) 189–195

Elsevier Titles in Chemistry

INORGANIC CHEMISTRY

A Guide to Advanced Study

Third, completely revised edition

by **R. B. Heslop** and **P. L. Robinson**

6×9″, viii+774 pages, 155 tables, 400 illus., 227 lit. ref., 1967, Dfl. 32.50, 65s.

Contents: Modern inorganic chemistry. The atomic nucleus: genesis of the elements. Radiochemistry. Electronic structures of atoms. The periodic table. Valency; nature and classification of chemical bonding. Structure and shape of molecules. Bonding and structure in compounds of non-transition elements. Bonding in transition-metal complexes. The solid state. Oxidation-reduction: redox reactions. Acids and bases. Hydrogen. The hydrides. The noble gases. The alkali metals. Beryllium, magnesium and the alkaline earth metals. Boron and aluminium. Gallium, indium and thallium. Carbon and silicon. Organometallic compounds. Germanium, tin and lead. Nitrogen and phosphorus. Arsenic, antimony and bismuth. Oxygen, sulphur, selenium, tellurium and polonium. The oxides. Peroxides and peroxo-compounds. The halogens. The halides and pseudohalides. The transition metals. Complex or co-ordination compounds and ions. Substitution reactions of metal complexes. The lanthanides, scandium and yttrium The actinides. Titanium, zirconium and hafnium. Vanadium, niobium and tantalum. Chromium, molybdenum and tungsten. Manganese, technetium and rhenium. Iron, cobalt and nickel. The platinum metals. Copper, silver and gold. Zinc, cadmium and mercury. Index.

INTRODUCTION TO THE ATOMIC NUCLEUS

Volume 3 in a collection of monographs on "*Topics in Inorganic and General Chemistry*" edited by P. L. Robinson

by **J. G. Cuninghame**

5½×8½, xi+220 pages, 3 tables, 58 illus., 170 lit. refs., 1964, Dfl. 15.00, 35s.

Contents: Historical introduction. General definitions and properties. Nuclear forces. Stable nuclides. Radioactivity. Nuclear models. Nuclear reactions. Fission. Alpha-decay. Beta-decay. Gamma-emission. Interaction of particles and rays with matter. Index.

INTRODUCTION TO NUCLEAR CHEMISTRY

by **D. J. Carswell**

5½×8½″, ix+279 pages, 23 tables, 69 illus., 1967, Dfl. 32.50, 70s.

Contents: The development of nuclear chemistry. Fundamental particles and nuclear structure. Nuclear reactions and radioactivity. Properties of nuclear radiations. The detection and measurement of nuclear radiation. Nuclear instrumentation. Radiation chemistry. Isotope measurement and separation methods. Charged particle accelerators, neutron sources, production and properties of the actinide elements. Uses of isotopes. Experimental nuclear chemistry. Index.

RADIOCHEMICAL SURVEY OF THE ELEMENTS

Principal Characteristics and Applications of the Elements and their Isotopes

by **M. Haïssinsky** and **J.-P. Adloff**

6×9″, ix+177 pages, 1965, Dfl. 32.50, 75s.

Contents: Introduction. The elements in alphabetical order. Element 102. Element 104.

THE STRUCTURE OF INORGANIC RADICALS

An Application of Electron Spin Resonance to the Study of Molecular Structure

by **P. W. Atkins** and **M. C. R. Symons**

6×9″, x+280 pages, 57 tables, 74 illus., 357 lit. refs., 1967, Dfl. 60.00, £7.0.0.

Contents: Introduction. An introduction to electron spin resonance. Formation and trapping of radicals. Trapped and solvated electrons. Atoms and monatomic ions. Diatomic radicals. Triatomic radicals. Tetra-atomic radicals. Penta-atomic radicals. Summary and conclusions.

Appendices: The language of group theory. The spin hamiltonian. Calculation of *g*-values. Determination of spin-density distribution and bond angles. Analysis of electron spin resonance spectra. Index.

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THE DETERMINATION OF MANGANESE IN A WIDE RANGE OF STEELS AND CAST IRONS BY ATOMIC ABSORPTION SPECTROSCOPY

A method is described for the determination of 0.1–2.0% of manganese in a wide range of steels and cast irons by atomic absorption spectroscopy. The sample solution is fumed with perchloric acid, silica is removed by filtration, and ethanol is added to the solution before the measurement. No interference from any of the other elements commonly found in these alloys was observed.

D. P. Hubbard and H. H. Monks,
Anal. Chim. Acta, 47 (1969) 197–202

DETERMINATION OF LEAD IN URINE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AFTER COPRECIPITATION WITH THORIUM

Lead is determined in urine by atomic absorption spectrophotometry after separation by coprecipitation with thorium, in the presence of copper(II); concentration of lead and removal of interferences are achieved simultaneously. Fresh urine or samples acidified with hydrochloric acid must be used. Precipitation is quantitative from the urine of subjects excreting coproporphyrins or treated with chelating agents, as the added copper liberates the chelated lead. The precision of the method is ±0.005 p.p.m. of lead

N. Zurlo, A. M. Griffini and G. Colombo,
Anal. Chim. Acta, 47 (1969) 203–208

EXTRACTION OF TETRABUTYLAMMONIUM TETRACHLOROAURATE(III) INTO CHLOROFORM SOLUTION OF TETRABUTYLAMMONIUM PERCHLORATE AND SPECTROPHOTOMETRIC DETERMINATION OF GOLD

The distribution equilibrium:

$$AuCl_4^- + (Bu_4N^+, ClO_4^-)_{HCCl_3} \rightleftarrows (Bu_4N^+, AuCl_4^-)_{HCCl_3} + ClO_4^-,$$

has been examined. With acidic aqueous chloride solutions in which $-\log \sqrt{[H^+]\,[Cl^-]}$ is greater than 2, the apparent equilibrium constant, K_A, is a constant equal to the equilibrium constant of the distribution reaction above; a value of $2.88 \cdot 10^3$ was obtained. Combination of the extraction with a direct spectrophotometric determination of $AuCl_4^-$ in chloroform at 312 nm provides a simple, rapid, and accurate analytical method for the separation and determining of gold in the μg-range.

O. Bravo and R. T. Iwamoto,
Anal. Chim. Acta, 47 (1969) 209–214

ADHESION AND ADHESIVES

2nd, completely revised, edition

edited by R. Houwink and G. Salomon

Volume 1

Adhesives

7 × 10", xvi + 548 pages, 72 tables, 150 illus., 1965, £ 8.0.0, Dfl. 67.50

The introductory chapter of this first volume is a concise guide to the scientific background of all adhesive processes. Surface science and bulk properties of solids, as related to adhesive bonding, are discussed and illustrated by recent examples from the technology of metals, glass, rubber and plastics. An annotated bibliography is provided for the reader who wants access to more highly specialized works. The further nine chapters, making up the volume, cover the basic materials used in adhesion technology. Greatest attention is paid to synthetic adhesives, especially the classical thermohardening and the new epoxy resins. Fields previously examined in the first edition have been extended, and a brief contribution added on the adhesion of glass and on glass-to-metal bonding.

CONTENTS:

1. Adhesion. 2. Animal glue and related protein adhesives. 3. Vegetable adhesives. 4. Synthetic organic adhesives. 5. Bituminous binders and coatings. 6. Rubbers. 7. Glass, enamels and ceramics. 8. Inorganic adhesives and cements. Part A: Soluble silicates. 9. Inorganic adhesives and cements. Part B: Miscellaneous inorganic materials. 10. Metallic adhesives. Appendix: Historical table. Subject index.

Volume 2

Applications

7 × 10", xiv + 590 pages, 21 tables, 300 illus., 196
£ 8.0.0, Dfl. 67.50

In this second volume the main trends i industrial application are outlined by sixtee specialists. Assessment of surface geome try, choice of surface treatment, and selec tion of the most economical bonding proces — the correct decision in each case is th basis for any successful engineering proces The introductory chapter deals with thi general background; it links the two volume and extends the annotated bibliography t 1966. Two compact "adhesives charts facilitate the choice of a candidate adhesiv and of processing methods. The work als contains a Subject Index to Volume 2 and a Author Index to both volumes.

CONTENTS:

Introduction. 11. Surface texture. 12. Surface treatme of adherends. 13. Adhesive bonding processes. 1 Wood, reconstituted wood and glued laminated stru tures. 15. Adhesive-bonded metal structures. 16. Bonde composite structures. 17. Pressure-sensitive adhesi tapes. 18. Rubber-textile structures. 19. The tack printing inks. 20. Adhesion in paint technology. 2 Miscellaneous applications. 22. Testing of adhesive 23. Mechanical testing of bonded joints. Appendi Adhesives charts. Subject index. Author index Volumes 1 and 2.

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SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TITANIUM IN ZIRCONIUM, ZIRCONIUM ALLOYS, HAFNIUM, NIOBIUM AND OTHER METALS, WITH DIANTIPYRINYLMETHANE

The reaction between titanium and diantipyrinylmethane to form a yellow-coloured complex in mineral acid solution, has been successfully applied to the direct spectrophotometric determination of titanium over the range 20–250 p.p.m., in zirconium, zirconium alloys and hafnium. Absorbance of the complex is measured at 390 nm. The proposed method is more sensitive than the peroxide method usually used for determining titanium in these materials. It is also less subject to interference from other metal ions, and can be applied to ZR 30 alloy without preliminary separation of molybdenum. Simple modifications have enabled the procedure to be extended to the determination of titanium in niobium, tantalum, tungsten and molybdenum. In the analysis of materials containing appreciable amounts of niobium or molybdenum, absorbances are measured at 430 nm.

D. F. Wood and J. T. Jones,
Anal. Chim. Acta, 47 (1969) 215–224

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF ARSENIC BY AN EXTRACTION METHOD

A general method is presented for the spectrophotometric determination of arsenic at trace levels. It involves extraction of the yellow molybdoarsenic acid with *n*-butanol and subsequent reduction to the blue complex. The yellow molybdophosphoric acid is removed by a preliminary extraction with isobutyl acetate or isoamyl alcohol. A comprehensive study of interferences was carried out and modifications are described which permit the determination of arsenic in a wide variety of salts, white metals, copper alloys and all types of steels.

P. Pakalns,
Anal. Chim. Acta, 47 (1969) 225–236

HYDROGEN FLAME CHEMILUMINESCENCE DETECTOR FOR SULFATE IN AQUEOUS SOLUTIONS

The instrument described is capable of detecting sulfate ion in aqueous solution at concentrations as low as 2 μg of sulfate per ml of solution. It is demonstrated to be of potential value for use as a specific sulfate analyzer in the hydrogen peroxide determination of sulfur dioxide. When used in conjunction with this analytical procedure, the detection limit for sulfur dioxide collected in 1-h samples is estimated to be 0.03 p.p.m. (v/v). Advantages over other methods presently in use are discussed.

W. L. Crider, N. P. Barkley, M. J. Knott and R. W. Slater, Jr.,
Anal. Chim. Acta, 47 (1969) 237–241

A STUDY OF THE DETERMINATION OF HAFNIUM IN ZIRCONIUM AND ITS ALLOYS BY X-RAY FLUORESCENCE

(in French)

The determination of hafnium in zirconium and its alloys by X-ray fluorescence is possible down to about 10 p.p.m. if a range of suitable standards is available. Either Hf Lα or Hf Lβ_1 can be used as the analytical line. The optimal experimental conditions are defined by means of statistical criteria.

G. Vos,
Anal. Chim. Acta, 47 (1969) 243–249

THE MASS SPECTRA OF ORGANIC MOLECULES

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

7 x 10", ix + 510 pages, 20 tables, 181 illus., 547 lit. refs., 1968, Dfl. 97.50

Contents: 1. The principles and methods of mass spectrometry. 2. Types of ions in the mass spectra of organic compounds. 3. The mass spectra of hydrocarbons. 4. The mass spectra of oxygenated compounds. 5. The mass spectra of nitrogen compounds. 6. The mass spectra of sulphur compounds. 7. The mass spectra of halogenated compounds. 8. The mass spectra of boron compounds. 9. The mass spectra of phosphorus compounds. 10. The mass spectra of silicon compounds. 11. Examples of structure determination from mass spectra. Appendix 1. Peaks commonly encountered in the mass spectra of organic compounds. Appendix 2. The masses and abundances of nuclides commonly encountered in the mass spectra of organic compounds. References. Indexes.

MASS SPECTROMETRIC ANALYSIS OF SOLIDS

edited by A. J. Ahearn, Member of Technical Staff, Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey, U.S.A.

5½ x 8½", viii + 175 pages, 13 tables, 46 illus., 242 lit. refs., 1966, Dfl. 30.00

Contents: 1. Introductory survey. 2. The production of ions from solids. 3. Photographic emulsions as ion detectors in quantitative mass spectrography. 4. Analysis of special samples. 5. Mass spectrographic microprobe analysis. Indexes.

ATOMIC-ABSORPTION SPECTROSCOPY

and Analysis by Atomic-Absorption Flame Photometry

by J. Ramírez-Muñoz, Principal Applications Chemist at Beckman Instruments Inc. and Scientific Research Collaborator of the C.S.I.C., Spain

6 x 9", xii + 493 pages, 23 tables, 156 illus., 950 lit. refs., 1968, Dfl. 80.00

Contents: *Part I: Fundamentals.* 1. Origins of the method and nomenclature. 2. General principles and characteristics. 3. Absorption and emission. 4. The literature of atomic-absorption spectroscopy. 5. Theory. *Part II: Instrumental Systems.* 6. Instrumental systems. 7. Emission systems. 8. Absorption system. 9. Selection system. 10. Photometric system. 11. Instruments. *Part III: Range and Limitations of Atomic Absorption Methods.* 12. Determinable elements. Choice of lines. 13. Sensitivity. 14. Limitations in atomic absorption. *Part IV: Experimental Methods.* 15. Experimental process. 16. Standard solutions. 17. Preparation of the sample. 18. Experimental measurements and calibration. *Part V: Applications.* 19. Applications. Appendix. Bibliography.

Still available:

MASS SPECTROMETRY AND ITS APPLICATIONS TO ORGANIC CHEMISTRY

by J. H. Beynon

7 x 10", xii + 640 pages, 11 tables, 185 illus., 2213 lit. refs., 1960, reprinted 1964 and 1967, Dfl. 85.00

TABLE OF META-STABLE TRANSITIONS FOR USE IN MASS SPECTROMETRY

by J. H. Beynon, R. A. Saunders and A. E. Williams

10 x 7", xix + 392 pages, 1965, Dfl. 50.00

MASS AND ABUNDANCE TABLES FOR USE IN MASS SPECTROMETRY

by J. H. Beynon and A. E. Williams

10 x 7", xxi + 570 pages, 1963, Dfl. 60.00

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ACCURATE SILICATE ANALYSIS BASED ON SEPARATION BY ION-EXCHANGE CHROMATOGRAPHY

A method is presented for the accurate determination of the major and some minor elements in silicate minerals. After sample dissolution and removal of silica, the elements are absorbed from an oxalic–hydrochloric–sulphuric acid mixture on a column of AG1-X8 anion-exchange resin in the oxalate–chloride–sulphate form and a column of AG50W-X8 cation-exchange resin in the hydrogen form. The columns are connected in series. Fe(III), Al(III), Ti(IV), Zr(IV), V(IV) and Mo(VI) are retained by the anion-exchange column, while Mg(II), Ca(II), K(I), Na(I) and Mn(II) pass through and are retained by the cation-exchange column. Phosphate passes through both columns. The columns are disconnected and both groups of elements completely separated by using only the volatile inorganic acids, hydrochloric and nitric acid, and the solvents ethanol and acetone as eluents. Selected titrimetric, spectrophotometric and atomic absorption methods are used for determinations. Very accurate results of analysis of synthetic mixtures and standard rocks are presented together with anion-exchange distribution coefficients in hydrochloric–oxalic acid mixtures and relevant elution curves.

F. W. E. STRELOW, C. J. LIEBENBERG AND F. VON S. TOERIEN,
Anal. Chim. Acta, 47 (1969) 251–260

DETERMINATION OF BISMUTH AND LEAD BY CONTROLLED-POTENTIAL COULOMETRIC OXIDATION

A method has been developed for the determination of lead and bismuth by controlled-potential coulometric oxidation. After simultaneous reduction of both metals into a mercury pool, lead and bismuth are determined by stepwise anodic stripping at -0.16 and $+0.20$ V *vs.* Ag/AgCl/sat. KCl electrode, respectively, in a supporting electrolyte of 0.4 *M* tartaric acid and 0.30–0.72 *M* perchloric acid. The reduction of lead and bismuth is carried out at -0.50 V or more negative potential. Bismuth alone can be reduced at -0.25 V. Polarography with a dropping amalgam electrode was advantageously applied to establish optimum conditions for coulometric oxidation of these metals. Solutions containing 0.02–0.2 meq of lead and/or bismuth were analyzed with an accuracy and precision of $\pm 0.2\%$ or better for lead and $\pm 0.3\%$ for bismuth. The method was applied to the analysis of glasses and thin films.

Y.-S. SU AND D. E. CAMPBELL,
Anal. Chim. Acta, 47 (1969) 261–266

ANALYTICAL UTILIZATION OF THE POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOR OF SOME SULFUR-CONTAINING PURINES

The polarographic and voltammetric behavior at the dropping mercury and pyrolytic graphite electrodes of 6-thiopurine, purine-6-sulfinic acid, purine-6-sulfonic acid, purine-6-sulfonamide and bis(6-purinyl) disulfide is discussed from the viewpoint of their analytical applicability. Procedures are described for the determination of the single compounds or mixtures of several compounds. The polarographic and voltammetric behavior of these compounds is so characteristic that the observed waves can be utilized for very sensitive qualitative identification.

G. DRYHURST,
Anal. Chim. Acta, 47 (1969) 267–274

INTRODUCTION TO NUCLEAR CHEMISTRY

by D. J. Carswell

ix + 279 pages, 23 tables, 69 illus., 1967, Dfl. 32.50, 70s.

Contents: 1. The development of nuclear chemistry. 2. Fundamental particles and nuclear structure. 3. Nuclear reactions and radioactivity. 4. Properties of nuclear radiations. 5. The detection and measurement of nuclear radiation. 6. Nuclear instrumentation. 7. Radiation chemistry. 8. Isotope measurement and separation methods. 9. Charged particle accelerators, neutron sources, production and properties of the actinide elements. 10. Uses of isotopes. 11. Experimental nuclear chemistry (including 16 selected experiments). Index.

STATISTICAL THERMODYNAMICS

An Introduction to its Foundations

H. J. G. Hayman

ix + 256 pages, 14 illus., 1967, Dfl. 47.50, 110s.

Contents: Preface. Nomenclature. 1. An introductory survey. 2. Some simple partition functions. 3. The microcanonical assembly. 4. The second law of thermodynamics. 5. The canonical assembly. 6. The third law of thermodynamics. 7. Dilute gases. 8. The grand canoinical assembly. 9. Fermi-Dirac, Bose-Einstein and imperfect gases. 10. The partition function method applied to Fermi-Dirac, Bose-Einstein and photon gases. 11. Classical statistical thermodynamics. 12. The relationship between classical and quantum statistics.
Appendices: 1. The probability integral. 2. Stirling's formula for ln n!. 3. The method of variation of constants. 4. The dynamic equilibrium of a microcanonical assembly. 5. The adiabatic principle. 6. Liouville's theorem. Index.

THE STRUCTURE OF INORGANIC RADICALS

An Application of Electron Spin Resonance to the Study of Molecular Structure

by P. W. Atkins and M. C. R. Symons

x + 280 pages, 57 tables, 74 illus., 357 lit. refs., 1967, Dfl. 60.00, £7.0.0.

Contents: 1. Introduction. 2. An introduction to electron spin resonance. 3. Formation and trapping of radicals. 4. Trapped and solvated electrons. 5. Atoms and monatomic ions. 6. Diatomic radicals. 7. Triatomic radicals. 8. Tetra-atomic radicals. 9. Penta-atomic radicals. 10. Summary and conclusions.
Appendices: 1. The language of group theory. 2. The spin Hamiltonian. 3. Calculation of g-values. 4. Determination of spin-density distribution and bond angles. 5. Analysis of electron spin resonance spectra. Index of data. Subject index.

FUNDAMENTALS OF METAL DEPOSITION

by E. Raub and K. Müller

viii + 265 pages, 10 tables, 138 illus., 245 lit. refs., 1967, Dfl. 60.00, £7.5.0.

Contents: 1. Chemical and electrochemical principles. 2. Electrode processes. 3. The cathodic discharge of ions. 4. The structure of electrolytic metal deposits. 5. Physical and chemical properties of electrolytic metal deposits. 6. Distribution of electrolytic metal deposits on the cathode. Index.

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APPLICATION OF ANODIC-STRIPPING VOLTAMMETRY TO THE DETERMINATION OF SOME TRACE ELEMENTS IN SEA WATER

The application of anodic-stripping voltammetry, with a hanging mercury drop electrode and a fast-sweep polarograph, to the determination of several trace elements in raw sea water is discussed. Advantages and disadvantages of the technique and the main sources of error are described. A comparison is made of analytical data for the trace elements zinc, cadmium, lead, and copper by the anodic-stripping technique and by the single-sweep polarographic technique. Precise measurements of concentrations of 10^{-8}–10^{-9} *M* can be made, if variables are carefully controlled.

G. C. Whitnack and R. Sasselli,
Anal. Chim. Acta, 47 (1969) 275–284

ELECTROCHEMICAL MASKING OF INDIUM IN A.C. POLAROGRAPHIC DETERMINATION OF CADMIUM

A polarographic method for the determination of cadmium without any previous separation of large amounts of indium is described. The anionic surfactant Benax serves as electrochemical masking agent for negatively charged metal citrate complexes but does not affect a.c. polarograms of uncomplexed cadmium ions. In citrate buffer at pH 3.5–4 with 0.03% Benax present, cadmium can be determined in the presence of 10,000-fold amounts of indium. No other frequently associated metals interfere in the determination.

E. Jacobsen and G. Tandberg,
Anal. Chim. Acta, 47 (1969) 285–290

SELECTIVITY OF ION-SPECIFIC MEMBRANE ELECTRODES

A theoretical interpretation is given for the selectivity constants of ion-selective electrodes. The validity of the theory is proved for halide-selective electrodes. The high selectivity of the halide electrodes to individual halide ions offers many applications of these electrodes in analytical chemistry.

E. Pungor and K. Tóth,
Anal. Chim. Acta, 47 (1969) 291–297

EXTRACTION STUDIES OF PLATINUM GROUP METALS WITH DIANTIPYRYLPROPYLMETHANE

Diantipyrylpropylmethane (DAPM) is easily synthesized and forms reasonably stable solutions in a number of common organic solvents. The solubility of DAPM in ten different solvents is reported. Solutions of DAPM react with the anionic chloro complexes of the platinum group metals in hydrochloric acid solution to form stable extractable complexes. The distribution of tracer quantities of the six platinum metals between hydrochloric acid solutions and a chloroform solution of the DAPM was studied. Distribution coefficients are reported as a function of the hydrochloric acid concentration; 98% of the Os, Pt or Pd can be extracted in a single pass, over an acid concentration range 0.1–12 *M*; 98% Ir can be extracted in one extraction over the acid range 0.1–6 *M*. Ruthenium can be extracted quantitatively in one extraction from 4–6 *M* hydrochloric acid with stronger DAPM solution. Rhodium is poorly extracted under all conditions tested.

DAPM is not promising for the selective separation of mixtures of platinum group metals, but may be used for group extraction.

A. D. Shendrikar and E. W. Berg,
Anal. Chim. Acta, 47 (1969) 299–304

Pigments

An Introduction to their Physical Chemistry

edited by David Patterson

Senior Lecturer, Department of Colour Chemistry, University of Leeds, Great Britai

$5\frac{1}{2} \times 8\frac{1}{2}''$, ix + 210 pages, 93 illus., 1967, Dfl. 32.50, 65s.

In this book the principles of physical chemistry are applied to the problems of making an using the insoluble organic and inorganic pigments manufactured for use in paints, printin inks, plastics and synthetic fibres. Development over many years has resulted in a high degre of technical quality in many of these pigments, achieved by purely empirical methods, but th use of such methods means that each case must be judged on its merits. On the other hand the application of physico-chemical theories can bring unifying concepts to a wide range o phenomena, and provide a deeper understanding of the processes involved.

It is quite insufficient to treat the making of pigments as the synthesis of certain compounds and to emphasize this the purely preparative chemistry of pigments has been left outside th scope of this book. Instead, pigments are regarded as substances produced to exert particula optical effects on certain media by colouring and opacifying them. The ways in which pigments can be prepared to carry out these functions, together with the appropriate technique for appraising their performance of them are consequently the main content of the book. A the problems cannot be solved at present, but this book by showing what can be achieve and attempting to provide signposts to some of the unexplored areas, will undoubtedly stimulate and encourage further work in a field that is of considerable industrial importance.

Contents

1. Introduction
2. The theory of the colour of inorganic substances
3. The colour and constitution of organic molecules
4. The colour of pigment crystals
5. Photoconduction and the degradation of organic molecules
6. The nucleation and growth of particles
7. Particle size measurements and their significance
8. Instrumental methods of colour measurement
9. Instrumental colour match prediction
10. The theory of surface activity
11. The theory of dispersion, flocculation and flotatio phenomena

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THE SOLVENT EXTRACTION OF VANADOMOLYBDOPHOSPHORIC ACID AS THE BASIS OF A SUBSTOICHIOMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS

The conditions for the extraction of phosphate as vanadomolybdophosphate, and the composition of the extract, have been studied with phosphorus-32 and vanadium-48. Reproducible extractions can be made with substoichiometric amounts of molybdate; such extractions can be adapted to the determination of either phosphorus or sulphur by means of neutron activation.

R. B. HESLOP AND A. C. RAMSEY,
Anal. Chim. Acta, 47 (1969) 305–314

SALT AND ACTIVITY EFFECTS ON THE PRECIPITATION OF TETRAPHENYLARSONIUM PERCHLORATE

Alkali metal chlorides in the concentration range 0.006–4 *M* influence the solubility, crystal form and filterability of precipitated tetraphenylarsonium perchlorate. Low salt concentrations increase, and high concentrations decrease the filterability and solubility. The mean activity coefficient of tetraphenylarsonium perchlorate is controlled by general and specific salt effects. Crystal nucleation is probably heterogeneous in low concentrations of salt and homogeneous in high concentrations.

KENNETH W. LOACH,
Anal. Chim. Acta, 47 (1969) 315–322

RAPID GRAVIMETRIC DETERMINATION OF MERCURY(I) SALTS

A rapid, reliable method for the analysis of mercury(I) salts is based on direct weighing of mercury formed by complete disproportionation of Hg_2^{2+}, accomplished by complexing the mercury(II) with bromide or iodide. The free mercury is obtained in the form of a bright metallic globule, which is easily washed and dried for weighing. The method has been applied to the analysis of mercury(I) chloride and mercury(I) nitrate, and has been compared with titrimetric methods involving oxidation of mercury(I) with iodate and with iron(III).

Y.-T. PENG AND G. H. AYRES,
Anal. Chim. Acta, 47 (1969) 323–331

HOMOGENEOUS PRECIPITATION OF BERYLLIUM BY MEANS OF TRICHLOROACETIC ACID HYDROLYSIS AND DETERMINATION AS PHOSPHATE

A solution of trichloroacetic acid, on heating, undergoes gradual decomposition to chloroform and carbon dioxide, accompanied by a rise in pH. This principle has been applied for the homogeneous precipitation of beryllium in presence of phosphate ions. The effect of alkali ions (Na and K) on the composition of the precipitate has been investigated. The method has been successfully applied for the determination of beryllium in beryls.

K. R. KRISHNAMOORTHY AND R. K. IYER,
Anal. Chim. Acta, 47 (1969) 333–338

Countercurrent Separation Processes

by **H. R. C. Pratt**

Chief, Division of Chemical Engineering, C.S.I.R.O., Melbourne, Australia

6 × 9″, xxii + 537 pages, 30 tables, 173 illus., 415 lit.refs., 1967, Dfl. 95.00, £11.0.0.

The countercurrent separation processes represent, in terms of invested capital, the most important single grou of operations in the chemical and process industries. Such operations, which must be clearly distinguished fro mechanical separations such as continuous countercurrent decantation and leaching, are normally restricted i the chemical engineering texts to distillation in its various forms (including azeotropic and extractive distillation) absorption and stripping, liquid-liquid extraction, and sometimes adsorption.

Since the 1940's, chemical engineers have become increasingly concerned with isotopic and other difficult separa tions. Furthermore, newer techniques, such as liquid thermal diffusion, etc. enable separations to be accomplishe which are difficult or unobtainable by other means. It became evident therefore that a text should be available whic generalises the treatment to cover all types of separation process, and this is in fact what the author hopes to hav achieved here. The list of processes dealt with in the various chapters does not exhaust all possibilities. However most of the remaining known processes are either of very limited application, or are as yet relatively undeveloped.

Although the book is fairly advanced in coverage, selected material can be used as the basis for a course for fina year chemical engineering students. It should also be of particular interest to research workers, both in stimulatin applications of the various processes to hitherto unachieved separations, and in development of entirely new type of separation process. Although not intended to be used as a design manual, it should prove of great value t practising chemical engineers and plant designers in providing a basic understanding of the principles involved i the design of equipment for these processes.

Contents: 1. Introduction and basic concepts. 2. Steady-state cascade theory: the ideal cascade. 3. Steady-stat cascade theory: square and squared-off cascades. 4. Distillation. 5. Equilibrium processes employing a separatin agent. 6. Other equilibrium processes. 7. Irreversible processes: gaseous diffusion. 8. Irreversible processes mass and thermal diffusion. 9. Other irreversible processes. 10. Multicomponent separations. 11. The unstead state. Appendix: Table of values of the separation potential. Subject index.

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AN ANALYTICAL STUDY OF A NEW TYPE OF HALIDE-SENSITIVE ELECTRODE PREPARED FROM SILVER HALIDES AND THERMOPLASTIC POLYMERS

A new type of halide-selective membrane electrode is described. Membranes selective for iodide, bromide and chloride can be prepared by thorough mixing of a silver halide precipitate with a thermoplastic polymer followed by heat treatment under pressure. The ranges of linear response to changes in halide concentration are similar to those for other types of silver halide membrane electrode. The selectivity of the electrodes and their behaviour in aqueous–organic solvents is described.

M. Mascini and A. Liberti,
Anal. Chim. Acta, 47 (1969) 339–345

N-ACETYLSALICYLOYL-N-PHENYLHYDROXYLAMINE AS AN ANALYTICAL REAGENT FOR TITANIUM(IV)

N-Acetylsalicyloyl-N-phenylhydroxylamine is readily prepared and can be used for the detection and the spectrophotometric or gravimetric determination of titanium(IV). The reagent forms a deep yellow chloroform-soluble complex with titanium(IV) and thiocyanate in 4.5–8 *M* hydrochloric acid media. The limit of identification of the spot test based on this reaction is 0.1 μg of titanium (dilution limit is $1:2\cdot10^6$). The spectrophotometric method is also highly selective, the sensitivity being 0.004 μg Ti/cm^2 at 390 nm. The optimum concentration range is 0.5–3.5 μg Ti/ml, the relative photometric error being 1.85. The complex is stable at room temperature for 24 h, and contains the metal, reagent and thiocyanate in the ratio 1:2:1. Commonly associated ions can be tolerated in amounts greater than 1000-fold. Gravimetric determination of titanium(IV) is also very selective; the yellow precipitate formed in 1–2 *M* hydrochloric acid media can be weighed directly after drying at 105–115°. Both methods can be applied to the determination of titanium in ilmenite.

C. P. Savariar and J. Joseph,
Anal. Chim. Acta, 47 (1969) 347–353

MASS SPECTRAL STUDIES OF SOME SUBSTITUTED PHOSPHINES

(Short Communication)

W. Z. Borer and K. Cohn,
Anal. Chim. Acta, 47 (1969) 355–359

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(Short Communication)

E. W. Berg and H. E. Moseley,
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AN ACID–BASE–ISOCYANATE METHOD FOR THE ANALYSIS OF ADMIXTURES OF HYDRAZINE WITH 1,1-DIMETHYLHYDRAZINE, AND MONOMETHYLHYDRAZINE WITH 1,1-DIMETHYLHYDRAZINE

(Short Communication)

H. E. Malone and D. M. W. Anderson,
Anal. Chim. Acta, 47 (1969) 363–366

COORDINATION CHEMISTRY REVIEWS

Editor: A.B.P. LEVER (Downsview, Ont., Canada)

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The effect of axial ligand fields on ground state properties of complexes with orbitally degenerate ground terms - G.A. Webb (Guildford, England)

CONTENTS Volume 4, No. 2, April 1969

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DETERMINATION OF IMPURITIES IN TITANIUM AND TITANIUM DIOXIDE BY NEUTRON ACTIVATION ANALYSIS

PART III. DETERMINATION OF VANADIUM AND ALUMINUM IN TITANIUM AND TITANIA BY PRESEPARATION

R. NEIRINCKX, F. ADAMS AND J. HOSTE
Institute for Nuclear Sciences, Ghent University, Ghent (Belgium)

(Received May 21st, 1969)

The determination of aluminum in titania is important for the study of the quality of titania as a pigment. Chalking of a paint film is influenced by the amount and properties of the added pigment. The breakdown of a paint film is dependent on the intensity of the light absorbed by the medium. The added pigment absorbs a relatively high fraction of the incident light but the surface of the pigment particles seems to catalyze the breakdown process. Therefore, metal oxides, usually alumina, are post-precipitated onto the titania pigment particles. This results in a markedly decreased corrosion rate. Vanadium has a negative effect on the quality of titania pigments, and the evaluation of its concentration may be of importance.

Vanadium and aluminum can be separated from titanium by precipitation of titanium hydroxide with sodium hydroxide. In this way, Al(III), V(V), Mo(VI), W(VI) and Cr(VI) remain in solution[1]. An anion-exchange separation of vanadium(V) and aluminum(III) from titanium(IV) was devised by Strelow[2] who eluted vanadium(V) with a mixture of hydrogen peroxide and 0.5 *N* sulphuric acid, followed by hydrogen peroxide and 1 *N* sulphuric acid, which elutes titanium(IV), while aluminum (III) remains on the resin. Kaimal and Shome[3] separated vanadium(V) and aluminum (III), together with many other elements, from titanium by precipitation of titanium (IV) with N-benzoyl-N-phenylhydroxylamine from a 0.5 *N* sulphuric acid—EDTA solution. Alimarin and Yakovlev[4] and Brooksbank *et al.*[5] determined vanadium in titania by neutron irradiation. These were non-destructive methods and cannot be applied for concentrations lower than about 20 o.p.m. or in the case of unfavourable Al/V weight ratios. The latter were encountered in different samples. Separation after irradiation is of course impossible since the half-life of both ^{52}V and ^{28}Al is too short. A preseparation of vanadium and aluminum is therefore required.

Nuclear data and interferences

A summary of the most important nuclear data is shown in Table I. Of the five stable isotopes of titanium, only the last one gives rise to a radioactive isotope, ^{51}Ti upon reactor irradiation. The (n, p), (n,2n) and (n,α) reactions are of minor importance in this case, as the cross-sections for these threshold reactions are rather small. Besides, under the irradiation conditions used, the fast neutron flux is three times smaller than the thermal neutron flux. Because hydrofluoric acid is used for the dis-

TABLE I

NUCLEAR DATA OF THE ISOTOPES, FORMED BY REACTOR IRRADIATION OF TITANIA, VANADIUM, ALUMINUM, FLUORINE AND LEAD

Reaction	*Activation cross-section (barn)*	*Half-life of the reaction product*	*Decay mode and energy (MeV)*
$^{46}Ti(n,\gamma)^{47}Ti$	0.6	Stable	—
$^{47}Ti(n,\gamma)^{48}Ti$	1.7	Stable	—
$^{48}Ti(n,\gamma)^{49}Ti$	8.3	Stable	—
$^{49}Ti(n,\gamma)^{50}Ti$	1.9	Stable	—
$^{50}Ti(n,\gamma)^{51}Ti$	0.14	5.8 min	β^- 2.13; γ 0.3200; 0.6084; 0.9285
$^{18}O(n,\gamma)^{19}O$	$2 \cdot 10^{-4}$	29.4 sec	β^- 3.25; 4.60; γ 0.122; 0.200; 1.36
$^{46}Ti(n,p)^{46}Sc$	$8 \cdot 10^{-3}$	84 d	β^- 0.357; γ 0.8894; 1.1203
$^{47}Ti(n,p)^{47}Sc$	$1.5 \cdot 10^{-2}$	3.43 d	β^- 0.439; γ 0.1600
$^{48}Ti(n,p)^{48}Sc$	$4 \cdot 10^{-3}$	1.83 d	β^- 0.65; γ 0.9835; 1.0376; 1.3118
$^{50}Ti(n,\alpha)^{47}Ca$	$4 \cdot 10^{-7}$	4.53 d	β^- 0.67; 1.979; γ 0.1600; 1.2969
$\xrightarrow{\beta^-} {}^{47}Sc$		3.43 d	β^- 0.439; 0.600; γ 0.1600
$^{46}Ti(n,2n)^{45}Ti$	$5 \cdot 10^{-6}$	3.07 h	β^+ 1.02; EC γ 0.718; 1.238; 1.408
$^{27}Al(n,\gamma)^{28}Al$	0.23	2.31 min	β^- 2.86; γ 1.7789
$^{51}V(n,\gamma)^{52}V$	4.5	3.76 min	β^- 2.47; γ 1.4344
$^{19}F(n,\gamma)^{20}F$	$9 \cdot 10^{-3}$	11.4 sec	β^- 5.42; γ 1.627
$^{204}Pb(n,\gamma)^{205m}Pb$	0.7	0.004 sec	IT γ 0.026; 0.284; 0.703; 0.99
$^{206}Pb(n,\gamma)^{207m}Pb$	0.03	0.8 sec	IT γ 0.569; 1.062
$^{208}Pb(n,\gamma)^{209}Pb$	$5 \cdot 10^{-4}$	3.3 h	β^- 0.635

solution of the samples, one has to deal with the ^{20}F activity, formed from the stable ^{19}F isotope upon reactor irradiation. Lead fluoride, which is used in one preseparation procedure, gives rise to ^{20}F and to some radioactive lead isotopes.

EXPERIMENTAL

The titania samples were dissolved by boiling the samples in small volumes of 29 *M* hydrofluoric acid in a teflon vessel whereas the titanium samples were dissolved in 1 *M* hydrofluoric acid, after which air was bubbled through the solution until the green colour of titanium(III) disappeared.

Vanadium-48 was used for the tracer experiments with vanadium. This isotope was produced by deuteron irradiation of titanium foil. For aluminum no long-lived tracer is known, except the ^{26}Al isotope, which is produced by deuteron irradiation of magnesium or silicon. The procedure yields only 1.4 disintegrations of ^{26}Al min^{-1} μA^{-1} h^{-1} and gives rise to 3,000,000 times[6] more ^{22}Na. For the present tracer work with aluminum and titanium, postirradiation was used as a means of checking the results of the different chemical separation procedures.

Three different methods for the preseparation of vanadium and aluminum from titanium were examined: (1) titanium hydroxide precipitation, (2) separation by anion-exchange chromatography, and (3) scavenging of vanadium with lead fluoride at pH 7–8.

Titanium hydroxide precipitation

Titanium hydroxide precipitates on addition of potassium hydroxide, leaving aluminum and vanadium in solution. The separation of vanadium and titanium was checked as a function of the amount of vanadium carrier, the digestion time and the relative amounts of potassium hydroxide and hydrofluoric acid. The results are given in Tables II and III. A precipitation with 1.2 equivalents of potassium hydroxide per 1 equivalent of hydrofluoric acid, followed by a digestion time of 1 h was found most satisfactory. Under these conditions, 2% of about 100-μg amounts of aluminum coprecipitated on the titanium hydroxide. A reactor irradiation of the filtrate cannot reveal the aluminum and vanadium impurities, as the major activity of the filtrate consists of ^{24}Na and ^{42}K.

A cation-exchanger Dowex 50W-X8, equilibrated with deionized water, was used for absorbing potassium and sodium from the filtrate. After percolation of the

TABLE II

CONTAMINATION OF THE TITANIUM HYDROXIDE PRECIPITATE WITH VANADIUM, AS A FUNCTION OF THE AMOUNT OF VANADIUM CARRIER

(100 mg of TiO_2; digestion time 30 min)

V carrier (μg)	*% Contamination on $Ti(OH)_4$*
53	0.15
5.2	0.20
0.85	0.40
0.20	0.10
Carrier-free	0.05

TABLE III

SEPARATION OF VANADIUM AND TITANIUM BY TITANIUM HYDROXIDE PRECIPITATION AS A FUNCTION OF THE DIGESTION TIME AND THE RATIO OF THE CONCENTRATION KOH/HF

(0.2 μg of vanadium carrier is added)

Digestion time (min)	*% V in solution*	*% Ti precipitated*
5	99.9	98.1
15	99.4	98.4
60	99.9	99.96
Equiv. KOH/equiv. HF		
1	99.8	99.5
1.1	99.8	99.8
1.2	99.8	99.9

TABLE IV

SEPARATION OF VANADIUM AND ALUMINUM FROM POTASSIUM AND SODIUM BY CATION EXCHANGE

Element	*% eluted*
V	>99.9
Al	99.5
K	< 0.7
Na	< 0.02

strongly basic filtrate, the column was washed with an additional 15 ml of water. The results of the tracer experiments for this separation are given in Table IV. This eluate was evaporated to a small volume, reactor irradiated, and counted. Figure 1 shows a Ge(Li) spectrum of an irradiated sample; it can be seen that ^{28}Al was present but that ^{52}V could not be detected on the high Compton continuum in the 1.4-MeV region.

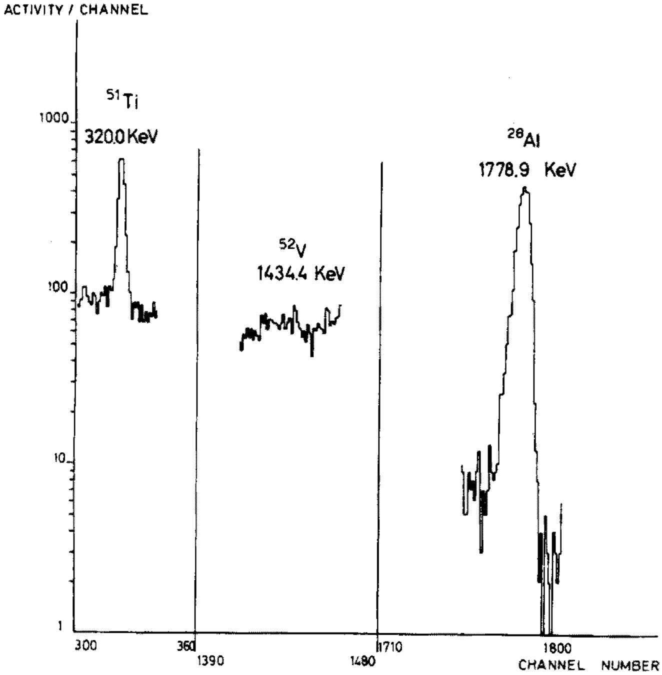

Fig. 1. Ge(Li) spectrum of an irradiated sample, preseparated by titanium hydroxide precipitation.

TABLE V

SEPARATION OF VANADIUM, ALUMINUM AND TITANIUM BY ANION EXCHANGE

Fraction	*Volume (ml)*	*Element*	*% in fraction*
1 *M* HF	80	V	> 99.96
0.5 *M* HF + 0.1 *M* HNO_3	20	Al	> 99
Resin	—	Ti(IV)	> 99.97

Separation by anion exchange

After dissolution of the sample, the hydrofluoric acid solution was diluted to 1 *M* and transferred to a Dowex 1-X8 anion exchanger. Vanadium was eluted with 1 *M* hydrofluoric acid, and aluminum with 0.5 *M* hydrofluoric acid + 0.1 *M* nitric acid, while titanium remained on the resin. The results are shown in Table V. The eluates were evaporated to a small volume, irradiated and counted. Figure 2 shows a Ge(Li) spectrum of the irradiated vanadium and aluminum fraction.

Separation of vanadium from titanium by scavenging as lead tetravanadate with lead fluoride

The samples were dissolved in small amounts of 29 *M* hydrofluoric acid. After dilution of the solution to 1 *M* hydrofluoric acid, the pH was varied between 0 and 11 by means of ammonium hydroxide, and lead acetate was added. Lead fluoride precipitated from the solution. The degree of coprecipitation of vanadium and aluminum was strongly dependent on the pH. This can be seen in Table VI and Fig. 3, which give the results for 400 µg of aluminum and 1 µg of vanadium. Above pH

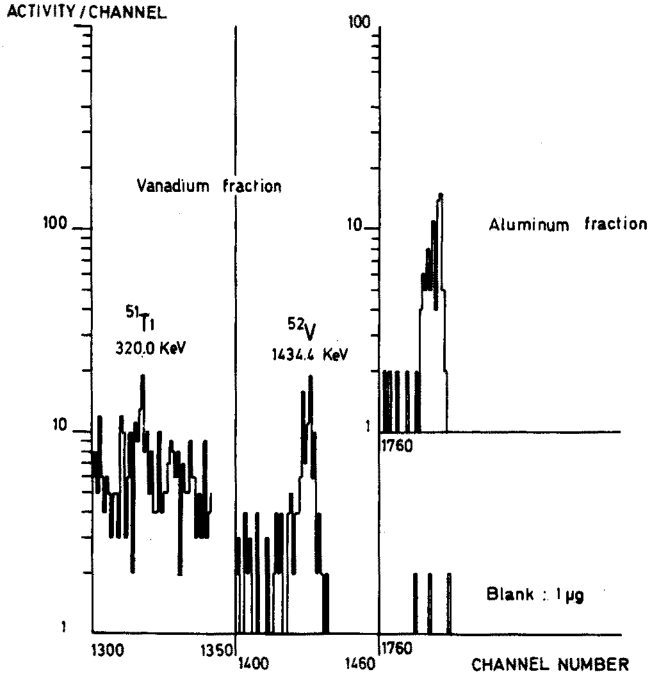

Fig. 2. Ge(Li) spectrum of the irradiated vanadium and aluminum fraction, separated by anion exchange.

TABLE VI

VANADIUM AND ALUMINUM COPRECIPITATION WITH LEAD FLUORIDE AS A FUNCTION OF pH

pH	*% V coprecipitated*	*% Al coprecipitated*
0	< 1	—
4	< 0.7	—
4.5	16	—
5.5	58	—
6	77	4
7	99.5	4
8	> 99.5	4
9	> 99.5	40
9.5	> 99.5	65
10	$Ti(OH)_4$ precipitates	40
11	$Ti(OH)_4$ precipitates	25

7 the coprecipitation of vanadium was quantitative, probably as the tetravanadate[7], $Pb_2V_4O_{12}$.aq. The decrease of coprecipitation of aluminum for pH values higher than 9.5 was probably due to the formation of aluminate. Moreover, titanium hydroxide precipitated in this pH region, so that the separation of vanadium from aluminum and titanium had to be accomplished in the pH interval 7–8.5. The lead fluoride precipitate was dissolved in a small volume of dilute nitric acid, reactor-irradiated and counted. Figure 4 shows a Ge (Li) spectrum of an irradiated sample; the sample was the same as the one preseparated by titanium hydroxide precipitation, shown in Fig. 1. In this case, ^{52}V could be easily determined from γ-spectrometry in the 1.4-MeV region.

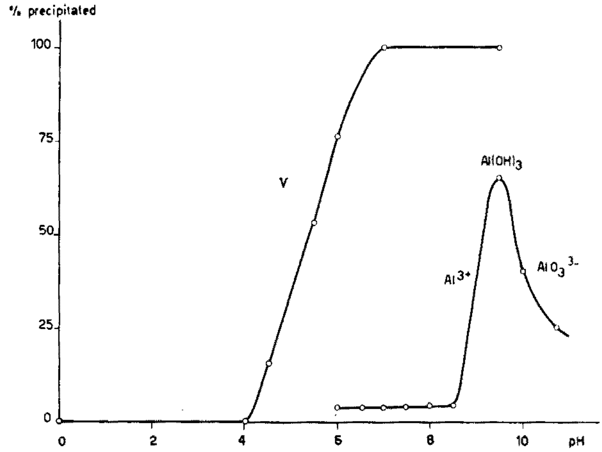

Fig. 3. Coprecipitation of vanadium and aluminum with lead fluoride as a function of pH.

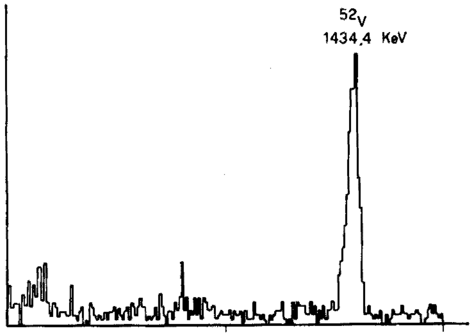

Fig. 4. Ge(Li) spectrum of a reactor-irradiated pure vanadium fraction, separated from titanium and aluminum by scavenging with lead fluoride.

Procedures

Titanium hydroxide precipitation. Dissolve the titania powder in 1 ml of 29 *M* hydrofluoric acid and dilute to 1 *M* hydrofluoric acid. Dissolve titanium metal or sponge in 29 ml of 1*M* hydrofluoric acid and pass an air stream through the solution until the green colour of titanium(III) disappears. Add 20 ml of a 10% potassium hydroxide solution, digest for 1 h and centrifuge the precipitate in a polypropylene tube. Wash the precipitate with small aliquots of 1% potassium hydroxide solution and add these to the main solution. Transfer to a Dowex 50 W-X8 cation-exchange column (diameter 1 cm, height 13 cm), equilibrated with water, and wash the column with 15 ml of water. Evaporate the eluate to a small volume, irradiate for 2 min, cool for 2 min and count for 3 min.

Anion-exchange separation. Dissolve the samples as described for the titanium hydroxide precipitation and dilute to 1 *M* hydrofluoric acid. Transfer to a Dowex 1-X8 anion-exchange column (1 cm diameter, height 13 cm), equilibrated with 1 *M* hydrofluoric acid. Elute with 50 ml of 1 *M* hydrofluoric acid; vanadium is collected, free from aluminum and titanium. For the aluminum fraction, wash the column with 20 ml of 0.5 *M* hydrofluoric acid + 0.1 *M* nitric acid. Evaporate both fractions, irradiate and count for ^{52}V or ^{28}Al.

Scavenging of vanadium with lead fluoride. Dissolve the samples as described for the titanium hydroxide precipitation. Dilute to 1 *M* hydrofluoric acid and adjust the pH to 7 by means of 6 *M* ammonia and 0.5 *M* ammonia. Add 150 mg of lead acetate; lead fluoride precipitates. Digest for 15 min on a hot water bath. Centrifuge in a polypropylene tube. Dissolve the precipitate in a small volume of 1 *M* nitric acid. Irradiate and count for ^{52}V.

Counting. The measurements were performed by means of either a NaI(Tl) detector or an 18-cm³ coaxial Ge(Li) detector. Especially in the case of the pure vanadium or aluminum fractions, the use of a NaI(Tl) detector is advisable, as its efficiency is roughly an order of magnitude higher than that of the Ge(Li) detector. Figure 5 shows the spectra of the same preseparated sample, counted respectively on a NaI(Tl) detector and on a 18-cm³ Ge(Li) detector. After reactor irradiation the purity of each sample was controlled by means of the Ge(Li) detector. Pure fractions were then

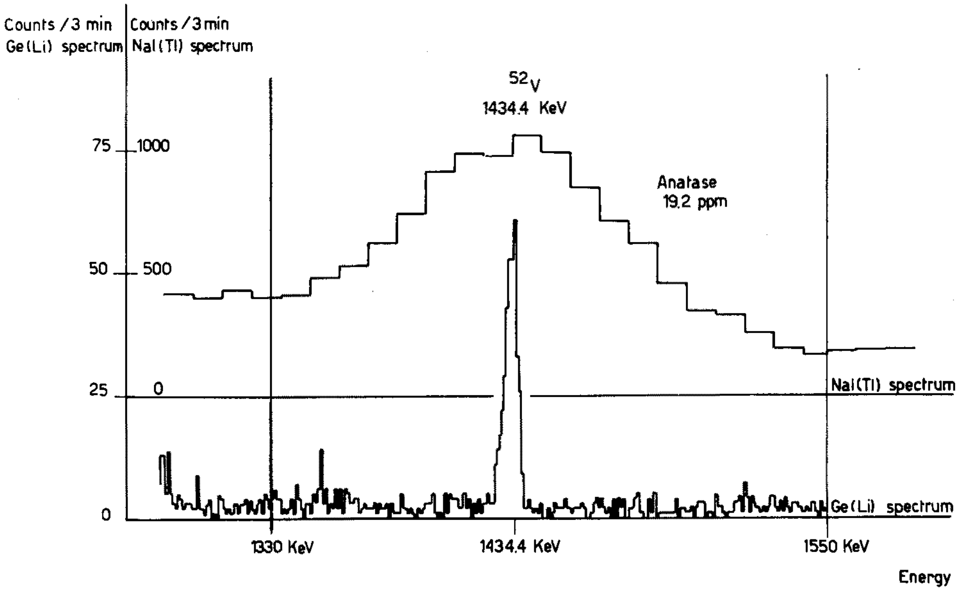

Fig. 5. Vanadium fraction, isolated by scavenging with lead fluoride, reactor-irradiated and counted for 3 min on a NaI(Tl) detector and a planar Ge(Li) detector.

irradiated again and counted on a NaI(Tl) detector. In most cases, no interfering impurities could be detected and the determinations could then be performed by scintillation spectrometry.

Irradiation conditions. The reactor irradiations were carried out at a neutron flux of *ca.* 10^{11} n cm^{-2} sec^{-1}. To ensure the complete decay of ^{20}F, ^{205m}Pb and ^{207m}Pb, the measurement of the sample started 2 min after the end of the irradiation. The reproducibility of the irradiation and counting was checked by means of an aluminum standard, irradiated and counted at regular intervals. The standard deviation for four standardisations was 2%.

Calculation of the results

Standards and samples were irradiated alternately. Because the preseparated samples and the standards had the same volume, and because the irradiation conditions, the cooling time and the measuring conditions were identical, the concentrations of vanadium and aluminum were easily derived from a comparison of the full-energy peak count rates of the samples and the standard. For the calculation of the limit of determination, the proposal of CURRIE[8] was adopted: $C_D = 4.65\sigma_B$ (C_D = counts under the full energy peak; σ_B = standard deviation of the background in the same energy region).

RESULTS AND DISCUSSION

The three preseparation techniques were applied to the analysis of three samples of titania powder, one sample of titanium metal and one sample of titanium sponge. The results are summarized in Table VII.

TABLE VII

COMPARISON OF THE RESULTS OF DIFFERENT PRESEPARATION METHODS OF ANALYSIS FOR VANADIUM AND ALUMINUM IN TITANIA POWDER, TITANIUM SPONGE AND TITANIUM METAL

Matrix	*Preseparation method*	*Element*	*Results of the analyses*		*Standard deviation of the mean (%)*
			Number of analyses	*median value $\tilde{x}$ (p.p.m.)*	
Rutile	Ti(OH)$_4$ precipitation	V	4	17.5	4
		Al	4	39.0	25
	Ion exchange	V	1	18.7	—
		Al	2	33.0	6
	Scavenging with PbF$_2$	V	3	19.8	7
Anatase	Ion exchange	V	2	18.2	5
		Al	3	33.0	6
	Scavenging with PbF$_2$	V	3	19.2	1.5
TiO$_2$ B	Ion exchange	Al	3	2,143	7
	Coprecipitation with PbF$_2$	V	8	12.7	6
Ti sponge	Ion exchange	V	2	4.3	2.5
		Al	2	< 4	—
Ti metal	Ion exchange	V	2	7.8	10
		Al	2	58	8

The determination of aluminum in titania powder and titanium metal can easily be done non-destructively, as the γ-ray energy of ^{28}Al is 1.7789 MeV. The most energetic ^{51}Ti γ-ray is 0.9285 MeV (Table I), while, after 2 min of reactor irradiation, the other impurities in titanium or titania rarely give rise to important activities in the high-energy region. The sensitivity can, however, be enhanced by the preseparation procedures, which make it possible to use larger samples (up to 1 g), while the non-destructive procedure is restricted to about 50 mg, because of the high ^{51}Ti activity.

For non-destructive determinations the determination limit of aluminum is 5 μg. For the preseparation procedures the sensitivity is determined by the blank, namely 1 μg for both the ion-exchange procedure and the titanium hydroxide precipitation method.

The sensitivity for the non-destructive determination of vanadium in titania powder and titanium metal is strongly dependent on the aluminum concentration in the sample, as the 1.4344-MeV γ-ray of ^{52}V is located on the Compton continuum of the 1.7789-MeV γ-ray of ^{28}Al. A comparison of the determination limits for vanadium, by means of several procedures, in samples containing 35 p.p.m. and 2.000 p.p.m. of aluminum respectively, is shown in Table VIII. It can be seen that the sensitivity for the vanadium determinations can be improved almost by a factor of 100 by the preseparation methods. The highest sensitivity reached was 0.15 p.p.m. at a neutron flux of 10^{11} n cm^{-2} sec^{-1}.

TABLE VIII

COMPARISON OF THE DETERMINATION LIMITS FOR VANADIUM, BY MEANS OF VARIOUS METHODS, IN SAMPLES CONTAINING 35 P.P.M. AND 2,000 P.P.M. OF ALUMINUM

Method	*Weight of sample (mg)*	*Determination limit (p.p.m.) with a Ge(Li) detector*	
		For samples containing 35 p.p.m. Al	*For samples containing 2,000 p.p.m. Al*
Non-destructive	50	5	40
$Ti(OH)_4$ precipitation	1,000	1	10
Anion-exchange separation	250	1	1
Scavenging with lead fluoride	1,000	0.15	0.5

Thanks are due to the "Instituut voor Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw" (IWONL) for financial support to one of us (R.N.).

SUMMARY

The determination of vanadium and aluminum by activation analysis was applied to titanium and titania samples. Three preseparation procedures, precipitation of titanium hydroxide, anion-exchange separation and scavenging with lead fluoride, were examined on different samples. The sensitivity of these methods is higher than for a non-destructive determination.

RÉSUMÉ

Le dosage du vanadium et de l'aluminium par activation neutronique a été appliqué à l'analyse d'échantillons de titane et d'oxyde de titane. On a examiné trois procédés de préséparation, précipitation de l'hydroxyde de titane, séparation par échange d'anions et entraînement avec fluorure de plomb, sur divers échantillons. La sensibilité de ces méthodes est supérieure à celle d'un dosage non-destructif.

ZUSAMMENFASSUNG

Mit Hilfe der Aktivierungsanalyse wurde Vanadin und Aluminium in Titan- und Titandioxid-Proben bestimmt. Folgende drei vorhergehende Abtrennungen wurden an verschiedenen Proben geprüft: die Fällung des Titanhydroxids, die Verwendung eines Anionenaustauschers und die Abtrennung mit Bleifluorid. Die Empfindlichkeit dieser Methoden ist grösser als die zerstörungsfreien Verfahren.

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THE DETERMINATION OF SULPHUR IN FLUOROCARBON POLYMERS BY NEUTRON ACTIVATION

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There has been interest here recently in the determination of sulphur in fluorocarbon compounds of rather high molecular weight containing less than 1% of sulphur. A gravimetric determination of the sulphuric acid produced by oxidation of the compound in an oxygen flask is not entirely satisfactory because of the low weights of barium sulphate produced. Moreover, the titration of sulphate with barium perchlorate[1] proved unsatisfactory for fluorine-containing compounds when the sulphur content falls below 5%. The possibility of determining the sulphur by neutron-activation of the samples to convert sulphur-32 to phosphorus-32, was therefore examined.

Sulphur has been determined by means of the $^{32}S(n, p)^{32}P$ reaction by GIBBONS AND SIMPSON[2], who determined sulphur in materials of high neutron-absorption cross-section, by BOUTEN AND HOSTE[3], who determined sulphur in steel, and by SOULIOTIS[4], who determined sulphur in high-purity paper and in beer.

Chemical separation of the phosphoric acid formed on combustion of the samples in an oxygen flask before proceeding to a radio-assay was examined. The precipitation of ammonium 12-molybdophosphate or magnesium ammonium phosphate after the addition of an inactive phosphate carrier proved time-consuming, particularly as the chemical yield of the precipitation from both test and standard samples had to be carefully determined. Solvent-extraction methods with either an excess of molybdate to convert the phosphate to 12-molybdophosphoric acid, or a vanadate–molybdate mixture to convert the phosphate to vanadomolybdophosphoric acid proved more satisfactory, but double extractions were required and results were not consistent.

In the more rapid and reliable method described below, less than the stoichiometric amount of molybdate necessary to convert the phosphate to vanadomolybdophosphoric acid in the presence of vanadate and perchloric acid, is used, thus avoiding the need for determining the chemical yield. The use of substoichiometry in radiochemical analysis has been reviewed by RŮŽICKA AND STÁRY[5], and a thorough study of the phosphorus method itself has been described[6].

EXPERIMENTAL

Reagents

Phosphate carrier solution. A 0.01 *M* phosphate solution was prepared by dissolving 1.36 g of dried A.R. potassium dihydrogen phosphate in 1 l of distilled water.

Ammonium molybdate reagent. A *ca.* 0.01 M solution of molybdenum was prepared by dissolving 1.8 g of powdered A.R. ammonium molybdate in water and making up to 1 l.

Ammonium vanadate solution. Ammonium metavanadate (A.R.; 0.58 g) was warmed with a little water until it had completely dissolved. The cooled solution was diluted to 500 ml with water to give a *ca.* 0.01 M vanadium solution.

Standard and test samples for neutron irradiation

Ammonium sulphate (A.R. grade) was used as standard; it must be irradiated in sealed silica tubes because the temperatures and radiation doses in the reactor may cause some decomposition which builds up hazardous pressures in the usual irradiation capsules. The ammonium sulphate standards (50–200 mg) and the samples (30–300 mg) were sealed in silica tubes (6 cm long; 3 mm i.d.). Care was taken to avoid contamination of the samples. The silica tubes were rinsed with nitric acid, distilled water and acetone several times, then ignited in an oxygen flame and cooled in a desiccator before use. By irradiating both the standards and samples in similar silica tubes in the same aluminium can or polythene container (7.5 cm × 2.5 cm), inhomogeneous flux effects were eliminated.

Irradiation conditions and counting equipment

The standards and samples were irradiated in the Universities Research Reactor, Risley, Warrington at a neutron flux of about $1.1 \cdot 10^{12}$ n cm^{-2} sec^{-1} for 6–8 h.

The β-emission from phosphorus-32 was counted with a 20th Century Electronics M6HST liquid counter and a Panax P7102 Automatic Scaler. Experiments were designed to give at least 10,000 counts so that the standard deviation did not exceed 1%. Each sample was counted two or three times and the average count rate was taken.

TABLE I

PERCENTAGE OF SULPHUR IN SOME STRAIGHT-CHAIN AND CYCLIC FLUORINE COMPOUNDS

Compounds analysed	*% S found*	*% S theor.*
S–Benzylthiouronium salt of C_3F_7COOH	8.50, 8.45, 8.4	8.42
S–Benzylthiouronium salt of $O(CF_2COOH)_2$	8.7, 8.7, 8.55	8.60
S–Benzylthiouronium salt of $CF_2(CF_2COOH)_2$	7.9, 7.7	7.88
Di-S-benzylthiouronium salt of $(CF_2)_3(COOH)_2$	11.0, 11.2	11.19
p-Phenylsulphonyl-perfluoropyridine	11.1, 11.0	11.00
S-Benzylthiouronium salt of 4-sulpho-2, 3, 5, 6-tetrafluoropyridine	16.3, 16.1	16.12
Sodium 2, 3, 5, 6-tetra-fluoropyridine 4-thiolate	15.9, 15.5	15.61

The determination of sulphur in some straight-chain fluorocarbon compounds

For preliminary tests, authentic compounds containing about 10% of sulphur were irradiated for 8 h in a neutron flux of 10^{12} n cm^{-2} sec^{-1}. The compounds studied (the first 4 samples in Table I) were carefully recrystallised before irradiation, and their carbon and hydrogen values were checked.

About 30 mg of the irradiated standard and 30–100 mg of the samples respectively were accurately weighed. The organic samples were oxidised completely by the oxygen-flask technique[1], in a 1-l Quickfit Pyrex conical flask containing 10 ml of 4 *M* nitric acid as the absorbent. The ammonium sulphate was dissolved in the same volume of 4 *M* nitric acid in a 100-ml beaker. To both the standards and the oxidised samples were added first 10 ml of 0.01 *M* phosphate solution and then 3 ml of saturated bromine water. The mixture was warmed on a hot plate, without boiling, so that the phosphorus was completely converted to orthophosphate and the excess of bromine was expelled. After cooling to room temperature, the solutions were carefully transferred to 50-ml volumetric flasks and made up to the mark with water. Each solution solution was shaken for 5 min and allowed to stand for 1 h before the next step.

To a 10.0-ml aliquot of each solution were added 1.0 ml of 60% perchloric acid, 4.0 ml of the 0.01 *M* vanadate solution and 12.0 ml of the 0.01 *M* molybdate solution, so that the pH was 0.7–0.8. The mixture was then extracted with 10 ml of isobutyl methyl ketone by shaking for three 1-min periods at 1-min intervals. A portion of the organic layer (8.0 ml) was counted in a liquid G.M. counter. Previous work with ^{32}P-labelled phosphate had shown that the activity extracted was reproducible.

As the amounts of phosphorus produced in the irradiated standard and the sample are very small compared with the amount of phosphorus in the added carrier, and as the same amount of phosphorus is extracted in each case[6], the ratio of the count-rates of sample and standard is the ratio of the respective induced activities. Thus the weight of sulphur in the sample, W, is given by $W'a/a'$, where a and a' are the count-rates obtained on the extracts of sample and standard respectively, and W' is the weight of sulphur in the standard.

Results. The results obtained for these fluorine compounds are shown in Table I. The presence of fluorine in the original compound did not affect the extraction. In the analysis of these compounds, the theoretical concentration of fluorine present in each aliquot taken was below $3 \cdot 10^{-3} M$; the actual fluorine content present may have been less because of the losses to the flask wall during the decomposition process and escape of hydrogen fluoride during the heating process specified.

The determination of sulphur in some cyclic fluorocarbon compounds

When the above method was applied to perfluoropyridine derivatives, the results were much too low. Evidently in this case the interference of fluorine was greater, and difficult to eliminate. Of several methods tried for eliminating this interference, fuming with hydrochloric acid proved most efficient, provided that the fluorine content was not too high.

The standards and samples were treated exactly as above, but a 10-ml aliquot of each prepared solution was transferred to a porcelain evaporating dish, and 5 ml of concentrated hydrochloric acid was added. The solution was slowly evaporated below 80°. The evaporation process was repeated twice. The final solid residue was dissolved in 10 ml of water and the extraction and counting were carried out as described above.

Results. The results (last 3 samples of Table I) obtained by three fuming processes with standard and test samples side by side on the hot plate were satisfactory. Independent experiments with labelled phosphate showed that at controlled temperatures below 80°, the loss of phosphate by volatilisation was negligible[6].

The determination of sulphur in fluorocarbon polymers

Fluorocarbon polymers of low sulphur content (less than 1%) were analysed. About 30–50 mg of the polymer sample was burned for each determination. The analyses were done exactly as described above for cyclic fluorine compounds.

The results obtained for four typical polymers are listed in Table II. Good precision is indicated by the agreement of duplicates.

TABLE II

PERCENTAGE OF SULPHUR IN FLUOROCARBON POLYMERS

Polymers analysed	*% Sulphur (found)*
Polymer VT1/A5	0.851, 0.846
Polymer VT1/A1	0.538, 0.526
Viton (3)	0.250, 0.248
Viton (1)	0.134, 0.130

Attempts were made to compare the results with those obtained by applying a gravimetric finish to the oxygen-flask combustion of larger samples of the polymers. The results so obtained were of the same order, but were much less reproducible than those obtained by the substoichiometric activation method. The percentages of sulphur found by the method described were also consistent with the method of preparation and subsequent treatment of the polymer in each case. The first two samples shown in Table II were co-polymers prepared from monomers of which one contained sulphur. The sulphur in the viton polymers arose entirely from the polymerisation initiators.

DISCUSSION

The determination of sulphur in fluorine compounds can be readily accomplished by neutron irradiation of samples and standards to convert some of the sulphur-32 to phosphorus-32 by the $^{32}S(n,p)^{32}P$ reaction. Irradiation for 8 h in a neutron flux of $1.1 \cdot 10^{12}$ n cm^{-2}sec^{-1} produced specimens with count-rates of 8000 counts/min per mg of sulphur originally present. It has been estimated that $5 \cdot 10^{-8}$ g of sulphur should be detected by this method if the sample is irradiated to saturation[7]; the present results confirm this.

The irradiated compounds were ignited in an oxygen flask to convert sulphur, phosphorus and fluorine to sulphuric acid, phosphoric acid and hydrofluoric acid respectively. Of the various methods available for separating the phosphoric and sulphuric acids, the quickest and most effective was one which made use of a substoichiometric technique.

After addition of a phosphate carrier to the active sample and standard solutions, sufficient ammonium vanadate was added to make the V:P ratio 2:1, and perchloric acid to reduce the pH to 0.7. The addition of ammonium molybdate, sufficient to convert only about one-half of the phosphate to 1-vanado-11-molybdophosphoric acid, enabled equal amounts of phosphate to be extracted from the solutions prepared from sample and standard.

The amounts of active phosphorus were very small compared with the amount of carrier, hence the prepared solutions contained effectively equal quantities of phosphate with specific activities proportional to the weights of sulphur in standard and sample. Extraction of the vanadomolybdophosphoric acid with equal volumes of isobutyl methyl ketone thus gave extracts which had count-rates proportional to the weights of sulphur irradiated.

The activity produced from the $^{34}S(n,\gamma)^{35}S$ reaction did not interfere with the method. The natural abundance of sulphur-34 is only 4.24%, the reaction has a low cross-section, the sulphuric acid produced in the oxygen flask is extracted hardly at all into the organic layer, and the soft β-radiation does not penetrate the wall of the liquid G.M. tube.

Careful evaporation with hydrochloric acid was satisfactory in removing the interference of fluorine, particularly if standard and test samples were treated under exactly the same conditions. This process added about 2 h to the time needed for a determination.

We thank the Manager and Staff of the Universities Research Reactor, Risley, Warrington, for carrying out the irradiations and for helpful advice on the preparation of samples for irradiation.

SUMMARY

Sulphur can be determined in fluorocarbon polymers and other fluorine compounds by neutron irradiation to convert sulphur-32 to phosphorus-32 by the (n,p) reaction. The phosphorus produced is determined by a substoichiometric extraction of vanadomolybdophosphoric acid, followed by measurement of β-emission. The method is satisfactory for sub-milligram quantities of sulphur irradiated for only 8 h.

RÉSUMÉ

Le soufre peut être dosé dans des hydrocarbures fluorés polymères et dans d'autres composés fluorés par irradiation neutronique pour convertir le soufre-32 en phosphore-32 par la réaction (n,p). Le phosphore produit est dosé par extraction de l'acide vanadomolybdophosphorique et mesure de l'émission β. La méthode convient pour des quantités de l'ordre du sub-milligramme de soufre irradié pendant 8 h seulement.

ZUSAMMENFASSUNG

Schwefel kann in fluorhaltigen Kohlenstoffpolymeren und anderen Fluorverbindungen mit Hilfe der Neutronenaktivierungsanalyse bestimmt werden. Dabei wird

der durch eine (n,p)-Reaktion entstandene Phosphor-32 durch substöchiometrische Extraktion von Vanadomolybdophosphorsäure und anschliessende β-Strahlen-Messung bestimmt. Die Methode ist für Submilligramme Schwefel, welche nur 8 Stunden bestrahlt wurden, zufriedenstellend.

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DETERMINATION OF TRACES OF SILVER IN WATERS BY ANION EXCHANGE AND ATOMIC ABSORPTION SPECTROPHOTOMETRY*

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The average content of silver in all fresh waters, according to BOYLE[1], is about 0.2 μg/l. However, regional variations both above and below this average appear to be normal. Some major streams or rivers generally carry a few tenths of a microgram per liter[2–6], while individual lakes, streams, or springs may have much higher values[1]. The concentration of silver in sea water commonly amounts to a few tenths of a microgram to a few micrograms per liter, with occasional higher values[1,7].

Numerous methods of analysis for silver have been recorded in the literature. Pre-concentration of samples of natural waters is usually required to determine trace amounts of silver. HAFFTY[8] has described a spectrographic method for the determination of many minor elements including silver in natural waters by the excitation of the water residue with a direct-current arc. WEST *et al.*[9] report a very useful method for the analysis of silver in water at concentrations between 10 and 1000 μg/l; ethylenediaminetetraacetic acid (EDTA) was used to stabilize the water sample to prevent adsorptive losses of silver to container walls. However, as indicated by the authors, the increase in adsorption of silver by the container walls beyond a 10-day to 2-week contact period restricts safe sample storage or handling to 10 days.

In a previous report[10] it has been shown that loss of silver by adsorption onto container walls poses a major concern in quantitative determinations of trace amounts of silver in water. A satisfactory method of analysis for silver in water should not only cope with the low silver concentrations but should also cope with the loss of silver by adsorption onto container walls at low concentrations. Because the fluvial geochemistry of silver has not been thoroughly or intensively studied, a method capable of accurately determining silver down to a few tenths of a microgram per liter of water is needed to facilitate further detailed hydrogeochemical investigations.

This paper is concerned with the development of such a method. It reports optimum conditions for the complete recovery of silver from water with an anion-exchange resin column, the quantitative elution of silver from the resin, and the measurement of silver by atomic absorption spectrophotometry after chelation of silver with ammonium pyrrolidine dithiocarbamate (APDC) and extraction of the chelate with methyl isobutyl ketone (MIBK).

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* Authorized for publication by Director, U. S. Geological Survey.

EXPERIMENTAL

Apparatus

The ion-exchange apparatus shown in Fig. 1 permits the automatic flow of water by gravity from the sample container through the resin column, and also allows the rate of flow to be adjusted by the lower Teflon stopcock. Twelve water samples can be conveniently processed simultaneously with an equal number of exchange column units as illustrated in Fig. 2.

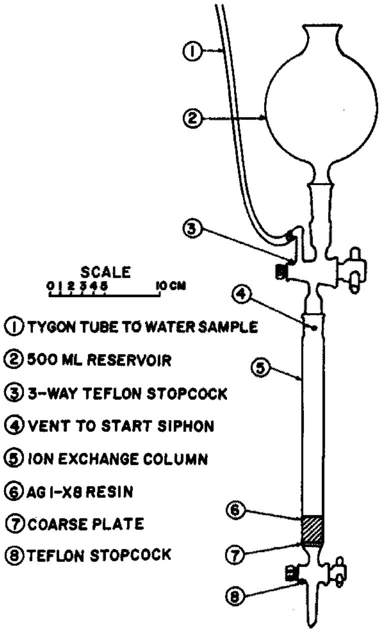


Fig. 1. Anion-exchange apparatus used for the concentration of silver from natural waters.

A Perkin-Elmer 303 atomic absorption spectrophotometer with a silver hollow-cathode lamp was used for silver determinations with the following operating conditions:

Grating—ultraviolet
Wavelength counter—328.1 (3281 Å)
Scale—10 X
Slit—4 (1 mm, 6.5 Å)
Lamp current—12 mA
Burner—Boling
Air pressure—28 psi, 6.0 on flowmeter
Acetylene pressure—8 psi, 4.0 on flowmeter
Response time control—1

A Tracerlab single-channel γ-ray spectrometer was employed to measure the radioactivity of silver-110m which served as a tracer at different stages in the development of the method.

A Radiometer pH meter Model 26 was used for pH measurement.

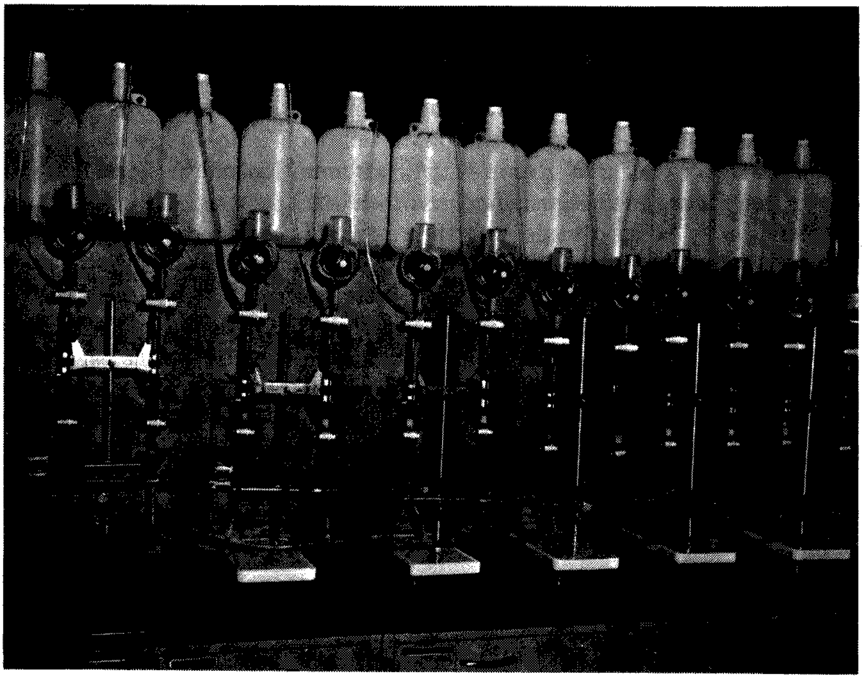


Fig. 2. Ion-exchange columns for concentration of silver.

Reagents

AG 1-X8 anion-exchange resin, 100–200 mesh, chloride form.

Silver standard solutions. Dissolve 0.1575 g of anhydrous silver nitrate in demineralized water. Add 6.5 ml of concentrated nitric acid and dilute to 1 l (1.00 ml = 100 μg Ag). Dilute 10.0 ml of the above silver solution and 6.5 ml of concentrated nitric acid to 1000 ml with demineralized water (1.00 ml = 1.0 μg Ag). Immediately before use, dilute 10.0 ml of the latter silver solution to 100 ml with demineralized water (1.00 ml = 0.1 μg Ag).

Concentrated nitric (s.g. 1.42) and hydrochloric (s.g. 1.19) acids were Mallinckrodt transistAR grade. Dilute nitric acid was prepared by mixing 20.0 ml of concentrated nitric acid with demineralized water and diluting to 1 l.

Dilute ammonia. Dilute 100 ml of concentrated reagent-grade ammonia to 500 ml with demineralized water.

Ammonium pyrrolidine dithiocarbamate (APDC). Dissolve 1.0 g of APDC in 100 ml of demineralized water. Prepare fresh daily.

Acetone and MIBK were of reagent grade.

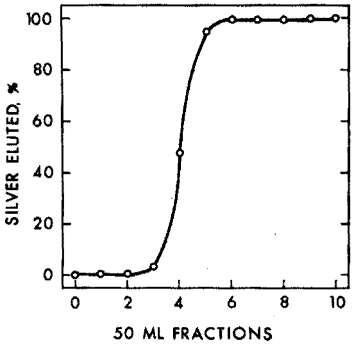
Optimum conditions for complete recovery of silver from water by a resin column

As reported previously[10], acidifying a water sample to pH 1 with hydrochloric acid may reduce adsorption of silver onto polyethylene containers to *ca.* 1% for at least 30 days. At pH 1, AG 1-X8 anion-exchange resin quantitatively removed silver from the water samples. Flow rate and column length affected the recovery of silver. Trials with different flow rates and column lengths showed that a 2.5-cm resin column (1.5

cm in diam.) containing 2.5 g of resin (40% moisture) completely recovered the silver from the sample when the water passed through the column at a flow rate of 5 ml/min.

Elution of silver from resin

Nitric acid (3 *N* and 4 *N*), and 5–10% sodium thiosulfate solutions only partially eluted the silver from the resin; 4 *N* hydrochloric acid was totally ineffective. Dry or wet ashing may be used to destroy the resin and recover the silver, but the ashing process is tedious and may also cause contamination or loss of the silver. An acetone–nitric acid (s.g. 1.42)–water mixture (volume ratio = 100:5:5)[11] successfully eluted the silver from the resin. Silver-110m was introduced onto the AG 1-X8 resin column as described above and eluted with the acetone–nitric acid–water mixture at a flow rate of 50 ml/h. The silver content of successive 50-ml fractions was determined and the percent silver eluted plotted against the volume of eluant (Fig. 3). Very little silver was recovered from the first two 50-ml fractions; however, the third through the seventh fractions contained all of the silver. With a total volume of 350 ml, silver was completely eluted from the resin. The elution curve was reproducible. If desired, the first 100 ml of eluate may be discarded.



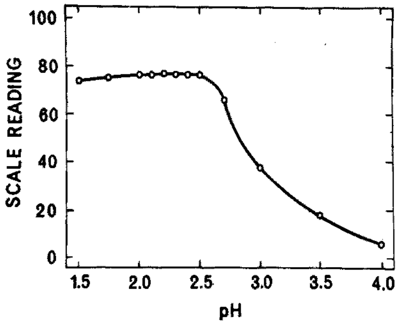


Fig. 3. Elution of silver from AG 1-X8 resin with acetone–nitric acid–water mixture as determined by silver-110m counting.

Fig. 4. Effect of pH on APDC–MIBK chelating extraction of silver.

Extraction of silver from nitric acid with APDC and MIBK

The acetone was evaporated in a constant-temperature bath, leaving silver in a nitric acid solution. The effect of pH on the extraction of silver with APDC–MIBK was investigated. A series of solutions containing 10 μg of silver was prepared and the pH of each solution adjusted with dilute nitric acid. The pH of these solutions varied from 1.5 to 4.0. APDC was then added; the silver–APDC chelate was extracted with MIBK, and silver determined by atomic absorption. The results obtained (Fig. 4) show that silver can be best extracted at pH 2.0–2.5. Above pH 2.5 silver extraction falls off rapidly. Similar results were obtained for the extraction of silver from ammonium nitrate solutions of similar concentration as provided in the procedure below. An initial pH of 2.3 ± 0.1 was therefore chosen for the extraction of silver with APDC–MIBK.

Proposed method

Collect one or more liters of water and filter it through a 4″ Gelman membrane filter (0.45-μ pore size) at the sampling site. The sample size depends on the concentration of silver in the water; 0.1–1 μg of silver per liter can be accurately determined with 1-l water samples. With lower concentrations of silver, the volume of water is proportionally increased. Immediately acidify the filtered sample with hydrochloric acid to pH 1. If silver associated with suspended materials is to be determined, save the filter for that purpose.

In the laboratory, pass the water through a 2.5-cm AG 1-X8 anion-exchange resin column (2.5 g of the resin with 40% moisture) at a flow rate of 5 ml/min using an automatic siphon system (Figs. 1 and 2). Rinse the resin column with 400 ml of demineralized water and drain the water completely. By turning the upper 3-way Teflon stopcock (Fig. 1), the column is opened to a 500-ml reservoir from which 350 ml of acetone–nitric acid–water mixture (volume ratio = 100:5:5) are allowed to elute the silver from the resin at a rate of 50 ml/h into a 400-ml Teflon beaker. Evaporate the acetone at 50–55° in a constant-temperature water bath.

Partially neutralize the nitric acid solution with concentrated ammonia (with Teflon beakers in an ice-water bath) and adjust the final pH of the solution to 2.3 ± 0.1 with dilute ammonia using a pH meter. Then transfer the solution to a 200-ml volumetric flask and dilute it to about 100 ml with water. Add 2.5 ml of 1% APDC and mix. Pipette 10.0 ml of MIBK into the flask and shake vigorously for 1 min. Allow the MIBK layer to separate and add demineralized water until the ketone layer is completely in the neck of the flask. Aspirate the MIBK layer into the flame of the atomic absorption spectrophotometer and determine the silver. Prepare silver reference standards by pipetting 1.0, 2.0, 3.0, 4.0, 5.0, 7.5 and 10.0 ml of the standard silver solution containing 0.1 μg silver per ml into 250-ml Teflon beakers. Add 15 ml of concentrated nitric acid and neutralize the solution with ammonia in the same manner as the sample. A demineralized water blank is similarly treated. Within the above range a linear relationship is observed between the scale reading and the silver concentration.

If the concentration of silver in water falls within the range of 1–10 μg/l, direct extraction of silver with APDC–MIBK is used without pre-concentration by the exchange column; 100 ml of water is adjusted to pH 2.3 ± 0.1 with dilute nitric acid and and then treated as above. The silver reference standards are similarly prepared but without adding 15 ml of concentrated nitric acid. The time required for the determination of silver at the higher concentration range (1.0–10.0 μg/l) is much shorter than at the lower concentration range (0.1–1.0 μg/l).

RESULTS AND DISCUSSION

Known amounts of silver or silver-110m were added to a natural water and synthetic solutions. These samples were then acidified and analyzed for silver by the proposed method or γ-counting of silver-110m. The results on recovery of silver under various conditions are presented in Table I.

The recovery of silver by the method described, in amounts ranging from 0.02 to 6 μg/l of silver, from waters or solutions of different compositions is satisfactory. The proposed method gives reproducible and accurate determinations, especially from

TABLE I

RECOVERY OF SILVER FROM WATERS OR SOLUTIONS BY THE PROPOSED METHOD

Ag added in water (μg/l)	*Type of water or solution*	*Volume of water used (l)*	*Ag found (μg/l)*			*Recovery (%)*		
By atomic absorption spectrophotometry								
0.020	Tap water[a]	5	0.018	0.018	0.019	90.0	90.0	95.0
0.040	Tap water[a]	5	0.039	0.040	0.039	98.0	100.0	98.0
0.10	Tap water[a]	5	0.094	0.096		94.0	96.0	
0.25	"Synthetic" water[b]	0.8	0.26	0.24	0.26	104.0	96.0	104.0
0 63	"Synthetic" water[b]	0.8	0.64	0.61	0.64	101.6	96.8	101.6
0.25	1% NaCl	0.8	0.25	0.25	0.24	100.0	100.0	96.0
0.63	1% NaCl	0.8	0.59	0.60	0.59	93.7	95.2	93.7
By γ-counting								
5.00	"Synthetic" water	0.5	4.97	5.02		99.4	100.4	
6.00	"Synthetic" water	0.5	5.94			99.6		
0.50	"Synthetic" water + 10 mg/l Fe^{3+}	0.5	0.49			98.0		
0.50	"Synthetic" water + 10 mg/l Zn^{2+}	0.5	0.52			104.0		
0.50	"Synthetic" water + 5 mg/l Cu^{2+}	0.5	0.50			100.0		
0.50	"Synthetic" water + 2.5 mg/l Pb^{2+}	0.5	0.49			98.0		
0.50	"Synthetic" water + 10 mg/l Fe^{3+}, 10 mg/l Zn^{2+}, 5 mg/l Cu^{2+} and 2.5 mg/l Pb^{2+}	0.5	0.49			98.0		

[a] Containing 12 mg/l Ca^{2+}, 2 mg/l Mg^{2+}, 3 mg/l Na^+, 26 mg/l HCO_3^-, 2 mg/l Cl^-, and 20 mg/l SO_4^{2-}.

[b] Containing 60 mg/l Ca^{2+}, 20 mg/l Mg^{2+}, 75 mg/l Na^+, 200 mg/l HCO_3^-, 20 mg/l Cl^-, and 195 mg/l SO_4^{2-}.

the standpoint of trace metal analysis. This method of analysis for silver in water is free from interferences, largely as a result of the separation of silver from other constituents in water by an ion-exchange reaction. The recovery of silver is not affected by the presence of Fe^{3+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} up to the concentrations indicated in Table I. Such heavy metals are commonly found in waters from mining areas.

As mentioned in the procedure, the minimum size of water sample required depends on the concentration of silver in water. Although it takes time to pass a large volume of water through the resin column and to elute subsequently the silver from the resin with the acetone–nitric acid–water mixture, no particular attention is required during this period of time using the equipment shown in Fig. 2.

SUMMARY

A method has been developed for the accurate determination of 0.1–1 μg of silver per liter of water. The method permits stabilization of silver in water without loss to container walls. Optimum conditions have been established for the complete recovery of silver from water with an anion-exchange column, for quantitative elution of silver from the resin, and for measurement of silver by atomic absorption spectrophotometry after chelation with ammonium pyrrolidine dithiocarbamate and extraction of the chelate with MIBK. Silver in the 1–10 μg/l range can be determined by extraction without pre-concentration on an ion-exchange resin.

RÉSUMÉ

Une méthode est proposée pour le dosage exact de 0.1–1 μg d'argent par litre d'eau. Elle permet de stabiliser l'argent dans l'eau sans perte sur les parois du récipient. Les conditions optima ont été établies 1. pour la récupération totale de l'argent dans l'eau à l'aide d'une colonne de résine échangeuse d'anions, 2. pour l'élution quantitative de l'argent de la résine et 3. pour le dosage de l'argent par spectrophotométrie par absorption atomique après chélation à l'aide de pyrrolidine dithiocarbamate d'ammonium et extraction de chélate au moyen de méthylisobutylcétone. L'argent (de 1 à 10 μg/l) peut être dosé par extraction sans préconcentration sur échangeur d'ions.

ZUSAMMENFASSUNG

Es wurde eine Methode zur genauen Bestimmung von 0.1–1 μg/l Silber entwickelt. Die Methode ermöglicht eine Stabilisierung des Silbers im Wasser ohne Verlust an den Behälterwänden. Optimale Bedingungen ergaben sich durch die vollständige Abscheidung des Silbers an einem Anionenaustauscher, anschliessende Elution des Silbers und Messung mit Hilfe der Atomabsorption nach Komplexbildung mit Ammoniumpyrrolidin-dithiocarbamat und Extraktion des Chelats mit Methylisobutylketon. Bei Silbergehalten van 1–10 μg/l ist eine vorherige Anreicherung mit einem Ionenaustauscher nicht erforderlich.

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THE DETERMINATION OF MANGANESE IN A WIDE RANGE OF STEELS AND CAST IRONS BY ATOMIC ABSORPTION SPECTROSCOPY

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BELCHER AND KINSON[1] have described a procedure for the determination of 0.001–2% manganese in low and high alloy steels, using a solution containing sulphuric acid, phosphoric acid and a little sulphurous acid to reduce any oxidised manganese salts. Interference from iron was practically eliminated by using a stoichiometric air–acetylene flame, and chromium interference at the 20% level was reduced by confining the absorption path to a small section of the flame. Results on N.B.S. samples obtained by SPRAGUE AND SLAVIN[2], who used aqua regia to dissolve the steel samples and a similar procedure to BELCHER AND KINSON showed poor precision and in certain cases unsatisfactory agreement with certificate values. In the latter study, silicon interference was eliminated by modifying the equipment so that only radiation passing through a restricted area of the flame was received by the detector. Phosphorus is thought to interfere with the determination of manganese in cast iron[3], although this has not been confirmed.

The present paper describes a method which involves, after initial acid dissolution, fuming with perchloric acid, filtering off the silica and spraying a 1:1 aqueous ethanol solution into an air–acetylene flame. No interference is found from any of the constituents of a wide variety of steels and cast irons. The method is simple and direct and could perhaps be used with advantage in the determination of some of the other elements present in steels. It does not involve the use of releasing agents, the addition of iron to the standard solutions or the use of restricted areas of the flame.

EXPERIMENTAL

Apparatus

A Unicam SP90 atomic absorption spectrophotometer and a manganese hollow-cathode lamp were used. The standard instrumental conditions were as given below:

Wavelength	279.5nm	Air pressure	30 p.s.i.
Slit width	0.08 mm	flow rate	5.5 l/min
Burner height	0.8 cm	Acetylene pressure	10 p.s.i.
Lamp current	12 mA	flow rate	1.7 l/min

Reagents

All of the reagents used were of analytical-reagent grade.

Standard manganese solution (100 p.p.m.). Dissolve 0.100 g of electrolytically pure manganese in 5 ml of concentrated hydrochloric acid and dilute the solution to 1 l with distilled water.

Standard iron solution (10, 000 p.p.m.). Dissolve 5.00 g of "Hilger" high-purity iron in 20 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid, evaporate to dryness, take up in 50 ml of concentrated perchloric acid and dilute to 500 ml with distilled water.

Analysis of steels and cast irons

For convenience, 0.1 g of alloy should be present in 100 ml of the final solution; this corresponds to 1000 p.p.m. of metal in the final solution and 1% of manganese in the alloy then corresponds to 10 p.p.m. of manganese in solution.

Method. Dissolve 1.00 g of the alloy in 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid with warming. Evaporate the solution first to dryness, cool, take up the residue in 10 ml of concentrated perchloric acid and allow to fume gently. Cool and add 50 ml of distilled water to dissolve the salts. Filter the solution into a 100-ml graduated flask and make up to the mark with distilled water. Pipette a 10-ml aliquot of this solution into a 100-ml graduated flask, add 50 ml of ethanol and make up to the mark with distilled water. Spray this solution into the flame in the usual way and determine the absorbance. Calculate the manganese content of the alloy by reading off the manganese concentration in the solution from a calibration curve (Note).

Note. The calibration graphs of flame optical density *vs.* concentration are curved over the two ranges studied, *i.e.* 0–5 p.p.m. and 0–20 p.p.m. manganese. However, the curves are constant over a period of several weeks provided that all the experimental parameters are kept constant.

RESULTS AND DISCUSSION

Effect of acids on the manganese absorbance

In the proposed method, after dissolution in hydrochloric and nitric acids, the solution is evaporated to dryness before being taken up in acid. The effects of sulphuric and perchloric acids on the manganese absorbance were studied.

The results are shown in Fig. 1 together with the effects of hydrochloric and phosphoric acids. All solutions contained 10 p.p.m. of manganese. It can be seen that perchloric acid depresses the absorbance less than the other acids and in fact up to 4% perchloric acid has no effect on the absorbance. The depressions of the absorbance by the other acids agree closely with the results obtained by BELCHER AND KINSON[1]. Fuming with perchloric acid produces a clear solution except for the dehydrated silica which is filtered off. Perchloric acid was therefore chosen as the most suitable medium.

Effect of other elements on the manganese absorbance

As it was intended to determine manganese in iron-base alloys, the effect of a large excess of iron on the manganese absorbance was first studied. The interference effects of other elements found in irons and steels were then studied by replacing part of the iron by another element. The concentrations of the elements were chosen so as to represent the maximum contents found in irons and steels from a 1-g sample, the dilution involved being considered. All solutions contained 1% or less perchloric acid. The results are shown in Table I.

In aqueous solution, iron depresses the manganese absorbance. The absorbance produced by a solution containing 10 p.p.m. manganese and 1000 p.p.m. iron was 0.293. Interference from other elements was considered to have occurred if the absorbance changed by 0.003 or more absorbance units when part of the iron was replaced by another element. From the results it is reasonable to assume that there would be no interference from the following: 1% chromium, 1% nickel, 2.5% aluminium, 3% copper, 5% titanium, and 5% vanadium. However, alloying elements in high concentrations gave quite large positive interference.

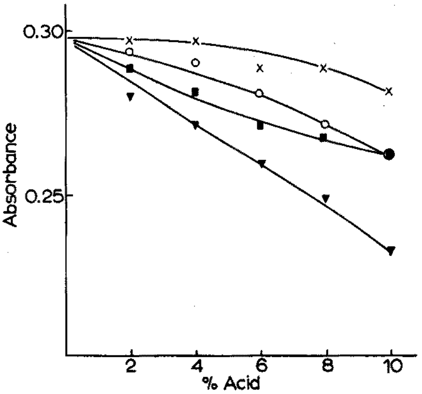

Fig. 1. Effect of acids on manganese absorbance. (×) Perchloric acid, (○) sulphuric acid, (■) hydrochloric acid, (▼) phosphoric acid.

TABLE I

EFFECT OF OTHER ELEMENTS ON THE MANGANESE ABSORBANCE IN AQUEOUS SOLUTION

(All solutions contained 10 p.p.m. manganese)

Element	*Concentration (p.p.m.)*	*Fe present (p.p.m.)*	*Absorbance*
—	—	—	0.297
—	—	1000	0.293
Cr	10	990	0.293
Ni	10	990	0.293
Cr	300	700	0.301
Ni	300	700	0.301
Co	200	800	0.305
W	200	800	0.305
Al	25	975	0.293
Cu	30	970	0.293
Ti	50	950	0.293
Al	25	975	0.293
Mo	100	900	0.301

Cobalt and tungsten at the 20% level both gave an absorbance of 0.305 which is 0.012 units higher than the standard manganese containing excess of iron. Chromium and nickel at the 30% and molybdenum at the 10% had similar effects.

Effect of organic solvents on the manganese absorbance

Organic solvents are well known to enhance the absorbance of many elements in atomic absorption spectroscopy[4]. It was thought that the use of an aqueous organic solution would increase the sensitivity of the method and might possibly eliminate some of the interferences encountered in aqueous solution. All solutions contained 50% (v/v) organic solvent and 10 p.p.m. manganese.

Acetone enhanced the signal to the greatest extent (absorbance 0.509 compared to 0.297 for aqueous solutions) but the meter readings were very unsteady. Ethanol enhanced the signal by over 50% (absorbance 0.464) and the ethanolic solution produced a very steady meter reading in some cases of superior stability to an aqueous solution. The enhancing effects of methanol, isopropanol and propanol were slightly less than that of ethanol. Although the effect of organic solvents was not studied extensively, ethanol was chosen as a most suitable solvent.

Effect of iron and other elements in a 50% (v/v) aqueous ethanol solution

The same procedure was adopted as for the study in aqueous solution. All solutions contained 10 p.p.m. manganese and 1% perchloric acid, and were 50% (v/v) in ethanol. The results are shown in Table II. It can be seen that in aqueous ethanol solution, the manganese absorbance is independent of the iron concentration and that the enhancement effects of 20% cobalt and 30% chromium have been eliminated. Moreover, the interference effects of nickel and tungsten have been reduced considerably and in fact be ignored, as the effects are less than 1%.

TABLE II

EFFECT OF OTHER ELEMENTS ON THE MAGNANESE ABSORBANCE IN AQUEOUS ETHANOL SOLUTION (1:1)

(All solutions contained 10 p.p.m. manganese)

Element	*Concentration (p.p.m.)*	*Fe present (p.p.m.)*	*Absorbance*
—	—	—	0.464
—	—	1000	0.464
Cr	300	700	0.464
Ni	300	700	0.467
Co	200	800	0.464
W	200	800	0.467
Mo	100	900	0.464

The use of a 50% (v/v) aqueous ethanol solution should enable the manganese content of irons and low and high alloyed steels to be determined accurately without the use of restricted areas of the flame, stringent control of the stoichiometry of the flame, or the addition of iron to the standard solutions. There is also no need to apply correction factors in certain highly alloyed steels.

Application to steels and cast irons

Results for the determination of manganese in a wide variety of cast irons and steels are shown in Table III. These results are considered to be extremely good. It seems very likely that this particular atomic absorption spectroscopic method could be applied to the determination of other elements in steels and other alloys.

TABLE III

RESULTS FOR THE DETERMINATION OF MANGANESE IN CAST IRONS AND STEELS BY ATOMIC ABSORPTION SPECTROSCOPY

Alloy	*Manganese content*	
	Certificate value (%)	*Found by a.a.s. (%)*
B.C.S.329 mild steel	0.12	0.12, 0.12
B.C.S.255/1 low alloy steel	0.16	0.16, 0.15(5)
B.C.S.252/1 low alloy steel	0.34	0.34, 0.34
B.C.S.254 low alloy steel	0.52(5)	0.52, 0.52(5)
B.C.S.224/1 chromium–vanadium steel	0.66	0.66, 0.66
B.C.S.253/1 low alloy steel	0.84	0.83, 0.83
B.C.S.220/1 high speed steel	0.29	0.29, 0.29
B.C.S.261 Nb stabilized "18012" stainless steel	0.66	0.65, 0.64
B.C.S.342 ferritic stainless steel	0.91	0.90, 0.90
B.C.S. austenitic stainless steel (20.6% Ni, 25.6% Cr)	0.85	0.84, 0.85
B.C.S.206 cast iron	0.32(5)	0.32, 0.32
B.C.S.234/4 high duty iron	0.54	0.53, 0.54
B.C.S.173 austenitic cast iron	1.01	1.01, 1.00
B.C.S.170 cast iron	1.64	1.64, 1.64

SUMMARY

A method is described for the determination of 0.1–2.0% of manganese in a wide range of steels and cast irons by atomic absorption spectroscopy. The sample solution is fumed with perchloric acid, silica is removed by filtration, and ethanol is added to the solution before the measurement. No interference from any of the other elements commonly found in these alloys was observed.

RÉSUMÉ

On décrit une méthode pour le dosage du manganèse (0.1 à 2.0%) dans divers aciers et fontes, par spectroscopie par absorption atomique. On évapore la solution à analyser avec de l'acide perchlorique; la silice est séparée par filtration. De l'éthanol est ajouté à la solution avant de faire la mesure. On n'observe aucune interférence des éléments accompagnant généralement ces alliages.

ZUSAMMENFASSUNG

Es wird die Bestimmung von 0.1–2.0% Mangan in einer grossen Zahl von Stählen mit der Atomabsorptionsspektroskopie beschrieben. Dabei wird die Probe mit Perchlorsäure und unter Zugabe von Äthanol verdampft. Siliciumdioxid wird durch Filtration abgetrennt. Störungen durch andere Elemente, die im allgemeinen in diesen Legierungen vorkommen, wurden nicht beobachtet.

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DETERMINATION OF LEAD IN URINE BY ATOMIC ABSORPTION SPECTROPHOTOMETRY AFTER COPRECIPITATION WITH THORIUM

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The determination of lead in urine by atomic absorption spectrophotometry is becoming increasingly preferred to the colorimetric dithizone and polarographic methods; both of these techniques are precise and sensitive, but are technically complex and require long ashing times. Solutions containing more than 0.1–0.2 mg of lead per litre can be directly analysed by atomic absorption in less than 1 min, but for lower concentrations, lead must be concentrated to fit the sensitivity range of the method. Only in theory can urine containing more than 0.2 p.p.m. of lead be directly analysed by atomic absorption spectrophotometry. In fact, urine contains Na, K, Ca, Mg and other components which interfere, causing spurious absorption readings corresponding to 0.3–0.6 p.p.m. of lead. When untreated urine is analyzed, spurious absorption causes errors of ±0.1 p.p.m., and the determination of lead is sufficiently accurate only in urine containing more than 0.5 p.p.m. of lead. It is exceptional for such concentrations to occur, though they may be found during therapy with chelating agents. Normal urine contains less than 0.05 p.p.m. of lead; subjects with occupational exposure seldom excrete more than 0.2 p.p.m. of lead; therefore, to determine lead by atomic absorption, it is necessary to extract lead from larger samples either in order to concentrate it, or to eliminate interfering components.

Lead can be extracted with chelating agents from urine into an organic solvent[1–3]; this technique avoids prior ashing, but requires additional sample preparation, so that the use of atomic absorption does not provide any special advantage over chemical and polarographic methods.

The coprecipitation of lead from urine has been used for its concentration as a preliminary step for many determinations by other techniques. For atomic absorption, KOPITO AND SHWACHMAN[4] suggested, as a rapid procedure with substantial advantages over other methods, the concentration of uninary lead by coprecipitation with bismuth. However, certain difficulties were found in the application of this method. Precipitation was not complete especially in samples from patients undergoing therapy with chelating agents, or excreting a large amount of coproporphyrin. Calcium and magnesium, which cause spurious absorption, precipitated with lead. The voluminous precipitate retained more than 10% of the original sample, with subsequent incomplete removal of insoluble salts, and the precipitate was soluble only in concentrated acid which subsequently damaged the nebulizer. Finally, the hydrolyzed bismuth precipitate often clogged the nebulizer capillary tube.

In view of the obvious advantages of coprecipitation, the above method was modified in order to provide a procedure which could be applied even when chelating agents are present, and in which a precipitate soluble in weak acid solutions without hydrolysis and not containing interfering elements, could be utilized.

Coprecipitation of lead with thorium

Urine contains about 3 g of phosphate per litre; on neutralization, all the cations present precipitate as phosphates except alkali metals. Except for calcium and magnesium, the precipitated cations do not interfere with the determination of lead by atomic absorption. In order to avoid spurious absorption caused by calcium and magnesium, the phosphates of which in urine precipitate only above pH 6, attempts were made to precipitate lead with cations which not only readily coprecipitate lead, but also precipitate as phosphate below pH 6.

Among metals with phosphates which are insoluble in weak acid, zirconium so readily coprecipitates lead as to prevent its reaction with dithizone; zirconium phosphate, however, is also insoluble in concentrated acid, and it is rather difficult to dissolve lead coprecipitated and partially coagulated with zirconium phosphate. Zirconium was, therefore, unsuitable.

In further tests, thorium was found to be particularly suitable for the coprecipitation of lead even from very dilute solutions. To keep reagent addition and precipitate volume to a minimum, the minimum amount of thorium required to assure complete precipitation of lead from urine at pH 5–6 was established. At pH 5–6, calcium and magnesium did not precipitate; thorium phosphate precipitated also below pH 4 and coprecipitation of lead phosphate was complete at pH 4. Table I gives the results obtained by precipitating 12.5 ml of urine with 0.5 ml of thorium nitrate solutions of different concentrations. Precipitation was complete with 2 mg of thorium; 4 mg of thorium per 12.5 ml of urine guaranteed a margin of safety, and the precipitate volume was reduced to a few mm³. With 2 mg of thorium in 12.5 ml lead was completely precipitated even from aqueous phosphate-free solutions, made weakly alkaline with ammonium hydroxide. Lead comes down with thorium hydroxide which precipitates from weakly alkaline solutions.

TABLE I

PRECIPITATION OF LEAD FROM 12.5 ml OF URINE WITH DIFFERENT CONCENTRATIONS OF THORIUM NITRATE

$Th(NO_3)_4 \cdot 6H_2O$ solution[a] *(%)*	*Th added (mg)*	*Pb in urine (dithizone) (μg/l)*	*Pb in precipitate μg/l urine (dithizone and a.a.s.)*	*Pb in supernatant μg/l urine (dithizone)*
0.5	1	110	80	28
1.0	2	110	110	—
2.0	4	110	110	—

[a] 0.5 ml added.

Coprecipitation of lead with thorium in the presence of copper

However, it was found that the precipitation of lead with thorium was incomplete in the urine of patients receiving EDTA therapy, as noted already by KOPITO AND SHWACHMAN[4] for coprecipitation of lead with bismuth. Moreover, the precipitation of lead was also incomplete in subjects excreting a large amount of coproporphyrin. In such urine specimens, only the same amount of lead was precipitated even with increased concentrations of thorium. Since thorium complexes are more stable than lead complexes, thorium should displace lead from EDTA and from other complex salts. Thorium, however, reacts slowly with chelating agents, and reacts immediately with phosphoric acid; if added to urine, thorium is precipitated instantaneously as an insoluble salt, without displacing the chelated lead. As a means of displacing chelated lead, copper(II) was tested; copper(II) not only forms more stable complexes than lead but also reacts rapidly with EDTA and coproporphyrins, and is not precipitated by phosphoric acid. In the presence of copper all the lead was coprecipitated with thorium even if EDTA or coproporphyrins are present at high concentration.

In urine containing a high concentration of coproporphyrin, 2–3 drops of a 2% copper(II) sulphate solution are sufficient; 0.5 ml of 2% copper sulphate produces complete coprecipitation of the lead contained in 12.5 ml of urine excreted within 24 h of the administration of 1 g of EDTA. Table II shows the recovery of lead by the dithizone method[5] and by coprecipitation with thorium and with thorium–copper solution, from the urine of normal subjects, of patients excreting more than 50 μg of coproporphyrin per 100 ml, and of patients treated with 1 g of EDTA. Below pH 6, copper(II) does not precipitate from urine, and so does not interfere with the lead determination; accordingly, the mixed solution was preferred in all cases.

TABLE II

DETERMINATION OF LEAD BY COPRECIPITATION OF 12.5 ml OF URINE WITH THORIUM OR THORIUM + COPPER

μg Pb/l of urine		
Coprecipitation with Th[a]	*Coprecipitation with Th–Cu*[b]	*Dithizone method*
70	68	70
87	85	85
75[c]	195	192
84[c]	148	150
430[d]	1480	1450
615[d]	2120	2180

[a] 4 mg of thorium added.
[b] 4 mg of thorium and 4 mg of copper added.
[c] Patients excreting > 50 μg of coproporphyrin per 100 ml.
[d] Patients undergoing therapy with 1 g of EDTA.

EXPERIMENTAL

Apparatus

A Unicam SP 90 Atomic Absorption Spectrophotometer was used with the following settings.

Wavelength	2170 Å
Slitwidth	0.4 mm
Burner height	1.4 cm
Propane	flow 250 ml/min
Air	flow 4.5 l/min
Sample flow	3 ml/min
Sample aspiration time	15–30 sec
Scale expansion	2 × : 1 p.p.m. corresponds to 9% absorption.

Reagents

Precipitating solution. Dissolve in 100 ml of deionized water 2 g of thorium nitrate hexahydrate and 2 g of copper sulphate; acidify with 2 drops of 1:1 hydrochloric acid.

Ammonium hydroxide (lead-free). Distil 100 ml of concentrated ammonia solution, collecting the distillate in 100 ml of deionized water.

Standard lead solutions. From 0.25 to 4 p.p.m.

Use lead-free glassware, carefully washed with hydrochloric acid and rinsed with deionized water.

Procedure

Add 0.5 ml of precipitating solution to 12.5 ml of urine at pH 5–6, in a 15-ml centrifuge tube and shake. After 5 min, centrifuge at 2500 r.p.m. for 5 min; discard the supernate, dissolve the precipitate with 0.5 ml of lead-free 1:1 hydrochloric acid, add 2 ml of water and determine lead by atomic absorption spectrophotometry under the above conditions. In the final hydrochloric acid solution, lead is 5 times more concentrated than in the original sample.

Lead can also be determined in urine samples kept for 10 days; before the storage, the urine is acidified with a few drops of 1:1 hydrochloric or nitric acid and before the analysis adjusted to pH 5–6 with ammonia solution. The complete removal of interfering salts allows calibration to be made with aqueous standard lead solutions (0.25–0.5 etc. p.p.m.). With the enrichment provided by the method, the recovery of lead from urine ranges from 0.03 to 0.05 p.p.m. with an error of ±0.005 p.p.m. When a more precise determination of lead in amounts below 0.03 p.p.m. is required, a tenfold concentration is necessary. This can be obtained by precipitating lead from 25 ml of urine, by means of the usual procedure.

The reagent blank is prepared by taking 12.5 ml of water made alkaline with a drop of ammonium hydroxide, through the same procedure. If reagents are lead-free, the blank peak is caused only by spurious absorption of thorium which, in the method described, is equivalent to 0.03 p.p.m. of lead. This spurious absorption from thorium can be checked at 2200 Å, where the peak produced is the same as that at 2170 Å, since there is no absorption by lead at 2200 Å.

A few minutes are necessary to dissolve the precipitate with hydrochloric acid; if stirred with a glass rod, the precipitate dissolves instantaneously. Sometimes the hydrochloric solution contains suspended particles from urine. In this case, the solution should be centrifuged for 3 min before it is sprayed into the burner, in order to avoid blocking the capillary tube. A run of 24 determinations can be made in about 2 h by a trained operator.

RESULTS

The reproducibility of the results obtained by the proposed procedure is excellent (Table III).

Lead from 20 urine samples was determined both by the coprecipitation–atomic absorption method and by the dithizone method[5]. The results (Table IV) show good agreement between the two methods. The atomic absorption method has, however, the advantage of being a much simpler and more rapid procedure.

TABLE III

REPRODUCIBILITY OF LEAD DETERMINATION AND RECOVERY OF LEAD ADDED TO URINE BY COPRECIPITATION

Subject	*μg Pb/l in urine*	*μg Pb/l added*	*μg Pb/l found*
1	25	50	80
	28	50	75
	26	50	78
2	50	80	127
	48	80	130
	51	80	126

TABLE IV

COMPARISON OF DITHIZONE AND ATOMIC ABSORPTION METHODS FOR DETERMINATION OF LEAD IN URINE

Specimen no.	*μg Pb/l dithizone*	*μg Pb/l a.a.s.*
1	132	128
2	65	64
3	50	50
4	414	380
5	126	130
6	376	390
7	130	125
8	310	315
9	70	60
10	30	35
11	10	10
12	90	90
13	90	84
14	65	61
15	10	13
16	40	33
17	430	400
18	130	125
19	63	65
20	85	88
Average	135	132.3

SUMMARY

Lead is determined in urine by atomic absorption spectrophotometry after separation by coprecipitation with thorium, in the presence of copper(II); concentration of lead and removal of interferences are achieved simultaneously. Fresh urine or samples acidified with hydrochloric acid must be used. Precipitation is quantitative from the urine of subjects excreting coproporphyrins or treated with chelating agents, as the added copper liberates the chelated lead. The precision of the method is ± 0.005 p.p.m. of lead.

RÉSUMÉ

Le plomb dans l'urine peut être dosé par spectrophotométrie par absorption atomique après séparation par coprécipitation, à l'aide de thorium, en présence de cuivre(II). La concentration du plomb et l'élimination des interférences se font simultanément. On doit utiliser de l'urine fraîche ou des échantillons acidifiés par l'acide chlorhydrique. La précipitation est quantitative dans les urines de sujets excrétant des coproporphyrines ou traitées par des agents chélatants: le couvre ajouté libère le plomb complexé. La précision de la méthode est ±0.005 p.p.m. de plomb.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Blei in Urin mit der Atomabsorptionsspektroskopie beschrieben. Das Blei wird durch Mitfällung mit Thorium in Gegenwart von Kupfer(II) konzentriert; dadurch werden gleichzeitig Störungen vermieden. Dazu müssen frische, mit Salzsäure versetzte Proben verwendet werden. Die Fällung ist quantitativ in solchen Proben, die gleichzeitig Coproporphyrin enthalten oder mit Chelatbildnern versetzt wurden, da das hinzugegebene Kupfer das komplexgebundene Blei freimacht. Die Genauigkeit der Methode beträgt 0.005 p.p.m. Pb.

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EXTRACTION OF TETRABUTYLAMMONIUM TETRACHLOROAURATE(III) INTO CHLOROFORM SOLUTION OF TETRABUTYLAMMONIUM PERCHLORATE AND SPECTROPHOTOMETRIC DETERMINATION OF GOLD

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In the course of a study of the chlorocomplexes of gold in this laboratory, we found that solutions of tetrabutylammonium perchlorate in chloroform can be used in an ion-association extraction[1] of tetrachloroaurate(III) as the tetrabutylammonium ion-pair. The extraction proceeds according to the equation:

$$\mathrm{AuCl_4^-} + (\mathrm{Bu_4N^+, ClO_4^-})_o \rightleftarrows (\mathrm{Bu_4N^+, AuCl_4^-})_o + \mathrm{ClO_4^-} \tag{1}$$

The equilibrium constant is given by the expression

$$K = \frac{[(\mathrm{Bu_4N^+, AuCl_4^-})_o]\,[\mathrm{ClO_4^-}]}{[(\mathrm{Bu_4N^+, ClO_4^-})_o]\,[\mathrm{AuCl_4^-}]}\,\frac{f_1 \cdot f_2}{f_3 \cdot f_4} \tag{2}$$

where f_1, f_2, f_3, and f_4 are the activity coefficients of $(\mathrm{Bu_4N^+, AuCl_4^-})_o$, $\mathrm{ClO_4^-}$, $(\mathrm{Bu_4N^+, ClO_4^-})_o$, and $\mathrm{AuCl_4^-}$, respectively, and subscript o denotes concentration in the organic phase. The thermodynamic and analytical aspects of this extraction system, represented by eqn. (1), are presented in this paper.

EXPERIMENTAL

Reagents

Tetrabutylammonium perchlorate was prepared by treating a solution of tetrabutylammonium bromide (Eastman) in chloroform with a slight excess of aqueous silver perchlorate (G. F. Smith Chemical Co.) solution 0.1 *M* in perchloric acid. After rapid filtration to remove the silver bromide, the chloroform phase was washed four times with distilled water and evaporated to dryness. The product was recrystallized twice from warm ethyl acetate and dried for 24 h *in vacuo* at 80°.

Gold metal was prepared by the addition of a saturated solution of oxalic acid to a hot solution of tetrachloroauric acid. The metal was washed with distilled water and dried at 110° for 6 h.

Tetrabutylammonium tetrachloroaurate(III) was prepared by the following procedure. Gold metal (1.01 mmol) was dissolved in hot concentrated hydrochloric acid by dropwise addition of nitric acid until complete dissolution occurred. The solution was evaporated to near dryness, then diluted to *ca.* 50 ml with water, and treated with tetrabutylammonium perchlorate (1.00 mmol) dissolved in 75 ml of chloroform (Baker, reagent grade). The chloroform layer was washed three times with an aqueous solution of 0.01 *M* hydrochloric acid, evaporated until crystals appeared, then cooled slowly, and finally filtered. The crystals obtained were washed twice with small amounts of cold chloroform and dried *in vacuo* at 50° for 4 h.

Analysis. Calcd. for $(C_4H_9)_4NAuCl_4$: Au, 33.9%. Found: Au, 33.8%.

In the course of this work, the tetraethylammonium salt Et_4NAuCl_4 was prepared. Because this tetrachloroaurate(III) salt can be obtained in high purity and is very stable and nonhygroscopic, it appears to be a good primary standard substance for gold. Tetraethylammonium tetrachloroaurate(III) was obtained by the slow addition of a saturated aqueous solution of tetraethylammonium perchlorate (0.205 *M* at 25°) to a *ca.* 0.2 *M* solution of tetrachloroauric acid (Baker) in water until no further precipitation occurred. The tetraethylammonium tetrachloroaurate(III) was washed five times with cold water and dried *in vacuo* at 50° for 4 h.

Analysis. Calcd. for $(C_2H_5)_4NAuCl_4$: Au, 42.00%. Found: Au, 41.98%.

Equilibrium study

Stock solutions of tetrabutylammonium perchlorate and of tetrabutylammonium tetrachloroaurate(III) in chloroform were prepared determinately, and those of perchloric acid and of hydrochloric acid were prepared with reagent-grade chemicals and appropriately standardized. Measured volumes of these solutions were placed into test tubes, and the tubes, stoppered tightly, were shaken mechanically in a constant temperature bath at $25.0° \pm 0.1°$ for 4 h. The samples were then removed from the bath, centrifuged, and placed back in the bath for a further 8 h. After this equilibration period, the phases were separated, and the aqueous phases were analyzed for gold. The concentrations of the other species in the system were calculated from their initial concentrations and the concentration of gold in the aqueous phase. The concentration of tetrachloroaurate(III) ion in the aqueous phase was determined by measurement of the absorbance at 312 nm. Beer's law was shown to hold at this wavelength for concentrations of tetrachloroaurate(III) up to $2.0 \cdot 10^{-4}$ *M* in 0.4 *M* hydrochloric acid solution, with the absorbance *vs.* concentration plot passing through the origin (molar absorptivity, 5,080). The absorbance of all solutions was measured with a 1-cm quartz cell and a Beckman DU spectrophotometer equipped with a hydrogen lamp.

Procedure for analysis

Dissolve the sample in aqua regia and evaporate the digested mixture to near dryness. (For this study, a standard gold solution containing 80 µg of gold per ml was prepared by dissolving a weighed amount of tetraethylammonium tetrachloroaurate(III) in a measured volume of aqueous 0.4 *M* hydrochloric acid solution.) Add a few ml of 2 *M* hydrochloric acid, boil the mixture for 5 min, filter if necessary, and dilute the sample to a known volume. Transfer an aliquot containing 20–120 µg of gold to a test tube (15 × 125 mm), and dilute to *ca.* 5 ml. Add 1 ml of a 0.10 *M* perchloric acid solution and 5.00 ml of a 0.02 *M* tetrabutylammonium perchlorate solution in chloroform. Stopper tightly and shake for 3 min. Allow the two phases to separate (centrifuge if necessary). Carefully siphon the aqueous phase with a water aspirator; avoid evaporation of the chloroform. Add *ca.* 5 ml of an aqueous 0.02 *M* perchloric acid, 0.02 *M* hydrochloric acid solution saturated with chloroform, stopper the tube, shake for 30 sec and then siphon the aqueous wash solution. Repeat the washing process four times. Centrifuge the tube (*ca.* 2,000 rev/min) and transfer some of the chloroform solution to a 1-cm quartz cell and measure the absorbance at 321 nm. It is recommended that, as a check, a sample of known gold content be processed simultaneously with the sample being analyzed.

RESULTS AND DISCUSSION

Typical data for the distribution equilibrium (eqn. (1)) are presented in Table I. (The initial concentration of hydrochloric acid in the aqueous phase was 0.02 *M*.) For the calculation of the equilibrium constant (eqn. (2)), it was assumed that (*a*) the tetrabutylammonium tetrachloroaurate(III) and tetrabutylammonium perchlorate ion-pairs are the only gold(III) and perchlorate species in chloroform and the tetrachloroaurate(III) and perchlorate ions are the only gold(III) and perchlorate species in the aqueous phase, and (*b*) the ratios of the activity coefficients of the two ion-association complexes and of tetrachloroaurate(III) and perchlorate ions are one because of the close similarity of the species in each of the pairs. The values of the constant obtained show no significant effects of variation of the concentrations of perchlorate ion, of tetrabutylammonium perchlorate in chloroform, and of tetrachloroaurate(III) ion, which indicate that the assumptions made in the calculation of K are valid and that the calculated values are good estimates of the equilibrium constant. The average value of K is $(2.88 \pm 0.05) \cdot 10^3$ over the ranges of concentration of the different species examined.

TABLE I

TYPICAL DATA FOR THE EQUILIBRIUM DISTRIBUTION REPRESENTED BY EQN. (1) AT 25°

Aqueous phase[a]		*Chloroform phase*		
$[AuCl_4^-] \cdot 10^5$	$[ClO_4^-] \cdot 10^1$	$[Bu_4NAuCl_4] \cdot 10^3$	$[Bu_4NClO_4] \cdot 10^3$	$K \cdot 10^{-3}$
1.89	0.385	4.63	3.37	2.79
3.64	0.769	4.60	3.40	2.87
5.39	1.154	4.56	3.44	2.84
6.94	1.54	4.53	3.46	2.90
8.56	1.92	4.50	3.50	2.89
13.86	2.00	4.44	2.23	2.88
7.66	2.00	4.54	4.13	2.87
5.17	2.00	4.59	6.08	2.92
3.96	2.00	4.61	8.06	2.89
3.18	2.00	4.62	10.05	2.89
1.93	2.00	0.90	3.36	2.78
3.74	2.00	1.81	3.39	2.85
5.59	2.00	2.71	3.42	2.83
7.28	2.00	3.61	3.45	2.87
9.13	2.00	4.52	3.48	2.85

[a] The initial concentration of hydrochloric acid in the aqueous phase was 0.02 *M*.

The effect of hydronium ion and chloride ion concentrations on the apparent distribution constant, K_A, is shown in Fig. 1.

$$K_A = \frac{(\text{total Au(III) species in chloroform})\,[ClO_4^-]}{(\text{total Au(III) species in aqueous phase})\,[(Bu_4N^+, ClO_4^-)_o]} \tag{3}$$

The shape of the curve may be explained by taking into consideration the hydrolysis of tetrachloroaurate(III) in the aqueous phase[2,3]

$$AuCl_4^- + H_2O \rightleftarrows AuCl_3OH^- + Cl^- + H^+ \tag{4}$$

$$K_h = \frac{[AuCl_3OH^-]\,[Cl^-]\,[H^+]}{[AuCl_4^-]} = 7 \cdot 10^{-7} \tag{5}$$

and assuming that the tetrachloroaurate(III) species is the only gold species extractable in the form of the tetrabutylammonium ion-pair into chloroform. The dashed curve in Fig. 1 was obtained from calculated values of K_A at various hydrochloric acid concentrations, by means of eqns. (2) and (5). Based on this study, a hydrochloric acid concentration of $1 \cdot 10^{-2}$ M in the aqueous phase should be sufficient to prevent any significant hydrolysis of tetrachloroaurate(III) ion.

From the equilibrium constants at 0, 6, 13, 19 and 25°, a ΔF value of -47.2 kcal at 25°, ΔH of -3.3 kcal, and ΔS of 4.6 cal/mol deg were obtained for the ion-association distribution system.

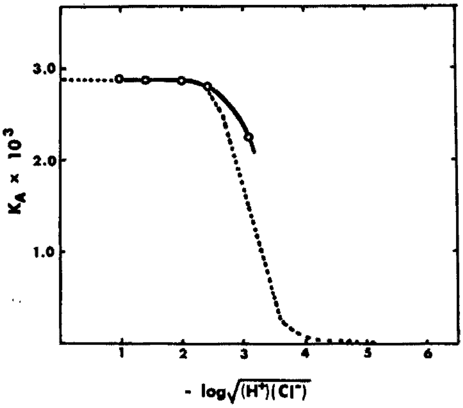

Fig. 1. Effect of hydronium ion–chloride ion concentration product on the apparent equilibrium constant, K_A.

Analytical application

On the basis of the studies described in the previous section, for the equilibrium expressed by eqn. (1), the distribution ratio, D, with acidic aqueous chloride solutions in which $-\log \sqrt{[H^+]\,[Cl^-]}$ is greater than 2 is equal to $[(Bu_4N^+, AuCl_4^-)_o]/[AuCl_4^-]$ and is a function of the concentrations of perchlorate ion in the aqueous phase and of tetrabutylammonium perchlorate in chloroform. With K for the distribution equilibrium (eqns. (1) and (2)) being $2.88 \cdot 10^3$, for a value of one for the ratio $[(Bu_4N^+, ClO_4^-)_o]/[ClO_4^-]$, and for equal volumes of chloroform and of aqueous phase, a quantitative extraction of gold of 99.97% should be attainable from aqueous solutions containing sufficient hydrogen and chloride ions to prevent hydrolysis of the tetrachloroaurate(III) ion.

The ultraviolet spectrum of tetrachloroaurate(III) ion in chloroform has an absorption maximum at 321 nm. At this wavelength, Beer's law holds over the range 0–24 μg of gold per ml; the molar absorptivity is 4,610. The gold complex is stable in the chloroform phase; there is no change in absorbance over 3 days. None of the other species involved in the extraction equilibrium absorbs at 321 nm.

The combination of this distribution equilibrium and direct spectral technique for an analytical method for separating and determining μg-quantities of gold appears to be satisfactory. The effect of 22 metal ions on the determination of gold by the procedure described in the EXPERIMENTAL section is summarized in Table II.

TABLE II

EFFECT OF SOME METALLIC IONS IN THE DETERMINATION OF GOLD (GOLD ADDED = 80 μg)[a]

Metal	*Metal added (mg)*	*Gold found (μg)*	*Metal*	*Metal added (mg)*	*Gold found (μg)*
Aluminum	20	79.7	Germanium	10	80.3
Calcium	20	80.1	Arsenic	30	79.5
Magnesium	20	79.6	Niobium	10	80.2
Vanadium	20	80.7	Palladium	3	80.9
Chromium	20	80.5	Cadmium	30	79.4
Manganese	30	79.8	Indium	30	80.5
Iron	30	80.8	Tin	30	79.8
Cobalt	30	79.7	Antimony	30	80.3
Nickel	30	80.4	Platinum	10	80.8
Copper	30	79.8	Mercury	30	80.1
Gallium	30	80.3	Thallium	10	97.3

[a] Duplicate samples taken for analysis.

Duplicate samples of 80 μg of gold and the metal ions were analyzed. Most of the metal ions studied have been shown in other studies to be extractable as chloridec omplexes[1]. Other metal ions were not studied because their behavior was expected to be similar to those examined or because they are rarely encountered in gold-containing samples. Only thallium(III) is extracted quantitatively together with gold(III), but because its molar absorptivity at 321 nm is much smaller than that of gold(III), it does not interfere when its concentration is less than 100 μg per ml. Platinum(IV), iron(III), nickel(II), vanadium(V), and palladium(II) are partially extracted, but they are eliminated in the backwashing step and do not interfere. (The oxidation state of palladium has been established by ultraviolet spectrophotometry to be II rather than IV.) Arsenic(V), antimony(V), and niobium(V) did not dissolve completely in the *ca.* 0.4 *M* hydrochloric acid solution after treatment with aqua regia. The insoluble material was filtered off before the extraction step. When the value of gold found in the presence of thallium is excluded, the relative standard deviation of the values of gold found in the presence of other metal ions in Table II is 0.51% at the 80-μg gold level (16 μg of gold per ml in the chloroform solution).

The method described is simple to perform and a large number of determinations can be carried out in a relatively short time. Since the distribution ratio can be increased to 30,000 by variation of the $[(Bu_4N^+, ClO_4^-)_o]/[ClO_4^-]$ ratio, the method can be extended and adjusted to the concentration and determination of the gold in dilute solutions of the metal, *e.g.*, 50 ml of 0.1 μg/ml aqueous solution with 2.0 ml of chloroform.

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SUMMARY

The distribution equilibrium:

$AuCl_4^- + (Bu_4N^+, ClO_4^-)_{HCCl_3} \rightleftarrows (Bu_4N^+, AuCl_4^-)_{HCCl_3} + ClO_4^-$,

has been examined. With acidic aqueous chloride solutions in which $-\log \sqrt{[H^+][Cl^-]}$ is greater than 2, the apparent equilibrium constant, K_A, is a constant equal to the equilibrium constant of the distribution reaction above; a value of $2.88 \cdot 10^3$ was obtained. Combination of the extraction with a direct spectrophotometric determination of $AuCl_4^-$ in chloroform at 312 nm provides a simple, rapid, and accurate analytical method for the separation and determining of gold in the μg-range.

RÉSUMÉ

Les auteurs ont examiné l'équilibre de partage:

$AuCl_4^- + (Bu_4N^+, ClO_4^-)_{HCCl_3} \rightleftarrows (Bu_4N^+, AuCl_4^-)_{HCCl_3} + ClO_4^-$.

En solutions aqueuses acide chlorhydrique où $-\log \sqrt{[H^+][Cl^-]}$ est plus grand que 2, la constante d'équilibre apparente K_A, est égale à la constante d'équilibre de la réaction de partage ci-dessus; une valeur de $2.88 \cdot 10^3$ a été calculée. La combinaison de l'extraction avec un dosage spectrophotométrique direct de $AuCl_4^-$ dans le chloroforme, à 312 nm, constitue une méthode d'analyse simple, rapide et précise pour la séparation et le dosage de l'or, à l'échelle du μg.

ZUSAMMENFASSUNG

Es wurde das Verteilungsgleichgewicht von $AuCl_4^-$ zwischen sauren Chloridlösungen und Chloroform, das Tetrabutylammoniumperchlorat enthält, untersucht. Durch direkte spektralphotometrische Bestimmung des $AuCl_4^-$ im Chloroform bei 312 nm ergab sich eine einfache, schnelle und genaue analytische Methode zur Trennung und Bestimmung des Golds im μg-Bereich.

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SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TITANIUM IN ZIRCONIUM, ZIRCONIUM ALLOYS, HAFNIUM, NIOBIUM AND OTHER METALS, WITH DIANTIPYRINYLMETHANE

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To meet the specification requirements for reactor-grades of hafnium, zirconium and zirconium alloys, the titanium content of these materials must not exceed 50 p.p.m. For some grades of niobium, a titanium content of up to 500 p.p.m. is permissible.

The titanium content of all these materials is usually well below the specified limit, and spectrographic analysis is usually adequate, but if the titanium content of the sample is shown (spectrographically) to be near the specified limit, a more precise determination is required. The method normally used in such cases is based on the spectrophotometric measurement of a yellow-coloured complex, formed by the reaction of titanium ions with hydrogen peroxide in mineral acid solutions[1]. This procedure is relatively free from interference by other ions, but its low sensitivity is a serious disadvantage. Other reagents have been recommended for determining titanium, *e.g.*, tiron and chromotropic acid, and they are more sensitive than hydrogen peroxide, but relatively unselective.

A reagent that has recently become fairly widely used for determining titanium, is diantipyrinylmethane*[2-5] and, from published data, it appeared that this reagent offered both high sensitivity and good selectivity. The application of diantipyrinylmethane to the determination of titanium in zirconium, hafnium, niobium and other metals of current interest was, therefore, investigated.

EXPERIMENTAL

Instrumentation and solutions

A Unicam S.P. 600 and 40-mm cells were used in these experiments.

Standard titanium solution. A 0.1-g sample of high-purity titanium (millings) was transferred to a 150-ml beaker, 50 ml of sulphuric acid (1 +4) was added, and the mixture was gently heated until the metal had dissolved. The solution was oxidised with about 5 ml of concentrated nitric acid, added dropwise, evaporated to fumes of sulphuric acid, fumed for 15 min, then cooled, transferred to a 100-ml calibrated flask, cooled, and diluted to the mark.

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* Sometimes called diantipyrylmethane.

A 5-ml aliquot of this solution was transferred to a 1-l calibrated flask containing 100 ml of sulphuric acid (1 + 1), and diluted to the mark (1 ml = 5 μg of titanium).

Diantipyrinylmethane solution (2%). 2 g of diantipyrinylmethane and 1 g of ascorbic acid were transferred to a 150-ml beaker and dissolved in 100 ml of hydrochloric acid (1 + 9). This reagent was prepared immediately before use. The presence of ascorbic acid reduces the tendency of solutions of diantipyrinylmethane to deteriorate and become yellow on standing.

Preliminary tests

Preliminary tests were made to establish suitable conditions for preparing a calibration graph.

To a 5-ml aliquot of the standard titanium solution (1 ml = 5 μg Ti) in a 50-ml calibrated flask, 5 ml of the 2% diantipyrinylmethane solution were added. The solution was diluted to the mark, and the absorbance was measured over the wavelength range 355–430 nm. Maximum absorbance was observed at 390 nm.

Subsequent tests showed that, in the presence of 5 ml of the reagent solution, the coloured complex was not fully developed, even after 8 h, but in the presence of 10 ml, development of the characteristic colour was complete within 1 h, and the colour was stable for at least 2 h.

It was anticipated that hydrochloric or sulphuric acid would be present in subsequent tests with solutions of the metals under consideration, and some preliminary tests were made to determine the effect of these acids. These tests showed that up to 5 ml of concentrated hydrochloric acid, or up to 4 ml of sulphuric acid (1 + 1), had no significant effect on the colour.

Calibration graph

Aliquots of the standard titanium solution (1 ml = 5 μg Ti), ranging from 0.5 to 5.0 ml, were transferred to 50-ml calibrated flasks. To each solution and a blank (5 ml of water), 4 ml of concentrated hydrochloric acid and 10 ml of the diantipyrinylmethane solution were added. The solutions were diluted to the mark and allowed to stand for 1 h, and absorbances were measured at 390 nm. After the absorbance of the reagent blank (0.016) had been deducted, the graph (absorbance *vs.* titanium) was a straight line that passed through the origin; an absorbance value of 0.242 corresponded to 10 μg of titanium.

An identical graph was obtained with solutions containing 4 ml of sulphuric acid (1 + 1), instead of the hydrochloric acid.

Application to zirconium and hafnium

Two solutions, each containing 0.1 g of high-purity zirconium, were prepared by heating the metal with a mixture of 2 g of potassium hydrogen sulphate and 2 ml of concentrated sulphuric acid. One of these solutions was used as a blank, and 2 ml of the standard titanium solution (1 ml = 5 μg Ti) were added to the other; a reagent blank was also prepared.

Tests with these solutions showed that the presence of zirconium completely suppressed the development of the colour; this was attributed to competition of zirconium ions for the reagent. The blank values were 0.04 (reagents only), and 0.055

(reagents + zirconium). Similar results were obtained with solutions containing 0.1 g of hafnium.

The possibility of preventing this interference by forming a complex of zirconium (or hafnium) with ethylenediaminetetraacetic acid (EDTA), before adding the diantipyrinylmethane reagent, was investigated. In the presence of 10 ml of a 5% solution of EDTA (sufficient to combine with 0.1 g of zirconium and provide a small excess), the effect of zirconium was considerably reduced, but development of the titanium–diantipyrinylmethane complex was very slow; the reaction was incomplete after 8 h. Attempts to increase the reaction rate by heating the test solutions in a boiling-water bath resulted in decomposition of the ascorbic acid and consequent formation of a soluble yellow compound that had a strong absorption at 390 nm.

The slow rate of the titanium – diantipyrinylmethane reaction was attributed to the presence of free zirconium ions, resulting from dissociation of the zirconium – EDTA complex. In general, the degree of dissociation of EDTA complexes decreases with decrease in acidity, and tests showed that when the acidity of the reaction medium was reduced, by partially neutralising the solution with 5 ml of ammonia solution before the diantipyrinylmethane reagent was added, development of the colour was complete within 1 h. After the absorbance of the blank (0.065), due to the reagents and 0.1 g of zirconium had been deducted, an absorbance value of 0.240 corresponded to 10 μg of titanium, which was almost identical with the value obtained in the absence of zirconium and EDTA (*cf.* previous tests).

These conditions were then applied to solutions containing 0.1 g of zirconium, and titanium in the range 2.5–25 μg; the graph (absorbance *vs.* titanium) was identical with that obtained in the absence of zirconium and EDTA.

Further tests showed that the established conditions were equally applicable to solutions containing up to 0.2 g of hafnium; this larger sample weight is permissible because of the relatively higher atomic weight of hafnium.

Effects of other metals. Tests were made with solutions containing 0.1 g of zirconium and 10 μg of titanium in the presence of other metals, and these showed that no significant interference was introduced by the presence of up to 10% of copper or tin, 1% of aluminium, cadmium, cobalt, lead, magnesium, manganese, nickel, vanadium or zinc, 0.5% of molybdenum, or 0.1% of chromium, iron, or uranium.

In similar tests with solutions containing 1% of niobium, hydrolytic precipitation of niobic acid occurred when the solutions were diluted, but it was shown that this precipitation could be prevented by adding 1 ml of tartaric acid solution (50%) to form a soluble niobium–tartrate complex, before the EDTA solution was added. The presence of niobium, however, caused a significant increase in the absorbance, and tests were made to determine if this could be minimised by measuring the absorbance at another wavelength.

Absorbance measurements in the range 350–480 nm showed that as the wavelength was increased, absorbance caused by the niobium decreased much more rapidly than that caused by the titanium–diantipyrinylmethane complex, and at 430 nm the effect of up to 10% of niobium was not significant. At this wavelength, the sensitivity of the procedure was lowered by about 30%.

Hydrolytic precipitation also occurred in solutions containing 1% of tantalum or tungsten; this was largely prevented by adding 1 ml of tartaric acid solution (50%) before addition of the EDTA solution, but the solutions became slightly turbid during the colour-development stage, and filtration was necessary before the absorbances were measured (at 390 nm). These tests showed that tantalum and tungsten caused a small increase in the absorbance, but the absorbance values obtained indicated that the effect of up to 0.5% of either metal was not significant.

Molybdenum above about 0.5%, caused a significant increase in the absorbance (at 390 nm), but its effect was considerably reduced by the presence of 1 ml of tartaric acid solution (50%), and further minimised by measuring the absorbance at 430 nm. With these modifications, up to 10% of molybdenum could be tolerated.

Application to niobium

Initial tests showed that hydrolytic precipitation of niobic acid from solutions containing 0.1 g of niobium, could be prevented by adding 10 ml of tartaric acid (25%), but in the presence of this amount of tartaric acid, development of the titanium–diantipyrinylmethane complex was retarded, presumably because of competition of the tartrate for titanium ions. Subsequent tests showed that the effect of tartaric acid decreased as the amount of concentrated hydrochloric acid in the test solution was increased from 1 to 5 ml; this was attributed to an increase in the degree of dissociation of the titanium–tartrate complex with progressive increase in acid concentration. Based on these preliminary observations, further tests were made as follows.

Three solutions, each containing 0.1 g of high-purity niobium were prepared by dissolving the metal in 2 g of potassium hydrogen sulphate and 1 ml of concentrated sulphuric acid, and extracting the cooled melt with 10 ml of tartaric acid solution (25%). To two of the solutions, 5 ml of the standard titanium solution (1 ml = 5 μg Ti) were added; the remaining solution was used as a blank. A solution containing reagents only, and another containing reagents and 5 ml of the standard titanium solution, were also prepared. The solutions were transferred to 50-ml calibrated flasks, 4 ml of concentrated hydrochloric acid and 10 ml of the diantipyrinylmethane solution (2%) were added, and each solution was diluted to the mark. After 1 h the absorbances were measured at 430 nm (the effect of absorbance due to niobium was minimised by measuring at this wavelength instead of 390 nm—*cf.* previous tests).

After the respective blanks (0.14 and 0.12) had been deducted, an absorbance value of 0.41 was obtained for the solutions containing niobium and titanium, compared with an absorbance value of 0.40 for the solution containing titanium only. These values show that the presence of 0.1 g of niobium causes a slight increase in absorbance (equivalent to about 10 p.p.m. of titanium). The procedure outlined above was then applied to solutions containing 0.1 g of niobium, and titanium in the range 5–25 μg; the graph (absorbance *vs.* titanium) was a straight line that passed through the origin.

Effect of other metals. Tests were made with solutions containing 0.1 g of niobium and 25 μg of titanium in the presence of other metals. No significant interference was introduced by the presence of up to 20% of tungsten, 10% of molybdenum, 2% of tin, 1% of aluminium, cadmium, cobalt, copper, lead, magnesium, manganese, nickel, tantalum, vanadium, or zinc, 0.5% of iron or chromium, or 0.1% of uranium.

In the presence of 10% of zirconium (or hafnium), development of the titanium–diantipyrinylmethane complex was considerably retarded. The effect of these metals was minimised by adding 5 ml of EDTA solution (1%) before addition of the diantipyrinylmethane reagent; with this slight modification, the effect of 10% of hafnium was not significant, but in the presence of 10% of zirconium, development of the colour was incomplete after 2 h. Application of the procedure to niobium–zirconium alloys, therefore, would necessitate a comparison of the absorbance of the sample solution with that of a reference solution containing niobium and the appropriate amount of zirconium, with a preferred colour-development time of 3 h.

Extension of the procedure to tantalum, tungsten and molybdenum

The procedure developed for application to niobium was applied to solutions containing separate 0.1-g additions of high-purity tantalum, tungsten and molybdenum, and 25 µg of titanium; appropriate blanks were also examined. Methods of preparing solutions of these metals are described in Method II.

In the presence of tantalum, a slight turbidity occurred during development of the colour, and the solutions were filtered before the absorbances were measured. Tantalum absorbed slightly, both at 390 and 430 nm, and the absorbance caused by 0.1 g of tantalum, at either wavelength, was equivalent to about 50 p.p.m. of titanium. In the application of this procedure to the determination of titanium in tantalum, therefore, it is essential to add 0.1 g of high-purity tantalum to the blank.

A slight turbidity also occurred in similar tests with solutions containing 0.1 g of tungsten, but absorbance values obtained on the filtrates showed that tungsten had no significant effect on the colour, and satisfactory results were obtained at 390 nm.

In tests with solutions containing 0.1 g of molybdenum, there was no tendency for hydrolytic precipitation to occur, even in the absence of tartaric acid, but tartaric acid was added to reduce the absorbance caused by molybdenum (*cf.* previous tests), and measurements were made at 430 nm to minimise the effect of molybdenum still further. Under these conditions, the absorbance caused by 0.1 g of molybdenum was equivalent to about 40 p.p.m. of titanium. In applying the procedure to molybdenum samples, therefore, a compensation must be made, for example, by adding an appropriate amount of ammonium molybdate solution to the blank.

RECOMMENDED METHODS

Determination of small amounts (25–250 p.p.m.) of titanium in zirconium, zirconium alloys and hafnium (Note 1)

Determine a reagent blank with each batch of samples and apply the procedure to a duplicate of one of the samples to which has been added 2.0 ml of the standard titanium solution (1 ml = 5 µg Ti) (Note 2). Transfer a 0.1-g sample (Note 3) to a 50-ml beaker, add 2 g of potassium hydrogen sulphate and 2 ml of concentrated sulphuric acid and heat gently, on a hot plate, until the sample has dissolved. Oxidise the solution with 1 ml of concentrated nitric acid added dropwise, evaporate to fumes of sulphuric acid, fume for 5 min, and then cool (Note 4).

Add 10 ml of EDTA solution (5%) to the sample and reference solutions (Note 3), and 10 ml of water (no EDTA) to the blank. Warm gently to dissolve salts, cool, add 5 ml of ammonia solution dropwise, and then cool. Transfer the solution to a 50-ml calibrated flask (rinse the beaker with a minimum volume of water), add 10 ml of the 2% diantipyrinylmethane solution (see EXPERIMENTAL) and dilute to the mark. Allow to stand for 1 h at room temperature, filter if necessary (note 5), then measure the absorbance at a wavelength of 390 nm (Note 6) in 40-mm cells. Deduct the blank value, and calculate the titanium content of the sample by comparison with the reference solution.

Notes. 1. No significant interference is caused by the presence of up to 10% of copper or tin, 1% of aluminium, cadmium, cobalt, lead, magnesium, manganese, nickel, vanadium or zinc, 0.5% of molybdenum, and 0.1% of chromium, iron or uranium.

2. If similar materials are analysed regularly, it is usually more convenient to prepare a standard calibration graph, instead of a reference solution with each batch of samples. If a graph is prepared, the calibration solutions must contain the same amount of parent metal and reagents that are used in the analysis of the sample.

3. In the examination of hafnium, a 0.2-g sample can be used for titanium contents below about 100 p.p.m. Where a 0.1-g sample *of hafnium* is used, reduce the volume of EDTA solution (5%) to 5 ml; 10 ml of the EDTA solution are required for 0.1 g of zirconium, because of its relatively lower atomic weight.

4. If the sample contains above about 0.1% of niobium, tantalum or tungsten, or above about 0.5% of molybdenum, add 1 ml of tartaric acid solution (50%) before adding the EDTA solution.

5. Filtration is usually necessary if alloying amounts of tantalum or tungsten are present, owing to the tendency for salts of these metals to hydrolyse and form insoluble acids during development of the coloured complex.

6. In the presence of above about 0.1% of niobium, or above about 0.5% of molybdenum, measure the absorbance of the blank, reference and sample solutions at a wavelength of 430 nm; this minimises the effect of these metals.

Determination of small amounts of titanium (50–250 p.p.m.) with diantipyrinylmethane in niobium, tantalum, molybdenum and tungsten (Note 1)

Determine a reagent blank with each batch of samples, and apply the procedure to a duplicate of one of the samples to which 2.0 ml of the standard titanium solution (1 ml = 5 μg Ti) has been added (Note 2).

Niobium. Niobium causes a slight increase in absorbance (0.1 g Nb $\simeq$ 10 p.p.m. Ti); when determining levels of titanium at which this effect is significant, add 0.1 g of high-purity niobium to the reagent blank.

Transfer a 0.1-g sample to a 50-ml beaker, add 2 g of potassium hydrogen sulphate and 0.5 ml of concentrated sulphuric acid, heat gently over a burner until the sample has dissolved, and then cool. Add 10 ml of tartaric acid solution (25%), warm until the melt has dissolved, then transfer the solution to a 50-ml calibrated flask; rinse the beaker with a minimum volume of water (Note 1). Add 4 ml of concentrated hydrochloric acid, cool, add 10 ml of the diantipyrinylmethane solution (2%), and dilute to the mark. Allow to stand for 1 h at room temperature, filter if necessary, and measure the absorbance at a wavelength of 430 nm, in 40-mm cells. Deduct the blank value and calculate the titanium content of the sample by comparison with the reference solution.

Tantalum. To compensate for absorbance caused by tantalum (0.1 g Ta $\simeq$ 50 p.p.m. Ti), add 0.1 g of high-purity tantalum to the blank. If the material is in the form of a fine powder, dissolve the sample (0.1 g) as described above for niobium. For coarse materials, *e.g.* drillings or millings, transfer a 0.1-g sample to a small platinum dish, add 1 ml of water, 3 ml of hydrofluoric acid, and 0.5 ml of concentrated nitric acid dropwise, and warm to assist solution of the sample. When the sample has dissolved, cool, add 1 ml of concentrated sulphuric acid, evaporate to fumes of sulphuric acid, continue the evaporation until most of the sulphuric acid has been expelled, and then cool. Add 2 g of potassium hydrogen sulphate, heat gently over a burner until the residue has dissolved, and then cool. Add 10 ml of tartaric acid solution (25%), and continue as described for *Niobium*, but measure the absorbance at a wavelength of 390 nm.

Tungsten. Transfer a 0.1-g sample to a 100-ml conical flask, add 2 g of potassium hydrogen sulphate, heat gently over a burner until the sample has dissolved, and then cool. Add 10 ml of tartaric acid solution (25%) and continue as described under *Niobium*, but measure the absorbance at a wavelength of 390 nm.

Molybdenum. To compensate for absorbance caused by molybdenum (0.1 g $Mo \simeq 40$ p.p.m. Ti), add 0.184 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, to the blank.

Transfer a 0.1-g sample to a 50-ml beaker, add 2 ml of water, then 2 ml of concentrated nitric acid dropwise, and warm gently to assist solution of the sample. After the sample has dissolved, cool the solution, add 1 ml of concentrated sulphuric acid, evaporate to fumes of sulphuric acid, and then cool. Add 10 ml of tartaric acid solution (25%), and continue as described for *Niobium*.

Notes. 1. In the procedure applied to niobium, no significant interference is caused by the presence of up to 20% of tungsten, 10% of molybdenum, 2% of tin, 1% of aluminium, cadmium, cobalt, copper, lead, magnesium, manganese, nickel, tantalum, vanadium or zinc, 0.5% of iron or chromium, or 0.1% of uranium.

Zirconium and hafnium suppress development of the colour, but this effect can be minimised by forming EDTA complexes of these metals. In the presence of 10% of zirconium, or hafnium, add 5 ml of EDTA solution (1%) before adding the 4 ml of concentrated hydrochloric acid; for lower contents, add proportionately less EDTA solution. Under these conditions zirconium still has a significant effect in retarding the development of the colour, and for zirconium contents above about 1%, a 3-h standing period should be allowed before measuring the absorbance.

2. If similar materials are analysed regularly, it is usually more convenient to prepare a standard calibration graph, instead of a reference solution (See Note 2, Method I). When analysing solutions containing alloying amounts of zirconium (or hafnium), an equivalent amount must be added to the calibration solutions, in addition to the parent metal.

APPLICATION

The first recommended method was applied to typical samples of zirconium, zirconium alloys (ZR 20 and ZR 30) and hafnium, containing about 20 p.p.m. of titanium, with and without additions of the equivalent of 50 and 100 p.p.m. of titanium. Typical samples of niobium, with and without additions of the equivalent of 100 p.p.m. and 200 p.p.m. of titanium were examined by the second recommended method. The recoveries of titanium compared favourably with those obtained by the hydrogen peroxide method, but better reproducibilities were obtained by the proposed methods (Table I).

TABLE I

DETERMINATION OF TITANIUM IN VARIOUS MATERIALS

Material	*Titanium (p.p.m.)*		
	Added	*Determined*	
		Diantipyrinylmethane procedure	*Hydrogen peroxide procedure*
Reactor-grade Zirconium	0	25, 27, 27	25, 30, 25
	50	75,	70,
	100	128	125
ZR 20[a]	0	22, 23, 22	25, 25, 20
	50	70	80
	100	125	120
ZR 30[b]	0	23, 25, 22	15, 20, 20
	50	74	75
	100	121	115
Niobium	0	60, 58, 61	55, 65, 60
	100	162	160
	200	265	270

[a] Zirconium + 1.5 % Sn + 0.1 % Fe + 0.1% Cr + 0.05 % Ni.
[b] Zirconium + 0.5 % Cu + 0.5 % Mo.

CONCLUSIONS

This work has shown that a direct procedure, based on the spectrophotometric measurement of the yellow-coloured complex formed by the reaction of titanium ions and diantipyrinylmethane in mineral acid solution, can be satisfactorily applied to the determination of about 20–250 p.p.m. of titanium in 0.1-g samples of zirconium, zirconium alloys and hafnium. Maximum absorbance of the complex occurs at 390 nm.

The presence of zirconium or hafnium suppresses development of the colour, but this effect is eliminated by forming EDTA complexes of these metals in a solution of low acidity. Slight modifications have enabled the procedure to be extended to the determination of titanium in niobium, tantalum, tungsten and molybdenum. Hydrolytic precipitation of niobic, tantalic, and tungstic acids is prevented by forming soluble tartrate complexes of the metals; interference caused by niobium and molybdenum ions is minimised by measuring the absorbance at 430 nm.

The inherent sensitivity of the titanium–diantipyrinylmethane reaction is about twenty times that of the titanium peroxide reaction currently used for determining titanium in the materials under consideration. Full advantage of this higher sensitivity cannot be taken, however, because the weight of sample is restricted to 0.1 g compared, with 0.5 g in the peroxide method. In practice, therefore, the sensitivity of the proposed method is only four times that of the peroxide method.

The method is relatively free from interference by other metal ions. There is no significant interference from up to 0.5% of molybdenum, and the procedure can, therefore, be directly applied to ZR 30 alloy without the preliminary separation of molybdenum that is necessary with the peroxide method.

The proposed method is simple and rapid; about twenty determinations can be completed in a normal working day.

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SUMMARY

The reaction between titanium and diantipyrinylmethane to form a yellow-coloured complex in mineral acid solution, has been successfully applied to the direct spectrophotometric determination of titanium over the range 20–250 p.p.m., in zirconium, zirconium alloys and hafnium. Absorbance of the complex is measured at 390 nm. The proposed method is more sensitive than the peroxide method usually used for determining titanium in these materials. It is also less subject to interference from other metal ions, and can be applied to ZR 30 alloy without preliminary separation of molybdenum. Simple modifications have enabled the procedure to be extended to the determination of titanium in niobium, tantalum, tungsten and molybdenum. In the analysis of materials containing appreciable amounts of niobium or molybdenum, absorbances are measured at 430 nm.

RÉSUMÉ

La réaction entre titane et diantipyrinylméthane formant un complexe jaune, en milieu acide minéral, a pu être appliquée avec succès au dosage spectrophotométrique direct du titane (20 à 250 p.p.m.) dans le zirconium, les alliages de zirconium et d'hafnium. On mesure l'absorption à 390 nm. Cette méthode est plus sensible que celle au peroxyde généralement utilisée. D'autre part, elle présente moins d'interférence avec les autres métaux; elle peut être appliquée à l'analyse de l'alliage ZR 30 sans séparation préalable du molybdène. Quelques modifications permettent le dosage du titane dans le niobium, le tantale, le tungstène et le molybdène; les mesures se font à 430 nm.

ZUSAMMENFASSUNG

Der gelb gefärbte Komplex, den Titan mit Diantipyrinylmethan in mineralsaurer Lösung bildet, wurde erfolgreich zur direkten spektralphotometrischen Bestimmung von 20–250 p.p.m. Titan in Zirkonium, Zirkoniumlegierungen und Hafnium angewandt. Die Absorption des Komplexes wurde bei 390 nm gemessen. Die vorgeschlagene Methode ist empfindlicher als die Peroxydmethode, welche im allgemeinen zur Bestimmung von Titan in diesen Materialien benutzt wird. Sie wird weiterhin nur wenig durch andere Metallionen gestört und kann bei der Analyse der Legierung ZR 30 ohne vorhergehende Abtrennung des Molybdäns verwendet werden. Das Verfahren lässt sich durch einfache Abwandlung auf die Bestimmung von Titan in Niob, Tantal, Wolfram und Molybdän ausdehnen. Bei den Materialien, die Niob oder Molybdän enthalten, wurde die Absorption bei 430 nm gemessen.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF ARSENIC BY AN EXTRACTION METHOD

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A review by SANDELL[1] shows that for the spectrophotometric determination of traces of arsenic, arsenic(III) can be separated from interfering ions by extraction with various solvents. Arsenic has been determined in nickel[2] and various ores[3] by extracting arsenic(III) as iodide in chloroform. All these methods require that arsenic(V), formed by dissolution of the sample in oxidizing acids, be reduced to the trivalent state, extracted in various solvents, reoxidized to the pentavalent state, and then determined as the blue molybdoarsenic acid complex. Also, separation of arsenic by distillation as arsenic(III) chloride or arsine can be used provided that no oxidizing agents are present. This last requirement limits the use of the distillation method in analysis of steels and ferro-alloys, where a lengthy procedure based on iodimetry is used[4]. KOVACS *et al.*[5] have determined arsenic in carbon steels by extracting arsenic(III) with sodium pyrrolidinedithiocarbamate in chloroform and measuring the colour of the organic layer, but the sensitivity is very low.

WADELIN AND MELLON[6] have shown that heteropoly acids of phosphorus(V), silicon, arsenic(V) and germanium can be extracted by various solvents and that *n*-butanol can be used to extract the yellow molybdoarsenic acid, provided that the interferences of the yellow molybdosilicate and yellow molybdophosphoric acid are previously removed. The formation of molybdosilicate can be prevented by increasing the acidity of the solution[7], and molybdophosphoric acid can be removed by extraction into isobutyl acetate[8] without loss of molybdoarsenic acid.

Arsenic has been determined in pure copper by extracting the yellow molybdoarsenic acid into *n*-butanol and measuring the colour directly[9], and in potatoes by reducing the yellow acid to the blue complex with tin(II) chloride[10]. The yellow molybdoarsenic acid has also been extracted with a mixture of *n*-butanol and diethyl ether and measured as the blue complex[11]. In all cases the yellow molybdophosphoric acid was first extracted with a chloroform–*n*-butanol mixture. Isobutyl acetate, which removes interference by silicon and phosphorus, is superior to chloroform–*n*-butanol because four extractions with chloroform–*n*-butanol do not remove the interference of 50 μg of silicon[10], and sub-milligram amounts of phosphorus interfere seriously after two extractions from nitric acid solutions[9].

The present paper describes a detailed investigation of the determination of arsenic at trace levels by extraction of the yellow molybdoarsenic acid with *n*-butanol and subsequent reduction to the blue complex. The method is applicable to the determination of arsenic in waters and in many metals, salts and alloys. Molybdophosphoric acid is removed by two preliminary extractions, either with isobutyl acetate, or with isoamyl alcohol if the solutions contain niobium and titanium. Hydroxylamine hydrochloride is used when oxidizing acids are present or when arsenic has to be determined in certain oxidizing agents, *e.g.*, dichromate, permanganate and cerium(IV) salts.

EXPERIMENTAL

Apparatus and reagents

A Unicam SP 600 spectrophotometer with 2-cm glass cuvettes was used. An E.I.L. Model 23A direct reading pH meter was used. For low pH work, new glass electrodes were left in 1 *N* hydrochloric acid for 24 h.

Demineralized water, further purified by a single distillation in the presence of permanganate, was used throughout.

Standard arsenic(V) solution. Prepare a stock solution containing 0.1 mg As/ml, by dissolving 0.4165 g of disodium hydrogen arsenate heptahydrate in 1 l of 0.04 *M* hydrochloric acid. Prepare a working solution (4 μg As/ml) by diluting 10 ml of stock solution to 250 ml.

Ammonium molybdate solution (5%). Prepare from $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and store in a polythene bottle.

Tin(II) chloride solution. Dissolve 10 g of $SnCl_2\cdot2H_2O$ in 25 ml of hydrochloric acid, and prepare fresh weekly.

Reducing solution. Add 20 ml of 10 *N* hydrochloric acid and 80 ml of water to 0.65 ml of tin(II) chloride solution.

Isobutyl acetate (May and Baker Ltd.; boiling range 115°–120°), isoamyl alcohol (May and Baker Ltd.; boiling range 128°–132°) and *n*-butanol (AnalaR; boiling range 116°–118°) were used.

Recommended procedure

Transfer an aliquot of the acidic sample solution (0–30 μg As) to a 250-ml beaker. Dilute with water to 25 ml. Adjust the pH to 0.10 with 9 *N* sulphuric acid (see also Table II, H_2SO_4 procedure). Add 10 ml of 5% ammonium molybdate solution and let stand for 5 min. Transfer to a 100-ml separating funnel and adjust the volume to 50 ml with water. Add 40 ml of isobutyl acetate, shake for 1 min and let stand for 2 min. Run the aqueous phase into a beaker and discard the organic phase. Repeat the extraction with 40 ml of isobutyl acetate. Return the aqueous phase to the 100-ml separating funnel. Add 25 ml of *n*-butanol, shake for 1 min and let stand for 2 min. Discard the aqueous phase. Add 50 ml of 0.3 *N* sulphuric acid, shake for 30 sec and let stand for 5 min. Transfer the organic phase to a 50-ml separating funnel. Swirl the organic extract to dislodge any water droplets and let stand for 2 min. Then remove the aqueous phase. Add 3 ml of reducing solution to the organic phase, shake for 45 sec and let stand for 5 min.

Run the contents of the funnel into a dry 25-ml volumetric flask, wash the funnel with methanol, and add the washings to the flask. Mix and dilute to volume with methanol. Measure the absorbance after 10 min against a blank at 740 nm in 2-cm cells.

Always make a standard addition of 20 μg of arsenic.

For interference by titanium and niobium in the presence of phosphorus, see p. 229.

DISCUSSION

Solvent extraction

n-Butanol is a very efficient extractant, and more than 99.5% of yellow molybdoarsenic acid is separated with one extraction. The total amount of *n*-butanol for extraction should not exceed 25 ml, otherwise it is not miscible with 3 ml of reducing solution when diluted to 25 ml with methanol. Two preliminary extractions with isobutyl acetate, each of 40 ml, reduce the absorbance of the blue molybdoarsenic acid by only 5%, and the washing step causes a further reduction by 2 to 5% depending on the acid medium.

Sensitivity and stability of the method

The blue molybdoarsenic acid formed in the *n*-butanol–methanol phase has an absorbance plateau in the region of 735–750 nm with a slight maximum at 740 nm. The molar absorptivity of the blue complex is $1.97 \cdot 10^4$ when formed in sulphuric acid and $2.13 \cdot 10^4$ in perchloric acid, corresponding to 0.0038 and 0.0036 As/cm^2, respectively, on the Sandell scale; Beer's law is obeyed to 5 μg As/ml. Solutions containing up to 50 μg of arsenic were used, but the range can be extended to 125 μg of arsenic by using 1-cm cells.

The blue molybdoarsenic acid in *n*-butanol–methanol solution is stable in the investigated temperature range 20°–28° for 2 h. The colour of the blue complex separated from copper solutions shows a slight drop in absorbance on standing, and the absorbance must be measured within 15 min of mixing. Hydroxylamine hydrochloride, being a relatively weak reducing agent compared to tin(II) chloride, does not interfere with the colour development.

Choice of pH and the effect of varying reagent concentrations

Constant absorbance for the blue molybdoarsenic acid is obtained when the yellow molybdoarsenic acid is formed in the investigated range of pH 0.15–1.25. After pH adjustment, a development time of 5 min is sufficient. A final pH of 0.25

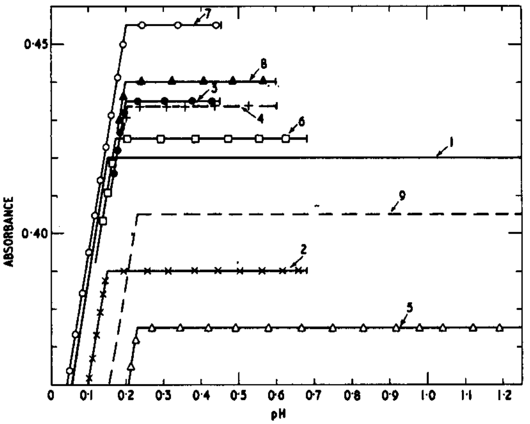

Fig. 1. Effect of salts and pH after ammonium molybdate addition on the absorbance (20 μg As/25 ml). Salts added (1.0 g): (1) standard curve; (2) NH_4Cl; (3) NH_4NO_3; (4) NH_4ClO_4; (5) $(NH_4)_2SO_4$; (6) NaCl; (7) $NaNO_3$; (8) $NaClO_4$; (9) Na_2SO_4.

(5.5 ml of 9 *N* sulphuric acid) after ammonium molybdate addition, is satisfactory even in the presence of 1 mg of silicon and large amounts of sulphates (Fig. 1).

Varying amounts of 9 *N* sulphuric acid were added to the solutions before extraction, and it was found that constant recoveries were obtained when the total amount of 9 *N* sulphuric acid was between 0.75 and 7.0 ml in 50-ml volume. No additional acid should be added before extraction, because the range of acidity for formation and extraction is the same. When the volume before extraction was 65 ml (initial volume 50 ml), the total amount of 9 *N* sulphuric acid necessary for constant recoveries was between 1.0 and 8.0 ml.

The specified amounts of tin(II) and hydrochloric acid in the reducing solution were found experimentally. The stability of the blue molybdoarsenic acid is excellent except when arsenic is determined in solutions containing large amounts of copper. Ascorbic acid or hydroxylamine hydrochloride should not be added to the reducing solutions, because they reduce sensitivity and the reproducibility of the method.

Extraction from media of various acids

Sulphuric acid cannot be used to dissolve all samples likely to be encountered, and other acids will often be required to effect dissolution. Also in many cases sulphuric acid cannot be added to adjust the acidity before extraction, *e.g.*, with white metals, and in other cases it is more advantageous to continue the procedure with one acid only, *e.g.*, nitric acid for copper alloys. Therefore the necessary parameters for various procedures in different acids were determined. A pH meter can be used in the pH adjustment with sulphuric acid, but not with hydrochloric, nitric or

TABLE I

DATA FOR FORMATION AND EXTRACTION OF THE YELLOW MOLYBDOARSENIC ACID
(25 ml initial volume)

	H_2SO_4[a] (9 *N*)	*HCl* (9 *N*)	HNO_3 (9 *N*)	$HClO_4$ (9 *N*)
1. Acid for formation and extraction (ml)	0.75–7.0	3.0–9.5	3.5–9.0	2.5–9.0
2. Acid required when P present (ml)	5.5–7.0	4.5–7.0	4.5–9.0	4.5–9.0
3. Acid required when P and Si present (ml)	5.5–7.0	6.0–7.0[b]	5.0–9.0[b]	7.0–9.0[b]
4. Recommended amount of acid (ml)	5.5[c,d]	6.0[c,d]	6.0[c]	7.5[c]
5. Adjust with acid to pH[e]	0.35 0.25	0.25 0.15	0.25 0.15	0.25 0.15
6. and add 9 *N* acid (ml)[e]	2.5 1.5	4.0 3.5	4.0 3.5	5.5 5.0
7. *n*-Butanol (ml)	25	25	25	25
8. *n*-Butanol washed with 50 ml of	0.3 *N* H_2SO_4[d,f]	0.3 *N* H_2SO_4[d,f]	H_2O	H_2O

[a] For 50-ml initial volume: (1) 1.0–8.0; (2) 6.5–8.0; (3) 6.5–8.0; (4) 7.0; (5) 0.45, 0.35; (6) 2.0, 1.0; (7) and (8) as above.

[b] For 50 ml initial volume (65 ml before extraction) increase the minimum and maximum of the range by 1.0 ml of acid.

[c] When Ge is present, use the highest acidity shown in line 3.

[d] For $CuSO_4$ or $CuCl_2$ solutions, replace 3 ml of 9 *N* acid by 3 ml of 9 *N* nitric acid and wash *n*-butanol with 50 ml of water.

[e] Before addition of ammonium molybdate.

[f] When large amounts of nitrates or perchlorates are present, wash with 50 ml of water.

perchloric acid, because of the large drop in pH on acid addition. The data for the determination in sulphuric, hydrochloric, nitric and perchloric acids are summarised in Table I. When the initial acidity is not known, this procedure calls for a preliminary pH adjustment, followed by the addition of a known amount of acid to obtain the optimum acid concentration for the formation and extraction of the yellow molybdoarsenic acid.

The *n*-butanol extracts various amounts of acids which cause interference (Table II). Water is also extracted and may contain coloured ions which produce a positive interference. These coloured cations, acids and free molybdic acid, which is extracted by *n*-butanol at lower acidities and interferes with the reduction by forming a blue colour, can be removed with an acid or aqueous wash. The amount of aqueous phase extracted into *n*-butanol from perchloric acid, especially at higher acid concentrations, is very large, and an aqueous wash is required before the organic phase is reduced with stannous chloride. The aqueous wash also removes the excess of acid present in the organic phase.

The *n*-butanol layer, when extracted from nitric or perchloric acid, must be washed with water, but 0.3 *N* sulphuric acid is used after extraction from hydrochloric or sulphuric acid to prevent hydrolysis of various metals and formation of emulsions (Table II).

TABLE II

EXTRACTION OF ACIDS BY VARIOUS ORGANIC SOLVENTS

(25 ml initial volume)

Acid added 9 N (ml)		*9 N acid extracted into*		
		Isobutyl acetate (ml)	*n-Butanol (ml)*	*n-Butanol after water wash (ml)*
H_2SO_4	5.5	0.00	0.3	0.02
HCl	6.0	0.01	0.8	0.03
HNO_3	6.0	0.25	1.3	0.11
$HClO_4$	7.5	0.08	2.2	0.33

Extraction of molybdophosphoric acid with isoamyl alcohol

The yellow molybdophosphoric acid cannot be extracted completely with isobutyl acetate from solutions containing titanium, niobium and tantalum ions[8,12]. Even amounts as small as 1 μg of titanium and niobium when associated with phosphorus cause appreciable positive interference. Niobium and titanium form strong complexes with phosphorus and molybdate, which are not extracted completely by isobutyl acetate but are extracted together with the yellow molybdoarsenic acid by *n*-butanol. This interference can be overcome by extracting the yellow molybdophosphoric acid complex with two aliquots, one 15 ml and one 10 ml, of isoamyl alcohol from sulphuric acid medium. The extraction can be carried out from solutions containing sulphuric acid (7 ml of 9 *N* sulphuric acid in a 50-ml initial volume) or from mixed acids containing a minimum amount of 5 ml of 9 *N* sulphuric acid. The recoveries from mixed acids decrease with reduction in the sulphuric acid concentration. Extractions from solutions containing only hydrochloric, nitric or perchloric acids give very low recoveries. Some yellow molybdoarsenic acid is also extracted and the absorbance of the blue molybdoarsenic acid, when 7 ml of 9 *N* sulphuric acid is used, is 75%, when compared with results obtained by the recommended procedure.

Standard addition

The change in absorbance depends on the cations and anions present, and also on the residual amounts of yellow molybdophosphoric acid and molybdosilicate extracted by the *n*-butanol (Table III). The standard addition procedure is used to correct for various effects arising from sample dissolution or extraction procedure.

A standard addition must be made for each determination, and the pH or acidity for the formation of the yellow molybdoarsenic acid in all aliquots must be strictly controlled. The proportionality of absorbance for the standard addition of 20 and 40 μg of arsenic was used to establish the feasibility of the method under various conditions. Tolerance levels were established for various ions and salts by the standard addition procedure (Table III).

Blanks

The blanks were low, depended on the acid medium used, and were between −0.010 and 0.015 absorbance units when measured against water.

Study of interferences

Because of the high acidity selected for the formation and extraction of the yellow molybdoarsenic acid, few modifications are necessary for determining arsenic in the presence of most cations and anions (Table III). In any determination the amount of any metal should not exceed 250 mg. When larger amounts of cations are taken, the initial volume should be increased to 50 ml. However some modifications are necessary when the following ions are present:

Antimony and bismuth require the addition of 0.2 g of tartaric acid for each 0.1 g of ion, to prevent hydrolysis.

Cerium must be present in the trivalent state which can be achieved by reduction with hydroxylamine hydrochloride.

TABLE III

EFFECT OF VARIOUS ELEMENTS

(Standard addition of 20 and 40 μg of As, no P added)

Foreign ion	*Amount taken (g)*	*Added as*[a]	*Absorbance (20 μg As)*	*Acid medium (Table I)*
—	—	—	0.420	H_2SO_4
—	—	—	0.445	HCl
—	—	—	0.455	HNO_3 or $HClO_4$
Al^{3+}	0.5	$Al(NO_3)_3 \cdot 9H_2O$	0.430	H_2SO_4
Bi^{3+}	0.25	$Bi(NO_3)_3 \cdot 5H_2O$[b]	0.410	HCl
BO_3^{3-}	1.5	H_3BO_3[c,g]	0.420	H_2SO_4
Ce^{4+}	0.25	$(NH_4)_2Ce(NO_3)_6$[d]	0.430	H_2SO_4
Co^{2+}	0.25	$Co(NO_3)_2 \cdot 6H_2O$	0.465	HNO_3 or $HClO_4$
Co^{2+}	0.25	$Co(NO_3)_2 \cdot 6H_2O$	0.420	H_2SO_4
Cr^{3+}	0.25	$CrCl_3 \cdot 6H_2O$	0.410	HCl
Cu^{2+}	0.25	$CuSO_4 \cdot 5H_2O$[e]	0.465	H_2SO_4–HNO_3
Cu^{2+}	0.25	$Cu(NO_3)_2 \cdot 3H_2O$	0.465	HNO_3

TABLE III (Continued)

Foreign ion	*Amount taken (g)*	*Added as*[a]	*Absorbance (20 μg As)*	*Acid medium (Table I)*
Cu^{2+}	0.25	$CuCl_2 \cdot 2H_2O^{e}$	0.470	HCl–HNO_3
F^-	0.20	$HF^{c,f}$	0.350	H_2SO_4
F^-	0.20	$HF^{c,f,g}$	0.420	H_2SO_4 or HNO_3
Fe^{3+}	0.25	$Fe(NO_3)_3 \cdot 9H_2O^{h}$	0.460	H_2SO_4
Fe^{3+}	0.25	$Fe(NO_3)_3 \cdot 9H_2O$	0.460	HNO_3 or $HClO_4$
Fe^{3+}	0.25	$FeCl_3$ (60% soln.)	0.460	HCl
Ge(IV)	0.0001	Metal[i]	0.420	H_2SO_4
Mn^{2+}	0.25	$KMnO_4^{j}$	0.430	H_2SO_4
Nb(V)	0.006	Metal[c,k]	0.295	H_2SO_4
Nb(V)	0.006	Metal[c,k,l,m]	0.175	H_2SO_4
Ni^{2+}	0.25	$NiSO_4 \cdot 6H_2O$	0.430	H_2SO_4
P(V)	0.0001	KH_2PO_4	0.435	H_2SO_4
P(V)	0.0003	KH_2PO_4	0.450	H_2SO_4
P(V)	0.0005	KH_2PO_4	0.470	H_2SO_4
Pb^{2+}	0.25	$Pb(NO_3)_2$	0.450	HNO_3
Sb(V)	0.25	Metal[b,n]	0.410	HCl
Se(IV)	0.0005	Na_2SeO_3	0.420	H_2SO_4
Si(IV)	0.001	Na_2SiO_3	0.430	H_2SO_4
Si(IV)	0.001	$Na_2SiO_3^{o}$	0.460	H_2SO_4
Si(IV)	0.001	$Na_2SiO_3^{p}$	0.500	H_2SO_4
Sn(IV)	0.25	Metal	0.420	HCl
Th^{4+}	0.25	$Th(NO_3)_4 \cdot 4H_2O$	0.475	H_2SO_4
Ti^{4+}	0.020	$Ti(SO_4)_2$ soln.	0.450	H_2SO_4
Ti^{4+}	0.005	$Ti(SO_4)_2$ soln.[l,m,r]	0.300	H_2SO_4
U(VI)	0.25	$UO_2(NO_3)_2 \cdot 6H_2O$	0.440	H_2SO_4
V(V)	0.020	$NH_4VO_3^{q}$	0.465	H_2SO_4
V(V)	0.001	$NH_4VO_3^{l,q}$	0.470	H_2SO_4
V(V)	0.050	$NH_4VO_3^{l,m,q}$	0.300	H_2SO_4
W(VI)	0.003	$Na_2WO_4 \cdot 2H_2O$	0.310	H_2SO_4
W(VI)	0.003	$Na_2WO_4 \cdot 2H_2O^{c,k,m}$	0.280	H_2SO_4
Zr^{4+}	0.20	$ZrOCl_2 \cdot 8H_2O^{g,k}$	0.420	H_2SO_4

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[a] Add 1 ml of 10% $NH_2OH \cdot HCl$ to all salts when present as nitrates or perchlorates.
[b] Add 0.2 g of tartaric acid to each 0.1 g of ion.
[c] Initial volume 50 ml.
[d] Reduce with 1 ml of 10% $NH_2OH \cdot HCl$.
[e] Replace 3 ml of 9 *N* H_2SO_4 with 3 ml of 9 *N* HNO_3, and wash *n*-butanol with 50 ml of water
[f] Add 7.5 ml of 4% H_3BO_3 for every 0.1 ml 40% HF.
[g] Wash *n*-butanol with water.
[h] 6 p.p.m. As in salt.
[i] For all acid media use highest acid concentration.
[j] Reduce with 2.5 ml of 10% $NH_2OH \cdot HCl$.
[k] Add 0.2 ml of 40% HF and 15 ml of 4% H_3BO_3.
[l] Add 200 μg P.
[m] Extract with 15 and 10 ml of isoamyl alcohol.
[n] 280 p.p.m. As.
[o] Add 4.5 ml of 9 *N* H_2SO_4.
[p] Add 4.0 ml of 9 *N* H_2SO_4.
[q] Add 2 ml of 10% $NH_2OH \cdot HCl$, boil for 2 min.
[r] 5 mg Ti ≡ 0.015 abs. units.

Copper when extracted from sulphate or chloride systems interferes in the final reduction stage by causing low and irreproducible results. This can be avoided by replacing 3 ml of 9 *N* sulphuric or hydrochloric acid with 3 ml of 9 *N* nitric acid. The *n*-butanol phase is then washed with 50 ml of water. It is possible to determine arsenic in a sample aliquot containing 0.1 g of copper as sulphate after extraction from sulphuric acid medium, but 0.1 ml of 40% sodium nitrate must be added to the *n*-butanol phase before reduction with tin(II) chloride. This procedure was used for checking the results for cupro-nickel sample BCS 180/1. The sample was analysed as recommended for steels when it was suspected that the high result was caused by interference from titanium, vanadium or niobium. However, the same arsenic content was found by the two different procedures (Table IV).

Hydrofluoric acid is added after dissolution to hold some metals (zirconium,

TABLE IV

SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC IN VARIOUS MATERIALS

Sample		*Certified As (%)*	*As found (%)*	*Absorbance on standard addition (20 μg As)*
Manganese brass	BCS 179	0.03	0.0239	0.475
Bronze	BCS 207/1	0.052	0.0512	0.465
Bronze	BCS 183/3	0.14	0.135	0.470
Cupro-nickel	BCS 180/1	0.006	0.013	0.465[a]
			0.013	0.310[a,b]
White metal (Sn based)	NBS 54d	0.088	0.090	0.450
White metal (Sn based)	BCS 178	0.04 (0.03–0.07)	0.0308	0.455
White metal (Pb based)	BCS 177	0.06	0.0602	0.455
White metal (Pb based)	BCS 177/1	$<$0.005 (0.001–0.01)	0.0060	0.430[a]
Antimony powder		—	0.0280	0.410
Ni–Cr–Mo steel	BCS 219/2	0.034	0.034	0.315
Ni–Cr–Mo steel	BCS 225/2	0.035	0.033	0.315
Cr–V steel	BCS 224	0.030	0.031	0.310
"18-8" stainless + Ti	BCS 235/1	—	0.020	0.290
Permanent magnet + Ti	BCS 233	—	0.024	0.290
Permanent magnet + Nb	BCS 312	—	0.013	0.300
7W–5Mo steel	BCS 220/1	0.030	0.030	0.300
			0.030	0.195[c]
Nb–Mo "18-12" stainless steel	BCS 246	—	0.022	0.290
Turbine steel (6W–3Nb)	SAA 125	—	0.022	0.270
			0.023	0.215[c]
Low alloy steel	NBS 1161	0.028	0.029	0.310
Low alloy steel	NBS 1162	0.046	0.046	0.310
Low alloy steel	NBS 1163	0.10	0.107	0.320
Low alloy steel	NBS 1164	0.018	0.017	0.300
Ingot iron	NBS 1165	0.010	0.010	0.270
Ingot iron	NBS 1166	0.014	0.014	0.270
Low alloy steel	NBS 1167	0.14	0.141	0.320
Low alloy steel	NBS 1168	0.008	0.009	0.270
Ferro-manganese	BCS 208	0.027 (0.02–0.031)	0.032	0.310
Ferro-molybdenum	BCS 231/2	—	0.011	0.300[c]
Ferro-vanadium	BCS 205	—	0.017	0.310

[a] 25 ml aliquot.
[b] Analysed as for steels, 0.1 ml of 400 mg $NaNO_3$ per ml solution added before reduction.
[c] After fuming 2 ml of HF added (complete dissolution method).

tungsten and niobium) in solution during the formation of the yellow molybdoarsenic acid. Free fluoride interferes with the determination of arsenic and 7.5 ml of 4% boric acid must be added for each 0.1 ml of 40% hydrofluoric acid to complex fluoride. The addition of boric acid to the sample aliquot produces lower recoveries, when the *n*-butanol phase is washed with 0.3 *N* sulphuric acid. The recoveries can be increased by washing the organic phase with water only.

Germanium. Molybdogermanic acid is formed at lower acidities than molybdosilicic acid and interferes unless the acidities are kept at the maximum of the range (Table I). Even then the maximum amount of germanium is limited to 100 μg per sample aliquot.

Niobium can be either filtered off as niobium pentoxide, after which the standard procedure can be used, or rendered soluble with hydrofluoric acid. In the second case two extractions, one 15 and one 10 ml, of isoamyl alcohol from sulphuric acid medium are required. The amount of niobium as fluoride is limited to 6 mg per aliquot.

Phosphorus gives a slight interference even after two preliminary extractions of the yellow molybdophosphorus acid with isobutyl acetate. The standard addition procedure corrects for the interference because the interference is proportional to the amount of arsenic present. The maximum amount of phosphorus is 500 μg per sample aliquot.

Silicon interference is negligible, because the yellow molybdoarsenic acid is formed at a much lower pH than that necessary for the formation of the yellow molybdosilicate complex[7].

Sodium and ammonium salts in amounts up to 1 g do not cause any interference. The *n*-butanol phase, after extraction from salts of nitrates and perchlorates, is washed with 50 ml of water (Table I, H_2SO_4 procedure).

Thorium solutions may form precipitates during adjustment of the pH. This can be overcome by adding 1 g of sodium sulphate to the sample aliquot for each 0.25 g of thorium.

Titanium as the molybdophosphoric acid complex can be extracted from sulphuric acid medium with two extractions, one 15 and one 10 ml, of isoamyl alcohol. Even then a small amount of this complex remains, and is extracted with the *n*-butanol causing slight interference (5 mg Ti$\equiv$0.015 abs. units).

Tungsten can be either filtered off as tungstic acid or rendered soluble with hydrofluoric acid. Because tungsten reduces the absorbance greatly, its amount should be kept below 6 mg per aliquot. Tungsten hydrolyses on standing in solutions containing boric acid, and therefore in the complete dissolution procedure for steels, the volumes were kept large to delay the formation of tungstic acid.

Vanadium(V) must be reduced to the tetravalent state to avoid the formation of molybdovanadophosphoric acid, which is not extracted completely by isobutyl acetate, but is extracted with *n*-butanol; 2 ml of 10% hydroxylamine hydrochloride is added and the solution is boiled for 2 min. It is then cooled, ammonium molybdate is added and the recommended procedure followed.

Zirconium must be held in solution with fluoride ion (0.2 g of zirconium requires 0.4 ml of 40% HF). Solutions containing phosphate and zirconium must be boiled with hydrofluoric acid in a Teflon beaker to form the zirconium fluoride complex and thus release phosphate for reaction with molybdate.

Hydroxylamine hydrochloride is used in the modified procedure to allow the determination of arsenic in the presence of cerium and vanadium, in solutions containing nitrates, perchlorates or oxidizing agents, and in oxidizing reagents such as potassium permanganate and potassium dichromate. It is recommended that 1 ml of 10% hydroxylamine hydrochloride be used as a general reducing agent for any oxidizing agents in solution.

Reproducibility of the method

Readings on a series of 10 standards showed the relative standard deviation at the 0.8 μg As/ml level (final solution) to be ±0.6%.

APPLICATIONS

The results obtained for a variety of materials are shown in Table IV.

It was found that when copper alloys are analysed it is important to add 10 ml of 10 *N* hydrochloric acid before the addition of 15 *N* nitric acid. Dissolution in 15 *N* nitric acid resulted in a very fast reaction and the arsenic results were low.

A general method for the determination of arsenic in steels is given which takes care of all types of steel and ferro-alloys. This method is recommended in all cases where the composition of the steel or ferro-alloy is unknown, because in the presence of 20 μg of phosphorus, 1 μg of vanadium(V) gives an error of 10%, 1 μg of titanium produces 20%, and 1 μg of niobium an exceptionally large error when the yellow molybdophosphoric acid is extracted with isobutyl acetate. Vanadium is reduced by boiling for 2 min with hydroxylamine hydrochloride, niobium and tungsten oxides are filtered off or dissolved with hydrofluoric acid, and the yellow molybdophosphoric acid is extracted with isoamyl alcohol. Steel samples must not be dissolved in hydrofluoric acid because on fuming with perchloric acid up to 20% losses of arsenic have been noted. Germanium in amounts of up to 100 μg does not interfere. Although a 10-ml aliquot of sample BCS 220/1 (7W–5Mo) gave an absorbance of only 0.195 for the standard addition of 20 μg of arsenic, this result was reproducible each time the determination was repeated.

Brass, bronze and cupro-nickel

Weigh 0.5 g of sample into a 250-ml beaker, and add 10 ml of hydrochloric acid followed by 10 ml of nitric acid. After dissolution, boil to expel nitrous oxides, add 2 ml of 20% hydrogen peroxide and boil for 1 min. Cool, transfer the sample to a 100-ml volumetric flask and dilute to volume (10 ml contain 2.5 ml of 9 *N* acid). Pipette an aliquot containing 15–25 μg of arsenic into a 250-ml beaker and add 9 *N* nitric acid to increase the total acidity to 6 ml of 9 *N* acid. Add 1 ml of 10% hydroxylamine hydrochloride, dilute to 25 ml and add 10 ml of ammonium molybdate with stirring. Continue as in the recommended procedure. Wash the organic phase with 50 ml of water. Prepare a blank and make a standard addition of 20 μg of arsenic.

White metal (lead or tin based)

Weigh 0.5 g of sample into a 250-ml beaker, add 25 ml of hydrochloric acid and then 5 ml of 20% hydrogen peroxide immediately. Heat to boiling and add further aliquots of 20% hydrogen peroxide in 1-ml lots until the sample has dissolved.

The small amount of residue can be dissolved by the addition of 0.5 ml of nitric acid. Dilute to 80 ml with water and heat to boiling. Cool, add 5 ml of 20% tartaric acid, transfer (filter if necessary) to a 100-ml volumetric flask and dilute to volume (10 ml contain 2.5 ml of 9 *N* acid). Pipette an aliquot containing 15–25 µg of arsenic into a 250-ml beaker and add 9 *N* hydrochloric acid to increase the total acidity to 6 ml of 9 *N* acid. Add 1 ml of 10% hydroxylamine hydrochloride. Dilute to 25 ml and add 10 ml of ammonium molybdate. Continue as in the recommended procedure, except for one isobutyl acetate extraction. Prepare a blank and make a standard addition of 20 µg of arsenic.

Antimony

Weigh 2.5 g of sample into a 250-ml beaker, add 15 ml of nitric acid and heat to boiling. After reaction ceases, add 30 ml of hydrochloric acid and boil until the precipitate dissolves. Cool, add 25 ml of 20% tartaric acid, transfer to a 100-ml volumetric flask and dilute to volume (10 ml contain 5 ml of 9 *N* acid). Pipette an aliquot containing 15–25 µg of arsenic and not more than 250 mg of antimony into 250-ml beaker. Continue as in the case of white metal.

Bismuth

Weigh 2.5 g of sample into a 250-ml beaker, add 15 ml of nitric acid and heat to dissolve. Add 2 ml of 20% hydrogen peroxide and boil for 1 min. Cool, add 25 ml of 20% tartaric acid, transfer to a 100-ml volumetric flask and dilute to volume (10 ml contain 2.5 ml of 9 *N* acid). Pipette an aliquot containing 15–25 µg of arsenic and not more than 250 mg of bismuth into a 250-ml beaker. Continue as in the case of white metal.

Steels, permanent magnets, ferro-manganese and ferro-vanadium

Weigh 0.5 g of sample into a 250-ml beaker and add 10 ml of hydrochloric and 10 ml of nitric acid. After dissolution, add 13 ml of perchloric acid and evaporate to fumes. Cover the beaker with a watch-glass and fume so that the perchloric acid refluxes on the side of the beaker for 5 min. Cool, add 25 ml of 9 *N* sulphuric acid, 15 ml of water and 2 ml of 10% hydroxylamine hydrochloride, and boil for 2 min. Cool. Filter into a 100-ml volumetric flask and dilute to volume (10 ml contain 3.5 ml of 9 *N* acid). Pipette an aliquot (not more than 20 ml) containing 15–25 µg of arsenic into a 250-ml beaker and add 9 *N* sulphuric acid to increase the total acidity to 7 ml of 9 *N* acid. Dilute to 50 ml and add 10 ml of ammonium molybdate. Continue as in the recommended procedure except for the extraction of the yellow molybdophosphoric acid with isoamyl alcohol, one 15 ml and one 10 ml aliquot. Wash the organic phase with 50 ml of water. Prepare a reagent blank and make a standard addition of 20 µg of arsenic.

Ferro-molybdenum and steels (complete dissolution of silica, tungstic acid and niobium pentoxide)

Weigh 0.5 g of sample and treat as in the case of steels. After fuming, add 25 ml of 9 *N* sulphuric acid, 15 ml of water, 2 ml of 10% hydroxylamine hydrochloride and 2 ml of 40% hydrofluoric acid, and boil for 2 min. Cool, transfer to a 250-ml volumetric flask containing 150 ml of saturated boric acid and dilute to volume (25 ml contain 3.5 ml of 9 *N* acid). Pipette an aliquot (not more than 50 ml) containing

15–25 μg of arsenic into a 250-ml beaker. Add 9 *N* sulphuric acid to increase the total acidity to 7 ml of 9 *N* acid. Dilute to 50 ml and continue as in the case of steels.

It is a pleasure to acknowledge the assistance given by Mrs. B. McALLISTER with the experimental work.

SUMMARY

A general method is presented for the spectrophotometric determination of arsenic at trace levels. It involves extraction of the yellow molybdoarsenic acid with *n*-butanol and subsequent reduction to the blue complex. The yellow molybdophosphoric acid is removed by a preliminary extraction with isobutyl acetate or isoamyl alcohol. A comprehensive study of interferences was carried out and modifications are described which permit the determination of arsenic in a wide variety of salts, white metals, copper alloys and all types of steels.

RÉSUMÉ

Une méthode générale est proposée pour le dosage spectrophotométrique de l'arsenic à l'état de traces. Elle consiste en une extraction de l'acide arsénomolybdique à l'aide de *n*-butanol et réduction en complexe bleu. L'acide phosphomolybdique jaune est séparé par extraction préliminaire au moyen d'acétate d'isobutyle et d'alcool isoamylique. On a examiné les interférences possibles. Les modifications décrites permettent le dosage de l'arsenic dans une grande variété de sels, de métaux blancs, d'alliages de cuivre et tous les types d'aciers.

ZUSAMMENFASSUNG

Es wird eine allgemeine Methode zur spektralphotometrischen Bestimmung von Spuren Arsen vorgeschlagen. Dabei wird die gelbe Molybdoarsensäure mit *n*-Butanol extrahiert und anschliessend zum blauen Komplex reduziert. Durch eine vorhergehende Extraktion mit Isobutylacetat oder Isoamylalkohol wird die gelbe Molybdophosphorsäure beseitigt. Störmöglichkeiten werden eingehend untersucht und Abwandlungen der Methode beschrieben, welche die Bestimmung von Arsen in einer grossen Zahl von Salzen, Weissmetallen, Kupferlegierungen und alle Arten von Stählen erlauben.

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HYDROGEN FLAME CHEMILUMINESCENCE DETECTOR FOR SULFATE IN AQUEOUS SOLUTIONS

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Previously developed methods for the analysis of sulfate in aqueous solution have employed color-developing reagents[1,2], titration[3], turbidimetry[4], or nephelometry[5]. When these methods are used for manual analysis of individual samples, they are tedious and time-consuming. Even when they are applied to automatic instrumental analysis, reagent preparation and stability can present problems. Instrumental analysis for sulfate by atomic absorption[6] has just recently been proved feasible at concentrations above 10 μg/ml.

The approach described in this paper is the development of a laboratory instrument that can be used easily and rapidly to analyze aqueous samples specifically for sulfate. SYTY AND DEAN[7] have recently disclosed an instrument for the detection of sulfur and phosphorus by a similar technique.

The present instrument, based on the principle of chemiluminescence of sulfur in a hydrogen-rich hydrogen–air flame, has been developed by modifying similar instruments[8–11] previously used in these laboratories. This new prototype instrument, which is operated in the same simple manner as other flame photometric and atomic absorption instruments, is demonstrated to be of specific value in the hydrogen peroxide method for sulfur dioxide analysis[12].

EXPERIMENTAL

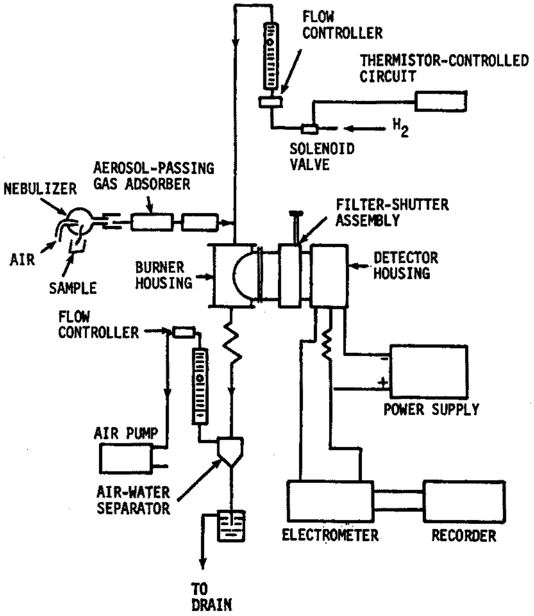
Apparatus

Figure 1 is a block diagram illustrating the relationship among instrument components. With the exception of the sample inlet system, the instrument is the same as the one previously described[10].

A Vaponefrin standard nebulizer was modified by extending the liquid take-up tube through the glass enclosure. This modification afforded a simple method for sample introduction and greatly facilitated rinsing of the nebulizer between samples.

The aerosol-passing gas adsorber (APGA) illustrated in Fig. 2 is a device designed to remove water selectively from the nebulized sample while permitting passage of the non-volatile sulfate particles to the detector. Maintaining a low humidity at the surface of the adsorber passage causes water in the aerosol to evaporate rapidly as it passes through.

Because of large differences between diffusion rates of the vapor and particles in the airstream, the water vapor quickly diffuses to the potassium hydroxide and magnesium perchlorate absorbents, whereas the sulfate particles are passed through unaffected. This APGA is a modification of one previously used successfully in our laboratories to remove sulfur dioxide selectively while allowing airborne droplets of sulfuric acid to pass into a sulfur detector.



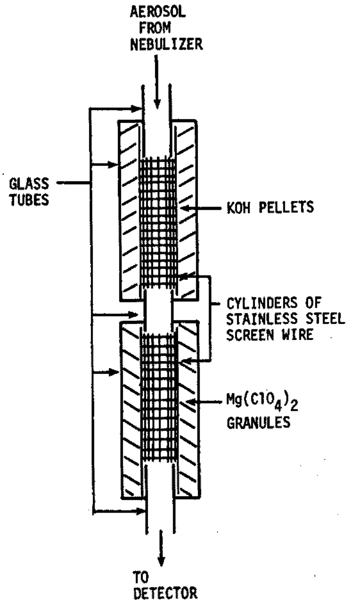


Fig. 1. Block diagram of apparatus.

Fig. 2. Aerosol-passing gas adsorber.

Reagents

Prepurified grade hydrogen fuel was used. The nebulizer and burner were supplied with pure air from a compressed gas cylinder. All sensitivity and calibration determinations were made with reagent-grade chemicals dissolved in distilled, deionized water.

Operating parameters

Recent work in this laboratory has indicated that maximum response to sulfur-containing compounds with minimum interference from other compounds was obtained with this burner when operated at a high hydrogen-to-oxygen ratio[11]. For this study the burner was operated at an hydrogen:oxygen ratio of 4.6, the highest ratio to give a stable flame. Air flow to the burner was 500 ml/min and hydrogen flow was 460 ml/min.

The nebulizer was operated at an inlet pressure of 10 psig. Under this condition, aqueous solutions were aerosolized at a rate of 0.2 ml/min with a total air flow of 4.9 l/min. The sample, in excess of that required by the burner, was exhausted through a hood.

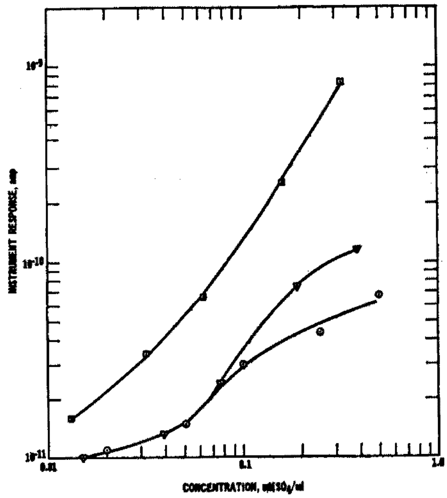
Procedure

Because the burner-detector used in this study responds sluggishly to sulfur-containing samples, a timed response rather than an equilibrium response was employed in all calibration and interference measurements. The procedure consisted of spraying the aqueous sample into the inlet for 30 sec, and determining the response. A stable baseline was allowed to be re-established (2–5 min) before the next sample was sprayed. The nebulizer was thoroughly rinsed with deionized, distilled water between samples. The average of duplicate measurements was used for each calibration determination.

The effectiveness of the APGA in increasing the sensitivity of the sulfate detector was determined by comparing the sulfuric acid calibration curve obtained with the APGA, with the sulfuric acid calibration curve obtained with a plain glass tube having the same length and internal diameter as the APGA. This comparison was made over the concentration range 10–50 μg/ml.

RESULTS AND DISCUSSION

Figure 3 illustrates the 30-sec responses obtained over a concentration range 2–50 μg/ml for sulfuric acid, ammonium sulfate and copper sulfate. In previous hydrogen flame studies, vapors other than those containing sulfur were demonstrated to have either an intensifying or quenching effect on gaseous sulfur chemiluminescence intensity[10]. The data presented in Fig. 3 indicate that other elements or radicals in solution with sulfate affect the intensity of sulfate chemiluminescence. Because copper sulfate gives a higher response than the other two sulfates, copper nitrate was tested as an intensifying agent. This compound, which alone in solutions as



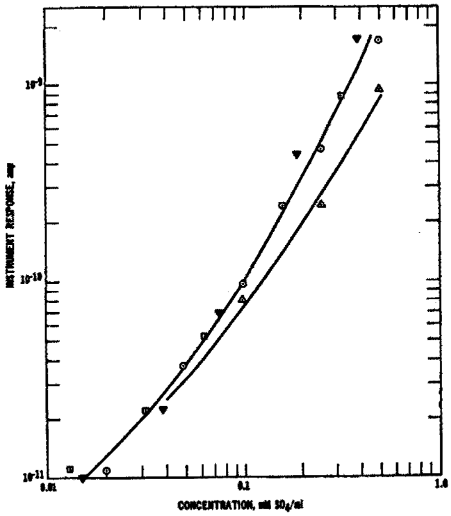


Fig. 3. Instrument calibration for sulfates in aqueous solutions. ⊙ H_2SO_4 with APGA; △ $(NH_4)_2SO_4$ with APGA; ⊡ $CuSO_4$ with APGA.

Fig. 4. Instrument calibration with 100 μg $Cu(NO_3)_2$ per ml of sulfate solution. ⊙ H_2SO_4 with APGA; ▼ $(NH_4)_2SO_4$ with APGA; ⊡ $CuSO_4$ with APGA; △ H_2SO_4 with plain inlet tube.

concentrated as 1,000 μg/ml, does not give any response, intensifies the emission of non-copper-containing sulfate solutions. A copper-to-sulfate mole ratio of between 1 and 2 in copper nitrate solutions of ammonium sulfate and sulfuric acid was found to give maximum intensification. At lower mole ratios, the intensifying effect dropped off sharply while at mole ratios as high as 10 the intensifying effect was only slightly reduced.

Figure 4 illustrates that by adding 100 μg of copper nitrate per ml to each of the concentrations of the three sulfate compounds, these calibration curves are now practically indistinguishable from each other. The effectiveness of the APGA in increasing instrument sensitivity to aerosols of aqueous sulfuric acid solutions is also illustrated by this Figure. At the higher concentrations, this twofold increase in sensitivity over the plain glass inlet tube is accomplished by removing water from the aqueous aerosol before it reaches the flame.

The precision with which sulfate concentrations can be determined by the use of this instrument was determined by comparing seven repetitive 30-sec responses to a solution containing 50 μg of sulfuric acid per ml. The extreme values among these seven determinations were within ±10% of the mean.

The detection limit of this instrument for aqueous sulfuric acid solutions is estimated to be 2 μg/ml (equivalent to 0.03 p.p.m. of sulfur dioxide collected in 75 ml of adsorbing reagent at a sampling rate of 28 l/min over a 1-h period). This estimate was obtained by extrapolating the calibration curve to the concentration that gives a response of $1.0 \cdot 10^{-11}$ A, which is twice the mean peak-to-peak background fluctuation.

In the selected hydrogen peroxide method for sulfur dioxide determination, the presence of strongly acidic or basic gases such as nitrogen dioxide, hydrogen chloride and ammonia is expected to give interference[12]. This instrument gave no detectable response to aqueous solutions of hydrochloric or nitric acid in concentrations as high as 1,000 μg/ml. In cases of simultaneous or sequential sampling of ammonia and sulfur dioxide, it is expected that ammonium sulfate will be a reaction product in the sampler. These data demonstrate that this instrument does not detect the normally expected gaseous interferents.

In comparing this instrumental aqueous sulfate detector to the NAPCA turbidimetric barium sulfate method selected to be specific for sulfate[13], it was found that this instrument is competitive in sensitivity with both the turbidimetric (50 μg sulfate) and nephelometric (2 μg of sulfate) analytical procedures. Analyses for sulfate can be made much more easily and quickly by the instrument described in this paper than by the selected barium sulfate method.

The feasibility of extending this sulfate analytical technique toward more general applications was investigated. While solutions of ammonium nitrate and sodium chloride in concentrations as high as 100 μg/ml gave no positive response, sodium chloride did depress the response of the three sulfates when mixed in solutions with them. Consequently, in applying flame chemiluminescence to general aqueous sulfate analysis, it may be necessary to develop an indirect method specific for the type of sample being studied.

By selecting appropriate burner operating conditions and optical filters, it is expected that this instrument can be used to detect selectively low concentrations of phosphates, chlorides, bromides, and iodides as well as sulfates in aqueous solution.

Consequently, it should be a valuable supplement to atomic absorption instruments, which are not capable of detecting these compounds[14].

SUMMARY

The instrument described is capable of detecting sulfate ion in aqueous solution at concentrations as low as 2 μg of sulfate per ml of solution. It is demonstrated to be of potential value for use as a specific sulfate analyzer in the hydrogen peroxide determination of sulfur dioxide. When used in conjunction with this analytical procedure, the detection limit for sulfur dioxide collected in 1-h samples is estimated to be 0.03 p.p.m. (v/v). Advantages over other methods presently in use are discussed.

RÉSUMÉ

L'appareil décrit permet de déceler les sulfates en solution aqueuse à des concentrations descendant jusqu'à 2 μg sulfate par ml de solution. Il convient également comme "analyseur" de sulfate spécifique lors du dosage de l'anhydride sulfureux au moyen de peroxyde d'hydrogène. Utilisé en relation avec ce procédé, la limite de détection pour des échantillons de SO_2 recueilli en une heure est estimée à 0.03 p.p.m. (v/v). On examine les avantages sur d'autres méthodes actuellement en usage.

ZUSAMMENFASSUNG

Es wird ein Gerät beschrieben, das fähig ist, Sulfationen in wässriger Lösung bei Konzentrationen von weniger als 2 μg Sulfat/ml Lösung, nachzuweisen. Es eignet sich als spezifischer Sulfatanalysator bei der Wasserstoffperoxydmethode zur Schwefeldioxidbestimmung. In Verbindung mit diesem analytischen Verfahren ergibt sich eine Nachweisgrenze für Schwefeldioxid von 0.03 p.p.m. (v/v). Vorteile gegenüber anderen Methode werden diskutiert.

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QUELQUES CONSIDERATIONS SUR LE DOSAGE DE L'HAFNIUM DANS LE ZIRCONIUM ET SES ALLIAGES PAR FLUORESCENCE X

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Les propriétés chimiques du zirconium et de l'hafnium étant très similaires, le dosage de faibles teneurs d'hafnium dans le zirconium n'est, en règle générale, pas facile.

Or, le zirconium à usage nucléaire ne peut renfermer plus que 200 p.p.m.[1] d'hafnium. Pour contrôler cette spécification, différentes méthodes physiques ont été proposées: l'analyse par activation[2], la spectrographie d'émission[3] et la spectrographie aux rayons X[4]. Toutes offrent cependant des difficultés à ces niveaux de concentration. L'analyse par activation nécessite, soit une séparation chimique préalable, opération longue et délicate, soit la manipulation d'un matériel irradié et par conséquent fortement activé. L'analyse par spectrographie d'émission de l'échantillon tel quel, c'est-à-dire sans séparation préalable, ne dépasse guère une limite de sensibilité de l'ordre de 50 p.p.m. Enfin, dans le cas de la spectrographie aux rayons X, les interférences provenant des raies de deuxième ordre du zirconium avec les raies analytiques de l'hafnium ($L\alpha$ et $L\beta_1$) rendent difficile la détermination directe de cet élément à des concentrations inférieures à 100 p.p.m.

En vue d'éliminer cet inconvénient, différents procédés ont été utilisés: la discrimination de hauteur d'impulsion réduisant l'intensité des raies de deuxième ordre, les monocristaux analyseurs de silicium ou de germanium, à faible pouvoir réflecteur dans le deuxième ordre, ou encore l'abaissement de la tension appliquée au tube à rayons X en dessous du niveau d'excitation des raies K du zirconium. NEUILLY ET FLORESTAN[5] ont montré que tous ces procédés comportent une perte d'intensité des raies de l'hafnium et par conséquent une diminution de la sensibilité de détection de ce dernier; en vue d'améliorer celle-ci, ils ont proposé l'utilisation de la combinaison: tube à anticathode d'or (en vue de l'excitation sélective de Hf $L\alpha$), monocristal de silicium, compteur à flux gazeux (peu sensible aux raies Zr $K\alpha$ et $K\beta$). Afin d'obtenir l'intensité la plus élevée possible de Hf $L\alpha$, cette raie n'est pas discriminée électroniquement, Zr $K\alpha$ du deuxième ordre n'est pas alors entièrement éliminée par le monocristal et se superpose à Hf $L\alpha$. Il se pose le problème du blanc, c'est-à-dire de l'échantillon d'une pureté en hafnium telle que seule demeure Zr $K\alpha$(II). Malheureusement, l'échantillon le plus pauvre en hafnium dont disposaient ces auteurs en renfermait encore 50 p.p.m. et une évaluation du fond continu devait se faire par extrapolation. De plus aucun test comparatif de la méthode par rapport à d'autres n'avait été effectué.

Récemment, FISCHER *et coll.*[6] ont mis au point une technique de séparation des traces d'hafnium à partir d'oxyde de zirconium, donnant ainsi la possibilité de doser soit par activation neutronique[1], soit par fluorescence X[6], des teneurs en hafnium dans le dioxyde de zirconium de l'ordre de 10 p.p.m. Cette méthode de séparation offre ainsi le grand avantage de permettre la préparation d'échantillons de ZrO_2 contenant moins de 20 p.p.m. de HfO_2, se rapprochant du blanc idéal.

Elle nécessite toutefois une préparation chimique préalable, moins apte à un travail de routine qu'une analyse directe et il était intéressant de vérifier si cette analyse était réalisable à l'aide de témoins synthétiques à faible teneur en hafnium. Différents échantillons de ZrO_2 purifiés en hafnium et contrôlés par activation et fluorescence X, ont été aimablement fournis par le professeur FISCHER. Ceci a permis dans le cadre de ce travail, la recherche des conditions optima de dosage par l'emploi de critères statistiques.

Choix des conditions expérimentales et critères de qualité

L'utilisation d'un spectromètre à rayons X comporte en général un certain nombre de conditions à choisir selon que l'on adopte tel ou tel cristal, tube excitateur ou détecteur. Certaines de ces conditions sont imposées par des raisons techniques inhérentes au problème considéré, telle par exemple la longueur d'onde de la raie analytique. Néanmoins, il demeure souvent plusieurs possibilités et il est souhaitable de déterminer de manière objective les conditions expérimentales les plus favorables. Dans ce but, SPIELBERG ET BRADENSTEIN[7] ont proposé un critère de qualité basé sur la définition classique de la limite de sensibilité égalée à trois fois l'écart type du fond continu. On assimile cet écart aux variations statistiques du comptage. On choisit par conséquent des conditions expérimentales telles que $R\sqrt{B}$ soit maxima, R étant égal au rapport pic sur fond et B à l'intensité du fond continu. Ce critère présente cependant des limites: d'abord il ne permet pas de choisir le temps de comptage, de plus la limite de détection calculée de cette manière ne tient pas compte d'un certain nombre de facteurs expérimentaux, tels que l'instabilité du tube excitateur et l'incertitude sur la valeur des témoins servant au calibrage. LAVRANTIEV ET VAINSHTEIN[8] ont élargi ce critère en y introduisant un terme supplémentaire traduisant les fluctuations de l'appareillage. Malheureusement ce terme n'est estimé que d'une manière approximative.

HUBAUX ET VOS[9] ont défini un critère expérimental à partir de la droite de calibrage calculée par régression. Ces calculs relativement laborieux sont effectués sur ordinateur. On assimile la limite de sensibilité à l'écart type sur l'ordonnée à l'origine de la droite de calibrage multiplié par le coefficient de FISCHER correspondant au nombre de degré de liberté (pour une probabilité de 95%). Ce nombre est équivalent au nombre de témoins utilisés moins deux. On trouvera dans le travail cité en référence une discussion plus détaillée de ce critère. Le but de cette étude a été de vérifier, comment à partir des standards utilisés, il est possible de rechercher les conditions de travail les meilleures.

PARTIE EXPÉRIMENTALE

Choix et préparation des témoins

Il existe quelques échantillons de zirconium métallique et de zircaloy fournis par le National Bureau of Standards avec indication des teneurs. Malheureusement, la gamme des concentrations est peu étendue, ce qui rend très aléatoire, le tracé d'une droite de calibrage. L'obtention des échantillons de ZrO_2 du professeur FISCHER a donné la possibilité de pallier à cet inconvénient. Ces échantillons sont tous à basse teneur de HfO_2. Par addition d'une quantité adéquate d'un oxyde de zirconium (Johnson-Matthey) de teneur connue en HfO_2, on a préparé une gamme de concentration de 17, 55, 118, 224 et 423 p.p.m. d'hafnium. Les mélanges s'opèrent, après addition de 10% en poids de cellulose en vue de faciliter le pastillage, pendant une heure dans un mélangeur Mixel-Mill. Chaque échantillon est pastillé dans une matrice de 31 mm de diamètre. Etant donné la faible quantité dont on dispose (4 à 5 g), on ajoute à la poudre étalon une dizaine de grammes de cellulose. On obtient ainsi une pastille plus aisée à manipuler.

Mise sous forme oxyde des échantillons métalliques

L'expérience montre que l'analyse directe des échantillons métalliques par comparaison avec des échantillons témoins d'oxydes n'est pas commode. En effet, on peut tenir compte, par le calcul, de l'influence de la matrice sur l'absorption de la raie analytique; toutefois, il est plus difficile de connaître exactement la valeur du fond continu c'est-à-dire du blanc. Dans ces conditions, on est amené à mettre les échantillons sous formes oxyde. Une prise de 2 g du métal est dissoute dans environ 100 cc d'un mélange 1:1 d'acide nitrique concentré et d'acide fluorhydrique. L'attaque se poursuit durant 3–4 h. On évapore ensuite presque à sec à deux ou trois reprises en reprenant chaque fois par l'acide nitrique. On amène à un volume de 50 cm^3 environ et on filtre si un résidu subsiste après l'attaque. L'examen du dépôt filtré ne permet pas de détecter la présence d'hafnium et de ce fait on peut l'écarter. Dans le filtrat, on reprécipite l'hydrate de zirconium par addition d'ammoniaque; on filtre et calcine pendant 2 h à 1100°. Le produit de calcination est pastillé comme précédemment, après addition de 10% en poids de cellulose.

Choix de la raie analytique

En principe, 3 raies d'hafnium, $L\alpha$, $L\beta_1$ et $L\beta_2$, ont une intensité suffisante pour servir à la détection de faibles teneurs de cet élément. La raie $L\beta_2$ n'est toutefois pas à considérer, étant donné qu'elle interfère avec la raie $K\alpha$ de deuxième ordre du niobium. Or, cet élément entre dans la composition d'un certain nombre d'alliages à base de zirconium. De plus son intensité n'est qu'environ la moitié de celle de l'hafnium $L\alpha$. En ce qui concerne Hf $L\alpha$, on peut craindre que la raie Cu $K\alpha$ provenant d'un autre élément d'alliage éventuel ne vienne interférer avec celle-ci si l'on utilise le cristal de silicium comme moyen dispersif. Les angles 2θ correspondant seront en effet 29°.10 et 28°.47. D'où découle l'intérêt d'étudier les possibilités analytiques des deux raies les plus intenses $L\alpha$ et Hf $L\beta_1$. Si l'on adopte les conditions expérimentales proposées par NEUILLY ET FLORESTAN[5] pour la raie Hf $L\alpha$, on obtient une sensibilité et une précision meilleures que celles données par la raie Hf $L\beta_1$ dans des conditions classiques (cristal LiF, tube W, discrimination électronique, toutes autres conditions égales), ainsi qu'on peut le voir sur le Tableau I. On notera cependant que les sensibilités et précisions calculées à partir des données de NEUILLY ET FLORESTAN sont moins bonnes, ce qui peut être attribué à une moindre réflectivité du cristal utilisé, ou à une évaluation trop élevée du fond continu. Rappelons qu'ultérieurement, on

TABLEAU I

COMPARAISON DES PERFORMANCES DES RAIES $L\alpha$ ET $L\beta_1$[a]

Raie analytique	*Tube*	*Cristal*	*D.H.I.*	*Ecart standard relatif sur la pente (%)*	*Limite de détection calculée d'après $R\sqrt{B}$ (p.p.m.)*	*Limite de détection calculée d'après la droite de calibrage (p.p.m.)*
$L\beta_1$	W	LiF	Oui	2.58	34	37
$L\alpha$	Au	Si	Non	1.05	19	17
$L\alpha$[b]	Au	Si	Non	—	36	—

[a] Toutes autres conditions étant identiques (Appareil Philips PW 1010).
[b] D'après les données de NEUILLY ET FLORESTAN.

a comparé également les deux modes d'évaluation de la sensibilité de détection: celui de SPIELBERG ET BRADENSTEIN[7] ($R\sqrt{B}$) et celui de HUBAUX ET VOS[9] (droite de calibrage). Dans ce cas, ceux-ci conduisent à des valeurs comparables de la limite de sensibilité.

On peut donc conclure que Hf $L\beta_1$, étant donné l'absence d'interférences gênantes, peut être utilisée comme raie analytique.

Optimisation des conditions expérimentales pour Hf $L\beta_1$

Cristal analyseur et détecteur. La comparaison effectuée entre les deux droites de calibrage obtenues avec les mêmes témoins, et les cristaux LiF et Si montre que l'usage de ce dernier cristal présente une perte de sensibilité et de précision. En effet de LiF à Si la précision relative sur la pente de la droite, ainsi que la limite de de sensibilité croissent d'un facteur 1.5 environ quel que soit le mode de calcul adopté pour celle-ci. On observe également une perte de sensibilité et de précision en substituant le compteur à flux gazeux par le scintillateur.

Anticathode et puissance appliquée. Normalement, on dispose de 2 tubes à anticathodes de tungstène ou d'or pour exciter dans les meilleures conditions les raies d'hafnium. Toutefois, ni l'un ni l'autre n'émet de raies caractéristiques de longueur d'onde plus courte et au voisinage de la discontinuité d'absorption L de l'hafnium. Ils ne peuvent donc pas exciter sélectivement Hf $L\beta_1$. L'expérience confirme d'ailleurs qu'ils ont des performances équivalentes dans ce domaine. Par contre, il est souhaitable d'appliquer au tube la puissance maxima de l'appareillage dont on

TABLEAU II

INFLUENCE DE LA PUISSANCE SUR LA SENSIBILITÉ DE DÉTECTION

Puissance appliquée (kW)	*Ecart type sur la pente de la droite de calibrage (%)*	*Limite de détection calculée d'après $R\sqrt{B}$ (p.p.m.)*	*Limite de détection calculée d'après la droite de calibrage (p.p.m.)*
1 (PW 1010)	2.37	34	37
1 (PW 1210)	1.58	24	26
2 (PW 1210)	1.29	18	20

dispose. L'emploi d'un appareillage plus stable et plus puissant apporte un gain de sensibilité dû au gain en précision. Le Tableau II donne un exemple d'essais comparatifs effectués avec les spectrographes PW 1010 et PW 1210, plus stable et plus puissant que le premier. Même à puissance égale, 1 kW, l'appareil le plus stable permet d'obtenir une plus grande sensibilité de détection.

Temps de comptage. Le critère de qualité de SPIELBERG ET BRADENSTEIN[7] ne permet pas de rechercher le temps de comptage optima, car il donne une évaluation trop optimiste de la sensibilité en choisissant un temps de comptage suffisamment long pour qu'interviennent les facteurs d'instabilité de l'appareillage. Effectivement la lecture du Tableau III indique clairement qu'une augmentation du temps de comptage de 100 à 400 sec améliore théoriquement la sensibilité d'un facteur 2; en réalité, ce gain, si l'on se réfère à la limite de détection calculée d'après la droite de calibrage, est beaucoup plus réduit.

TABLEAU III

UTILISATION DU RAPPORT D'INTENSITÉ DES RAIES Hf $L\beta_1$ ET Zr $K\beta$(II) POUR LA DROITE DE CALIBRAGE

Méthode de calcul	*Ecart type sur la pente de la droite de calibrage (%)*	*Limite de détection calculée d'après $R\sqrt{B}$ (p.p.m.)*	*Limite de détection calculée d'après la droite de calibrage (p.p.m.)*
Hf $L\beta_1$ 100 sec	1.30	18	20
Hf $L\beta_1$/Zr $K\beta$(II) 100 sec	1.19	18	10
Hf $L\beta$ 400 sec	1.10	9	17
Hf $L\beta_1$/Zr $K\beta$(II) 400 sec	0.79	9	7

Utilisation d'une raie de zirconium comme étalon interne. L'utilisation de la raie Zr $K\beta$(II) comme étalon interne, améliore nettement la précision et la sensibilité de la détermination pour des temps de comptage de 100 à 400 sec (voir Tableau III). On se trouve ici également en présence d'un cas où le critère calculé d'après $R\sqrt{B}$ n'est pas utilisable pour des raisons évidentes: on ne peut pas en effet considérer la variation statistique du fond continu comme égal à $\sqrt{B}$ car il s'agit d'un rapport de deux intensités prises à des moments différents. Ce gain de précision et de sensibilité peut être attribué à la diminution de l'influence de facteurs tels que l'état de surface de l'échantillon ou sa position relative au tube à rayons X. Il faut toutefois remarquer que l'emploi de zirconium comme étalon interne n'est possible que pour autant que cet élément soit en quantité identique dans les témoins et l'échantillon à analyser.

Reproductibilité et exactitude

Deux échantillons d'alliage de zirconium à 2.5% de niobium ont été analysés de façon répétée, afin de tester la reproductibilité de la méthode. Les résultats indiquent un écart type relatif de l'ordre de 20% pour des concentrations voisines de 50 p.p.m.

Trois étalons du "NBS" et un échantillon provenant d'une firme privée (Heraeus) analysé par celle-ci, ont été transformés à l'état d'oxyde; l'hafnium a été

TABLEAU IV

DOSAGE DU HAFNIUM SUR 4 ÉCHANTILLONS

Origine	*Teneurs indiquées (p.p.m.) recalculées pour* ZrO_2	*Valeurs obtenues à partir des témoins synthétiques (p.p.m.)*[a]
NBS 1210	67 ± 2	74 ± 8
NBS 1211	106 ± 1	101 ± 4
NBS 1213	66 ± 1	64 ± 2
H (Heraeus)	60	70 ± 7

[a] Moyenne de 8 mesures.

dosé. Les résultats obtenus figurent dans le Tableau IV. La concordance entre les valeurs proposées et expérimentales est très satisfaisante, si l'on tient compte du domaine de concentration. Il faut se rappeler également que les témoins eux-mêmes sont entachés de l'incertitude liée aux déterminations du niveau de concentration de l'hafnium, incertitude estimée à 4 p.p.m. environ.

DISCUSSION

GOSHI[10] a adapté à un spectromètre à rayons X commercial un deuxième cristal, augmentant notablement ainsi le pouvoir de résolution. Il parvient à éliminer complètement l'interférence de la raie Zr Kα(II) sur la raie Hf Lα et obtient une limite de sensibilité théorique de l'ordre de 10 p.p.m. (calculée d'après $R\sqrt{B}$). La solution proposée est intéressante mais ne parait pas donner de résultat supérieur. Une autre possibilité d'éliminer les interférences gênantes consiste à utiliser la technique de "l'émission directe", c'est-à-dire l'excitation directe du rayonnement X par bombardement électronique. GRIFFOUL ET RABILLON[11] ont effectivement appliqué cette technique, malheureusement le petit nombre de données expérimentales ne permet qu'une évaluation très grossière de la limite de sensibilité. Celle-ci parait cependant nettement plus élevée que par fluorescence. En vue de vérifier ce point, on a repris cette étude en utilisant les témoins "NBS". Effectivement l'expérience a montré qu'il n'était pas possible de détecter moins de 100 p.p.m. d'hafnium, sensibilité que se compare défavorablement à celle obtenue par fluorescence X, alors que cette dernière permet par contre, de mesurer des concentrations de l'ordre de 10 p.p.m. Deux facteurs sont importants pour atteindre ce but, d'abord la possession d'un appareillage doté d'une bonne stabilité, ensuite des étalons de valeur aussi exacte que possible. Tous ces paramètres jouent en effet un rôle important sur la précision et par conséquent la sensibilité de la méthode, caractéristiques d'une méthode analytique dont l'interdépendance n'a pas toujours été suffisamment mise en évidence.

Conclusion

On peut employer pour le dosage de l'hafnium dans le zirconium et ses alliages les deux raies analytiques Hf Lα et Hf Lβ_1. Celles-ci donnent des sensibilités de détection comparables, ce qui permet d'éviter des interférences provenant d'un des éléments d'alliage. Si l'on dispose d'un générateur bien stabilisé et d'une gamme de témoins adéquate, on peut doser sans précaution particulière jusqu'à 7 p.p.m. de cet élément.

Nous exprimons tous nos remerciements au Professeur W. FISCHER qui a bien voulu nous procurer les échantillons témoins à basse teneur en hafnium et à M. W. DE SPIEGELEER qui s'est occupé de la partie technique de ce travail.

RÉSUMÉ

Le dosage par fluorescence X de l'hafnium dans le zirconium et ses alliages est possible jusqu'à une teneur de l'ordre de 10 p.p.m. si l'on dispose d'une gamme de témoins appropriée. On peut utiliser comme raies analytiques aussi bien Hf $L\alpha$ que Hf $L\beta_1$. Les conditions expérimentales optima sont définies par l'emploi d'un critère statistique.

SUMMARY

The determination of hafnium in zirconium and its alloys by X-ray fluorescence is possible down to about 10 p.p.m. if a range of suitable standards is available. Either Hf $L\alpha$ or Hf $L\beta_1$ can be used as the analytical line. The optimal experimental conditions are defined by means of statistical criteria.

ZUSAMMENFASSUNG

Die Bestimmung von Hafnium in Zirkonium mittels Röntgenfluoreszenzanalyse ist hinab bis zu einem Gehalt von 10 p.p.m. möglich, wenn man über eine Reihe adäquater Standardproben verfügt. Man kann als analytische Linie sowohl Hf $L\alpha$ als auch Hf $L\beta_1$ benutzen. Die optimalen experimentellen Versuchsbedingungen werden durch statistische Kriterien gegeben.

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ACCURATE SILICATE ANALYSIS BASED ON SEPARATION BY ION-EXCHANGE CHROMATOGRAPHY

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The first complete ion-exchange procedure for the separation of main elements in silicate minerals probably has been described by YOSIMURA AND VAKI[1]. Results obtained with the method are of moderate accuracy. Its weak points are: (*a*) the operating distribution coefficient for retaining manganese(II) as the chloride complex is quite small ($D \approx 7$); (*b*) some of the operating separation factors also are rather small ($\alpha_{Na}K = 2.1$, $\alpha_{Mg}Ca = 2.2$); and (*c*) aluminium(III) does not appear quantitatively in the desired eluate fraction because of partial hydrolysis in the ammonium acetate eluent. Furthermore, the method is rather long. A shorter method has been devised by OKI *et al.*[2], who extracted iron(III) as the chloride complex into ethyl ether and then separated the other elements by a single column procedure. This method appears to be more accurate but still does not satisfy the requirements for reference analysis. Some of the separation factors are rather low again and only small amounts of sample (0.1 g) have been used.

MAINES[3] has described an ion-exchange procedure for silicate analysis which has been shown to give fairly accurate results. He employs adsorption of the sulfosalicylate complexes of iron(III), titanium(IV), and aluminium(III) on Dowex 1 anion-exchange resin for separation of these elements from Mn(II), Mg(II), Ca(II), K(I) and Na(I). The operating distribution coefficient for aluminium (III) unfortunately is rather small, and large columns (50 cm resin bed) are necessary to avoid losses of aluminium(III). On continued use of columns, erratic and low results are obtained, nevertheless, and fresh resin therefore has been used for every analysis. Furthermore, the destruction of the organic reagents used is time-consuming and unattractive. None of the above methods seems to be quite satisfactory for accurate reference analysis.

During a systematic study of the anion-exchange distribution coefficients of elements in oxalic–hydrochloric acid mixtures, it was found in this laboratory that this system seemed to offer excellent prospects for a group separation of multivalent elements such as Al(III), Fe(III), Ti(IV), Zr(IV), V(IV) and Mo(VI) from Mn(II), Mg(II), Ca(II), K(I) and Na(I). The method therefore was investigated in detail and procedures to separate the two main groups into their components were developed, utilizing available knowledge of distribution coefficients[4-6]. Combined with selected methods of determination for the single elements, the analysis scheme was applied to synthetic mixtures and standard silicates.

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** This is part of a D.Sc. thesis by the third author at the Department of Inorganic and Analytical Chemistry of the University of Pretoria.

EXPERIMENTAL

Apparatus and reagents

Only analytical reagent grade chemicals were used. Bromic acid was prepared by passing an aqueous solution of potassium bromate through a cation-exchange column in the hydrogen form. The resins used were the AG1-X8 anion-exchanger and the AG50W-X8 cation-echanger (BIO-RAD Laboratories, Richmond, Calif.) and are equivalent to the Dowex 1 and Dowex 50 resins. Resin of 200–400 mesh particle size was used for column work and of 100–200 mesh particle size for equilibrium experiments. Borosilicate glass tubes of about 20 or 24 mm inner diameter, fitted with a glass sinter of No. 2 porosity and a stopcock at the bottom and a B19 ground-glass joint at the top, were used as columns. A Perkin-Elmer 303 atomic absorption spectrometer and a Zeiss PMQII spectrophotometer were used for atomic absorption and spectrophotometric determinations, respectively.

Distribution coefficients

Distribution coefficients were determined by the batch method with 2.500 g of AG1-X8 resin (dry weight at 105°) in the chloride form, with a total volume of 250 ml of solution, 1.0 mmole of the element and a shaking time of 24 h at 20°. Shaking

TABLE I

ANION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 0.05 *M* OXALIC ACID CONTAINING VARIOUS AMOUNTS OF HYDROCHLORIC ACID

Element	*0.01 M*	*0.1 M*	*0.2 M*	*0.5 M*	*1.0 M*	*2.0 M*	*3.0 M*	*4.0 M*
Mo(VI)[a]	$>10^4$	$>10^4$	$>10^4$	$>10^4$	2310	920	660	950
Ti(IV)	$>10^4$	$>10^4$	$>10^4$	639	26.5	0.8	0.5	<0.5
Zr(IV)	$>10^4$	$>10^4$	4040	138	11.4	1.4	0.7	0.4
Fe(III)	$>10^4$	2790	1580	105	14.5	6.0	9.5	39.0
V(V)[a]	5830	620	174	19.2	2.5	0.6	<0.5	<0.5
Ti(IV)[a]	$>10^4$	1420	320	38.6	6.4	0.5	<0.5	<0.5
Al(III)	$>10^4$	1840	211	5.4	0.5	<0.5	<0.5	<0.5
Mn(II)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
[also Mg(II), Ca(II), Na(I), K(I)]								

[a] 0.1 % H_2O_2 present.

TABLE II

ANION-EXCHANGE DISTRIBUTION COEFFICIENTS IN 0.25 *M* OXALIC ACID CONTAINING VARIOUS AMOUNTS OF HYDROCHLORIC ACID

Element	*0.01 M*	*0.1 M*	*0.2 M*	*0.5 M*	*1.0 M*	*2.0 M*	*3.0 M*	*4.0 M*
Ti(IV)	$>10^4$	7800	5200	1450	213	6.2	2.1	<0.5
Zr(IV)	$>10^4$	$>10^4$	6800	348	18.4	3.1	1.7	0.9
Fe(III)	$>10^4$	3920	1450	236	35.2	6.6	8.1	27.6
V(V)[a]	3370	483	201	41.3	8.3	1.6	0.5	<0.5
Ti(IV)[a]	2340	1280	457	80	15.0	2.8	1.1	0.6
Al(III)	4250	1840	571	36.6	1.8	<0.5	<0.5	<0.5
Mn(II)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
[also Mg(II), Ca(II), Na(I) and K(I)]								

[a] 0.1% H_2O_2 present.

times of only 2 h were used in the case of iron (III) to reduce the amount of reduction to iron(II). Coefficients for molybdenum(VI) and vanadium(V) were determined in the presence of 0.1% hydrogen peroxide to avoid precipitation, and those for titanium (IV) in the presence and in the absence of hydrogen peroxide. Coefficients in 0.05 *M* and 0.25 *M* oxalic acid containing 0.01 *M*–4.0 *M* hydrochloric acid were determined and are presented in Tables I and II.

Elution curves

Group separation. From the results in Tables I and II it was concluded that it should be possible to elute Mn(II), Mg(II), Ca(II), K(I) and Na(I) from an AG1-X8 resin column partly in the oxalate form, while Al(III), Fe(III), Ti(IV), Zr(IV), V(IV), Mo(VI) should be retained quantitatively. Figure 1 shows an elution curve for manganese(II), the element forming the most stable oxalate complexes of the nonabsorbed group, and aluminium(III), the least strongly absorbed element of the other group.

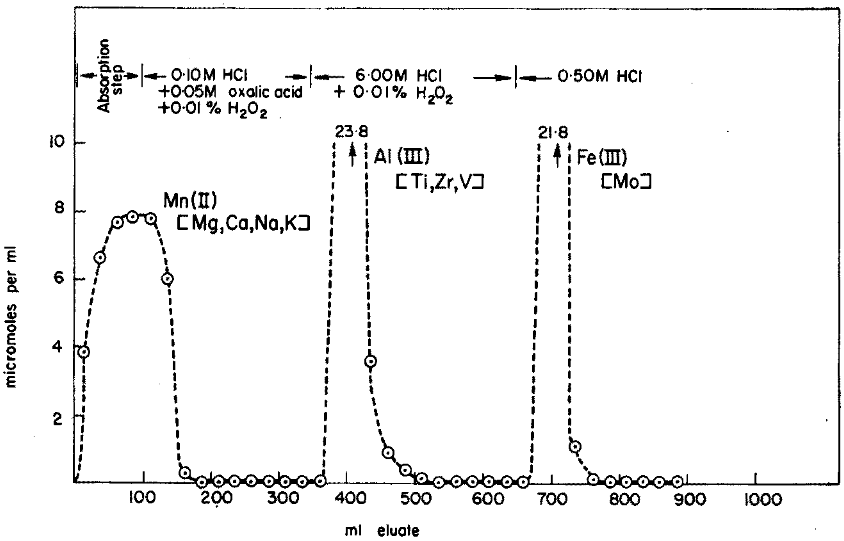

Fig. 1. Elution curve for Mn(II)–Al(III)–Fe(III). Column 23 ml (10 g) AG1-X8, 200–400 mesh, resin. Length 7.5 cm; diameter 2.0 cm; flow rate 3.0 ± 0.3 ml per min.

Adsorption took place from 100 ml of 0.25 *M* hydrochloric acid containing 0.25 *M* oxalic acid and 0.03% hydrogen peroxide on a column of 23 ml (10 g) of AG1-X8 anion-exchange resin of 200–400 mesh particle size. The resin column was about 7 cm in length and 2.0 cm in diameter and had been partially converted from the chloride to the oxalate form by passing through 100 ml of 0.25 *M* oxalic acid. After adsorption the elements were eluted with 250 ml of 0.10 *M* hydrochloric acid containing 0.05 *M* oxalic acid and 0.03% hydrogen peroxide. Subsequently, aluminium(III) was eluted with 250 ml of 6.0 *M* hydrochloric acid containing 0.03% hydrogen peroxide. Mg(II), Ca(II), K(I) and Na(I) have elution curves very similar to those of Mn(II), while Ti(Iv), Zr(IV) and V(IV) accompany Al(III) quantitatively and Fe(III) and Mo(VI) are retained by the column. Normally, molybdenum(VI) will be a trace element and iron(III) can be eluted quantitatively with 250 ml of 0.10 *M* hydrochloric acid.

When molybdenum(VI) has to be determined, iron(III) is eluted with 250 ml of 1.0 M nitric acid containing 0.05 M oxalic acid and 0.03% hydrogen peroxide, while molybdenum(VI) is retained and then can be eluted with 200 ml of 2.0 M ammonium nitrate containing 0.5 M aqueous ammonia.

Mn(II), Mg(II), Ca(II), Na(I), K(I). These elements do not form oxalate complexes in dilute hydrochloric acid and therefore can be absorbed quantitatively on a cation-exchange resin when the eluate from the anion-exchange resin is passed through it directly, provided that the column is large enough and/or the concentration of strong acid small enough to prevent leakage of sodium(I). A combination of methods described in the literature previously[7-9], was applied to obtain a complete separation of the group. Figure 2 shows a typical elution curve. About 1 mmole of each Mn(II), Mg(II), Ca(II), K(I) and Na(I) in 200 ml of 0.1 M hydrochloric acid containing 10 ml of 2.5 M sulphuric acid, 10 ml of 0.3% hydrogen peroxide and 7.9 g of oxalic acid were passed through a column of 60 ml (20 g) AG50W-X8 cation-exchange resin of 200–400 mesh particle size. The resin was in the hydrogen form and the column 13.5 cm in length and 2.4 cm in diameter. Oxalic acid was removed from the column by washing with 100 ml of water and the elements then were eluted with the following sequence of reagents: 900 ml of 0.50 M nitric acid for sodium (I) followed by potassium(I), 400 ml of 0.75 M hydrochloric acid in 90% acetone for manganese(II), 400 ml of 3.00 M hydrochloric acid in 60% ethanol for magnesium(II), and 400 ml of 2.00 M nitric acid for calcium(II). The flow rate was kept at 3.0 ± 0.3 ml per min throughout, with the exception of the 3.00 M hydrochloric acid in 60% ethanol, where a flow rate of 2.0 ± 0.3 ml per min was used.

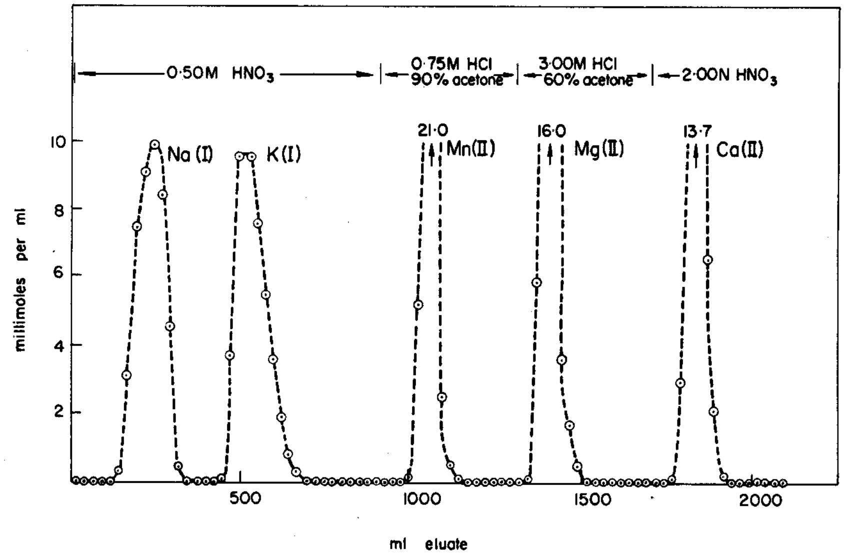

Fig. 2 Elution curve for Na(I)–K(I)–Mn(II)–Mg(II)–Ca(II). Column 60 ml (20 g) AG50W-X8, 200–400 mesh, resin. Length 14 cm; ϕ2.4 cm; flow rate 3.5 ± 0.5 ml per min; 2.0 ± 0.3 ml per min for Mn(II).

V(V), Ti(IV), Al(III), Zr(IV). The eluate containing these elements contains oxalate which has to be destroyed before further separations are carried out.

This was achieved by evaporating the solution to a small volume, adding 30 ml of nitric acid and expelling the chloride, then adding 10 ml of perchloric and enough bromic acid to effect a complete oxidation of the oxalate, and finally evaporating to fumes of perchloric acid. Vanadium(IV) is oxidized to vanadium(V) during this treatment. The solution is then diluted to about 0.5 *M* perchloric acid, about 10 ml of 0.3% hydrogen peroxide are added and the solution is then ready for separation. Figure 3 shows a typical elution curve for this group with a column of 30 ml (10 g) of AG50W-X8 cation-exchange resin of 200–400 mesh particle size. The column length was 9.5 cm and the diameter was 2.0 cm; 1 mmole of each V(V), Al(III) and Zr(IV) and 0.5 mmole of Ti(V) were present and adsorbed from 250 ml of 0.5 *M* perchloric acid containing 0.03% hydrogen peroxide. Vanadium(V) passed through the column during the absorption step. The elements then were eluted with the following eluents: 200 ml of 0.01 *M* nitric acid containing 10 ml of 3% hydrogen peroxide for residual vanadium(V), 300 ml of 1.25 *M* nitric acid for titanium(IV), 225 ml of 2.50 *M* hydrochloric acid for aluminium(III) and 350 ml of 5.0 *M* hydrochloric acid for zirconium(IV).

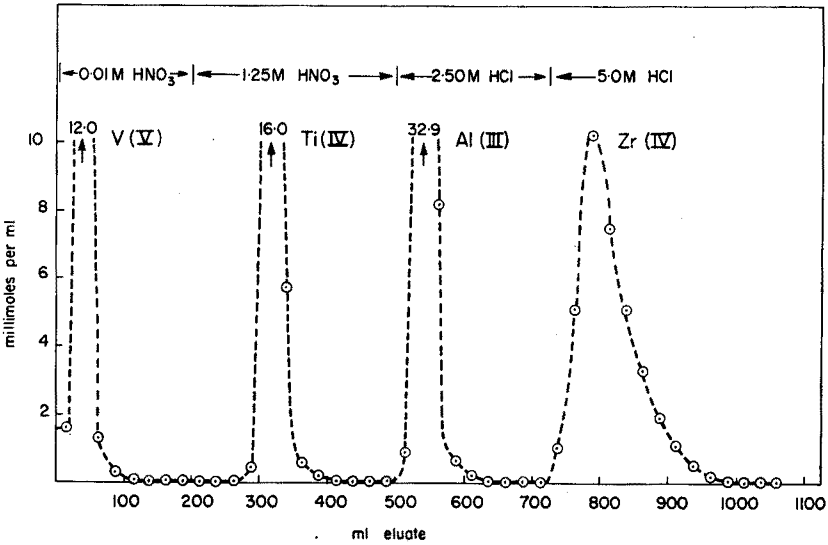

Fig. 3. Elution curve for V(V)–Ti(IV)–Al(III)–Zr(IV). Column 30 ml (10 g) AG50W-X8, 200–400 mesh, resin. Length 9.5 cm: diam. 2.0 cm; flow rate 3.0 ± 0.3 ml per min.

Analysis of synthetic mixtures and standard silicates

Separation procedure. From the above the following method was developed and applied to the analysis of synthetic mixtures and standard silicates. About 1-9 samples were weighed out and dissolved by heating with mixtures of hydrofluoric, hydrochloric and sulphuric acids in teflon beakers using an oven which enclosed the beakers up to 3/4 of their height. Insoluble residues were dissolved in hydrofluoric–perchloric acid or phosphoric–perchloric–hydrofluoric acid (chromite) mixtures. Iron was oxidized by bromine water, and hydrofluoric and perchloric acids were removed by evaporation in the presence of sulphuric or phosphoric acid. Finally the solution was adjusted to a volume of about 200 ml containing about 10 ml of 2.5 *M* sulphuric acid, 4 ml of 5 *M* hydrochloric acid, 10 ml of 0.3% hydrogen peroxide and 12 g of boric acid. After addition of 60 ml of 0.5 *M* oxalic acid to the cool solution, the mixture was immediately passed through a column of 46 ml of AG1-X8 anion-exchange resin and a column of 60 ml of AG50W-X8 cation-exchange resin connected in series. Both resins were of 200–400 mesh particle size. The anion-exchange column was about 10.5 cm in length and 2.4 cm in diameter and had been partially converted from the chloride to the oxalate form by equilibrating with 100 ml of 0.25 *M* oxalic acid. The cation-exchange column was in the hydrogen form and was 13.5 cm in length and 2.4 cm in diameter. It contained a head of about 100 ml of 0.05 *M* hydrochloric acid above the resin bed. The elements were washed onto the anion-exchange column and Mn(II), Mg(II), Ca(II), K(I) and Na(I) were then eluted with 150 ml of 0.10 *M* hydrochloric acid containing 0.05 *M* oxalic acid and 5 ml of 0.3% hydrogen peroxide.

The columns were disconnected, the solution head was allowed to drain through the cation-exchange column and the oxalic acid was washed from the column with 100 ml of water. The elements on the cation-exchange column then were eluted as described above, for Mn(II) etc., but with only 800 ml of 0.50 *M* nitric acid, for potassium(I) plus sodium(I) and 400 ml of 3.00 *M* hydrochloric acid for calcium.

From the anion-exchange column, Al(III), Ti(IV), Zr(IV) and V(IV) were eluted with 100 ml of 0.5 *N* hydrochloric acid containing 0.05 *M* oxalic acid and 5 ml of 0.3% hydrogen peroxide followed by 400 ml of 6.0 *M* hydrochloric acid containing 20 ml of 0.3% hydrogen peroxide. Iron(III) then was eluted with 300 ml of 0.50 *M* hydrochloric acid. The eluate containing aluminium(III) etc. was treated and oxalate destroyed as described for vanadium(V) etc. above, but the elements then were separated on a larger column containing 60 ml (20 g) of AG50W-X8 resin. The following elution sequence was used: 250 ml of 0.01 *M* nitric acid containing 10 ml of hydrogen peroxide for vanadium(V), 400 ml of 1.25 *M* nitric acid containing 10 ml 3% hydrogen peroxide for titanium(IV), 400 ml of 2.50 *M* hydrochloric acid for aluminium(III) and 600 ml of 6.0 *M* hydrochloric acid for zirconium(IV). A flow rate of 3.5 ± 0.5 ml per min was used throughout.

Determinations

Sodium and potassium. The eluate was received in a 1000-ml volumetric flask and made up to volume and fractions were taken for dilution. Both elements were determined by atomic absorption spectrometry with a Perkin Elmer 303 instrument, a propane–butane flame, a flat water-cooled burner as described by BUTLER[10], and the 5890 Å and 7665 Å absorption lines, respectively; 500 p.p.m. of specpure potassium(I) were added to the sodium samples and standards. When only low amounts of the alkalies were present, the free acid was removed by evaporation.

The free acid from the eluates of the other elements also was removed by evaporation, and the following methods were applied for determination.

Aluminium(III). Addition of excess DCyTA, and back-titration with zinc sulphate using xylenol orange as indicator [11,12].

Iron(III). Reduction with tin(II) chloride and titration with potassium dichromate using barium diphenylamine-sulphonate as indicator.

Titanium(IV). Spectrophotometrically as hydrogen peroxide complex or as the complex with sodium alizarin sulphonate in 6 *M* hydrochloric acid after reduction with tin(II) chloride (small amounts)[13].

Zirconium(IV). Spectrophotometrically as xylenol orange complex[14].

Vanadium(V). Spectrophotometrically as the 4-(2-pyridylazo)-resorcinol complex[15].

Calcium(II) and Magnesium(II). Compleximetric titration with DCyTA using methylthymol blue as indicator. Atomic absorption spectrophotometry with an air–acetylene flame for small amounts.

Manganese(II). Atomic absorption spectrophotometry with an air–acetylene flame.

The method was applied to a synthetic mixture and to six standard rock samples. The results are presented in Tables III and IV.

DISCUSSION

The described method provides an excellent means for the accurate determination of the above elements in silicate rocks and is very well suited for accurate reference analysis. Critical separation factors are appreciably higher than those operating in other ion-exchange methods published for silicate analysis[1–3]. Reasonably large samples (1 g) therefore can be separated on smaller columns. The destruction of oxalic acid with bromic acid is very effective and more attractive than the destruction of large amounts of sulphosalicylic acid. While results for major amounts of elements are at least as accurate as those obtained by classical silicate analysis at its best, results for smaller amounts are considerably more accurate and also are superior to those obtained by X-ray fluorescence spectroscopy or atomic absorption spectrometry without separations. When 2.595 mg of aluminium, which are equivalent to 0.490% Al_2O_3 in a 1-g rock sample, were separated from a synthetic mixture of the kind described in Table III, 2.588 ± 0.013 mg of aluminium, equivalent to 0.489 ± 0.003% Al_2O_3 were found. Furthermore, zirconium(IV), vanadium(V), potassium(I) and sodium(I) which were not included by MAINES[3] are separated in the above scheme. Silica, iron oxide and phosphorus pentoxide can be determined by standard methods on separate samples.

The amount of calcium which may be present is limited to about 50 mg in 250 ml of 0.1 *M* hydrochloric acid containing 0.1 *M* sulphuric acid and 60 ml of 0.5 *M* oxalic acid. Slow precipitation of calcium oxalate which can lead to losses by retainment on the columns occurs with larger amounts. No precipitation of calcium oxalate occurs within 90 min when as much as 200 mg of calcium are present in 250 ml of solution containing the above reagents plus 12 g of boric acid. The boric acid has to be added before the addition of oxalic acid, and the solution should be kept cool after the addition of oxalic acid. When only small amounts of aluminium(III), iron(III) and titanium(IV) are present, the amounts of calcium which may be present also can be increased to 200 mg by using only 15 ml of 0.5 *M* oxalic acid instead of 60 ml.

The total amounts of elements of the oxalate group which can be handled are about 6 moles, of which up to 4 mmoles may be aluminium(III). A total of 10 mmoles, of which 7 may be aluminium(III), can be present when 100 ml of 0.5 *M* oxalic acid, instead of 60 ml, are present in 250 ml of solution during the absorption step, but the titanium(IV) in this case has to be eluted from the cation-exchange column (second step) with 500 ml of 1.00 *M* nitric acid containing 10 ml of 3% hydrogen peroxide, to prevent a premature breakthrough of aluminium(III). As much as 10 mmoles of di-

TABLE III

RESULTS OF QUANTITATIVE ANALYSES OF A SYNTHETIC MIXTURE

Element	*mg present*	*mg found*	*Coefficient of variation (7 results)*
K(I)	26.00	26.12 ± 0.16	0.62
Na(I)	48.30	48.16 ± 0.24	0.50
Mg(II)	27.61	27.57 ± 0.05	0.18
Ca(II)	39.42	39.40 ± 0.05	0.13
Mn(II)	13.47	13.53 ± 0.06	0.44
Fe(III)	64.43	64.32 ± 0.18	0.28
Al(III)	51.89	51.93 ± 0.15	0.29
V(V)	12.63	12.70 ± 0.12	0.95
Ti(IV)	12.20	12.16 ± 0.09	0.74
Zr(IV)	29.68	29.73 ± 0.09	0.30

TABLE IV

RESULTS OF QUANTITATIVE ANALYSES OF STANDARD ROCKS[a]

Element	*W 1*		*AGV-1*		*PCC-1*	
	Standard	*Found*	*Standard*	*Found*	*Standard*	*Found*
Na_2O	2.07	2.17	4.33	4.29	0.053	< 0.02
K_2O	0.67	0.66	2.87	2.84	0.019	< 0.005
MgO	6.55	6.57	1.49	1.50	43.35	43.09
CaO	10.91	10.87	4.98	4.97	0.534	0.528
Al_2O_3	15.00	15.01	17.01	17.07	0.65–0.85	0.711
Total Fe as Fe_2O_3	11.06	11.02	6.65	6.70	8.20–10.86	7.74
MnO	0.16	0.123	0.09	0.101	0.12	0.121
TiO_2	1.07	1.09	1.05	1.03	0.02	0.007
V_2O_5	0.045	0.049	0.022	0.022	21 –40(p.p.m.)	29.2 (p.p.m.)
ZrO_2	0.022	0.015	0.031	0.025	< 4–< 100(p.p.m.)	5.9 (p.p.m.)

Element	*DTS-1*		*GR*[b]		*51*[c]	
	Standard	*Found*	*Standard*	*Found*	*Standard*	*Found*
Na_2O	0.046	< 0.02	3.51	3.52	3.38	3.43
K_2O	0.033	< 0.005	4.50	4.54	2.60	2.64
MgO	49.85	49.89	2.34	2.34	4.05	4.04
CaO	0.158	0.121	2.47	2.40		
Al_2O_3	0.25–0.55	0.211	14.53	14.46	9.01	8.70
Total Fe as Fe_2O_3	8.85	8.31	4.02	4.02	8.32	8.30
MnO	0.12	0.122	0.056	0.055	0.41	0.426
TiO_2	0.02	0.018	0.62	0.624	0.47	0.475
V_2O_5	6–30(p.p.m.)	6.8(p.p.m.)	0.010	0.010	0.015	0.014
ZrO_2	< 10–< 100(p.p.m.)	3.2(p.p.m.)	0.008	0.024	0.47	0.52

[a] The results are averages of 4 determinations.
[b] Granite from University of Nancy (France).
[c] Syenite from Canadian Association of Applied Spectroscopy.

valent elements plus 10 mmoles of total alkalies can be present, but the amount for each single element should not be more than about 5 mmoles.

SUMMARY

A method is presented for the accurate determination of the major and some minor elements in silicate minerals. After sample dissolution and removal of silica, the elements are absorbed from an oxalic–hydrochloric–sulphuric acid mixture on a column of AG1-X8 anion-exchange resin in the oxalate-chloride–sulphate form and a column of AG50W-X8 cation-exchange resin in the hydrogen form. The columns are connected in series. Fe(III), Al(III), Ti(IV), Zr(IV), V(IV) and Mo(VI) are retained by the anion-exchange column, while Mg(II), Ca(II), K(I), Na(I) and Mn(II) pass through and are retained by the cation-exchange column. Phosphate passes through both columns. The columns are disconnected and both groups of elements completely separated by using only the volatile inorganic acids, hydrochloric and nitric acid, and the solvents ethanol and acetone as eluents. Selected titrimetric, spectrophotometric and atomic absorption methods are used for determinations. Very accurate results of analysis of synthetic mixtures and standard rocks are presented together with anion-exchange distribution coefficients in hydrochloric–oxalic acid mixtures and relevant elution curves.

RÉSUMÉ

Une méthode est proposée pour le dosage précis d'éléments dans les silicates. Après dissolution de l'échantillon et séparation de la silice, les éléments en milieu acides oxalique-chlorhydrique et sulfurique sont absorbés sur résine, échangeur d'anions AG1-X8 (forme oxalate–chlorure–sulfate) et sur échangeur de cations AG50W-X8 (forme hydrogène). Les colonnes sont connectées en série. Fe(III), Al(III), Ti(IV), Zr(IV), V(IV) et Mo(VI) sont retenus sur l'échangeur d'anions, tandis que Mg(II), Ca(II), K(I), Na(I) et Mn(II) passent et restent sur l'échangeur de cations. Les phosphates traversent les deux colonnes. On utilise les acides chlorhydrique et nitrique, et les solvants éthanol et acétone comme éluants. Le dosage de ces éléments se fait finalement par volumétrie, spectrophotométrie et absorption atomique. Des résultats très précis ont été obtenus.

ZUSAMMENFASSUNG

Es wird eine Methode zur genauen Bestimmung der Haupt- und einiger Nebenelemente in Silikaten beschrieben. Nach Auflösung der Probe und Abtrennung des Siliciumdioxids werden die Elemente aus einer Mischung von Oxal-, Salz- und Schwefelsäure an einem AG1-X8-Anionenaustauscher als Oxalat, Chlorid, bzw. Sulfat und an einem AG50W-X8-Kationenaustauscher als Säure absorbiert. Fe(III), Al(III), Ti(IV), Zr(IV), V(IV) und Mo(VI) wirden am Anionenaustauscher, Mg(II), Ca(II), K, Na und Mn(II) am Kationenaustauscher absorbiert; Phosphat läuft durch. Die vorher verbundenen Kolonnen werden getrennt und danach diese beiden Gruppen der Elemente durch Verwendung von Salzsäure und Salpetersäure und Äthanol und Aceton als Lösungsmittel eluiert. Mit ausgewählten Methoden der Massanalyse der Spektralphoto-

metrie und der Atomabsorption werden Bestimmungen durchgeführt, die zu sehr genauen Ergebnissen führen, was am Beispiel von synthetischen Mischungen und Standardgesteinen gezeigt werden konnte.

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DETERMINATION OF BISMUTH AND LEAD BY CONTROLLED-POTENTIAL COULOMETRIC OXIDATION

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An accurate method for determining bismuth and lead as major constituents in glasses and thin films was needed in this laboratory. Numerous controlled-potential coulometric methods for bismuth and lead in various electrolytes have been reported and reviewed by RECHNITZ[1]. Most previous studies have been based on controlled-potential deposition of the metal onto a platinum or mercury cathode. When a mercury pool is used as the working electrode, the determination of a metal by anodic oxidation of its amalgam after previous reduction is often preferred[2–5]. Anodic stripping usually proceeds more rapidly than the reduction of an ion to the elemental state. Thus, the oxidation background current usually comprises a smaller fraction of the total current than the reduction background current. This leads to a smaller blank and better accuracy.

Lead has been determined by anodic oxidation in either perchloric acid[4] or sodium bromide–tartaric acid media[5]. Determination of bismuth by controlled-potential anodic oxidation, on the other hand, has never been reported in the literature. KOZLOVSKII AND TSYB[6] did report that quantitative stripping of bismuth can be achieved in a sulfuric acid medium. In this Russian work, however, stripping was conducted under uncontrolled-potential electrolysis conditions until oxidation of mercury was observed; bismuth recovery was established by gravimetry. Their work suggested the possibility of determining bismuth by controlled-potential oxidation. A sulfuric acid medium, however, is not ideal because of the low solubilities of bismuth and lead in this electrolyte. In evaluating various supporting electrolytes employed for the polarographic and coulometric determination of lead and bismuth, the acidic tartrate medium[7,8] appeared to be most promising.

The objectives of this investigation were threefold: to examine the possibility of determining bismuth by controlled-potential coulometric oxidation; to explore the applicability of this technique for the determination of lead and bismuth by stepwise stripping after simultaneous reduction of both metals into the mercury; and to develop procedures for the analysis of glasses and thin films.

EXPERIMENTAL

Apparatus

A Nuclear Materials and Equipment Corporation electronic controlled-potential coulometric titrator (Model 6000) and a John Fluke D.C. differential voltmeter were used for most of the coulometric analyses. An Analytical Instruments potentiostat and current integrator were also employed for the glass analysis when larger amounts of sample were available. The performance of the Analytical Instruments equipment was improved through the incorporation of the modifications recommended by WISE AND WILLIAMS[3].

A Leeds and Northrup Type E Electro-Chemograph was used to scan the potential ranges for reduction and oxidation curves.

Silver–silver chloride reference electrodes were prepared as described by LINGANE[9]. All voltages are given with respect to this electrode.

The electrolysis cell, the working and auxiliary electrodes, and the stirring device were similar to those described by WISE AND WILLIAMS[3]. Perchloric acid (1 M) was used in the auxiliary electrode compartment.

Reagents

A 0.02 N bismuth solution was prepared by dissolving 0.6966 g of pure bismuth in 40 ml of 6 M perchloric acid and 1.0 ml of 16 M nitric acid. The solution was fumed to dryness on a hot plate. Perchloric acid (20 ml of 12 M) was added and the fuming was repeated to remove the last traces of nitrate. The residue was dissolved in 20 ml of 12 M perchloric acid and diluted to 500 ml.

A 0.02 N lead solution was prepared by dissolving 1.036 g of pure lead in a perchloric–nitric acid mixture and following the fuming procedure described above. The residue was dissolved in 10 ml of 12 M perchloric acid and diluted to 500 ml.

Procedure

Preparation of samples. Each lead–bismuth oxide film was dissolved off its substrate with 1–2 ml of 12 M hydrochloric acid; 5 ml of 12 M perchloric acid was added and the solution was evaporated to near dryness on a hot plate. The residue was dissolved in 2.5–6.0 ml of 12 M perchloric acid and 20 ml of 2.0 M tartaric acid, and diluted to *ca.* 100 ml with distilled water before coulometric analysis. Part of the supporting electrolyte was used in transferring the sample solution into the electrolysis cell.

The ground glass sample was dissolved by heating on a steam bath with 2.0 ml of water, 5.0 ml of 12 M perchloric acid, and 5.0 ml of concentrated hydrofluoric acid. Subsequently, the solution was fumed to near dryness on a hot plate and the residue was dissolved in the perchloric–tartaric acid mixture as described above.

Coulometric analysis. Ca. 40–45 ml of mercury having a surface area of 30 cm^2 was used as the working electrode. The sample solution was transferred into the cell and the reference and auxiliary electrodes were positioned in the solution. The stirrer and stream of nitrogen gas were turned on, and the reduction of bismuth and lead was carried out at -0.50 V for 2–3 h.

After complete reduction of the bismuth and lead, the polarity of the electrodes was reversed, and the lead and bismuth were determined by stepwise stripping. The lead was oxidized at -0.16 V until zero electrolysis current was indicated. The bismuth was then oxidized at $+0.20$ V until the zero current was again obtained. A blank containing all reagents was carried through the entire procedure and their corresponding values were subtracted from the lead and bismuth results. If only bismuth is to be determined in the presence of lead, it can be reduced at -0.25 V and determined by oxidizing at $+0.20$ V.

RESULTS AND DISCUSSION

Current–voltage curves of bismuth, lead, and cadmium

Frequently, cathodic current–voltage curves obtained by polarography are used in the selection of optimum conditions for coulometric reduction. On the other hand, relatively few anodic current–voltage curves have been studied by dropping amalgam electrodes[10]. This technique was found to be equally useful for deducing optimum potentials for coulometric oxidation.

The oxidation of bismuth, lead, and cadmium was studied by standard polarographic technique. The amalgam was prepared by quantitative deposition of the metals from a 1.0 *M* perchloric acid–0.4 *M* tartaric acid supporting electrolyte into the mercury cathode at −1.00 V. Typical polarographic waves for the oxidation of cadmium, lead, and bismuth are shown in Fig. 1.

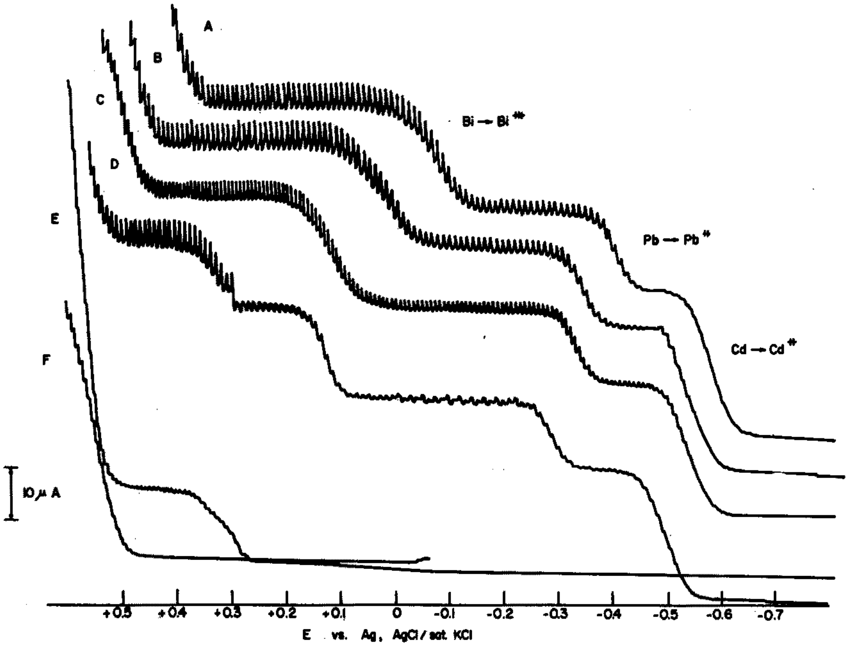

Fig. 1. Anodic current–potential curves with dropping amalgam electrode in 0.4 *M* tartaric acid media of various acidities. The amalgam contains *ca.* 0.09 meq Bi, 0.10 meq Pb and 0.20 meq Cd in 50 ml Hg. (A) pH 5.0; (B) pH 2.5; (C) pH 0.5; (D) 1 *M* in $HClO_4$; (E) residual current of mercury alone in the same medium as D with chloride ion present; (F) same as E except no chloride present.

Critical evaluation of the waves was not intended, since the primary objective of this study was to establish the optimum potentials for coulometric oxidation of bismuth and lead. Well defined and well separated waves were obtained for cadmium, lead and bismuth in 0.40 *M* tartrate solutions at different acidities. No maxima were observed under the conditions studied. The half-wave potentials of these metals shifted to more positive values with increasing acidity. The wave preceding the anodic current of mercury in curves D and E was caused by the chloride ion which diffused from the reference electrode (Ag/AgCl/sat. KCl). The diffusion of the chloride ion can be minimized by filling the lower half of the reference electrode with potassium sulfate–agar gel instead of potassium chloride (see curve F). However, the chloride diffusion from the reference electrode does not perturb the coulometric analysis.

Current potential curves of bismuth and lead were also obtained with a large stirred mercury pool electrode as described by MEITES[11]. A typical curve for the reduction and oxidation of bismuth is shown in Fig. 2.

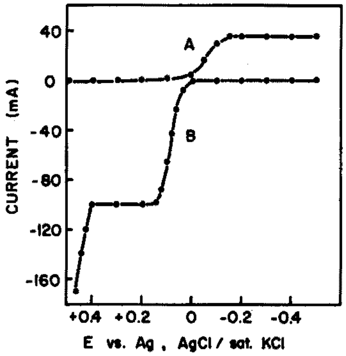

Fig. 2. Current–potential curves for a large stirred mercury working electrode in 1 *M* perchloric–0.4 *M* tartaric acid. (A) reduction of 0.18 meq Bi in 100 ml; (B) oxidation of Bi amalgam prepared by the quantitative reduction of solution A with 50 ml of mercury at −0.25 V *vs.* the Ag/AgCl electrode.

TABLE I

ANALYSES OF STANDARD SOLUTIONS

meq taken		*meq found*		*% Recovery*		*Procedure*[a]
Lead	*Bismuth*	*Lead*	*Bismuth*	*Lead*	*Bismuth*	
	0.1794		0.1794		100.0	A
	0.1794		0.1793		99.94	A
	0.1794		0.1792		99.8_9	A
	0.1794		0.1794		100.0	A
	0.0179_7		0.0179_7		100.0	A
	0.0179_7		0.0179_5		99.8_9	A
0.1984	0.1794		0.1796		100.1	A
0.2019	0.1794	0.2017		99.9_0		B
0.1984	0.1794	0.1983	0.1796	99.9_5	100.1	C
0.1984	0.1794	0.1981	0.1799	99.8_5	100.3	C
0.1984	0.1794	0.1984	0.1798	100.0	100.2	C
0.1984	0.1794	0.1983	0.1794	99.9_5	100.0	D
0.0991_5	0.0896_7	0.0990_1	0.0896_5	99.8_8	99.9_8	C
0.0991_5	0.0896_7	0.0991_7	0.0900_0	100.0	100.4	D
0.0991_5	0.0896_7	0.0992_2	0.0896_3	100.1	99.9_6	D
0.0198_7	0.0179_7	0.0198_7	0.0180_4	100.0	100.4	D
				Av. $99.9_6 \pm 0.08$	$100.0_8 \pm 0.18$	

[a] (A) Bi reduced at −0.25 V and determined by oxidation at +0.20 V; (B) Pb plus Bi reduced at −1.00 V and Pb oxidized at −0.16 V; (C) Pb plus Bi reduced at −1.00 V and Pb oxidized at −0.16 V, followed by oxidation of Bi at +0.20 V; (D) Pb plus Bi reduced at −0.50 V and determined as in C.

It can be seen that optimum potentials for coulometric analysis can be readily deduced from either method. However, the polarographic approach is more advantageous in that it is rapid, more reproducible, and capable of scanning several metals at once.

Coulometric analysis

Because the oxidation potentials of bismuth and lead vary with acidity, it is necessary to select an acidity range for coulometric analysis. The supporting electrolytes used in the present study were 0.30–0.72 *M* in perchloric acid (pH 0.50–0.14) and *ca.* 0.4 *M* in tartaric acid.

Table I shows the results obtained in the analysis of pure bismuth and/or lead solutions. Some typical results obtained for glasses and thin films are given in Table II to indicate the precision of the method on actual samples. An average recovery of 99.9_8% with a relative standard deviation of 0.08% was obtained in analyzing nine samples containing lead from 0.20 to 0.020 meq (20–2.0 mg). For fifteen samples that were analyzed for bismuth ranging from 0.18 to 0.018 meq (14–1.4 mg) the average recovery and relative standard deviation were 100.0_8% and 0.17%, respectively.

TABLE II

DETERMINATION OF LEAD AND BISMUTH IN THIN FILMS AND GLASSES

Type of sample	*Lead*	*Bismuth*
Thin film	*mg Pb*	*mg Bi*
No. 1	1.56, 1.56 Av. 1.56	2.93, 2.91 Av. 2.92
No. 2	5.38, 5.34 Av. 5.36	2.46, 2.48 Av. 2.47
No. 3	5.12, 5.10 Av. 5.11	2.41, 2.42 Av. 2.42
Glass	% *PbO*	% *Bi_2O_3*
No. 1		59.0_4, 59.0_3 Av. 59.0_4
No. 2		76.1_9, 76.1_6, 76.3_0 Av. 76.2_2
No. 3	53.5_9, 53.6_8 Av. 53.64	19.6_5, 19.7_0 Av. 19.6_8
No. 4	50.3_5, 50.3_0 Av. 50.3_3	26.3_7, 26.4_2 Av. 26.4_0
No. 5	47.0_9, 47.0_7, 47.1_2 Av. 47.0_9	32.9_2, 32.9_5, 32.8_8 Av. 32.9_2
No. 7	44.3_0, 44.3_0 Av. 44.3_0	38.6_9, 38.6_6 Av. 38.6_8
No. 8	41.8_7, 41.7_7 Av. 41.8_2	43.9_4, 43.8_7 Av. 43.9_1
No. 9[a]		34.6_2, 34.6_1 Av. 34.6_2
No. 10[a]		64.6_7, 64.6_0 Av. 64.6_4

[a] In the absence of bismuth, lead alone can be determined in basic tartrate medium (2 *M* NaOH–0.25 *M* tartrate) by reducing the lead at −0.95 V and oxidizing at −0.55 V. Lead results obtained by this procedure for glass No. 9 and 10 were 34.5_0 and 64.6_5%, respectively.

The background current correction for bismuth was approximately 0.13 μeq when the sample solution was reduced at −0.50 V for 2.0 h and oxidized at +0.20 V. However, the correction for lead was negligible even when the solution was reduced at −1.00 V. Although a tartaric acid concentration of 0.4 *M* was selected, its concentration is not critical; analyses were also performed in solutions as dilute as 0.20 *M*.

SUMMARY

A method has been developed for the determination of lead and bismuth by controlled-potential coulometric oxidation. After simultaneous reduction of both metals into a mercury pool, lead and bismuth are determined by stepwise anodic stripping at −0.16 and +0.20 V *vs.* Ag/AgCl/sat. KCl electrode, respectively, in a supporting electrolyte of 0.4 *M* tartaric acid and 0.30–0.72 *M* perchloric acid. The reduction of lead and bismuth is carried out at −0.50 V or more negative potential. Bismuth alone can be reduced at −0.25 V. Polarography with a dropping amalgam electrode was advantageously applied to establish optimum conditions for coulometric oxidation of these metals. Solutions containing 0.02–0.2 meq of lead and/or bismuth were analyzed with an accuracy and precision of ±0.2% or better for lead and ±0.3% for bismuth. The method was applied to the analysis of glasses and thin films.

RÉSUMÉ

Une méthode est proposée pour le dosage du plomb et du bismuth par coulométrie d'oxydation, à potentiel contrôlé. Après réduction simultanée des deux métaux par le mercure, le plomb et le bismuth sont dosés par "Stripping" anodique respectivement à −0.16 et +0.20 V *vs.* électrode Ag/ AgCl/KCl sat., dans une solution acide tartrique 0.4 *M* et acide perchlorique 0.30–0.72 *M* comme électrolyte de base. La réduction du plomb et du bismuth s'effectue à −0.50 V ou à un potentiel encore plus négatif. Le bismuth seul se réduit à −0.25 V. La polarographie avec électrode à goutte d'amalgame est utilisée pour établir les conditions optima de l'oxydation coulométrique de ces métaux. Précision de ±0.2% au moins pour le plomb et ±0.3% pour le bismuth pour des concentrations de 0.02–0.2 meq. Ce procédé a été appliqué à l'analyse de verres et de films minces.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Bestimmung von Blei und Wismut durch coulometrische Oxidation bei kontrolliertem Potential entwickelt. Nach gleichzeitiger Reduktion beider Metalle in Quecksilber wurden sie durch schrittweises anodisches Stripping bei −0.16 (Pb) und +0.20 V (Bi) gegen eine Ag/ AgCl/gesät. KCl-Elektrode in einem Trägerelektrolyten aus 0.4 *M* Weinsäure und 0.30–0.72 *M* Perchlorsäure bestimmt. Die Reduktion von Blei und Wismut wurde bei −0.50 V oder negativeren Potentialen durchgeführt. Wismut allein kann polarographisch bei −0.25 V mit einer tropfenden Amalgam-Elektrode reduziert werden. Lösungen, die 0.02–0.2 mäquiv. Blei bzw. Wismut enthielten, wurden mit einer Genauigkeit von besser als ±0.2% beim Blei und ±0.3% beim Wismut analysiert. Die Methode wurde bei der Analyse von Gläsern und dünnen Filmen angewandt.

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APPLICATION OF ANODIC-STRIPPING VOLTAMMETRY TO THE DETERMINATION OF SOME TRACE ELEMENTS IN SEA WATER*

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Although the single-sweep polarographic method of analysis with the dropping mercury electrode (D.M.E.) can be used to determine rapidly a number of trace elements in raw sea water[1,2], the method is restricted to concentrations of the trace element greater than 10^{-7}–10^{-8} M.

Anodic-stripping voltammetry has been successfully applied to the determination of trace element concentrations in the range of 10^{-8}–10^{-10} M[3-10] and recently in such complex media as brines[11] in the concentration range of 10^{-8} M. The technique thus allows one to determine a large number of trace elements whose concentrations are below the limit of detection and analysis by single-sweep polarography. Anodic-stripping voltammetry like the single-sweep method has the advantage over classical wet methods of trace element analysis in that very few errors are introduced during the analysis through contamination from glassware, chemical reagents, and concentration techniques.

It is the purpose of this paper to describe an anodic-stripping technique with a "hanging" mercury drop electrode (H.M.D.E.) and a fast-sweep polarograph that has been successfully applied in our laboratories to the determination of several trace elements in raw sea water. The sources of error and advantages and disadvantages of the method are discussed. A comparison of results is shown for some of the trace elements in sea water obtained by this technique and those determined by single-sweep polarography.

EXPERIMENTAL

Apparatus and materials

The polarograph used to record the anodic-stripping data was the Sargent Model FS Polarograph (E. H. Sargent and Company, Chicago, Ill.). It is designed for either fast-sweep polarography or anodic stripping. The instrument has a span e.m.f. of ±3 V, continuously variable, and scan rates of 16, 25, 33, 41, and 50 mV/sec respectively. A built-in 10-inch chart recorder with a range of 0–250 mm and sensitivity ranges of 0.4 to 0.0004 μA/mm graduated in 19 steps is available in the instrument. The maximum scanning period is 60 sec, allowing a maximum scan of 3 V in one continuous sweep. The single-sweep polarograph used in this study is the Davis

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Differential Cathode-Ray Polarotrace (Model A1660, Southern Analytical Instruments, Ltd., England).

The cell assembly used is shown in Fig. 1. All electrodes and tubes were inserted through O-rings into the solution. The cell was made of fused quartz to prevent loss of the trace elements to the glass or increase of trace elements in solution through a leaching effect of the sea water on the glass. The total capacity of the cell was 100 ml.

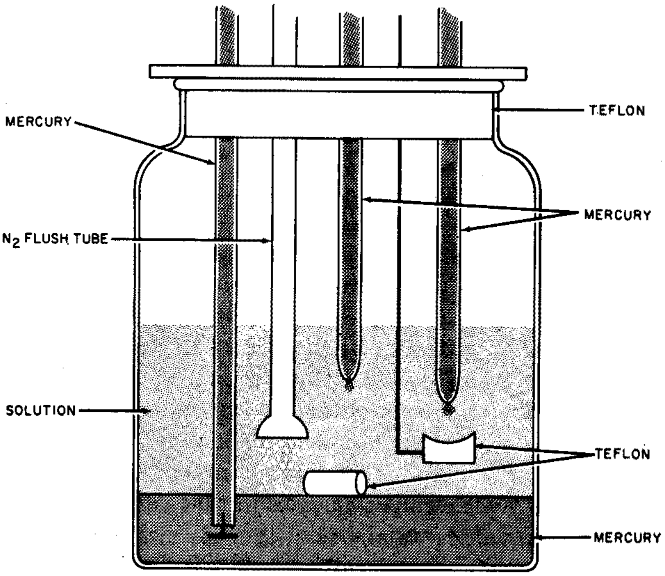

Fig. 1. Quartz cell assembly.

A teflon spoon on a quartz tube was used to transfer drops of mercury from the D.M.E. to the H.M.D.E. The contact electrode was made of quartz and has a tungsten tip. All voltages were referred to a mercury pool (S.C.E. *vs.* Hg pool $= -0.058$ V in standard sea water)[12]. The nitrogen flushing tube was also made of quartz. The cell was immersed in a water bath at 30° ± 0.1° during analysis.

Anodic-stripping voltammetry requires the use of a substantial amount of pure mercury. In general, it was found that regular triple distilled mercury was not pure enough for this method. Contaminated mercury produced a much larger wave than normal; in some cases the waveheight was double what it should be. All the mercury used in this work was purified by the following method.

The triple distilled mercury was first filtered through filter paper with a small pin hole in the bottom of the paper. The mercury (1–2 in.) was then placed in a filter flask and covered with about 2 in. of 10% sodium hydroxide solution. The flask was fitted with a 1-hole stopper through which a glass tube extends down into the mercury, through which filtered compressed air was pumped. The mercury was treated in the 10% sodium hydroxide solution for about 24 h, and was then rinsed and treated in the same manner with 10% nitric acid for 12 h, rinsed, and treated again in 10% nitric acid for 24 h. It was then rinsed well with distilled water and filtered twice through filter paper to remove the water.

Because of the sensitivity of the method, treating the solution to remove all traces of oxygen is extremely important. Standard tank nitrogen was used for removal of traces of oxygen from the sample. The nitrogen was purified by allowing it to flow over metallic copper heated to 450°. It was then cooled and passed over more metallic copper heated to 350°. The nitrogen was then saturated with distilled water and passed directly into the cell. The nitrogen system was made almost entirely of glass. The use of the second lower temperature copper furnace was found necessary when analyzing for trace elements in a concentration range of 10^{-8} *M* or less. The zinc analysis was particularly affected by any residual oxygen in the nitrogen. All the samples were flushed for at least 20 min with the purified nitrogen before analysis. The flushing tube was then raised (Fig. 1) out of the solution so that nitrogen flowed over the solution during the analysis.

The H.D.M.E. used in this work was the type described by SHAIN *et al.*[3]. The D.M.E. used to collect drops of mercury for the H.M.D.E. had a drop rate of 5 sec in distilled water and $m^{2/3}t^{1/6} = 1.45$ mg$^{2/3}$ sec$^{-1/2}$. Two drops of mercury were collected in the teflon spoon (Fig. 1) from the D.M.E. when immersed in the sample. The drops of mercury were then transferred to the platinum tip of the H.M.D.E. Each analysis was made with two fresh drops of mercury as the H.M.D.E.

Pre-electrolysis periods of 10 min for zinc and 30 min for copper, lead, and cadmium were employed throughout most of this work. A 30-sec period of time was used in each analysis between the end of the pre-electrolysis period and the start of the anodic scan.

The cell was placed on a magnetic stirring device and a round teflon stirrer (Fig. 1) was placed on the mercury in the cell for stirring the solution during the pre-electrolysis period. The magnetic stirring unit contained a 1/20-HP constant speed motor, which drove a gear reduction box, so that a final speed of 175 r.p.m. was maintained. The speed was held constant at 175 ± 2 r.p.m. during each analysis.

Procedure

Place 50 ml of sea water in the quartz cell, fit the teflon stopper assembly in place and place the cell on the stirring device. Bubble a steady flow of pure nitrogen through the solution. After flushing, pull up the flushing tube so that nitrogen flows over the solution. Regulate the stirring device to 175 r.p.m. and set an initial potential on the FS polarograph that is *ca.* 0.2 V more negative than the peak potential of the ion obtained by fast-sweep polarography. For example, if a determination for zinc is desired, the initial potential is set at -1.20 V *vs.* Hg. Apply this potential to the cell for precisely 10 min with the solution stirred at 175 r.p.m.; 30 sec before the 10 min are up, stop the stirring and allow the solution to equilibrate. Then, immediately reverse the potential from -1.20 V to zero at a scan rate of 16 mV/sec. The anodic scan for zinc produces a peak at about -1.0 V. Then make a standard addition of a known zinc concentration to the solution in the cell and repeat the procedure with two fresh mercury drops on the H.M.D.E. Obtain the concentration of zinc from the ratio of the known and unknown peak heights *vs.* concentration.

RESULTS AND DISCUSSION

The trace amounts of copper, lead, cadmium, and zinc reported on in this

TABLE I

PEAK POTENTIALS OF SOME TRACE ELEMENTS IN SEA WATER
(V *vs.* Hg pool)

Technique	*Copper*	*Lead*	*Cadmium*	*Zinc*
Single-sweep polarography[a]	−0.25	−0.50	−0.67	−1.09
Anodic-stripping voltammetry[b]	−0.31	−0.48	−0.65	−1.01

[a] Trace element = $5 \cdot 10^{-8}$ g/ml.
[b] Trace element = $5 \cdot 10^{-9}$ g/ml.

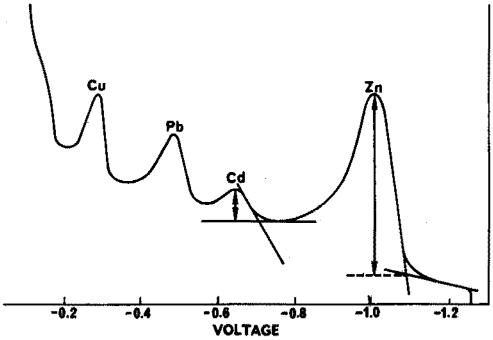

Fig. 2. Simultaneous analysis of some trace elements in raw sea water by anodic-stripping voltammetry. Pre-electrolysis period, 30 min at −1.20 V, anodic scan rate, 16 mV/sec.

study were obtained from surface samples of sea water collected from the Pacific Ocean off the coast of California. The ions were identified by adding known concentrations of the ions to the raw sea water and measuring the increase in peak height at the same peak potential as the unknown. An increase in peak height at the same potential identified the peaks. It was found that the peak heights for standard additions of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} were directly proportional to concentration over the range 10^{-7}–10^{-9} *M* in raw sea water. The peak potentials of these ions determined by the anodic stripping technique and the single-sweep polarographic technique are shown in Table I. Good agreement between the values was obtained. A simultaneous analysis of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} in raw sea water is shown in Fig. 2. It can be seen that flat plateaus are reached before the current increases for the next ion, which allows one to measure the peak height with good accuracy. The anodic scan rate here was 16 mV/sec and this slower rate proved best for well-formed and separated waves. Fast scans tended to produce large, complicated, and overlapping waves. If the waves are well formed and separated, with good plateaus between peaks, simultaneous analysis can be made on the ions Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. If these conditions cannot be obtained, then an analysis for zinc is made, followed by a simultaneous analysis for cadmium, lead, and copper. For the simultaneous analysis of the latter three ions, a constant potential of −0.8 V *vs.* Hg is maintained for 30 min before the 16-mV anodic scan is made.

The variables reported here must be carefully studied and controlled to obtain the best results for each single or simultaneous analysis and will vary with the ion and the media. Table II gives the concentrations obtained by single-sweep polaro-

TABLE II

CONCENTRATION OF SOME TRACE ELEMENTS IN A SURFACE SAMPLE OF PACIFIC SEA WATER

Concentration found (g/ml) (average for 5 determinations)		
Trace element	*Single-sweep polarography*	*Anodic-stripping voltammetry*
Copper	$8.2 \cdot 10^{-9}$	$9.0 \cdot 10^{-9}$
Lead	$< 5 \cdot 10^{-9}$	$4.0 \cdot 10^{-9}$
Cadmium	$< 5 \cdot 10^{-9}$	$1.0 \cdot 10^{-9}$
Zinc	$3.1 \cdot 10^{-8}$	$3.0 \cdot 10^{-8}$

graphy and anodic-stripping voltammetry for some of the trace elements in surface sea water. Pre-electrolysis periods of 10 min for zinc and 30 min for cadmium, lead, and copper respectively were used in this study. Scan rates of 16 mV/sec were used to obtain the anodic-stripping waves. The data are the average of five separate determinations for each ion. Lead and cadmium concentrations were too low to be detected by the single-sweep method but gave clearly measurable waves by the anodic-stripping technique. The data are accurate to within ±5% of the amount present in the 10^{-8} g/ml range and to within ±10% in the 10^{-9} g/ml range. The values for zinc are about one order of magnitude greater than those obtained for the other trace elements reported here. Other investigators[11–13] have reported varying values for total zinc as low as 0.6–0.7 μg/l and ionic zinc in the range of 2–6 μg/l and total zinc values as high as 1–30 μg/l. ARIEL AND EISNER[11] found a concentration of $5.7 \cdot 10^{-7}$ *M* for zinc in dead sea brine. The two analytical methods used in this work determine only the ionic form of the trace element. Copper values in the range 1–20 μg/l have previously been reported[12] and the values reported here are in good agreement. The higher zinc values reported here may result from the presence of several other ions that are present in sea water and can form amalgams during the pre-electrolysis period at −1.2 V. Nickel is an example of an ion that may interfere. Further work on the interference of other trace elements in sea water is needed to establish the accuracy of the anodic-stripping technique for zinc. The values for zinc obtained by the single-sweep polarographic technique check extremely well with those obtained by the anodic-stripping technique (Table II). This suggests that the electrode process is the same at a single drop of mercury with a rapid cathodic sweep as at the H.M.D.E. (2 drops Hg) with a 10-min controlled applied voltage pre-electrolysis period followed by an anodic scan. The presence of standard additions of nickel(II) to sea water[1] produces a double wave by the single-sweep method at about −1.15–1.20 V (*vs.* Hg) but the waves tend to overlap and are difficult to measure. Thus, the data reported here by the single-sweep method for zinc include the nickel concentration as well. Lead cannot be determined in sea water by single-sweep polarography in the 10^{-8}–10^{-9} g/ml range because of the large increase in current due to the electrocapillary maximum at about −0.5 V[14]. The data reported here for lead by anodic-stripping voltammetry are in fair agreement with those reported previously[12]. The data obtained for cadmium in sea water by anodic-stripping voltammetry are considerably higher than those reported by other investigators[12]. About twenty samples of surface sea water were analyzed for cadmium in these laboratories by the two procedures. Cadmium could not be detected in any of these samples by single-sweep polarography, but with anodic-stripping voltammetry a consistent value of 1–$2 \cdot 10^{-9}$ g/ml was obtained. This is in good agreement with data reported by ARIEL AND EISNER for cadmium in Dead Sea brine[11]. It is possible that other ions, which can form amalgams at the -0.8 V pre-electrolysis potential used for cadmium in this work, interfere in the analysis. Further work is necessary to establish the accuracy of the cadmium results.

Advantages and disadvantages

Anodic-stripping voltammetry has two distinct advantages over most analytical methods for the determination of trace elements in sea water. These are (*1*) trace elements in concentrations as low as 10^{-10} *M* can be determined, and (*2*) the analysis is relatively free from errors due to contamination in concentration procedures and from glassware and chemical reagents used in most methods of trace element analysis. For example, all wet chemical methods suffer from the sources of error above and in addition are usually not sensitive enough unless large volumes of sea water are used to concentrate the trace element before the final analysis is made.

The anodic-stripping technique also has an advantage over most other methods in that the technique can simultaneously determine a number of trace elements in a given sample of sea water. It is also very selective for the particular ion or species that is determined. The method is more time-consuming than is single-sweep polarography but its sensitivity allows one to determine several of the trace elements in sea water that cannot be determined by the single-sweep method. Because of the sensitivity of the anodic-stripping method, it is not always necessary to concentrate sea water before analyzing for some of the trace elements, and the work reported on in this study requires only 50-ml volumes of unconcentrated sea water for analysis. The method does suffer from the fact that with a H.M.D.E. it is applicable to only those trace elements in sea water which will form amalgams. In addition, a very large number of variables must be precisely controlled if reliable and reproducible data are to be obtained.

Sources of error

There are many sources of error in anodic-stripping voltammetry with the H.M.D.E.; the following were found critical and had to be very carefully controlled to obtain precise and reproducible data.

(*1*) *Oxygen removal.* This source of error is discussed in the EXPERIMENTAL section.

(*2*) *Time of pre-electrolysis.* Pre-electrolysis periods must be accurately timed with a stop watch. A 30-sec period should be allowed at the end of the pre-electrolysis period, with no stirring, for the solution to equilibrate. The optimum period of pre-electrolysis must be established and then strictly maintained for each ion and its concentration in the sample before reliable data can be obtained. In raw sea water these periods were established as 10 min for zinc and 30 min for copper, lead, and cadmium, respectively, in this work.

(*3*) *Rate of voltage scan.* The optimum anodic voltage scan rate should be established for each ion and its concentration range. In this work an anodic voltage scan rate of 16 mV/sec was found best. This rate provided well-formed and separated waves for the ions. Faster scan rates gave nonreproducible data and complicated overlapping waves.

(*4*) *Initial pre-electrolysis voltage.* This voltage is most important in order to form a good amalgam at the H.M.D.E. for stripping. The initial voltage must be more negative than the peak voltage established by fast-sweep polarography but not too negative, as other ions present may then form amalgams that interfere in the stripping process. A series of trial and error experiments can best establish this voltage for precise and accurate results. In raw sea water an initial pre-electrolysis voltage of -1.2 V for zinc and the simultaneous analysis of zinc, cadmium, lead, and copper was found to be the best for reproducible data and well-formed waves with flat base lines for measurement of the peak heights. When only cadmium, lead, and copper were desired, then -0.8 V was found to be the best.

(*5*) *Purity of mercury and nitrogen.* This is discussed in the EXPERIMENTAL section.

(*6*) *Rate of stirring.* The rate of stirring is very critical and must be precisely controlled. With the arrangement described in the experimental section, it was found that variations of ± 10 r.p.m. in the recommended 175-r.p.m. rate could produce errors as high as 20%.

(*7*) *Reproducibility of mercury drops.* For each analysis two drops of mercury from the D.M.E. are used as the H.M.D.E. These drops must be maintained very reproducibly from the D.M.E. The drop rate and weight of two drops of mercury from the D.M.E. should be checked frequently to be sure that the D.M.E. is forming reproducible drops for the H.M.D.E. Erratic drops from a D.M.E. were found to produce errors of as much as 100% in the analysis. The use of more than two drops of mercury increased the chances of error considerably and for this work two drops of mercury were established as the best for the H.M.D.E.

(*8*) *Reference electrode.* The use of a S.C.E. was another source of error. The calomel solution that slowly diffuses into the sample contains enough trace elements to interfere considerably in the analysis. A mercury pool electrode, into which is placed a platinum contact electrode, was found very satisfactory and used throughout this work. It was found that in 1 h the calomel electrode could introduce errors of as high as 50% in the analysis.

(*9*) *Cell material.* Soft glass or pyrex could not be used in this work because of contamination and ion adsorption errors. The cell, flushing tube, platinum contact electrode, D.M.E., H.M.D.E., and mercury transfer spoon are all made of fused quartz. Teflon is used on the tip of the spoon to collect the mercury drops from the D.M.E. and a teflon magnetic stirring bar is used to stir the solution. The stopper for the cell is also made of teflon.

(*10*) *Temperature.* A temperature variation of more than 0.5° introduced errors, and the solution in the cell was maintained at $30° \pm 0.5°$ throughout this work.

(*11*) *Formation of intermetallic compounds.* Some ions cannot be analyzed by anodic-stripping voltammetry because of the formation of intermetallic compounds[7]. In this work no evidence for the formation of such compounds with zinc, cadmium, lead, and copper at the H.M.D.E. was observed. The fact that the contact time for two drops of mercury with the platinum tip of the H.M.D.E. was short and that the pre-electrolysis periods were held to a maximum of 30 min may have made this source of error negligible in these studies.

(*12*) *Electrolysis media.* For best results the media should have an ionic strength considerably greater than the concentration of the ion to be determined. Sea water is about 0.5 M in sodium chloride and has a total ionic strength of about 1.0 M. Thus, it provides an excellent medium for stripping analysis. Serious errors can result if the medium is not at least 100 times more concentrated than the ion.

SUMMARY

The application of anodic-stripping voltammetry, with a hanging mercury drop electrode and a fast-sweep polarograph, to the determination of several trace elements in raw sea water is discussed. Advantages and disadvantages of the technique and the main sources of error are described. A comparison is made of analytical data for the trace elements zinc, cadmium, lead, and copper by the anodic-stripping technique and by the single-sweep polarographic technique. Precise measurements of concentrations of 10^{-8}–10^{-9} M can be made, if variables are carefully controlled.

RÉSUMÉ

On examine la possibilité d'application de la voltammétrie anodique-"Stripping", avec électrode à goutte de mercure pendante et la polarographie à balayage rapide pour le dosage de plusieurs éléments en traces dans l'eau de mer. On indique les avantages et les inconvénients de cette technique, ainsi que les principales sources d'erreur. On compare les valeurs obtenues par cette méthode avec celles de la polarographie à balayage simple, pour des traces de zinc, cadmium, plomb, et cuivre. On arrive à des résultats précis de 10^{-8} à 10^{-9} M si les divers facteurs sont contrôlés soigneusement.

ZUSAMMENFASSUNG

Es wird die Anwendung der anodischen Stripping-Voltametrie mit hängender Quecksilber-Elektrode und schnellem Polarographen bei der Bestimmung mehrerer Spurenelemente im Seewasser diskutiert. Vor- und Nachteile dieser Technik und die Hauptfehlerquellen werden beschrieben. Unterschiedliche polarographische Techniken werden miteinander verglichen. Konzentrationen von 10^{-8}–10^{-9} M können unter sorgfältiger Berücksichtigung der Nebenbedingungen genau gemessen werden.

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ANALYTICAL UTILIZATION OF THE POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOR OF SOME SULFUR-CONTAINING PURINES

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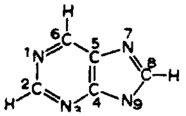
Various sulfur-containing purines are of special interest because of their use in the treatment of various types of cancer. For example, 6-thiopurine is particularly effective in acute leukemia. Recently, the degree of parallelism between metabolic breakdown of various purines and their electrochemical oxidation has been investigated[1–3]. During a study of the electrochemical oxidation of 6-thiopurine[3], it became necessary to characterize and determine a number of purines containing exocyclic sulfur in a higher state of oxidation than in the parent compound. This paper summarizes the work of analytical significance based on the reduction of these sulfur-containing purines at the dropping mercury electrode (D.M.E.) and oxidation at the pyrolytic graphite electrode (P.G.E.).

The polarographic and voltammetric procedures described have been employed to follow the course of chemical or biological reactions of four purines of special interest, namely, 6-thiopurine, purine-6-sulfinic acid, purine-6-sulfonic acid and purine-6-sulfonamide. Data are also presented for bis(6-purinyl)disulfide, although its rather poor stability at most pH values precludes accurate evaluation of any quantitative procedure.

The fundamental structure of the purines is as follows (the numbering shown is that used in chemical abstracts):



With the exception of 6-thiopurine, the electrochemical oxidation or reduction behavior of these compounds has not previously been described. HORN AND ZUMAN[4] reported that 2-hydroxy-6-thiopurine did not show typical catalytic waves for hydrogen evolution in ammoniacal cobalt solutions such as those observed for various thio-pyrimidines and for 2,6-dithiopurine[5]. 2-Hydroxy-6-thiopurine also gave an anodic wave over most of the pH range owing to formation of a mercury salt with the compound[4]. HUMLOVA[6] studied the oscillographic polarography of 6-thiopurine, and VACEK[7] suggested that 6-thiopurine could be determined polarographically by utilizing the height of the wave observed in McIlvaine buffer pH 7.1.

DETERMINATIONS AT THE DROPPING MERCURY ELECTRODE

6-Thiopurine, purine-6-sulfinic acid, purine-6-sulfonic acid, purine-6-sulfonamide and bis(6-purinyl) disulfide are all polarographically reducible at the D.M.E. in aqueous solution. The mechanisms of the polarographic reduction of 6-thiopurine, purine-6-sulfinic acid and purine-6-sulfonic acid have been thoroughly investigated[8].

6-Thiopurine

Some typical polarographic data for 6-thiopurine between pH 1 and 9 are given in Table I. Below pH 2.3, 6-thiopurine exhibits[8] two very close waves; wave I is a 4-electron process ($E_{1/2} = -0.79 - 0.116$ pH) to form 1,6-dihydropurine and wave II is a 2-electron process ($E_{1/2} = -1.00 - 0.048$ pH) involving formation of 1,2,3,6-tetrahydropurine which is then hydrolyzed to form a 4-aminoimidazole. Because wave II shifts, with increasing pH, to less negative potentials than wave I, the two waves merge at pH 3 and give a composite 6-electron wave, which up to pH 5.5 shows the same pH dependence as wave I (Table I).

TABLE I

EFFECT OF pH ON THE $E_{1/2}$ AND DIFFUSION CURRENT CONSTANT OF 6-THIOPURINE, PURINE-6-SULFINIC ACID AND PURINE-6-SULFONIC ACID[a]

6-Thiopurine				*Purine-6-sulfinic acid*[h]				*Purine-6-sulfonic acid*			
pH	*Wave*	*I*	$E_{1/2}$ (*V*)	*pH*	*Wave*	*I*	$E_{1/2}$ (*V*)	*pH*	*Wave*	*I*	$E_{1/2}$ (*V*)
<0[b]	I	24.4	0.810	3.6[e]	I	4.57	0.710	1.0[c]	I	2.74	0.500
	II	30.7	0.975		III	4.32	1.280	2.0[c]	I	3.43	0.600
1.0[c]	I	24.5	0.910	5.4[e]	I	4.23	0.890		III	10.00	1.170
	II	34.7	1.060		III	4.45	1.420	2.3[d]	I	3.36	0.640
2.3[d]	I	8.3	1.010	7.0[f]	I	2.91	1.060		III	5.23	1.120
	II	9.1	1.120		III	3.77	1.560	3.6[e]	I	4.52	0.750
3.4[e]	I	14.3	1.180	8.0[f]	I	1.62	1.130		II	1.60	0.960
4.4[e]	I	14.8	1.260		II	1.35	1.400		III	3.04	1.170
5.7[e]	I	14.2	1.430	9.1[g]	I	3.41	1.230	5.4[e]	I	4.68	0.890
6.0[f]	III	12.7	1.450		III	3.02	1.720		II	2.72	1.125
7.0[f]	III	5.4	1.480	9.0[i]	II	3.28	1.460		III	4.84	1.320
8.0[f]	III	1.8	1.510		III	—[k]	1.770	6.9[f]	I	1.36	0.970
9.1[g]	IV	14.8	1.740	11.6[j]	II	2.79	1.660		II	4.39	1.230
				12.3[j]	II	2.32	1.710		III	7.86	1.400
								8.0[f]	II	3.82	1.355
									III	6.80	1.400
								8.9[i]	II	5.30	1.405
									III	3.82	1.580
								9.1[g]	II	3.25	1.310
									III	3.32	1.560
									IV	3.58	1.460
								11.6[j]	II	2.86	1.560
								12.3[j]	II	3.38	1.660

[a] Except in the case of 1 *M* sulfuric acid and 1 *M* acetic acid, all buffers were 0.5 *M* in ionic strength.
[b] 1 *M* sulfuric acid. [e] Acetate buffer.
[c] Chloride buffer. [f] McIlvaine buffer.
[d] 1 *M* acetic acid. [g] Ammonia buffer.
[h] Below pH 3.6 decomposition of purine-6-sulfinic acid is too rapid to allow accurate analytical data to be gathered.
[i] Carbonate media. [j] Hydroxide media.
[k] This wave was too indistinct to allow calculation of I.

Above pH 5.5 wave III appears ($E_{\frac{1}{2}} = -1.29 - 0.027$ pH) but disappears above pH 8; a single further wave IV is observed at pH 9.1. At low pH values, the reduction process is accompanied by a catalytic hydrogen discharge which is shown by large catalytic currents.

Because of the involvement of catalytic hydrogen current at low pH and the closeness of waves I and II, the most useful pH range for the determination of 6-thiopurine is pH 3.5–5.7. Some typical analytical data in acetate buffer pH 3.5 are shown in Table II. Because the limiting current shows deviations from linear dependence on concentration, either the concentration range should be restricted to below $1 \cdot 10^{-4}\,M$ or a calibration curve should be used. The observed deviation is probably associated with the lowering of the hydrogen overpotential by 6-thiopurine. As the 6-thiopurine concentration increases, hydrogen becomes more readily reduced so that there is a much poorer separation between the 6-thiopurine and hydrogen discharge waves.

Purine-6-sulfinic acid

Below pH 3.7 purine-6-sulfinic acid is extremely unstable and decomposes mainly to sulfur dioxide, 6-thiopurine and hypoxanthine, although at some pH values purine and purine-6-sulfonic acid may be produced[8]. Some typical polarographic data are presented in Table I. All three polarographic waves observed for purine-6-sulfinic acid shift linearly more negative with increasing pH. Between pH 2 and 9.1, a reduction wave I ($E_{\frac{1}{2}} = -0.37 - 0.094$ pH) is observed which is attributed to a 2-electron reduction of the monoanionic species to 1,6-dihydropurine-6-sulfinic acid which dehydrates fairly slowly to purine-6-sulfenic acid, which is immediately further reduced in a 2-electron process to 6-thiopurine. Wave II appears between pH 8 and 13 ($E_{\frac{1}{2}} = -0.79 - 0.075$ pH), and is attributed to a 2-electron reduction of the dianionic species to the corresponding 1,6-dihydro derivative which breaks down to yield purine and the sulfoxylate anion. These were accompanied between pH 3 and 9 by the wave III ($E_{\frac{1}{2}} = -0.99 - 0.080$ pH) which is attributed to a 4-electron reduction of the product formed in the preceding step[8]. In terms of clarity of waves and stability of purine-6-sulfinic acid, the optimum background for the determination of the compound is in buffers containing ammonia and ammonium chloride at pH 9.1. Some typical data are presented in Table II. At pH 9.1, the values of i_d/C for concentrations in the range 1.9–$9.5 \cdot 10^{-4}\,M$ were found to be constant, 5.9 ± 0.1 μA/mM for wave I and 6.4 ± 0.5 μA/nM for wave III. The values for wave III tend to decrease with increasing purine concentration. This is related to the closeness of the current due to discharge of ammonium ions from the background electrolyte and the consequent difficulty in accurate measurement of the current, and to the rather erratic droptime at these very negative potentials.

Purine-6-sulfonic acid

At pH 1.0 and below, purine-6-sulfonic acid decomposes to hypoxanthine and sulfur dioxide, although the decomposition is much slower than for the sulfinic acid. The variation of the diffusion current constant and half-wave potential with pH is shown in Table I; three of the waves shift linearly more negative with increasing pH. Wave I ($E_{\frac{1}{2}} = -0.45 - 0.078$ pH) appears between pH 1 and 7; this wave is attributed to a 2-electron reduction of the monoanionic species to the 1,6-dihydrosulfonate

TABLE II

VARIATION OF CURRENT WITH CONCENTRATION FOR VARIOUS SULFUR-CONTAINING PURINES AT THE DME

Conc. (mM)	*Background*	*pH*	*Current mean (μA)*[a]	i_d/C *(μA/mM)*
6-Thiopurine				
0.028	Acetate	3.5	1.16 ± 0.01	41.4
0.084			3.23 ± 0.05	38.5
0.168			5.76 ± 0.04	34.3
0.252			8.51 ± 0.05	33.8
0.420			12.98 ± 0.30	30.9
Purine-6-Sulfinic Acid				
0.19	Ammonia	9.1	I[b] 1.17 ± 0.03	6.0
			III 1.33 ± 0.05	7.0
0.38			I 2.25 ± 0.03	5.9
			III 2.62 ± 0.18	6.9
0.57			I 3.30 ± 0.00	5.8
			III 3.63 ± 0.09	6.4
0.76			I 4.57 ± 0.09	6.0
			III 4.50 ± 0.25	5.9
0.95			I 5.68 ± 0.08	6.0
			III 5.42 ± 0.22	5.7
Purine-6-Sulfonic Acid				
0.20	Ammonia	9.1	II[b] 1.29 ± 0.00	6.5
			IV 1.76 ± 0.03	8.8
			III 1.28 ± 0.03	6.4
0.39			II 2.37 ± 0.03	6.1
			IV 3.57 ± 0.09	9.1
			III 2.24 ± 0.02	5.7
0.59			II 3.76 ± 0.00	6.4
			IV 4.66 ± 0.02	7.9
			III 3.68 ± 0.08	6.3
0.78			II 5.10 ± 0.20	6.5
			IV 6.00 ± 0.50	7.7
			III 4.80 ± 0.20	6.2
0.98			II 6.22 ± 0.07	6.3
			IV 7.61 ± 0.03	7.8
			III 6.00 ± 0.15	6.1

[a] At least three replicate determinations at each concentration level were carried out.
[b] Roman numerals refer to wave designation as outlined in text and in references 3 and 8.

which decomposes to purine[8]. Between pH 3.6 and 12.5, wave II appears ($E_{\frac{1}{2}} = -0.68 - 0.079$ pH); this is ascribed to a 2-electron reduction of the dianionic sulfonate to the 1,6-dihydro derivative which decomposes to purine[8]. Wave III appears between pH 1 and 9 ($E_{\frac{1}{2}} = -0.98 - 0.064$ pH), and involves a 4-electron reduction of the product of the first 2-electron step to a 4-aminoimidazole. A fourth wave, wave IV, was observed at pH 9.1 only, between waves II and III.

It is clear from Table I that the analytical determination of purine-6-sulfinic acid could be readily accomplished at many pH values by utilizing one or several waves. From the point of view of determining the sulfonic acid in the presence of the sulfinic acid, an ammonia buffer pH 9 seems to offer the greatest potential. Analytical data for the sulfonic acid at pH 9 are presented in Table II. The values of i_d/C for the concentration range shown were found to be constant: 6.3 ± 0.2 μA/mM for wave II, 8.2 ± 0.8 μA/mM for wave IV, and 6.1 ± 0.3 μA/mM for wave III. Clearly all three waves are linearly dependent upon concentration and can be successfully utilized analytically.

Purine-6-sulfonamide

Purine-6-sulfonamide was only investigated at pH 9 (ammonia). At this pH it gave three diffusion-controlled waves at $E_{\frac{1}{2}} = -1.04$ V, -1.47 V and -1.58 V. The most positive first wave could be employed to determine the sulfonamide in the presence of all the other purines studied.

Bis(6-purinyl) disulfide

Bis(6-purinyl) disulfide rapidly decomposes in alkaline solution to purine-6-sulfinic acid or, if ammonia is present, to a mixture of purine-6-sulfinic acid and purine-6-sulfonamide[8]. Even at low pH the compound is rather unstable and it has been suggested[8] that at pH 2.3 it decomposes to either a disulfone or disulfoxide. At pH 2.3, the compound gives two very characteristic waves at $E_{\frac{1}{2}} = -0.05$ V and -1.05 V, but because of the instability of the compound, these waves were not utilized for quantitative analysis although they do serve to characterize the compound for qualitative purposes.

DETERMINATION OF PURINES AT THE PYROLYTIC GRAPHITE ELECTRODE

Only two of the purines examined gave analytically useful anodic waves at the P.G.E. The mechanisms of the processes giving rise to these waves have been determined[3].

6-Thiopurine

Some typical voltammetric data for 6-thiopurine at the stationary PGE between pH 0.0 and 12 are shown in Table III. The first two pH-dependent anodic waves I and II have been attributed to 1-electron processes resulting in the formation of bis(6-purinyl) disulfide; the height of wave I is limited by adsorption of the disulfide[3]. The disulfide decomposes[3] rapidly in ammonia pH 9 and the overall result is that, under coulometric conditions, somewhat in excess of 4 electrons are transferred. Wave III observed in ammonia buffer pH 9 has been ascribed to a 6-electron oxidation, in which the primary product can undergo further chemical reactions[3]. Typical concentration data are shown in Table IV at the stationary P.G.E. For analytical purposes, wave II in 1 M acetic acid or wave III at pH 9.1 can be used. Waves I and II are well separated in acetic acid media, which is important since only wave II is directly proportional to concentration.

In an attempt to increase the sensitivity of the method, the electrode was rotated at about 600 r.p.m. At pH 9, three waves were then observed and the current was increased very considerably (Table IV); the current for all three waves ($E_{p/2} =$ 0.06 V, 0.30 V and 0.50 V, respectively, for wave I, II and III) increased linearly with concentration over the range studied.

Purine-6-sulfinic acid

Purine-6-sulfinic acid is oxidized in ammonia buffer pH 9 primarily to purine-6-sulfonamide and a trace of purine-6-sulfonic acid[3]. The pH dependence of the single

TABLE III

EFFECT OF pH ON THE PEAK POTENTIAL AND LIMITING CURRENT OF 6-THIOPURINE AT THE STATIONARY P.G.E.

Background	*pH*	*Current for wave*		*Peak potential (V)*
		i_p (μA)	i_p/AC ($\mu A/mM \cdot mm$)	
1 M H_2SO_4	< 0.00	II 1.10	0.202	0.79
1 M HOAc	2.3	I 0.57	0.104	0.35
		II 1.23	0.225	0.70
		III —[a]	—[a]	1.57
Acetate	3.6	I 0.88	0.161	0.39
		II 1.34	0.245	0.62
Acetate	4.4	II 1.05	0.192	0.62
Acetate	5.4	I 0.68[b]	0.125	0.28
		II 1.32	0.241	0.52
		III —[a]	—[a]	1.10
McIlvaine	6.1	I 0.56	0.102	0.25
		II 1.21	0.221	0.48
McIlvaine	6.9	I 0.88	0.161	0.15
		II 1.26	0.230	0.42
McIlvaine	8.1	I 0.58	0.106	0.13
		II 1.25	0.229	0.34
Ammonia	9.2	II 1.35	0.237	0.30
		III 3.32	0.607	0.62
Hydroxide	9.9	II 1.82	0.333	0.29
		III 3.80	0.694	0.93
Hydroxide	12.0	II 1.30	0.237	0.20

[a] At these pH values wave III appeared as a sharp spike on the voltammogram. A current could not be measured because generally the background trace showed a greater current than that in the presence of 6-thiopurine.

[b] Often this peak did not appear.

TABLE IV

VARIATION OF CURRENT WITH CONCENTRATION FOR VARIOUS SULFUR-CONTAINING PURINES AT THE P.G.E.

Concn. (mM)		*Mean current (μA)*	i_1/C ($\mu A/mM$)
6-Thiopurine at stationary P.G.E. in 1 M HOAc			
0.08	I[a]	0.24 ± 0.12	3.0
	II	0.27 ± 0.01	3.4
0.17	I	0.31 ± 0.08	1.8
	II	0.57 ± 0.03	3.4
0.25	I	0.21 ± 0.07	0.8
	II	0.86 ± 0.08	3.4
0.42	I[b]		
	II	1.39 ± 0.07	3.3
6-Thiopurine at stationary P.G.E. in ammonia pH 9.1			
0.08	II[c]		
	III	0.90 ± 0.10	11.2
0.17	II[c]		
	III	1.95 ± 0.10	11.5
0.25	II	1.00 ± 0.04	4.0
	III	2.84 ± 0.10	11.4
0.42	II	1.61 ± 0.03	3.8
	III	4.61 ± 0.20	11.0

TABLE IV (*continued*)

Concn. (mM)		*Mean current (μA)*	i_l/C *(μA/mM)*
6-Thiopurine at rotating[d] *P.G.E. in ammonia pH 9.1*			
0.20	I	3.30 ± 0.20	1.7
	II[e]		
	III	8.1 ± 0.50	40
0.41	I	7.1 ± 1.0	1.7
	II	4.1 ± 0.4	10.0
	III	17.9 ± 1.5	44
0.61	I	10.7 ± 0.2	1.8
	II	5.6 ± 0.4	9.2
	III	22.5 ± 0.8	37
0.81	I	15.3 ± 0.1	1.9
	II	8.0 ± 0.4	10.0
	III	30.3 ± 0.7	37
1.01	I	16.8 ± 1.2	1.7
	II	12.0 ± 1.8	11.9
	III	36.7 ± 1.9	36
Purine-6-sulfinic acid at stationary P.G.E. in ammonia pH 9.1			
0.19		1.80 ± 0.02	9.5
0.38		4.09 ± 0.18	10.8
0.57		4.30 ± 0.03	7.6
0.76		6.45 ± 0.30	8.5
0.95		8.05 ± 0.05	8.5

[a] Roman numerals refer to waves as described in text and references 3 and 8.

[b] In these experiments this wave appeared as a very indistinct inflection on the rising portion of wave II.

[c] At these concentrations wave II was too indistinct to allow accurate measurement of the peak current.

[d] Rotation speed: 600 r.p.m.

[e] No wave observed at this concentration level.

anodic wave observed for the compounds has not been studied. However, in ammonia buffer pH 9.1, the compound shows a single anodic wave at the stationary P.G.E. ($E_{p/2} = 0.70$ V). The current for this peak was approximately a linear function of concentration at least up to the 1 m*M* concentration level ($i_l/C = 9.0 \pm 1.8$ μA/m*M*; Table IV).

ANALYSIS OF MIXTURES

A mixture of purine-6-sulfinic acid and purine-6-sulfonic acid can be analyzed by a single polarographic method. At pH 9 (ammonia) the first polarographic waves of these compounds are indistinguishable to give a composite wave at $E_{\frac{1}{2}} = -1.30$ V; the height of this wave is proportional to the sum of the sulfinic and sulfonic acid concentrations. The second and third waves to appear are due to the sulfonic acid and can be used to determine its concentration; then by difference the current due to sulfinic acid in the first wave can be calculated and hence its concentration. Alternatively, the sulfinic acid can be determined through the height of its anodic wave at the P.G.E. (Table V).

TABLE V

ANALYSIS OF MIXTURES OF 6-THIOPURINE, PURINE-6-SULFINIC ACID AND PURINE-6-SULFONIC ACID

Sample taken (mM)			*Sample found (mM)*		
6-Thiopurine	*Sulfinic acid*	*Sulfonic acid*	*6-Thiopurine*	*Sulfinic acid*	*Sulfonic acid*
—	0.47	0.49	—	0.46[a]	0.50[b]
—	0.21	0.80	—	0.17[a] 0.22[c]	0.78[b]
—	0.76	0.20	—	0.72[a] 0.74[c]	0.20[b]
0.51	—	0.49	0.55[d]	—	0.52[e]
0.81	—	0.22	0.80[d]	—	0.22[e]
0.20	—	0.86	0.22[d]	—	0.89[e]
0.81	0.21	—	0.80[f]	0.20[g]	—
0.20	0.85	—	0.22[f]	0.82[g]	—
0.51	0.53	—	0.55[f]	0.54[g]	—
0.34	0.36	0.36	0.36[f]	0.32[a]	0.34[b]

[a] Based on current for first polarographic wave corrected for sulfonic acid concentration obtained from second and third polarographic waves, background ammonia pH 9.

[b] Based on second and third polarographic waves at D.M.E. at pH 9.

[c] Based on single anodic wave at stationary P.G.E. at pH 9.

[d] Based on height of voltammetric oxidation waves at rotating P.G.E. at pH 9.

[e] Based on height of polarographic reduction waves at D.M.E. at pH 9.

[f] Based on three anodic waves at rotating P.G.E. at pH 9.

[g] Based on first polarographic wave at pH 9.

Mixtures of purine-6-sulfonic acid and 6-thiopurine are readily analyzed in ammonia buffer pH 9; the sulfonic acid is determined through the height of any of its three polarographic waves; 6-thiopurine is determined through the height of any of its three anodic waves at the rotating P.G.E. (Table V).

Purine-6-sulfinic acid is determined in the presence of 6-thiopurine at pH 9 through the height of its first polarographic reduction wave at the D.M.E.; the 6-thiopurine can be determined in such a mixture based on either of the three oxidation waves at the rotating P.G.E. (Table V).

By utilizing the same general principles, a mixture containing purine-6-sulfinic and sulfonic acids and 6-thiopurine can also be determined (Table V). If purine-6-sulfonamide is present in any of these mixtures it is most satisfactorily determined at pH 9 through its first polarographic wave, $E_{\frac{1}{2}} = -1.04$ V.

EXPERIMENTAL

Chemicals

6-Thiopurine was obtained from Calbiochem. Bis(6-purinyl) disulfide, purine-6-sulfinic acid (sodium salt) and purine-6-sulfonic acid (potassium salt) were prepared as described by DOERR *et al.*[9]; the latter compound was most conveniently prepared from 6-chloropurine (Calbiochem). Purine-6-sulfonamide was supplied as a gift from Dr. ROLAND K. ROBINS (University of Utah).

Buffer solutions were prepared from reagent-grade chemicals. Argon (Linde) used for deoxygenating purposes was equilibrated with water; no further purification or treatment was necessary.

Apparatus

Polarograms and voltammograms were automatically recorded on a Sargent Model XVI Polarograph employing a water-jacketed polarographic cell maintained at 25° ± 0.2°. A saturated calomel reference electrode was employed throughout the study and all potentials are referred to this electrode.

The preparation of the 4-mm diameter P.G.E has been described earlier[2].

General polarographic procedure

Test solutions were prepared by diluting a suitable stock solution with the desired buffer; unless otherwise specified the ionic strength in the final test solutions was 0.5 M. About 15 ml of this test solution was transferred to the polarographic cell, purged with argon for at least 10 min, and then polarographed. A portion of the buffer solution was treated in an identical fashion to obtain a background curve. The residual current was subtracted arithmetically from the total current; $E_{\frac{1}{2}}$ and i_l were determined graphically, from the average of the recorder trace.

General voltammetric procedure

Test solutions were prepared in the same way as in the General Polarographic Procedure. The P.G.E. was resurfaced before each run by polishing it on a 600-grade silicon carbide disc mounted on a motor-driven plate. The surface was then washed free of any loose adhering graphite particles with a jet of distilled water; the electrode was then very carefully dried by touching the surface on a soft paper tissue. The electrode was then immersed in the cell and the initial potential (usually 0.00 V) was applied for 10 sec after which time the voltammetric scan was begun.

When a rotating P.G.E. was employed, a rotation rate of 600 r.p.m. was maintained. Background electrolyte solutions were treated identically to obtain the residual current, which was subtracted arithmetically from the total current to obtain i_p and E_p or $E_{p/2}$.

Simultaneous determination of 6-thiopurine, purine-6-sulfinic acid and purine-6-sulfonic acid

Simple calibration curves are prepared for each compound over the desired concentration range (*e.g.* 0.1–1.0 mM) as follows. Polarograph appropriate concentrations of the sulfinic acid in ammonia buffer pH 9.1 and prepare a calibration curve of diffusion current *vs.* concentration for the first polarographic wave, $E_{\frac{1}{2}} = -1.23$ V. Repeat the same procedure for purine-6-sulfonic acid and prepare three calibration curves for the waves at $E_{\frac{1}{2}} = -1.31$ V, -1.46 V and -1.56 V.

Calibration curves for the three anodic waves of 6-thiopurine at the rotating P.G.E. are prepared, again in ammonia buffer pH 9.1.

The concentration of purine-6-sulfonic acid in an unknown solution buffered to pH 9.1 with ammonia is obtained from the height of the second and third polarographic waves. Once the sulfonic acid concentration has been calculated, the appropriate current is subtracted from that observed for the first wave; the difference is the current due to the first wave of purine-6-sulfinic acid which is then used to calculate the concentration of this compound. The concentration of 6-thiopurine is determined from the height of any of the three anodic waves observed at the rotating P.G.E.

The author would like to thank Professor ROLAND K. ROBINS, University of Utah, for a sample of purine-6-sulfonamide; Dr. JACK J. FOX, Sloan Kettering Institute for Cancer Research, for samples of purine-6-sulfinic acid and purine-6-sulfonic acid; and the National Science Foundation for financial support.

SUMMARY

The polarographic and voltammetric behavior at the dropping mercury and pyrolytic graphite electrodes of 6-thiopurine, purine-6-sulfinic acid, purine-6-sulfonic acid, purine-6-sulfonamide and bis(6-purinyl) disulfide is discussed from the viewpoint of their analytical applicability. Procedures are described for the determination of the single compounds or mixtures of several compounds. The polarographic and voltammetric behavior of these compounds is so characteristic that the observed waves can be utilized for very sensitive qualitative identification.

RÉSUMÉ

On examine le comportement polarographique et voltammétrique à la goutte de mercure et aux électrodes de graphite pyrolytique des composés suivants: 6-thiopurine, acide purine-6-sulfinique, acide purine-6-sulfonique, purine-6-sulfonamide et bis(6-purinyl)disulfure. Des procédés sont décrits pour le dosage de ces substances, individuellement et en mélange. Les vagues observées sont si caractéristiques qu'elles peuvent permettre une identification très sensible de ces composés.

ZUSAMMENFASSUNG

Unter dem Gesichtspunkt ihrer analytischen Anwendbarkeit werden das polarographische und voltametrische Verhalten der tropfenden Quecksilber- und pyrolytischen Graphit-Elektrode im Hinblick auf folgende Substanzen diskutiert. 6-Thiopurin, Purin-6-Sulfinsäure, Purin-6-Sulfonsäure, Purin-6-Sulfonamid, Bis(6-purinyl)disulfid. Es werden Verfahren zur Bestimmung der einzelnen Verbindungen oder Mischungen verschiedener Verbindungen beschrieben. Das polarographische und voltametrische Verhalten dieser Verbindungen ist so charakteristisch, dass die beobachteten Stufen zur sehr empfindlichen qualitativen Identifizierung benutzt werden können.

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ELECTROCHEMICAL MASKING OF INDIUM IN A.C. POLAROGRAPHIC DETERMINATION OF CADMIUM

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The half-wave potentials of indium and cadmium are very close to each other and their simultaneous determination is very difficult by conventional d.c. polarography. Even a.c. polarograms show well separated reduction waves only when the concentration of the two elements is about equal. Hence, indium is usually removed by precipitation as hydroxide[1] or by extraction with isopropyl ether[2-4] before the determination of cadmium. DOLEŽAL[5] recommends ethylenediamine in potassium hydroxide as supporting electrolyte for the determination of cadmium in the presence of excess of indium; in this medium the waves are well separated but at higher concentrations a precipitate of indium hydroxide is formed on which cadmium ions are adsorbed. The waves of cadmium and indium are well separated also in alkaline solutions of bis(2-hydroxybutyl)-2-hydroxyethylamine. However, when this electrolyte is used, the lead wave appears at the same potentials as that of cadmium and interferes in its determination[6].

In non-complexing electrolytes like phosphoric, perchloric or nitric acid, indium is irreversibly reduced at the dropping mercury electrode and does not produce any a.c. polarographic wave. Hence, cadmium can be determined in the presence of large amounts of indium by the a.c. polarographic method[7-9]. However, in the presence of even small amounts of chloride, or other complex-forming anions, the indium wave appears on the polarogram and interferes in the determination of cadmium.

The present work was carried out in order to find a suitable electrochemical masking agent for indium which would permit polarographic determination of cadmium without any previous separation of indium.

EXPERIMENTAL

Polarograms were recorded with a Metrohm E 261 R Polarecord connected to a Metrohm E 393 A-C modulator. An external saturated calomel electrode (S.C.E.) served as reference electrode and a tungsten electrode was employed as auxiliary electrode. All a.c. polarograms were obtained with an a.c. amplitude of 10 mV r.m.s. The capillary characteristics of the dropping mercury electrode, measured in 0.1 M potassium nitrate (open circuit) at a mercury height of 60.1 cm, were $m = 2.389$ mg/sec and $t = 3.99$ sec. All experiments were performed at $25 \pm 0.1°$. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis.

Citric acid (0.2 M) was used as supporting electrolyte in most experiments. The pH of the electrolyte was adjusted to the desired value by addition of sodium hydroxide and measured with a Beckman Zeromatic pH meter. Stock solutions of cadmium were prepared by dissolving the appropriate amount of reagent-grade cadmium sulphate in distilled water, and standardized by EDTA titration. Solutions (1%) of Benax (sodium dodecyldiphenyletherdisulphonate; Dow Chemical Co., Midland, Mich., U.S.A.) and of Aerosol AY (sodium diamylsulphosuccinate; American Cyanamide Co., New York, U.S.A.) were prepared by dissolution of the commercial products in distilled water. The remaining chemicals were of reagent grade and were used without further purification.

RESULTS AND DISCUSSION

Recent investigations indicate that the electrode reaction of negatively charged complexes is inhibited in the presence of certain anionic surfactants like Benax and Aerosol AY, whereas the polarographic waves of uncomplexed metal ions are practically unaffected by the presence of the same surfactants[10,11].

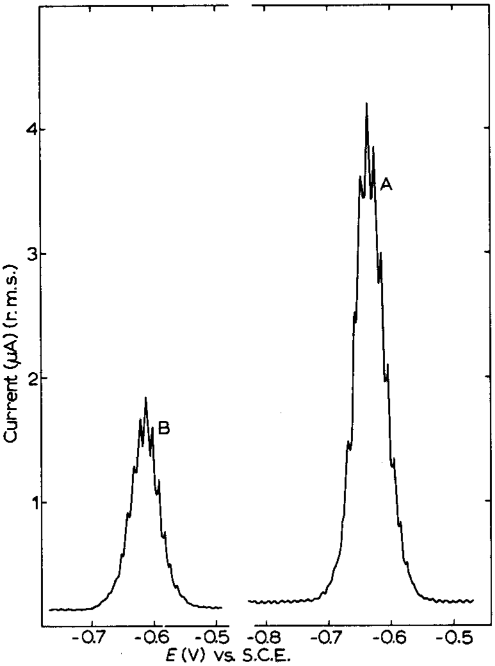

Fig. 1. A.c. polarograms of 10^{-4} M cadmium and 10^{-4} M indium in 0.2 M citrate buffer, pH 3.5 in the absence (curve A) and in the presence of 0.03% Benax (curve B).

Citric acid which forms a stable complex with indium was chosen as supporting electrolyte. Both cadmium and indium give rise to well-defined a.c. polarographic waves in this medium but the electrode reactions occur at the same potentials. As indicated in Fig. 1, curve A, a mixture of cadmium and indium in citrate buffer pH 3.5 produces only one a.c. polarographic wave. The same result is observed over the entire pH range 2–6. At pH values above 6 the indium wave disappears, but in slightly acidic and neutral solutions the height of the cadmium wave is very dependent on the excess of citrate present and on the pH of the electrolyte. These experiments are in excellent agreement with earlier data on the polarographic behaviour of cadmium in citrate and tartrate buffers[12,13] and imply that the determination of cadmium is restricted to acidic solutions in which the indium wave is not masked by some complexing agent.

The effect of anionic surfactants on the height of the a.c. polarographic waves is given in Fig. 2. As indicated in the figure, the electrode reaction of indium is completely inhibited in the presence of 0.02% of either Benax or Aerosol AY. However, the peak current of cadmium in the same supporting electrolyte is only slightly decreased in the presence of Aerosol AY and completely independent of even large amounts of Benax.

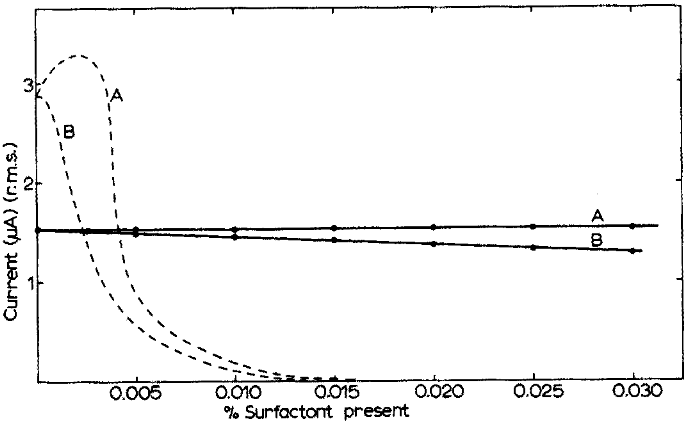

Fig. 2. Effect of surfactants on peak height of a.c. polarographic waves of 10^{-4} *M* indium (dashed lines) and of 10^{-4} *M* cadmium (solid lines) in 0.2 *M* citrate buffer, pH 3.5. (A) Benax; (B) Aerosol AY.

The effect of pH of the supporting electrolyte was investigated by recording a.c. polarograms of indium and of cadmium in citrate buffers containing 0.03% Benax. The pH of each solution was adjusted to the desired value by addition of sodium hydroxide. At low pH values the indium wave is only partly depressed, but above pH 3.5 the electrode reaction of the indium citrate complex is completely inhibited in the presence of Benax. On the other hand, the cadmium wave is not affected by the surfactant at pH values less than 4. Above pH 4 the peak height decreases, probably because a cadmium citrate complex is formed at these pH values. In the following experiments 0.2 *M* citrate buffer with pH 3.6–3.9 containing 0.03% Benax was used as supporting electrolyte. In this buffer, cadmium exhibits well-defined d.c. and a.c. polarographic waves (Fig. 1, curve B), the summit potential, E_s, coincides with the half-wave potential, $E_{\frac{1}{2}} = -0.62$ V *vs.* S.C.E., and the height of the wave is not affected by the presence of excess of indium.

As indicated in Fig. 3, the diffusion current of cadmium increases linearly with the concentration in the range 10^{-4}–10^{-3} *M*. However, the peak height of the a.c. polarographic wave is proportional to the concentration only in the range 10^{-6}–$2.5 \cdot 10^{-4}$ *M* cadmium. At higher concentrations, the a.c. current is less than expected, but the peak height is perfectly reproducible and independent of the excess indium present.

The effect of drop time was investigated by recording a.c. and d.c. polarograms at various heights of the mercury column. The limiting d.c. current of cadmium in citrate buffer, pH 3.7 and 0.03% Benax present, increases with increasing height of mercury and the value $i/\sqrt{h_{corr}}$, where h_{corr} is the height of the column after correction for the "back pressure", is constant, indicating that the limiting current is diffusion-controlled (Table I). However, the a.c. peak current decreases with decreasing drop time (increasing height of the column). This effect might be the result of a slow step in the overall electrode reaction but was not investigated further. These experiments imply that in quantitative a.c. polarographic determination of cadmium in this medium, it is important to keep the mercury head at a constant level.

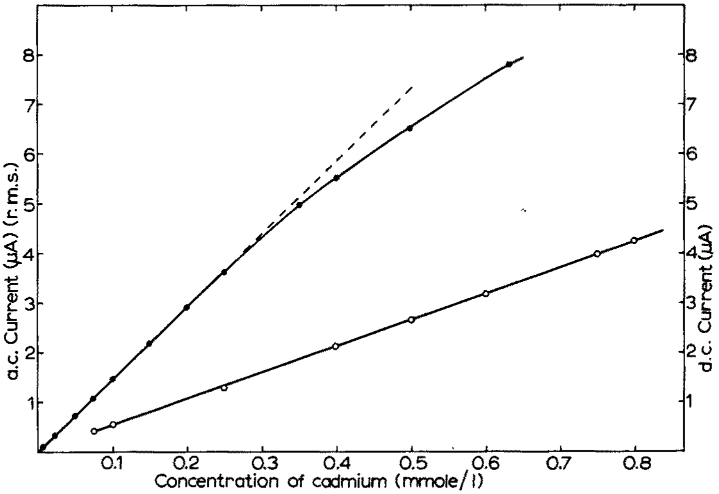

Fig. 3. Calibration curve of cadmium in 0.2 *M* citrate buffer, pH 3.7 with 10^{-2} *M* indium and 0.03% Benax present. (○) d.c. current; (●) a.c. current.

TABLE I

EFFECT OF PRESSURE OF MERCURY ON POLAROGRAPHIC WAVES OF $2.5 \cdot 10^{-4}$ *M* CADMIUM IN 0.2 *M* CITRATE BUFFER, pH 3.75 AND 0.03% BENAX PRESENT

h_{corr} (cm)	i_p (r.m.s) (μA)	i_d (μA)	$i_d/\sqrt{h_{corr}}$
41	3.56	0.94	0.147
46	3.48	0.99	0.146
51	3.42	1.05	0.147
56	3.34	1.09	0.145
61	3.26	1.14	0.146
66	3.20	1.18	0.146
71	3.14	1.22	0.145
76	3.12	1.28	0.147

Cobalt, nickel, manganese and tungsten are polarographically inactive in citrate buffer at pH 3.5–4, and zinc and arsenic are reduced at potentials considerably more negative than that of cadmium[14]. Copper, iron(III) and bismuth are reduced at potentials more positive than cadmium in citrate buffer. However, as these cations form stable complexes with citrate at pH 3.5, the electrode reactions are completely inhibited in the presence of Benax. Lead and thallium do not form stable negatively charged complexes with citrate at pH 3.5 and the waves of these cations are only slightly affected by the presence of Benax. The summit potentials of lead ($E_s = -0.45$ V) and thallium ($E_s = -0.47$ V) are considerably more positive than that of cadmium and even large excesses of these cations do not interfere in the a.c. polarographic determination of cadmium. Consequently, the suggested method is very selective and may be of practical analytical value. Provided that there is a sufficient excess of citrate to complex interfering elements and that the mercury head is kept at a constant level, cadmium can be determined in the presence of at least 10,000-fold amounts of indium and large amounts of a number of other cations. Anions which do not form stable negatively charged complexes with cadmium at pH 3.5 (chloride, nitrate, sulphate, etc.) do not interfere. Experiments showed that the peak height of the cadmium wave is slightly dependent on the concentration of the supporting electrolyte. Hence, in the most precise work cadmium should be determined at constant citrate concentration or by the standard addition method.

A few data of a.c. polarographic determination of cadmium in synthetic mixtures are given in Table II. The solutions were prepared by addition of 50 ml of 0.4 *M* citrate buffer to the sample solutions and adjusting the pH to 3.5–4 with sulphuric acid or sodium hydroxide; 3 ml 1% Benax was added to each solution before dilution to 100 ml with distilled water.

The authors wish to thank the Dow Chemical Co., Midland, Mich. U.S.A. for a gift of the Benax sample.

TABLE II

DETERMINATION OF CADMIUM IN SYNTHETIC MIXTURES

(0.2 *M* citrate buffer pH 3.6 and 0.03% Benax present)

Cd taken (mM)	*Added species (mM)*	*Cd found (mM)*	*Error (%)*
0.250	10 In^{3+}	0.254	+1.6
0.025	10 In^{3+}	0.0248	−0.8
0.001	10 In^{3+}	0.00095	−5.0
0.050	10 In^{3+} 0.5 Cu^{2+} 0.5 Bi^{3+}	0.047	−0.6
0.100	0.1 In^{3+} 1.0 Pb^{2+} 0.1 Tl^{+}	0.995	−0.5
0.050	10 In^{3+} 0.5 Fe^{3+}	0.0505	+1.0
0.100	10 In^{3+} 100 Cl^{-} 100 NO_3^{-} 10 SO_4^{2-}	0.1004	+0.4

SUMMARY

A polarographic method for the determination of cadmium without any previous separation of large amounts of indium is described. The anionic surfactant Benax serves as electrochemical masking agent for negatively charged metal citrate complexes but does not affect a.c. polarograms of uncomplexed cadmium ions. In citrate buffer at pH 3.5–4 with 0.03% Benax present, cadmium can be determined in the presence of 10,000-fold amounts of indium. No other frequently associated metals interfere in the determination.

RÉSUMÉ

Une méthode est décrite pour le dosage polarographique du cadmium sans séparation préalable de l'indium (même en fortes proportions). On utilise le surfactant anionique Benax comme agent de masquage électrochimique pour des complexes citriques métalliques chargés négativement: ce qui n'influence pas les polarogrammes c.a. des ions cadmium non complexés. En milieu citrique, à pH 3.5–4, avec 0.03% de Benax, il est possible de doser le cadmium en présence d'indium à des concentrations 10000 fois supérieures à celles de l'indium. Aucun métal, l'accompagnant généralement ne gêne le dosage.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode zur Bestimmung von Cadmium ohne vorherige Abtrennung grosser Mengen Indium beschrieben. Das anionische grenzflächenaktive Benax dient als elektrochemisches Maskierungsmittel für negativ geladene Metallzitrat-Komplexe, aber es beeinflusst nicht die a.c.-Polarogramme der nichtkomplexierten Cadmiumionen. In einem Citratpuffer mit dem pH 3.5–4 und 0.03% Benax kann Cadmium in Gegenwart eines 10,000-fachen Überschusses an Indium bestimmt werden. Andere häufig auftretende Begleitmetalle stören die Bestimmung nicht.

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SELECTIVITY OF ION-SPECIFIC MEMBRANE ELECTRODES

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A great deal of effort has recently been expended on the development of ion-selective electrodes reversible to various cations or anions[1,2]. On the analogy of the glass electrode, materials with ion-exchanger properties have been used first in homogeneous or heterogeneous form as the electrode matrix[3-7]. Except for some liquid ion-exchange electrodes[8,9], all ion-exchange electrodes lack sufficient selectivity to individual ions. In further work, precipitate-exchange phenomena of various materials have been utilized to prepare homogeneous or heterogeneous ion-selective electrodes. The words "homogeneous" and "heterogeneous" do not relate to the function but to the composition of the electrode material. The behaviour of both types of electrode can be interpreted in the same way, thus it is undesirable to discriminate between solid state and silicone rubber membrane electrodes theoretically.

Since one of the most important parameters of ion-selective electrodes is their selectivity, the aim of this paper is to summarize our theoretical and experimental findings concerning the selectivity constants of precipitate-containing membrane electrodes.

THEORY

The theoretical studies on precipitate-based ion-selective electrodes lead to the conclusion that all membrane electrodes behave similarly. The ion-exchange phenomenon has become generally accepted for the interpretation of the behaviour of cation-selective glass electrodes since it was introduced by NIKOLSKI AND TOLMACHEVA[10-12]. EISENMAN's equation derived for the membrane potential has generally extended the validity of the NIKOLSKI equation[13-15].

EISENMAN has also derived an equation for calculating the selectivity ratios of glass electrodes to various cations. His work is extremely important, because it gives a basis for evaluating the practical value of the individual electrodes. For a mixture of hydrogen and other ions, the equation can be written as:

$$E_{\mathrm{H}}-E_{\mathrm{A}}= -\frac{RT}{F}\ln K_{\mathrm{HA}} \qquad (1)$$

where E_{H} is the electrode potential measured in 0.1 M hydrochloric acid; E_{A} is the membrane potential measured when the concentration of H^+ converges to zero in a solution containing the cation A^+ and the anion Cl^-; and K_{HA} is the selectivity constant for the ions A^+ and H^+.

The behaviour of precipitate-based ion-selective electrodes is interpreted on the basis of the precipitate-exchange equilibrium. In solutions containing more than one ion, every ion takes part in the exchange reaction and together they determine the value of the membrane potential. For 1:1 electrolytes, the equation for the membrane potential is:

$$E=E_0+\frac{RT}{nF}\ln a_i\sum_n K_{ik}\cdot\frac{a_k}{a_i} \tag{2}$$

$$E_0=\frac{(\mu_0)_s-(\mu_0)_m}{F}+\frac{RT}{F}\ln\left[(a_i)_m+(a_k)_m\right] \tag{3}$$

where E_0 is the normal potential of the electrode, which involves the difference in the standard chemical potentials of the ion in the solution and the membrane phase, respectively, and the total exchange capacity of the membrane (The total exchange capacity of the electrode is the sum of the exchangeable ions in the membrane.); R, T, F have their usual physico-chemical meanings; a_i and a_k are the activities of the i-th and k-th ions; n is the number of ions taking part in the exchange reaction; K_{ik} is the selectivity constant; K_{ii} is the selectivity constant of the electrode to the i-th ion, the value of which is always equal to 1; s and m denote the solution and membrane phase, respectively; μ_0 is the standard chemical potential.

The selectivity constant of an electrode shows unambiguously at which concentration an ion can be determined with the electrode in the presence of a certain amount of another ion. A general equation can be deduced for the calculation of the selectivity constant of the ion-selective electrodes by considering the precipitate-exchange reaction for ions of valency more than one. The basis reaction is:

$$\frac{1}{a}\left[(I_j)_a(I_i)_b\right]+\frac{m}{n}(I_k)\rightleftharpoons\frac{1}{n}\left[(I_j)_n(I_k)_m\right]+\frac{b}{a}(I_i) \tag{4}$$

where I_j represents the cation of the precipitate built into the membrane (*e.g.* Ag); I_i and I_k are two anions taking part in the precipitate exchange reaction; a, b, n, m are the stoichiometric constants of the precipitates built into the membrane or formed during the exchange reaction, respectively.

When co-precipitation starts, the anions are in equilibrium with the solid phase in the swollen boundary layers of the membrane, and the equilibrium can be expressed simply as follows:

$$K_{ik}=\frac{[I_i]^{b/a}}{[I_k]^{m/n}} \tag{5}$$

If it is assumed that the activities of the anions in the swollen boundary phases and in the bulk solution are equal to each other, then

$$K_{ik}=\frac{(I_i)_s{}^{b/a}}{(I_k)_s{}^{m/n}} \tag{6}$$

Square brackets and curved brackets, denote the solution phase and membrane phase, respectively.

K_{ik} can be expressed as the function of the solubility products of the precipitates incorporated in the membrane and formed during the exchange reaction. If it is assumed that the composition of the two precipitates is $(I_j)_a(I_i)_b$ and $(I_j)_n(I_k)_m$, where S_{ji} and S_{jk} are the appropriate solubility products, then:

$$S_{ji} = (I_j)^a \cdot (I_i)^b \tag{7}$$

and

$$S_{jk} = (I_j)^n \cdot (I_k)^m \tag{8}$$

If the same solubility products are valid in the swollen boundary phases of the membrane as in water, then

$$[I_j] = \frac{S_{ji}{}^{1/a}}{[I_i]^{b/a}} \tag{9}$$

or

$$[I_j] = \frac{S_{jk}{}^{1/n}}{[I_k]^{m/n}} \tag{10}$$

In equilibrium, the I_j concentration is the same for both precipitates, so

$$\frac{[I_i]^{b/a}}{[I_k]^{m/n}} = \frac{S_{ji}{}^{1/a}}{S_{jk}{}^{1/n}} \tag{11}$$

and

$$K_{ik} = \frac{S_{ji}{}^{1/a}}{S_{jk}{}^{1/n}} \tag{12}$$

When monovalent ions form the precipitate, then eqn. (12) reduces

$$K_{ik} = \frac{S_{ji}}{S_{jk}} \tag{13}$$

Equations (12) and (13) can be used for the theoretical calculation of the selectivity constants of ion-specific electrodes. The validity of the equations can be proved potentiometrically.

From the general membrane potential equation, it follows that the selectivity constant of an ion-selective electrode can be determined on the basis of the e.m.f. values measured in solutions containing both the ion to which the electrode is reversible, and the other ion. The e.m.f. measurements can be carried out as follows: (1) in solutions containing a constant amount of the ion, to which the electrode is reversible, and varying amounts of the other ion (Method I); (2) in solutions containing a constant amount of the other ion and varying amounts of the ion to which the electrode is reversible (Method II).

In the former case the potential measurements are carried out directly at various other ion concentrations, and the e.m.f. values *vs.* $-\log c_X$ (where X is the concentration of the other ion) are plotted. From the break-point of the curve, the concentration ratio at which the other ion starts to disturb the behaviour of the membrane electrode, can be determined. This ratio is equal to the selectivity constant.

In the latter case two different procedures are theoretically available. The e.m.f. measurements can be carried out either by the direct method or by a titration method. If the selectivity constant of the electrode studied differs very much from unity, then the potentiometric titration method should be employed. As titrant a soluble salt of the cation of the precipitate built into the membrane is used. The concentration ratio (K_{Ik}) is determined from the point at which the co-precipitation can easily be observed.

EXPERIMENTAL

Apparatus

A Radelkis (Hungary) Universal pH-meter Model OP-240 on the expanded scale was used for all potentiometric measurements (input resistance 10^{12} Ω). Radelkis OP-I-711, OP-Br-711 and OP-Cl-711 indicator electrodes, and a Radelkis saturated calomel electrode or a silver–silver chloride electrode with a potassium nitrate salt bridge were employed in this study. Before measurements all electrodes were pretreated in the appropriate 0.1 *M* alkali halide solutions for at least 2 h. The silver halide-based cyanide electrodes were pretreated by soaking them in a 0.1 *M* potassium nitrate solution of pH 11. After the electrodes had been carefully washed with distilled water, they were ready for measurements and were calibrated in the standardizing solutions. Between measurements, the electrodes were kept either dry or in the appropriate soaking solution.

Reagents

All chemicals used were of analytical grade. Approximately 0.1 *M* potassium iodide, bromide, chloride and cyanide stock solutions were prepared and standardized potentiometrically with silver nitrate as titrant. The stock solutions were stored in polythene bottles. The standardizing solutions were made by serial dilutions.

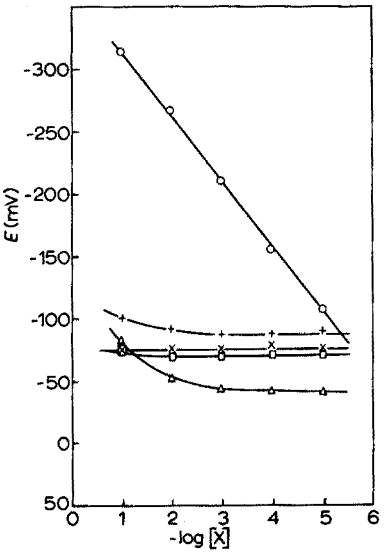
Methods

For measurements of the selectivity of the bromide electrode, solutions containing a constant amount (10^{-4} *M*, 10^{-5} *M*, etc.) of potassium bromide and 10^{-1}–10^{-6} *M* potassium chloride were prepared by a series of dilutions. For the other selectivity measurements, appropriate solutions were made analogously. The pH of the solutions containing cyanide and halide ions[16] was 11. The ionic strength of all solutions was maintained at 0.1 with potassium nitrate.

RESULTS

The selectivities of the iodide membrane electrode to chloride and bromide and the selectivity of the bromide electrode to chloride are shown in Figs. 1 and 2. The measurements were carried out by Method I. From the break-points of the curves, the selectivity constants were determined. A comparison between the calculated and measured selectivity constants of the bromide and iodide membrane electrodes is given in Table I. The calculation was carried out with eqn. (13).

All halide-selective electrodes can be used for the determination of cyanide as is discussed in another paper[16]. Figure 3 shows the selectivity of the bromide and iodide electrodes for cyanide, while Table II shows a comparison of the selectivity constants of the iodide membrane electrode to various other ions in the presence of iodide or cyanide ions.



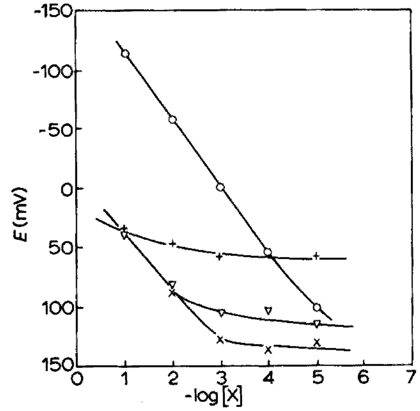


Fig. 1. Potentiometric selectivity of the iodide membrane electrode to iodide in I^-/Cl^- and I^-/Br^- binary mixtures. Potential measured *vs.* Ag/AgCl (0.1) electrode with a potassium nitrate salt bridge. X = halide. (○) Calibration curve for the iodide electrode. (+) 10^{-5} *M* KI in bromide solution. (△) 10^{-6} *M* KI in bromide solution. (×) 10^{-5} *M* KI in chloride solution. (□) 10^{-6} *M* KI in chloride solution.

Fig. 2. Potentiometric selectivity of the bromide membrane electrode to bromide in Br^-/Cl^- binary mixtures. Potential measured *vs.* Ag/AgCl (0.1) with a potassium nitrate salt bridge. (○) Calibration curve for the bromide electrode. (+) 10^{-4} *M* KBr in chloride solution. (△) 10^{-5} *M* KBr in chloride solution. (×) 10^{-6} *M* KBr in chloride solution.

TABLE I

COMPARISON OF THE SELECTIVITY CONSTANTS

(Data taken at 25°)

Anion pair		*log of selectivity constant*		
$[Br^-]$	$[Cl^-]_{at\ the\ break}$	*Real*	*Apparent*[a]	*Calculated*
10^{-6}	$7.11 \cdot 10^{-4}$	2.85		
10^{-5}	$5.6 \cdot 10^{-3}$	2.75	2.0	2.6
10^{-4}	$5.6 \cdot 10^{-2}$	2.75		
$[I^-]$	$[Br^-]_{at\ the\ break}$			
10^{-6}	$5 \cdot 10^{-3}$	3.7		3.75
10^{-5}	$4.25 \cdot 10^{-2}$	3.63		

[a] Measurement carried out by RECHNITZ AND KRESZ[17].

DISCUSSION

Table I shows a good agreement between the calculated and measured K_{Ik} values, which proves the validity of eqn. (13), as well as the general statement that the selectivity measurements of ion-selective electrodes must be carried out in solutions containing two ionic species: the ion to which the electrode is reversible and the ion which is being investigated.

On the basis of Table II, it can be said that the silver iodide-based cyanide electrode shows the same selectivity to cyanide as to iodide in the presence of other ions.

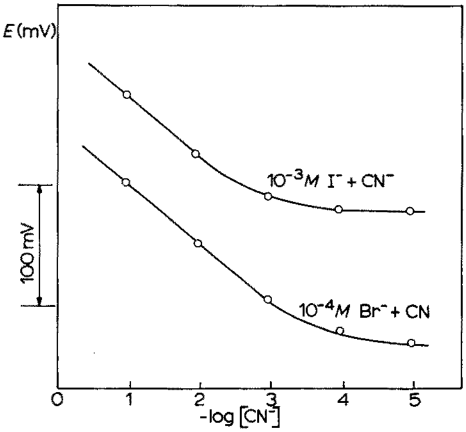


Fig. 3. Selectivity of the bromide and iodide membrane electrodes to cyanide in CN^-/Br^- and CN^-/I^- binary mixtures. Potential measured *vs.* Ag/AgCl (0.1) electrode with a potassium nitrate salt bridge.

TABLE II

SELECTIVITY OF IODIDE MEMBRANE ELECTRODE TO VARIOUS IONS IN THE PRESENCE OF CYANIDE OR IODIDE IONS

(Data taken at 25°)

Ion	*Selectivity constant in the presence of*	
	CN^-	*I^-*
Cl^-	10^{-5}–10^{-6}	10^{-6}
Br^-	10^{-3}–10^{-4}	10^{-4}
I^-	1	
CN^-		1
NH_4^+	10^{-5}–10^{-6}	10^{-6}
SO_4^{2-}	10^{-5}–10^{-6}	10^{-6}

With respect to the application of these ion-selective electrodes, it is also necessary to know how complexing agents which form complexes with silver, influence the electrode behaviour. From Fig. 3 it is obvious that the selectivity constants of the halide-selective electrodes for cyanide are equal to 1, because the β value ($-\log K_d$ is the dissociation constant) of the silver dicyanide complex is higher than the negative logarithm of the solubility product of the silver halide precipitates incorporated in the appropriate membrane; in other words, because the cyanide completely dissolves all silver halide precipitates.

At the beginning of the development of ion-selective electrodes, RECHNITZ AND KRESZ[17] used EISENMAN's method, which, strictly, can only be employed for ion-exchange electrodes, for measuring the selectivities of some ion-selective electrodes developed by PUNGOR[2]. The selectivity values measured by RECHNITZ AND KRESZ can be accepted only as apparent selectivity values.

SUMMARY

A theoretical interpretation is given for the selectivity constants of ion-selective electrodes. The validity of the theory is proved for halide-selective electrodes. The high selectivity of the halide electrodes to individual halide ions offers many applications of these electrodes in analytical chemistry.

RÉSUMÉ

Une interprétation théorique est donnée pour les constantes de sélectivité des électrodes ioniques sélectives. La validité de la théorie est confirmée par les électrodes sélectives-halogénure. La grande sélectivité de ces électrodes permet de nombreuses applications en chimie analytique.

ZUSAMMENFASSUNG

Die Selektivitätskonstanten von ionenselektiven Elektroden werden theoretisch interpretiert. Die Gültigkeit der Theorie wird für halogenidselektive Elektroden bewiesen. Die hohe Selektivität der Halogenid-Elektroden für die einzelnen Halogenid-Ionen lässt die Anwendung dieser Elektroden in der analytischen Chemie als geeignet erscheinen.

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EXTRACTION STUDIES OF PLATINUM GROUP METALS WITH DIANTIPYRYLPROPYLMETHANE

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Basic dyes are among the several types of new organic compounds which increasingly are being used in inorganic analyses. They possess the property of reacting with metallohalide or metallocyanide complex anions to form compounds which are sparingly soluble in water and which can be extracted into common organic solvents. These properties prompted an investigation of the use of diantipyrylpropylmethane (DAPM) for the solvent extraction separation of platinum metal chloro complexes.

Typical of the basic dyes used in analyses are the triphenylmethane dyes[1], but they are not stable in acidic medium which restricts their use in analytical procedures[2]. ZHIVOPISTSEV AND CHELNOKOVA[3] worked to improve the acid stability of these dyes by introducing heterocyclic radicals into the molecules. Starting with antipyrine, as a basic substance, they synthesized and studied a series of diantipyryl derivatives as potential organic reagents.

BUSEV AND TIPTSOVA were the first, however, to synthesize DAPM which they used for the gravimetric determination of thallium[4] in a bromide solution and the quantitative precipitation of gallium[5] from 6 M hydrochloric acid solution. SOKOLOVA *et al.*[6] used DAPM to determine cobalt spectrophotometrically in bronze and cast iron.

Relatively little work has been done on DAPM in extraction studies, although it and its metal derivatives are soluble in common organic solvents. Tellurium[7] was found to extract from 3 M hydrochloric acid into a dichloroethane solution containing DAPM and some pairs of elements among the platinum group metals have been separated by selective extraction of the metals into dichloroethane–DAPM solution[8,9].

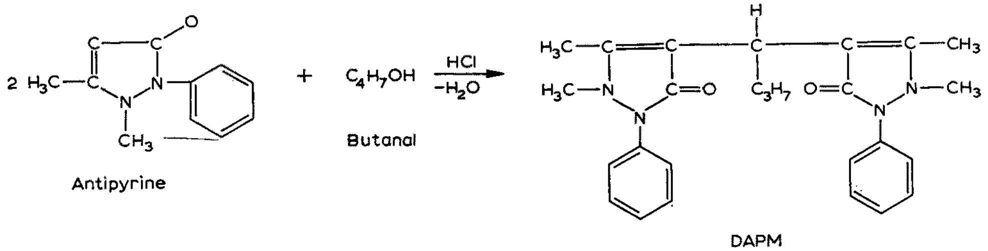
The object of this paper is to explore the use of DAPM further as a selective reagent for the extraction of platinum group metals from hydrochloric acid solutions.

EXPERIMENTAL

Synthesis of DAPM

DAPM was synthesized by the procedure recommended by BUSEV AND TIPTSOVA[4] with only minor modifications.

The condensation reaction leading to the formation of DAPM may be written as follows:



Antipyrine (5 g) was dissolved in a minimum amount of water. To this 2 ml of concentrated hydrochloric acid and 2 ml of freshly distilled butanal were added; the mixture was heated for 30 min on a water bath and then diluted to 200 ml with water. Busev and Tiptsova[4] recommended that DAPM be precipitated from the solution by the addition of 1:1 ammonia:water, but an oily substance separated from solution under these conditions which was rather difficult to collect and crystallize. However, when 1:10 ammonia:water was substituted for the 1:1 reagent and added slowly with constant stirring to an ice-cooled solution, a crystalline precipitate of DAPM formed immediately. After 3–5 min the light brown precipitate was filtered, washed with water and dried at 110°. Yield, 5.5 g; theoretical yield, 5.7 g. The crude DAPM can be recrystallized from methanol, ethanol, benzene, acetone and a 1:1 acetone:water mixture. Experience indicated that the best solvent for recrystallization is the 1:1 acetone:water mixture. Elemental analysis of the recrystallized DAPM gave 72.6% C, 7.0% H, 12.8% N; (calculated: 72.56% C, 6.97% H, 13.02% N); m.p. 155–156°. NMR and IR solution spectra supported the structure proposed above for DAPM.

Reagents

Rhodium-102, ruthenium-103 and iridium-192 were obtained by irradiating the metal chlorides in a high neutron flux. Stock solutions were prepared by dissolving the salts in 5 *M* hydrochloric acid. Platinum-188 and palladium-103 isotopes were obtained by neutron irradiation of the pure metals. Stock solutions of the radioactive platinum and palladium were prepared by dissolving the metals in aqua regia. The excess of nitric acid and oxides of nitrogen were removed by boiling and the stock solutions were made up with 5 *M* hydrochloric acid. Osmium-191 was obtained from the Oak Ridge National Laboratory as a solution of sodium osmate. The osmate solution was dissolved in 5 *M* hydrochloric acid to form a stock solution.

All other reagents were reagent grade.

Apparatus

A Baird-Atomic Inc. well-type scintillation counter was used for determining the activity of the radioisotopes used in this study. Solutions (2 ml) were counted in small snap-top polyethylene capsules (1.2 cm diameter and 5.5 cm length) which were placed in the well of a sodium iodide (thallium-activated) scintillator.

A vibrator mechanical shaker was used to agitate phases in the establishment of phase equilibria.

Procedure

The solubility of DAPM in various solvents was determined. Solvent was added to the reagent from a buret and the solution was shaken between each addition of solvent until total dissolution of DAPM was noted.

Distribution coefficients for the platinum metals were determined by adding several drops of the stock radio-isotope solution of the metal to 10.0 ml of hydrochloric acid solution. Only enough stock solution was added to the hydrochloric acid solution to give a satisfactory counting rate. The aqueous phase was equilibrated with an equal volume (10.0 ml) of a chloroform solution of DAPM in a polyethylene bottle. The heterogeneous system was shaken for 15 min in the mechanical shaker before the two phases were transferred to a separatory funnel and separated. The aqueous phase was washed twice with 5-ml portions of chloroform and the chloroform extracts were combined. Aliquots (2 ml) of each phase were taken for analysis in the scintillation counter. The distribution coefficient, K, was defined by the expression:

$$K = \frac{\text{counts per minute/ml of the chloroform solution}}{\text{counts per minute/ml of the HCl solution}}$$

A detailed description of the procedure followed in the extraction studies is given in the work by LYLE AND SHENDRIKAR[10].

RESULTS AND DISCUSSION

Diantipyrylpropylmethane (DAPM) slowly decomposes and turns brown when exposed to daylight for as much as two days but when stored in darkness is stable for periods up to two months. The reagent is quite soluble in a number of common solvents (see Table I) but the solutions are unstable in daylight and must be stored in darkness. DAPM is readily decomposed in nitric acid solution but is stable in hydrochloric, sulfuric and perchloric acid solutions at room temperature. Thus, little difficulty is experienced in preparing and storing solutions of the reagent for use.

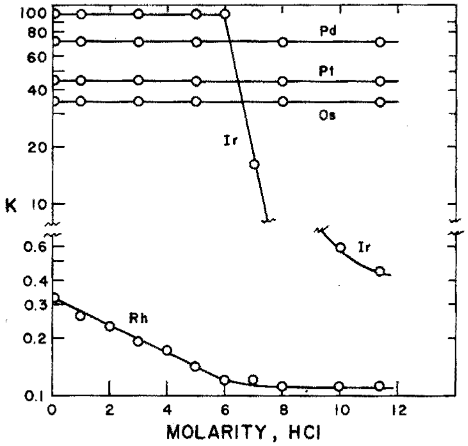
TABLE I

SOLUBILITY OF DAPM IN VARIOUS ORGANIC SOLVENTS AT 26°

Solvent	*Solubility g/100 ml of solvent*	*Solvent*	*Solubility g/100 ml of solvent*
Water	0.004	Benzene	7.10
Boiling water	0.051	Ethanol	18.50
1:1 acetic acid	3.25	Methanol	25.20
Acetone	4.00	Chloroform	26.40
Carbon tetrachloride	4.80	Carbon disulfide	4.9

Preliminary extraction experiments indicated that chloroform solutions of DAPM would be suitable for the extraction of the chloro complexes of the platinum metals. It was expected that the extractions would be very dependent on the hydrochloric acid concentration in the aqueous phase, therefore a systematic study of the effect that the hydrochloric acid concentration would have on the distribution coefficients for the individual metals was undertaken. A 1% solution of DAPM in chloroform was chosen for the extractant and 1–2 drops of the stock radioisotope solutions were added to 10.0 ml of hydrochloric acid solution of the appropriate concentration for the raffinate. After equilibration, the phases were separated and analyzed.

Figures 1 and 2 give the distribution coefficient and percentage of metal extracted for each element studied as a function of the hydrochloric acid molarity. The distribution coefficients for these metals in the chloroform–hydrochloric acid solvent system are uniformly high at all acid concentrations except for rhodium and iridium. For some unexplained reasons the distribution coefficient for iridium falls off very rapidly with hydrochloric acid concentrations greater than 6.0 *M*. Even so, the efficiency of extraction is quite good for all the elements except rhodium at hydrochloric acid concentration below 6 *M*. A single extraction will extract 97–98% of the Pt, Pd, Os or Ir from 0.1–6 *M* hydrochloric acid solution. These data are similar to the data obtained with dichloroethane as a solvent[4].



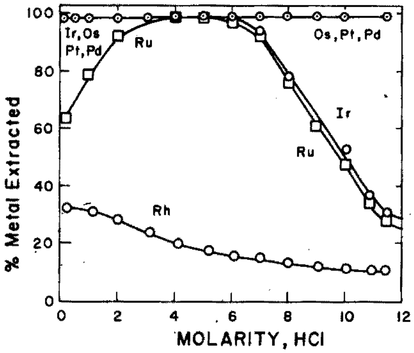


Fig. 1. Distribution coefficients of various platinum group metals as a function of hydrochloric acid concentration.

Fig. 2. Percentage of metal extracted as a function of hydrochloric acid concentration.

The extraction of ruthenium was not studied as a function of hydrochloric acid concentration under exactly the same conditions as the other elements. Ruthenium was extracted into a 5% (w/v) solution of DAPM in chloroform instead of a 1% (w/v) solution used for the other metals. It was shown that only 39% of the ruthenium was extracted from 5 *M* hydrochloric acid solution into a 1% DAPM solution. It is clear from Fig. 2, however, that ruthenium can be extracted quite efficiently from 4–6 *M* hydrochloric acid solution with a 5% (w/v) solution of DAPM in chloroform.

Inasmuch as rhodium was the only platinum metal not efficiently extracted over a broad hydrochloric acid range, some experiments were performed to find satisfactory conditions for the extraction of rhodium. The extraction of rhodium was not enhanced either by salting with sodium chloride or by extending the pH range over which extraction was considered to an alkaline medium. Neither a change of solvent to benzene nor the addition of oxalate, tartrate, citrate or ethylenediaminetetraacetate to the sample had the desired effect of increasing the extractability. No conditions were found that gave an efficient extraction of the DAPM complex of rhodium into chloroform.

Additional work has shown that virtually the same conclusions can be reached by equilibrating the two phases for extraction by hand shaking in a separatory funnel for only 3 min. Shaking the phases together for 15 min in a mechanical shaker is an unnecessarily long equilibration time.

In conclusion, it is clear that tracer quantities of iridium, osmium, palladium and platinum can be efficiently extracted from 4–6 *M* hydrochloric acid solution with a 1% (w/v) solution of DAPM in chloroform and ruthenium with a 5% (w/v) solution of DAPM in chloroform. Rhodium extracts under the same conditions but with a limited efficiency of about 20%.

DAPM in chloroform solution does not appear to be a promising reagent for the solvent extraction separation of the platinum group metals from one another although it does possess the potential to isolate or recover various platinum group metals from base metals by solvent extraction.

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SUMMARY

Diantipyrylpropylmethane (DAPM) is easily synthesized and forms reasonably stable solutions in a number of common organic solvents. The solubility of DAPM in ten different solvents is reported. Solutions of DAPM react with the anionic chloro complexes of the platinum group metals in hydrochloric acid solution to form stable extractable complexes. The distribution of tracer quantities of the six platinum metals between hydrochloric acid solutions and a chloroform solution of the DAPM was studied. Distribution coefficients are reported as a function of the hydrochloric acid concentration; 98% of the Os, Pt or Pd can be extracted in a single pass, over an acid concentration range 0.1–12 *M*; 98% Ir can be extracted in one extraction over the acid range 0.1–6 *M*. Ruthenium can be extracted quantitatively in one extraction from 4–6 *M* hydrochloric acid with a stronger DAPM solution. Rhodium is poorly extracted under all conditions tested.

DAPM is not promising for the selective separation of mixtures of platinum group metals, but may be used for group extraction.

RÉSUMÉ

Le diantipyrylpropylméthane (DAPM) peut se préparer facilement et forme des solutions relativement stables dans un certain nombre de solvants organiques courants. On donne la solubilité de DAPM dans dix solvants différents. Ces solutions de DAPM réagissent avec les chlorocomplexes anioniques des métaux du groupe du platine, en solution acide chlorhydrique pour former des complexes stables que l'on peut extraire. On examine le partage de traces des six métaux du groupe du platine entre acide chlorhydrique et chloroforme. Les coefficients de partage sont donnés en fonction de la concentration d'acide chlorhydrique: 98% de Os, Pt ou Pd peuvent être extraits en une fois avec des concentrations en acide 0.1–12 *M*; 98% Ir en une extraction avec acide 0.1–6 *M*; Ru est extrait quantitativement en une fois de solutions acide chlorhydrique 4–6 *M* avec une solution plus concentrée de DAPM. L'extraction du rhodium est faible dans les conditions essayées. DAPM ne semble pas convenir pour une séparation sélective des métaux du groupe du platine mais il permet de faire une extraction du groupe.

ZUSAMMENFASSUNG

Diantipyrylpropylmethan (DAPM) lässt sich leicht synthetisieren und bildet ziemlich stabile Lösungen mit einer Zahl gängiger organischer Lösungsmittel. Die Löslichkeit von DAMP in 10 verschiedenen Lösungsmitteln wurde untersucht. Lösungen von DAPM reagieren in salzsauren Lösungen mit anionischen Chlorokomplexen der Metalle der Platingruppe und bilden stabile extrahierbare Komplexe. Die Verteilung von Spuren der 6 Platinmetalle zwischen salzsauren Lösungen und einer Lösung von DAPM in Chloroform wurde untersucht. Es werden die Verteilungskoeffizienten in Abhängigkeit von der Salzsäurekonzentration angegeben. 98% Os, Pt oder Pd werden aus 0.1–12 *M* Säure in einem einzigen Schritt extrahiert. Das gleiche erreicht man beim Iridium im Bereich von 0.1–6 *M*. Ruthenium wird quantitativ aus 4–6 *M* Salzsäure mit stärkerer DAPM-Lösung extrahiert Rhodium wird unter all diesen genannten Bedingungen schlecht extrahiert. DAPM ist für die selektive Trennung der Platinmetalle nicht geeignet, aber es kann zur Gruppenextraktion verwendet werden.

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THE SOLVENT EXTRACTION OF VANADOMOLYBDOPHOSPHORIC ACID AS THE BASIS OF A SUBSTOICHIOMETRIC METHOD FOR THE DETERMINATION OF PHOSPHORUS

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The formation of a yellow complex acid between phosphate, vanadate and molybdate ions in acidic aqueous media has found use in many methods for determining phosphorus. ELWELL AND WILSON[1] based a colorimetric determination on the extraction of vanadomolybdophosphoric acid into an organic layer. A modified procedure was adopted as a British Standard method[2] for the determination of phosphorus in steel.

Despite the wide application of vanadomolybdophosphoric acid in analysis, there are no details in the literature on the reasons for the choice of solvent, the effect of pH on the efficiency of extraction, or the composition of the complex which is extracted. This last point is of particular interest because COURTIN *et al.*[3] found that there were three triheteropolyacids containing vanadium, molybdenum and phosphorus, their compositions being $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and $H_6PV_3Mo_9O_{40}$.

In the present paper, studies of the extraction of vanadomolybdophosphoric acid by means of the radioisotopes phosphorus-32, vanadium-48 and molybdenum-99 as tracers are described.

Experiments on the amount of molybdate needed for maximum extraction of the acid, in which substoichiometric amounts of molybdate were added to acidic aqueous solutions of vanadate and phosphate, enabled a substoichiometric method for the determination of phosphate to be developed.

EXPERIMENTAL

Reagents

Preparation of potassium dihydrogen phosphate solutions. Phosphorus-32 was obtained as orthophosphate (Radiochemical Centre, Amersham); to ensure that the radiophosphorus was in the same oxidation state as the orthophosphate used in the experiments, it was warmed with hydrochloric acid, hydrogen peroxide and carrier phosphate[4]. In some later experiments bromine water and nitric acid were preferred to the acid–peroxide mixture, because residual traces of hydrogen peroxide were found to react with the vanadate to form peroxocompounds.

Standard labelled solutions were made from the active solution and weighed quantities of potassium dihydrogen phosphate. Unlabelled 0.02 *M*, 0.01 *M*, 0.005 *M*, and 0.001 *M* solutions were also used.

Preparation of ammonium metavanadate solutions. The required weight of ammonium metavanadate for 0.04 *M* and 0.01 *M* solutions, and about 10 μCi of the radioisotope vanadium-48, which was obtained as the oxotrichloride, were diluted to 100 ml with water. Unlabelled 0.05 *M*, 0.04 *M*, 0.02 *M*, 0.01 *M* and 0.002 *M* solutions were also used.

Preparation of ammonium molybdate solutions. The solutions prepared were 0.20 *M*, 0.10 *M*, 0.05 *M* and 0.01 *M* with respect to molybdate (MoO_4^{2-})ions. (In this paper vanadate and molybdate will be formulated as simple, uncondensed ions for the purpose of expressing concentrations.) A 0.10 *M* solution labelled with molybdenum-99 was used in some experiments.

Counting equipment. The β-emission from phosphorus-32 was counted in a 20th Century Electronics M6HST liquid counter using a Panax P7102 scaler. The γ-emission from vanadium-48 and molybdenum-99 was counted by means of a Panax scintillation counter and a P7102 scaler. Experiments were designed to give at least 10,000 counts so that the standard deviation did not exceed 1%.

EXTRACTION STUDIES

The extraction of vanadomolybdophosphoric acid

The percentage of phosphorus extracted as vanadomolybdophosphoric acid into isobutyl methyl ketone[2] was investigated with phosphorus-32.

Perchloric acid (1.0 ml of 60%) was added to 5.0 ml of 0.002 *M* phosphate solution labelled with phosphorus-32, followed by 2.0 ml of 0.01 *M* ammonium vanadate and 4.0 ml of 0.10 *M* ammonium molybdate. Isobutyl methyl ketone was used to extract vanadomolybdophosphoric acid by shaking 10.0 ml of solvent with the aqueous layer for 1 min and allowing to stand for 1 min, intermittently over a total time of 6 min. The layers were separated, and 8.0-ml aliquots of each layer were counted. The distribution of phosphorus was calculated after correcting for lost-counts and volume differences. The percentage extraction at pH 0.3 was 99.9%.

Further experiments on solvents were not made. The solvent used in the British Standard method is obviously efficient at low pH.

The effect of pH on the percentage of phosphorus extracted as vanadomolybdophosphoric acid

A PYE model No. 79 pH meter was used with a glass electrode and a calomel reference electrode for measurements in the range 1.0–5.0. Below pH 1.0 the value was estimated from the known concentration of perchloric acid.

Appropriate aliquots of 0.002 *M* phosphate solution labelled with phosphorus-32, perchloric acid, 0.01 *M* vanadate and 0.10 *M* molybdate were mixed in that order so that, at the required acidity, the stoichiometric proportions were $PO_4^{3-}:VO_3^-:MoO_4^{2-} = 1:1:40$. Earlier work[5] on the extraction of $H_3PMo_{12}O_{40}$ suggested that a large excess of molybdate might be necessary; furthermore, the British Standard method[2] uses a very large excess of molybdate. Isobutyl methyl ketone (10.0 ml) was used to extract the vanadomolybdophosphoric acid, as described above, and the volumes of the separated phases were noted. Counts taken on 8.0-ml aliquots of the aqueous and organic phases were corrected for lost-counts and volume differences. The distribution of phosphorus was then calculated and finally the pH of the aqueous phase was read.

For the lower acidities, freshly prepared 2 *M* ammonia solution was used to adjust the pH. All the experiments were conducted at laboratory temperature (20 ± 1°). Figure 1 shows the extraction curve for vanadomolybdophosphoric acid.

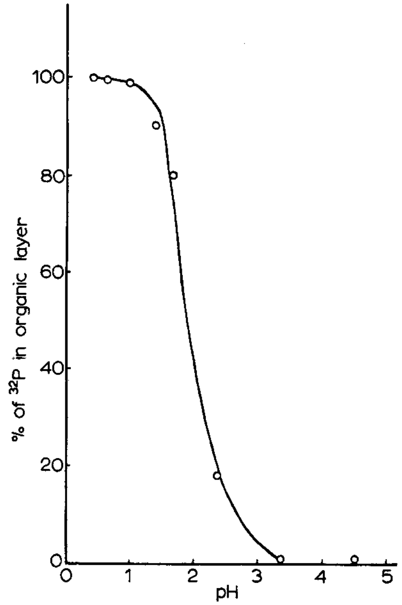

Fig. 1. The extraction of vanadomolybdophosphoric acid: dependence on pH.

Determination of the P: V ratio in the vanadomolybdophosphoric acid extracted

A series of extraction experiments were carried out with isobutyl methyl ketone on solutions containing different proportions of PO_4^{3-}:VO_3^-:MoO_4^{2-}. Experiments were carried out with phosphorus-32, vanadium-48 and molybdenum-99 as tracers. In all cases the pH was about 0.3. Table 1 shows the percentages of phosphorus-32 extracted into the organic layer from the various solutions and also the percentages of vanadium-48 for several cases.

The ratio Mo:P varied from 10.2 to 10.5 and never reached the theoretical value of 11.0. Too much reliance should not be placed on the experimental figures in this case because the count-rates were made on ^{99}Mo in equilibrium with its radioactive daughter nuclide, ^{99m}Tc.

Determination of the P:Mo and V:Mo ratio in vanadomolybdophosphoric acid

A 0.02 *M* phosphate solution labelled with ^{32}P (10.0 ml) was mixed with 1.0 ml of 60% perchloric acid, to adjust the pH to about 0.5, followed by 10.0 ml of 0.04 *M* vanadate solution. The mixture was then extracted with 10.0 ml of isobutyl methyl ketone as described above. A 10.0-ml aliquot of the aqueous layer was then counted. The contents of the liquid counter were completely returned to the separating funnel,

TABLE I

THE EXTRACTION OF PHOSPHORUS-32 AND VANADIUM-48 INTO ISOBUTYL METHYL KETONE FROM ACIDIFIED (pH 0.3) AQUEOUS SOLUTIONS OF PHOSPHATE, VANADATE AND MOLYBDATE

$PO_4^{3-}:VO_3^-:MoO_4^{2-}$ *in aqueous solution*	% *P extracted into organic layer*	% *V extracted into organic layer*	*V:P ratio*
1:1:40	99.7	69.1	0.69
1:2:40	99.9	46.0	0.92
1:3:40	99.9	32.6	0.98
1:4:40	99.8	25.5	1.02
1:1:15	73.2		
1:2:15	79.8		
1:3:15	81.4		
1:4:15	82.1		

the liquid counter having been coated with a silicone film, "Repelcote", to make this possible. A 0.2 *M* molybdate solution was then added in 2.0-ml portions from a burette. The extraction was repeated after each addition until an end-point was reached, *i.e.* the count-rate for the aqueous layer, corrected for lost-counts and change in volume, remained approximately constant after successive additions of ammonium molybdate (Fig. 2A).

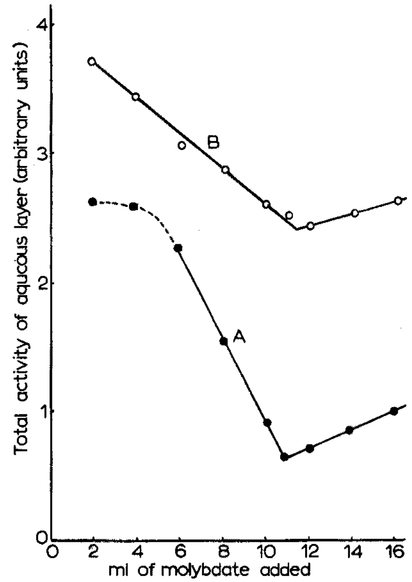

Fig. 2. Radiometric titration of acidified phosphate/vanadate solution with molybdate. Organic solvent: isobutyl methyl ketone (10 ml). Aqueous layer: 10 ml 0.02 *M* KH_2PO_4+1 ml 60% $HClO_4$+10 ml 0.04 *M* NH_4VO_3 titrated with 0.2 *M* $(NH_4)_2MoO_4$. (A) ^{32}P as tracer; (B) ^{48}V as tracer.

A similar experiment was carried out with labelled vanadate instead of labelled phosphate (Fig. 2B).

In these graphs the total activity of the aqueous layer tended to rise after the Mo:P ratio reached 11.0:1 (Fig. 2A) and the Mo:V ratio reached 11.4:1 (Fig. 2B).

From the activity of the phosphate and that of the excess of vanadate remaining in the aqueous phase, it appeared that the P:V ratio in the extract was unity, thus confirming the previous set of experiments.

TABLE II

TYPICAL RADIOMETRIC TITRATION OF 0.01 M PHOSPHATE (LABELLED WITH ^{32}P) AND 0.02 M VANADATE WITH 0.1 M MOLYBDATE AT pH < 1.0.

ml of 0.1 M MoO_4^{2-} added	2	6	10	11	12	14
Corrected counts/min for whole aq. layer	7173	4385	1581	1087	587	605

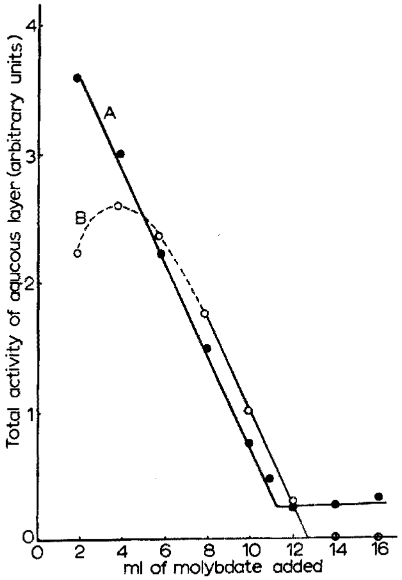

Fig. 3. Radiometric titration of acidified phosphate with molybdate: (A) in the presence of vanadate; (B) in the absence of vanadate. Organic solvent: isobutyl methyl ketone (10 ml). Aqueous layer: 10 ml 0.01 M KH_2PO_4 (labelled with ^{32}P) +1 ml 60% $HClO_4$ (+10 ml 0.02 M NH_4VO_3 in case A) titrated with 0.1 M $(NH_4)_2MoO_4$.

Titration experiments were also carried out with phosphate, vanadate and molybdate solutions of one-half (Table II, Fig. 3A), one-quarter and one-twentieth of the strengths described above. With 0.01 M solutions, the activity of the aqueous layer remained practically constant after the Mo:P ratio reached 11.4. With very weak solutions the "end-point" was indistinct.

Experiments were also carried out with the same solutions as in Table II but omitting the vanadate (Fig. 3B). The lower part of this line is similar to A, though rather further to the right, suggesting that $H_3PMo_{12}O_{40}$ is being extracted, but the upper part curves over, indicating that ^{32}P is being extracted in some form other than 12-molybdophosphoric acid.

The titration curve obtained for the extraction of phosphate in the presence of vanadate suggested the possibility of developing a radiometric titration method for analysing phosphate, but the idea was rejected because the titrations took too long to complete, and not all the phosphate was extracted — earlier results indicated that an excess of molybdate is necessary to extract all the phosphate. However, the fact that for a given concentration of phosphate the curve was highly reproducible suggested that it might be possible to develop a method for phosphorus analysis based on a substoichiometric quantity of molybdate.

THE SUBSTOICHIOMETRIC DETERMINATION OF PHOSPHORUS

The effect of time of shaking

A series of solutions with equal content of phosphate were substoichiometrically extracted at constant pH for different intervals of time; 10.0 ml of isobutyl methyl ketone was used to extract 10.0 ml of 0.002 *M* phosphate (labelled with ^{32}P), 1.0 ml of 60% perchloric acid, 4.0 ml of 0.01 *M* vanadate and 12.0 ml of 0.01 *M* molybdate. Counts were taken on the organic extract separated after different extraction times.

TABLE III

EFFECT OF TIME OF SHAKING

Shaking time (sec)	*counts/min org. layer*	*Shaking time (sec)*	*counts/min org. layer*
30	4995	240	6304
60	5489	300	6384
120	5967	600	6613
180	5846	1200	6840

The mean values for duplicate experiments are shown in Table III. Equilibrium was not reached quickly, but after shaking for 3 min, the increase of extraction with time was slow enough to enable reproducible extractions to be obtained.

Reproducibility of the method at constant phosphate concentration

Experiments were done in which 0.4–0.8 ml of very dilute, high-activity phosphate solution, labelled with ^{32}P, was added to exactly 2.0 ml of 0.01 *M* potassium dihydrogen phosphate, made up to 12.0 ml with water, acidified with 1.0 ml of 60% perchloric acid and mixed with 4.0 ml of 0.01 *M* vanadate followed by 12.0 ml of 0.01 *M* molybdate, making the P:V:Mo ratio 1:2:6. Counts were made on the solution and on the organic extract obtained by intermittent shaking for 6 min with 10.0 ml of isobutyl methyl ketone. The distribution of phosphorus-32 was calculated from the corrected count-rate on the whole organic layer and that of the original aqueous layer. The results (Table IV) show the extraction to be reproducible. When the total period of extraction was increased to 10 min (shaking for 1 min, standing for 1 min, five times), the percentage of phosphorus-32 extracted increased to 46.8.

Reproducibility of the method over a range of phosphate concentrations

A series of solutions were made containing 10 ml of 0.002 *M* phosphate labelled with phosphorus-32, and diluted to 20 ml with water (where necessary) after the addition of 0, 2, 4, 6, 8 and 10 ml of inactive 0.005 *M* phosphate solution. To each was added 4.0 ml of 0.01 *M* vanadate, 12.0 ml of 0.01 *M* molybdate and sufficient

TABLE IV

PERCENTAGE OF PHOSPHORUS EXTRACTED IN THE SUBSTOICHIOMETRIC METHOD

Phosphorus-32 solution (ml)	*Total activity counts/min (corrected)*	*Extracted activity counts/min (corrected)*	*% P extracted*
0.4	7771	3515	45.2
0.5	10014	4541	45.4
0.6	12093	5401	44.7
0.7	13783	6193	44.9
0.7	14042	6282	44.7
0.8	15320	6878	44.9
0.8	15417	6945	45.0
0.8	15156	6842	45.1

TABLE V

REPRODUCIBILITY OF THE SUBSTOICHIOMETRIC EXTRACTION OVER A RANGE OF PHOSPHATE CONCENTRATIONS

Volume of inactive 0.005 M PO_4^{3-} added (ml)	*Isotope dilution ratio*[a]	*Count-rate*[b] *(counts/min)*	*Isotope dilution ratio × count-rate*[b]
0	1	14039	$1 \times 14039 = 14039$
2	1.5	9458	$1.5 \times 9458 = 14387$
4	2	7234	$2.0 \times 7234 = 14468$
6	2.5	5648	$2.5 \times 5648 = 14120$
8	3	4648	$3 \times 4648 = 13944$
10	3.5	4120	$3.5 \times 4120 = 14420$

[a] Total phosphate as a multiple of the amount in the solution containing no added inactive phosphate.
[b] On 8-ml aliquot.

perchloric acid to make the pH 0.3. Each was extracted as before with 10.0 ml of isobutyl methyl ketone. Counts were made on 8.0 ml of each organic extract. The count-rates decreased in the series because of the addition of inactive phosphate to the original solution. The results summarized in Table V are mean values for duplicate experiments and show that the same amount of phosphate was extracted into the organic layer over the whole range of concentration.

The effect of interfering ions

To 10.0-ml portions of 0.002 *M* phosphate, labelled with ^{32}P, were added interfering ions. The anions were introduced as solid sodium salts, and the transition-metal ions as solid nitrates. In some case, several different concentrations of interfering ions were tried. The solid was dissolved in the aqueous phosphate solution, and to each solution 1.0 ml of 60% $HClO_4$, and the above specified amounts of vanadate and molybdate were added. The mixture was extracted in each case with isobutyl methyl ketone and the count-rate on the organic layer was compared with the count-rate obtained by exactly similar treatment of a similar solution containing no interfering ion. The results are summarized in Table VI. Duplicate experiments were performed in every case. The standard deviation inherent in the counting method was about 0.5 %, as about 40,000 counts were taken on each extract.

The removal of the interference due to fluoride ions

Attempts were made to remove fluoride ions by evaporation. A 10.0-ml portion of ^{32}P-labelled 0.002 *M* phosphate solution was pipetted into each of two evaporating dishes. To one solution was added sufficient sodium fluoride to make the solution 0.002 *M* in fluoride. To each solution 5 ml of concentrated hydrochloric acid were added and both were heated to dryness on the same hot plate; after cooling they were fumed twice more with hydrochloric acid, the whole procedure requiring about 90 min. In another experiment the evaporation was carried out four times in all. After the residues had been dissolved in 10.0 ml of water, the usual extraction procedure was applied to both solutions. The discrepancy in the count-rates on the organic layers was reduced from 12.1% to 0.5± 0.3%. Furthermore, the count-rates showed that phosphate had been lost in the fuming-off. It was found sufficient to evaporate three times; the fourth fuming made no difference.

TABLE VI

THE EFFECT OF INTERFERING IONS ON THE EXTRACTION OF PHOSPHORUS-32

Ratio: $\frac{\textit{molarity of interfering ion}}{\textit{molarity of phosphate ion}}$	*100*	*10*	*2*	*1*
Interfering ion	*% reduction in extraction of* ^{32}*P*			
Cl^-	3.4±0.3	1.3±0.8		1.6±0.2
F^-				12.1±0.5
SO_4^{2-}			0.7±0.4	
NO_3^-			1.1±0.2	
AsO_4^{3-}		30.1±0.5		
Fe^{3+}		29.9±0.2		1.5±0.5
Co^{2+}		2.2±0.5		2.2±0.7
Mn^{2+}		3.9±0.4		0.9±0.3
Cr^{3+}		2.1±0.3		0.6±0.4

In an attempt to avoid the time-consuming evaporation various transition-metal ions were added to samples of the fluoride-containing phosphate solution. Even those which were known to form strong fluorocomplexes in acidic solution were unsatisfactory because they themselves interfered markedly with the extraction of vanadomolybdophosphoric acid.

DISCUSSION

For the extraction of the vanadomolybdophosphoric acid, isobutyl methyl ketone is a satisfactory solvent, and the pH must be below 1.0. The ratio P:V in the extract is 1 even in the presence of a ten-fold excess of vanadate. Radiometric titrations show that the extraction of phosphorus reaches a maximum at a Mo:P ratio of just over 11. Titrations in the absence of vanadate show a maximum extraction of phosphorus at an Mo:P ratio of 12, but extraction of 12-molybdophosphoric acid does not occur at low molybdate concentrations, whereas the vanadomolybdophosphoric acid which is formed appears to be extracted almost quantitatively from solutions less than 0.01 *M* even when the molybdate present is only a small fraction of that required to complex all the phosphate.

Reproducible extractions of phosphorus with isobutyl methyl ketone can be made from solutions of phosphate mixed with an excess of vanadate below pH 1.0 to which a substoichiometric amount of molybdate is added. It is obvious from the results that the molybdate ions are not used quantitatively; *but* the molybdate ions are always used to the *same* extent provided that the extraction procedure is standardised, as the extent of extraction is only slightly dependent on the time of shaking.

Of the ions which have been studied for interferences, only arsenate, fluoride and iron (III) interfere grossly. Fluoride can be fumed off as hydrofluoric acid without loss of phosphate.

The extraction of phosphate as vanadomolybdophosphate with a substoichiometric amount of molybdate forms the basis of a method for determining the phosphorus after neutron activation, with the advantages which are inherent in substoichiometric methods[6]. The principle has been applied with success to provide a radiometric finish for the estimation of traces of sulphur in carbon–fluorine–sulphur compounds which have been irradiated[7].

SUMMARY

The conditions for the extraction of phosphate as vanadomolybdophosphate, and the composition of the extract, have been studied with phosphorus-32 and vanadium-48. Reproducible extractions can be made with substoichiometric amounts of molybdate; such extractions can be adapted to the determination of either phosphorus or sulphur by means of neutron activation.

RÉSUMÉ

On a examiné les conditions d'extraction des phosphates comme vanadomolybdophosphate et la composition des extraits, à l'aide de phosphore-32 et de vanadium-48. Des extractions reproductibles peuvent être effectuées avec des quantités substoechiométriques de molybdate. Ces extractions peuvent être adaptées au dosage du phosphore ou du soufre par activation neutronique.

ZUSAMMENFASSUNG

Die Bedingungen für die Extraktion von Phosphat als Vanadomolybdophosphat und die Zusammensetzung des Extrahierten, wurde unter Verwendung von Phosphor-32 und Vanadin-48 untersucht. Reproduzierbare Extraktionen erhält man mit substöchiometrischen Mengen von Molybdat. Diese Extraktionen können auch sowohl bei der Bestimmung von Phosphor als auch Schwefel mit der Neutronenaktivierungsanalyse verwendet werden.

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SALT AND ACTIVITY EFFECTS ON THE PRECIPITATION OF TETRAPHENYLARSONIUM PERCHLORATE

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A study has been made of the effects of a wide range of concentrations of potassium, sodium and lithium chlorides on the solubility, crystal form and filterability of precipitated tetraphenylarsonium perchlorate. Its purpose was to find which salt concentrations were preferable as precipitation media for the detection and determination of perchlorate.

Tetraphenylarsonium chloride has been recommended as a titrimetric and gravimetric reagent for the precipitation of anions of large radius and low charge density from aqueous solution[1-8]. It was first used in a back-titration procedure[1,2] in which the anion was precipitated with excess reagent and the excess was precipitated as the triiodide by titration to a potentiometric end-point. Other workers used direct titrations to conductimetric[7] or specific-ion electrode[8] end-points. Arsonium salts have also been used in gravimetric procedures[3-6].

The first methods for the use of tetraphenylarsonium chloride recommended the addition of sodium chloride to the medium. Titrations were usually finished in saturated sodium chloride solution although some anions were satisfactorily precipitated at salt concentrations of 0.5 M to 3 M[1,2]. Later methods specified the use of a variety of supporting electrolytes (sodium chloride[3,5], ammonium hydroxide[3,4] and hydrochloric acid[6] in a variety of concentrations (0.3 M to 11 M).

The reasons advanced for the use of these added electrolytes have been various. They have been described as improving the rate of coagulation of the precipitate[1] and the crystal form and filterability[1,2,4-6] and reducing the solubility[1,2]; in some papers no reasons were given for their use[3].

METHODS

Tetraphenylarsonium chloride dihydrate was synthesised by a published procedure[9]. After precipitation from sodium chloride solution, the crude chloride was purified via the hydrodichloride[10,11] and finally recrystallised from water and air-dried to give the dihydrate. Potassium perchlorate (reagent grade) was recrystallised from water and dried at 110°. All other reagents were standard reagent grade. All solutions were filtered through retentive filter paper (Eaton-Dikeman 613) before use and stored in polyethylene bottles.

Solubility products

Apparent solubility product (K'_{sp}) values were determined in aqueous solution by the measurement of the molar detection limit for perchlorate ion in the presence of a known excess concentration of tetraphenylarsonium chloride and salt.

Each sample was made by mixing 10.0 ml of $2.00 \cdot 10^{-3}$ *M* tetraphenylarsonium chloride and 10.0 ml of salt solution of twice the final required concentration; 0.50–0.010 ml of potassium perchlorate ($1.00 \cdot 10^{-3}$ *M* or $0.500 \cdot 10^{-3}$ *M*) was added quickly. The mixture was shaken vigorously and placed in a thermostatted water bath at 25.0° ± 0.1°. The samples were contained in flat-bottomed screw-capped glass vials (85 mm × 26 mm o.d.). These vials just floated with 20 ml of mixture inside. The final nominal concentrations in each vial were $1.00 \cdot 10^{-3}$ *M* in tetraphenylarsonium chloride, 10^{-4}–10^{-6} *M* in potassium perchlorate and up to 4 *M* in salt. In each run, samples were made to give a perchlorate concentration sequence with successive vials differing by p[ClO_4] concentration unit intervals of 0.1. Precipitation did not occur for 15–30 min after mixing, by which time the mixture temperatures had already changed to 25.0° ± 0.1°.

After 90 min, the vials were removed from the bath, shaken vigorously to suspend the precipitates, wiped with tissue paper and then allowed to stand undisturbed for 5 min to allow bubbles to disappear. Longer reaction times, up to two days, made no apparent difference to the results.

Each vial was examined for the presence of a precipitate. The vial was held upright over a lamp (Bausch and Lomb Micro-Lite, 75 W bulb and blue filter) with the light shining vertically through the bottom of the vial. The contents of the vial were swirled gently, without introducing air-bubbles, and observed at right angles to the path of illumination against a dark background. A positive result was recorded when very fine evenly-sized flocs or crystalline needles were seen. A negative result was recorded when no precipitate or only irregular dust particles could be seen. The conditions of observation were critical and some practice was required before reproducible results were obtained.

When decision was difficult the sample was compared with those above and below it in perchlorate concentration, using them as positive and negative standards respectively. Replicate experiments for each perchlorate concentration series were made until the detection limit was established; usually 5–7 replicate runs were required. The detection limit was taken to be the lowest perchlorate ion concentration at which half or more of the replicate samples showed the precipitation of tetraphenylarsonium perchlorate.

The apparent solubility product exponent (pK'_{sp}) values were calculated from the product of the nominal arsonium ion concentration (10^{-3} *M*) and the nominal perchlorate ion concentration (10^{-4} *M* to 10^{-6} *M*) at the detection limit. The p[ClO^-_4] values were set at 0.1 unit intervals so the pK'_{sp} values had a nominal uncertainty of ±0.1 units.

Crystal form and filterability

The effects of salt concentrations on the settling rate, crystal form and filterability of precipitated tetraphenylarsonium perchlorate were measured for a series of precipitation mixtures differing only in the concentrations of salt within each series. Each sample was made by diluting 25.0 ml of 0.0200 *M* potassium perchlorate with 50.0 ml of salt solution (twice the final required concentration) and adding with stirring 25.0 ml of 0.0240 *M* tetraphenylarsonium chloride at room temperature. After a final stirring, the samples were left to settle for 1 h. The appearance of the settled samples was noted and, after stirring, one-drop samples were taken for microscopic examination.

Crystals were observed at approximately 200 × and 430 × magnification with a microscope fitted with a calibrated filar micrometer eyepiece. The largest crystals were measured for their length and breadth.

The samples were filtered on 30M sintered glass crucibles under water-pump vacuum. The filtration times, in minutes, were recorded as measures of filterability. The empty crucibles had previously been checked and unusually fast- and slow-running crucibles were discarded; those used had filtration times of 45 ± 15 sec for 100 ml of water.

The lower salt concentrations were corrected by addition of the 0.006 *M* concentration of chloride formed by the reaction of the potassium perchlorate and tetraphenylarsonium chloride.

Molar activity coefficients of the salts were calculated by interpolation from standard solution density tables[12] and molal activity coefficient tables[13].

RESULTS

Solubility products

The pK'_{sp} values were plotted against the square root of the molar salt concentration (Fig. 1). This gave a set of curves reminiscent of the familiar graphs of mean ionic activity coefficient against the square root of the ionic strength for most

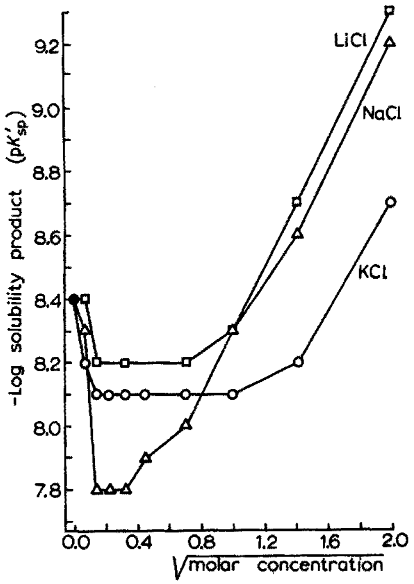


Fig. 1. Variation of solubility product exponent (pK'_{sp}) of tetraphenylarsonium perchlorate in alkali halide solution. (○) potassium chloride; (△) sodium chloride; (□) lithium chloride.

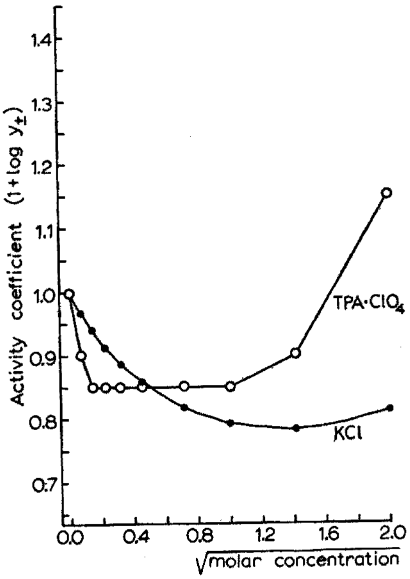


Fig. 2. Molar activity coefficients ($1 + \log y_{\pm}$) in potassium chloride solution. (○) tetraphenylarsonium perchlorate; (●) potassium chloride.

electrolytes. This suggested that the pK'_{sp} values could be used to calculate the trace activity coefficients of tetraphenylarsonium perchlorate as a function of salt concentration provided that the pK'_{sp} values could be taken as equal to equilibrium values. It seemed reasonable to do this; the pK'_{sp} value in the absence of added salt agreed well with values calculated from independent determinations of the solubility of tetraphenylarsonium perchlorate in water (Table I) and the pK'_{sp} values in general were not dependent on the time of reaction.

TABLE I

SOLUBILITY AND pK_{sp} VALUES FOR TETRAPHENYLARSONIUM PERCHLORATE IN WATER

pK_{sp}	7.92	8.40	8.40	8.33	8.59
Molar soly ($\cdot 10^9$)	12	3.98	4.0	4.63	2.60
Ref.	7	14	This work	15	16

$$K_{sp} = (a_{TPA^+})(a_{ClO_4^-}) = [TPA^+][ClO_4^-] \cdot y_\pm^2 = K'_{sp} \cdot y_\pm^2$$

$$\log y_\pm = 1/2(pK'_{sp} - pK_{sp})$$

If the ionic strength is negligible in the absence of salt and if K_{sp} is independent of ionic strength then

$$pK_{sp} = pK^0_{sp} = 8.4$$

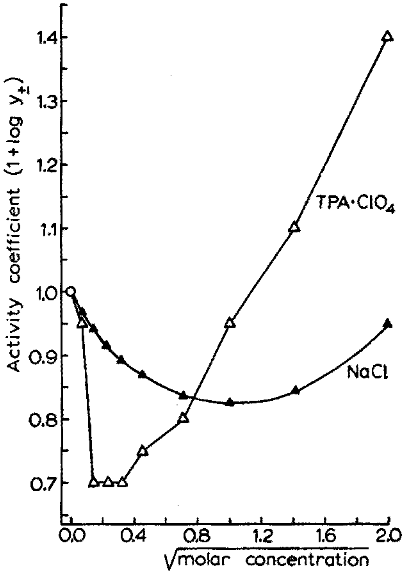
$$\log y_\pm = 1/2(pK'_{sp} - 8.4)$$

where K_{sp} is the equilibrium activity product, K'_{sp} the apparent solubility product, K^0_{sp} the apparent solubility product in the absence of salt, a the activity, $y_\pm$ the mean molar activity coefficient, and TPA^+ tetraphenylarsonium.

In this way the activity coefficients of tetraphenylarsonium perchlorate were calculated from the corresponding pK'_{sp} values and plotted against the square root of the molar concentration (Figs. 2–4) and on the same axes were plotted the corresponding molar activity coefficients of the added salts. The corresponding curves clearly differ but the tetraphenylarsonium perchlorate values approach those of the added salt more nearly for lithium chloride than for potassium chloride.

STOKES AND STOKES[17,18] found that the activity coefficient of a trace electrolyte could tend to that of a swamping electrolyte at high ionic strength. This was confirmed by WEEKS[19] who also found that the trend was not a predictable one. Hydrochloric acid trace activity coefficients did not show a regular trend in the presence of the group IIA perchlorate series magnesium through barium and the relative forms of the trace activity coefficient curves could not be predicted with the use of the "structure making or breaking" model of ion–solvent interaction.

It is concluded that the effects of added salts on the solubility of tetraphenylarsonium perchlorate are a consequence of the effect of the salt on the activity coefficient of tetraphenylarsonium perchlorate. Added electrolytes should all increase the solubility of tetraphenylarsonium perchlorate at low ionic strengths and decrease the solubility at high ionic strengths but the magnitude of the effect should depend on the electrolyte present.



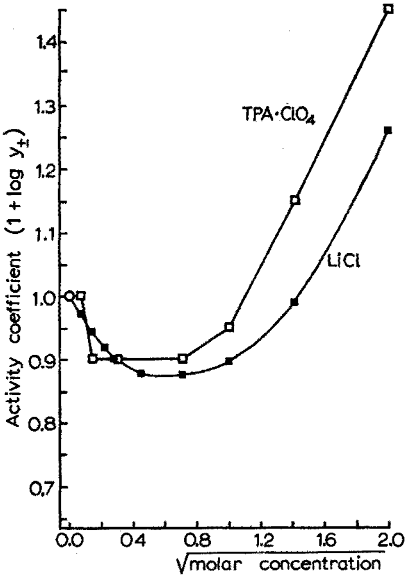


Fig. 3. Molar activity coefficients $(1 + \log y_{\pm})$ in sodium chloride solution. (△) tetraphenylarsonium perchlorate; (▲) sodium chloride.

Fig. 4. Molar activity coefficients $(1 + \log y_{\pm})$ in lithium chloride solution. (□) tetraphenylarsonium perchlorate; (■) lithium chloride.

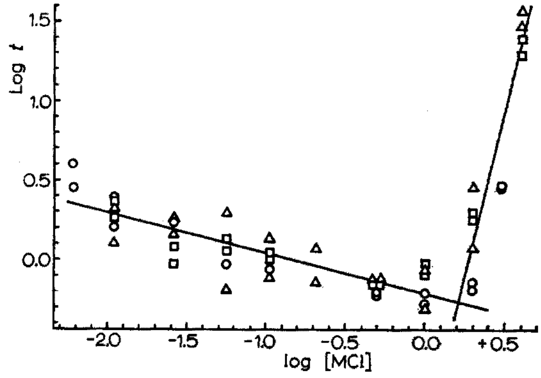


Fig. 5. Filtration time of tetraphenylarsonium perchlorate precipitates in alkali chloride solutions. (○) potassium chloride; (△) sodium chloride; (□) lithium chloride. Some coincident points have been offset side by side so as to show clearly.

Crystal form and filterability

It was clear, by inspection of the filtration times, crystal sizes and forms and settling behaviour of the precipitates, that there were no obvious differences between the effects of the three salts. For the rest of this discussion no distinctions will be made between them. (This is in interesting contrast to the specific effects of the salts on the precipitate solubility.)

At the lowest salt concentration (0.006 *M*) the crystals were rosettes and laths ($10 \times 2\ \mu$). As the concentrations increased to 0.2 *M* the precipitates formed weak dendrites and irregular needles ($40 \times 3\ \mu$). From 0.5 *M* to 1.0 *M*, needles ($100 \times 3\ \mu$) were formed. In 2–4 *M* solution, the acicular habit persisted but the needles became very small (from $50 \times 1\ \mu$ to $6 \times 0.2\ \mu$). The suspended precipitates settled most readily and compactly in 1 *M* solution; settling was progressively poorer at higher and lower concentrations. At concentrations below 1 *M* the precipitate had a strong tendency to form on the beaker wall; at 1 *M* and higher concentrations the beaker walls were free of adhering crystals.

The logarithmic filtration time ($\log_{10}t$) of each sample was plotted against the logarithmic molar salt concentration ($\log_{10}$[MCl]) for each salt (see Fig. 5). The points fell into two regions, each of which could be fitted to a straight-line graph by the standard least-squares method[20]. The regression equations of $\log_{10}t$ on $\log_{10}$[MCl] and the corresponding standard error of estimate and coefficients of correlation were: for [MCl] $\leq$ 1.0

$$\log_{10}t = -0.216 - 0.254 \log_{10}[\mathrm{MCl}];\ \hat{s}_{y.x} = 0.101,\ r = -0.841$$

and for [MCl] $>$ 1.0

$$\log_{10}t = -1.138 + 4.174 \log_{10}[\mathrm{MCl}];\ \hat{s}_{y.x} = 0.190,\ r = 0.923$$

The corresponding equations and statistics were calculated for each of the salts separately; the regression coefficients did not differ significantly at the 99% confidence level from that of the combined data.

All this evidence suggested strongly that there were different controlling processes of crystal formation above and below a salt concentration of 1 *M*.

At less than 1 *M* concentration, change of concentration altered the crystal form *i.e.* the relative rates of growth of crystal faces, but did not markedly alter the number of crystals formed. When the reagents were first mixed there was a barely noticeable induction period (of less than a second) before the precipitate formed and the precipitate showed a definite tendency to grow on the beaker wall.

Above 1 *M* in salt concentration, the number of crystals increased markedly and their size decreased with salt concentration. The precipitate formed noticeably faster than before, the crystals were much more evenly sized and the precipitate showed no tendency to grow on the beaker wall.

All these facts can be explained most simply by assuming that the nucleation of the precipitate is heterogeneous in salt solutions up to 1 *M* in concentration and is homogeneous above 1 *M*.

DISCUSSION

It seems clear that the main effect of added salt is to control the crystal form and the consequent filterability of tetraphenylarsonium perchlorate and that there is also an effect on the precipitate solubility.

Moderate salt concentrations (0.01–1.0 *M*) improve the filterability of the precipitate by controlling the rates of crystal face growth following heterogeneous nucleation. The solubility is increased by low concentrations of salt ($<$ 0.05 *M*) but this effect is unimportant at moderate concentrations (0.5–1.0 *M*). Hence for gravimetric separations of tetraphenylarsonium perchlorate, the better medium is 1.0 *M* sodium chloride; lithium and potassium chlorides afford no especial advantage and are more expensive.

High concentrations (2–4 *M*) cause a more rapid precipitation following homogeneous nucleation. The solubility of the precipitate is lowest at high concentrations but the crystals are very fine and unsuitable for filtration. Hence saturated sodium chloride is the better medium for a precipitation titration, as recommended by WILLARD *et al.*[1,2] and a high salt concentration will improve the sensitivity of tetraphenylarsonium chloride as a qualitative precipitating reagent for perchlorate.

SUMMARY

Alkali metal chlorides in the concentration range 0.006–4 *M* influence the solubility, crystal form and filterability of precipitated tetraphenylarsonium perchlorate. Low salt concentrations increase, and high concentrations decrease the filterability and solubility. The mean activity coefficient of tetraphenylarsonium perchlorate is controlled by general and specific salt effects. Crystal nucleation is probably heterogeneous in low concentrations of salt and homogeneous in high concentrations.

RÉSUMÉ

Les chlorures de métaux alcalins en concentration de l'ordre de 0.006 à 4 *M* influencent la solubilité, la forme cristalline, la filtrabilité du perchlorate de tétraphénylarsonium précipité. Le coefficient d'activité moyen du perchlorate de tétraphénylarsonium est contrôlé par des effets de sels. La nucléation cristalline est probablement hétérogène aux faibles concentrations de sels et homogène aux fortes concentrations.

ZUSAMMENFASSUNG

Alkalimetallchloride im Konzentrationsbereich von 0.006–4 *M* beeinflussen die Löslichkeit, Kristallform und Filtrierbarkeit von gefälltem Tetraphenylarsoniumperchlorat. Geringe Salzkonzentrationen verbessern die Filtrierbarkeit und Löslichkeit, hohe Konzentrationen verschlechtern beide. Der mittlere Aktivitätskoeffizient des Tetraphenylarsoniumperchlorats wird durch allgemeine und spezifische Salzeffekte bestimmt. Die Kristallkeime sind wahrscheinlich bei niedrigen Salzkonzentrationen heterogen und bei hohen Konzentrationen homogen.

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RAPID GRAVIMETRIC DETERMINATION OF MERCURY(I) SALTS

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Among the determinations of mercury(I) compounds, only a few methods have used metallic mercury as the weighing form. EVANS AND CLARKE[1] displaced the mercury with metallic copper, and then volatilized the mercury as a grayish black deposit on the bottom of a platinum crucible for weighing. FIALKOV[2] used the disproportionation of mercury(I) salts to obtain finely divided mercury, which was filtered onto a previously washed, dried, and weighed filter paper; filter and precipitate were then dried to constant weight. ROBINSON[3] reduced mercury compounds with hypophosphorous acid; the free mercury was absorbed on paper pulp, but the determination was completed titrimetrically with iodine. TRAVAGLI[4] used hot pyridine–hydrochloride to effect the disproportionation of calomel, obtaining the mercury as a single drop; however, the metal was then dissolved in nitric acid and determined gravimetrically as mercury(II) sulfide or mercury(I) chloride. All of the above methods are tedious, some requiring up to many hours for completion.

The disproportionation of mercury(I):

$$Hg_2^{2+} \rightleftarrows Hg^{2+} + Hg$$

can proceed quantitatively in the presence of a sufficient amount of ligand, such as Cl^-, Br^-, I^-, SCN^-, or CN^-, to form a mercury(II) complex of the general formula HgX_4^{2-}. In the method reported below, the free mercury is obtained as a bright metallic globule, which is washed, dried, and weighed. The entire procedure requires only about 30 min.

EXPERIMENTAL

Reagents

All chemicals used were reagent grade. Mercury(I) chloride, Hg_2Cl_2, was weighed out for direct use. Mercury(II) nitrate ($Hg(NO_3)_2 \cdot H_2O$, assay 99.0%) consisted of white crystals that were somewhat hygroscopic. Two samples of mercury(I) nitrate, $Hg_2(NO_3)_2 \cdot 2H_2O$, were used. A recently purchased supply consisting of translucent crystals and lumps, had a manufacturer's assay of 98.5%; another sample, probably some 20 years old, consisted of lemon-yellow crystalline lumps, indicating considerable deterioration to basic salt and/or mercury(II) compounds. Solutions of the nitrates were prepared, and aliquots taken for analysis.

General procedure

Into a 100-ml beaker, transfer 0.5–1.0 g (accurately weighed) of solid mercury(I) chloride, or 10–15 ml of mercury(I) nitrate solution. Add 10–20 ml of acid (HCl, HBr, or HI) and/or alkali halide solution. Heat the mixture to gentle boiling, with constant stirring, until small shiny mercury globules appear, no muddy precipitate remains, and the supernatant solution is clear. Carefully decant most of the solution, and remove the remainder with a dropper pipet. Wash the inner wall of the beaker and the mercury globules three times with 10–20 ml of distilled water, and then with about 10 ml of ethanol. (If, during washing, fine particles are observed floating on the liquid surface, stir with a glass rod to cause them to coalesce and fall.) Dry with a stream of air, or in a 40–50° oven for a few minutes. Gentle shaking or swirling causes the small mercury droplets to coalesce into a shiny ball. If the mercury globule is contaminated with a gray coating, wash with 2 or 3 ml of 2 *M* hydrochloric acid, then with water and finally with alcohol, and dry again. Transfer the mercury to a small weighing bottle or test tube for weighing.

RESULTS

Analysis of mercury(I) chloride

Because no assay value was available for the mercury(I) chloride, and for comparison with results of the gravimetric method, the mercury(I) chloride was analyzed by titration with potassium iodate in hydrochloric acid solution, to the disappearance of the iodine color in carbon tetrachloride, according to the reaction[5]:

$$2\ Hg_2Cl_2 + KIO_3 + 6\ HCl \rightarrow ICl + KCl + 4\ HgCl_2 + 3\ H_2O$$

The results are shown in Table I. In calculating the results of the gravimetric analysis of mercury(I) chloride reported below, a purity factor of 98.7% has been applied to the sample weights.

TABLE I

TITRIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE

Titrant: 0.02406 *M* KIO_3

Hg_2Cl_2 taken (g)	*6 M HCl (ml)*	*KIO_3 (ml)*	*Hg_2Cl_2 found (g)*	*% Recovery*
0.3940	10	17.15	0.3896	98.87
0.5077	13	21.81	0.4956	97.62
0.7090	12	31.30	0.7110	100.32
0.7971	12	34.70	0.7884	98.87
0.9552	14	41.40	0.9407	98.46
1.0707	15	46.16	1.049	97.95
			Average:	98.7

Hydrochloric acid reagent. The general procedure was followed, with variations in the amount of hydrochloric acid added. The results are shown in Table II. With hydrochloric acid at less than about 6 *M*, the reaction was quite incomplete and scattered results were obtained. Although the precision of the results shown in Table II is satisfactory, the error is far outside acceptable accuracy.

Hydrobromic acid reagent. Three series of samples, varying in the amount of hydrobromic acid added, gave the results shown in Table III. The mercury globules were very easily obtained by the use of hydrobromic acid; 2 *M* hydrobromic acid was sufficient for quantitative reaction, and higher concentrations could be used without adverse effect.

Hydriodic acid reagent. The general procedure was followed, with 20 ml of 2 *M* hydriodic acid. The reaction was complete without heating, although heating was advantageous in causing coalescence of the small mercury globules. Results are shown in Table IV.

TABLE II

GRAVIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE WITH HYDROCHLORIC ACID REAGENT

Hg_2Cl_2 *taken (g)*	*HCl added*	*Hg obtained (g)*	*% Recovery*
0.5433	40 ml, 6 *M*	0.2140	93.9
0.6372	40 ml, 12 *M*	0.2493	93.3
0.7694	50 ml, 12 *M*	0.3025	93.8
1.0192	50 ml, 6 *M*	0.4320	92.6
		Average:	93.4

TABLE III

GRAVIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE WITH HYDROBROMIC ACID REAGENT

Hg_2Cl_2 *taken (g)*	*HBr added*	*Hg obtained (g)*	*% Recovery*
0.1077	20 ml, 1 *M*	0.0442	97.8[a]
0.1914		0.0795	99.1
0.2957		0.1225	98.8
0.3926		0.1633	99.2
0.4820		0.2000	99.6
0.5028		0.2075	99.4
0.5145		0.2139	99.1
		Average:	99.3
0.2018	20 ml, 2 *M*	0.0845	99.9
0.2265		0.0950	99.8
0.3658		0.1530	99.7
0.4995		0.2094	100.0
0.5535		0.2311	99.6
0.6584		0.2756	99.8
0.7621		0.3186	99.7
1.0277		0.4296	99.7
1.1736		0.4916	99.9
		Average:	99.8
0.2786	10 ml, 4 *M*	0.1177	100.8
0.4589	15 ml, 4 *M*	0.1920	100.0
0.5954	15 ml, 4 *M*	0.2482	99.4
0.4853	10 ml, 8.8 *M*	0.2020	99.3
0.5115	10 ml, 8.8 *M*	0.2205	102.8[a]
1.0533	10 ml, 8.8 *M*	0.4358	99.3
1.1719	10 ml, 8.8 *M*	0.4892	99.5
		Average:	99.7

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[a] Not included in average.

Alkali halides and thiocyanate reagents. In these tests the reagent was a solution of potassium chloride, potassium bromide, potassium iodide, or potassium thiocyanate. The mercury was washed first with acid (HCl, HBr, or HI), then with water and with alcohol. Sometimes a fine gray residue was observed floating on the liquid; addition of

TABLE IV

GRAVIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE WITH HYDRIODIC ACID REAGENT
20 ml of 2 *M* HI used for all samples

Hg_2Cl_2 taken (g)	*Hg obtained (g)*	*% Recovery*
0.3089	0.1298	100.2
0.4505	0.1900	100.6
0.5423	0.2285	100.5
0.5623	0.2367	100.4
0.6006	0.2531	100.5
0.7583	0.3198	100.6
0.7760	0.3274	100.6
0.7901	0.3327	100.4
0.8444	0.3550	100.3
0.9985	0.4205	100.4
	Average:	100.4

TABLE V

GRAVIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE WITH ALKALI SALT REAGENTS

Hg_2Cl_2 taken (g)	*Reagent used*	*Hg obtained (g)*		*% Recovery*
Potassium chloride reagent				
0.4853	20 ml, satd.	0.1967		96.7
1.0105	20 ml, satd.	0.4075		96.2
0.5558	40 ml, 2 *M*	0.2158		92.6
0.9119	40 ml, 2 *M*	0.3521		92.1
Potassium bromide reagent				
0.5645	20 ml, satd.	0.2375		100.3
0.9917	20 ml, satd.	0.4160		100.0
0.4119	20 ml, 2 *M*	0.1722		99.7
0.7613	20 ml, 2 *M*	0.3196		100.1
			Average:	100.0
Potassium iodide reagent				
0.4708	20 ml, 4 *M*	0.1981		100.4
1.0108	20 ml, 4 *M*	0.4213		99.4
0.5023	20 ml, 2 *M*	0.2100		99.7
1.1024	20 ml, 2 *M*	0.4629		100.1
			Average:	99.9
Potassium thiocyanate reagent				
0.4639	20 ml, 4 *M*	0.1938		100.0
1.0030	20 ml, 4 *M*	0.4184		99.5
0.6295	20 ml, 2 *M*	0.2584		97.9[a]
1.0714	20 ml, 2 *M*	0.4465		99.4
			Average:	99.6

[a] Not included in average.

dilute acid, especially hydrobromic or hydriodic acid. caused this material to condense into mercury droplets. From reactions with potassium thiocyanate the mercury drop had a dark luster which was not removed by washing with hydrobromic acid. Results of these tests are given in Table V.

Potassium iodide and hydrochloric acid reagent. The reagent in this test was a solution *2 M* in potassium iodide and 2 *M* in hydrochloric acid, added in different volumes. Table VI shows the results.

TABLE VI

GRAVIMETRIC ANALYSIS OF MERCURY(I) CHLORIDE WITH POTASSIUM IODIDE–HYDROCHLORIC ACID REAGENT

Hg_2Cl_2 *taken (g)*	*Reagent used (ml)*	*Hg obtained (g)*	*% Recovery*
0.4020	15	0.1688	100.2
0.5837	14	0.2457	100.4
0.9957	20	0.4182	100.2
1.0571	20	0.4450	100.4
		Average:	100.3

Analysis of mercury(I) nitrate

Although potassium iodide or bromide can be used in the analysis of solid samples of mercury(I) nitrate, the corresponding hydro acids cannot be used because of oxidation of the free mercury in acid solution by nitrate or by iodine or bromine formed by oxidation of the halides. Furthermore, solid samples of mercury(I) nitrate may not be uniform in composition because of slow conversion to basic salt and/or to mercury(II) compounds, and uncertainty in amount of hydrate water. Precise analysis therefore requires use of the solution, which will nevertheless contain more or less mercury(II), depending upon the condition of the solid chemical used for preparation of the solution. Mercury(II) in the solution does not interfere in the analysis if sufficient complexing anion is added. Mercury(I) nitrate is not appreciably soluble in water, but is readily soluble in dilute nitric acid, which prevents formation of the basic salt.

A weighed quantity of the mercury(I) nitrate dihydrate was dissolved in water containing nitric acid, and then diluted to known volume; aliquots of the solution were taken for analysis. For comparison with the present gravimetric method, the solutions were analyzed titrimetrically by the method of BELCHER ABD WEST[6], in which an excess of standard iron(III) alum is added followed by addition of excess of ammonium thiocyanate; the excess of iron(III) is back-titrated with standard mercury(I) nitrate to disappearance of the red color of the iron(III) thiocyanate complex. For gravimetric analysis, aliquots of the solution were treated with alkali halide to precipitate the mercury(I) halide. The solution was neutralized (to methyl orange) with dilute sodium hydroxide, and then a large excess of alkali halide was added to effect the disproportionation of the mercury(I). The free mercury was washed, dried, and weighed, as described earlier. The results shown in Tables VII and VIII are for a sample of mercury(I) nitrate, many years old, consisting of bright yellow lumps of crystals. Table IX gives the results of similar analyses of a solution of a relatively

TABLE VII

ANALYSIS OF MERCURY(I) NITRATE

(Solution: 14.430 g $Hg_2(NO_3)_2 \cdot 2H_2O + 10$ ml 6 *M* HNO_3, diluted to 250 ml. Aliquots taken for analysis)

(A) GRAVIMETRIC METHOD, KBr REAGENT

$Hg_2(NO_3)_2 \cdot 2H_2O$ taken (g)	*Pptd. with 0.5 M KBr (ml)*	*KBr reagent added*	*Hg obtained (g)*	*% Recovery*
0.5772	10	20 ml, 2 *M*	0.1585	76.8[a]
0.5772	8	20 ml, 2 *M*	0.1615	78.3
0.5772	8	20 ml, 2 *M*	0.1625	78.8
0.5772	8	10 ml, 4 *M*	0.1621	78.6
			Average:	78.6

(B) TITRATION WITH 0.1021 *N* IRON(III) alum

Sample taken		*Titrant used (ml)*	*$Hg_2(NO_3)_2 \cdot 2H_2O$ found (g)*	*% Recovery*
(ml)	*(g)*			
15.20	0.8775	25.00	0.7162	81.6[a]
15.15	0.8746	24.10	0.6905	78.9
14.50	0.8372	23.10	0.6618	79.1
12.80	0.7390	19.95	0.5716	77.4
9.98	0.5761	15.72	0.4504	78.2
			Average:	78.4

[a] Not included in average.

TABLE VIII

ANALYSIS OF MERCURY(I) NITRATE

(Solution: 14.337 g $Hg_2(NO_3)_2 \cdot 2H_2O + 12$ ml 6 *M* HNO_3, diluted to 250 ml. Aliquots taken for analysis)

(A) GRAVIMETRIC METHOD, KI REAGENT

$Hg_2(NO_3)_2 \cdot 2H_2O$ taken (g)	*Hg_2^{2+} pptd. with 0.5 M*	*KI reagent added*	*Hg obtained (g)*	*% Recovery*
0.5735	KBr	20 ml, 2 *M*	0.1601	78.1
0.5735	KBr	20 ml, 2 *M*	0.1606	78.8
0.5735	HCl	24 ml, 2 *M*	0.1600	78.0
0.5735	NaCl	20 ml, 2 *M*	0.1600	78.0
			Average:	78.2

(B) TITRATION WITH 0.1021 *N* IRON(III) ALUM

Sample taken		*Titrant used (ml)*	*$Hg_2(NO_3)_2 \cdot 2H_2O$ found (g)*	*% Recovery*
(ml)	*(g)*			
11.70	0.6710	18.17	0.5205	77.6
8.75	0.5018	13.50	0.3867	77.1
10.05	0.5762	16.15	0.4626	80.3[a]
8.35	0.4789	13.15	0.3767	78.7
			Average:	77.8

[a] Not included in average.

TABLE IX

ANALYSIS OF MERCURY(I) NITRATE

(Solution: 16.964 g of new supply of $Hg_2(NO_3)_2 \cdot 2H_2O + 1.6300$ g $Hg(NO_3)_2 \cdot H_2O + 17$ ml 6 M HNO_3, diluted to 500 ml. Aliquots taken for analysis)

(A) GRAVIMETRIC METHOD, KBR REAGENT

$Hg_2(NO_3)_2 \cdot 2H_2O$ (g)	*KBr added*	*Hg obtained (g)*	*% Recovery*
0.3393	15 ml, 2 M	0.1066	87.7[a]
0.3393	20 ml, 2 M	0.1064	87.6[a]
0.5090	20 ml, 4 M	0.1609	88.2
0.5090	20 ml, 4 M	0.1647	90.3
0.5090	20 ml, 4 M	0.1636	89.8
0.5090	20 ml, 4 M	0.1639	89.9
0.5090	20 ml, 4 M	0.1641	90.0
0.5090	20 ml, 4 M	0.1641	90.0
		Average:	89.7

(B) GRAVIMETRIC METHOD, KI REAGENT

$Hg_2(NO_3)_2 \cdot 2H_2O$ (g)	*KI added*	*Hg obtained (g)*	*% Recovery*
0.5090	20 ml, 4 M	0.1642	90.1
0.5090	10 ml, 4 M	0.1643	90.1
0.5090	10 ml, 4 M	0.1644	90.2
0.5090	10 ml, 4 M	0.1653	90.7
0.5090	10 ml, 4 M	0.1652	90.6
0.5090	10 ml, 4 M	0.1646	90.2
		Average:	90.3

(C) TITRATION WITH 0.1021 N IRON(III) ALUM

Sample taken		*Titrant used*	*$Hg_2(NO_3)_2 \cdot 2H_2O$ found (g)*	*% Recovery*
(ml)	*(g)*	*(ml)*		
13.20	0.4479	13.94	0.3994	89.2
13.22	0.4485	14.05	0.4025	89.7
10.02	0.3399	10.95	0.3138	92.3[a]
9.28	0.3149	9.97	0.2856	90.7
18.30	0.6210	19.68	0.5639	90.8
18.95	0.6432	20.00	0.5729	89.1
			Average:	89.9

[a] Not included in average.

new supply of mercury(I) nitrate, the solution containing also some mercury(II) nitrate.

The validity of the gravimetric method is confirmed by good agreement with the iron(III) titrimetric method. Percentage recovery is calculated on the assumption that the weighed sample taken was pure $Hg_2(NO_3)_2 \cdot 2H_2O$. It is to be noted that the precision of the gravimetric method is in each case better than the precision of the titrimetric determination. Low recovery (purity) of the old sample was to be expected, because the material had obviously suffered deterioration. The new supply, labelled "Assay $Hg_2(NO_3)_2 \cdot 2H_2O$, 98.5%", was analyzed to only about 90% by both the gravimetric and titrimetric methods. Presence of a significant amount of hygroscopic moisture could account for the low results.

DISCUSSION

For the disproportionation equilibrium,

$$Hg_2^{2+} \rightleftarrows Hg + Hg^{2+},\ K_{eq} = [Hg^{2+}]/[Hg_2^{2+}] = 6 \cdot 10^{-3}$$

extensive reaction can be accomplished by "removal" of mercury(II) through formation of complex ions of the general formula HgX_4^{2-}. The formation constants of the chloro, bromo, and iodo complexes are, respectively, 10^{16}, 10^{22}, and 10^{30}. In the gravimetric method proposed here, reliable results were obtained by the use of HBr, HI, KBr, and KI to furnish the complexing anion. Quantitative reaction was not obtained by chloride ion, which is consistent with the lower formation constant of the tetrachloromercurate(II) complex. In our experience, better precision was attained by this gravimetric method than in the titrimetric oxidation of mercury(I) with iodate or with iron(III). The method can be carried out in the presence of mercury(II) compounds. Strong oxidizing agents, especially in acid solution, interfere with this gravimetric method. Interference is also experienced from cations (Ag^+, Pb^{2+}) that form insoluble halides, and from those (*e.g.*, Bi^{3+}, Sb^{3+}) that form insoluble basic salts.

Appreciation is expressed to the National Science Foundation for participation by Mr. Peng in the 1967–1968 Academic Year Institute at The University of Texas at Austin.

SUMMARY

A rapid, reliable method for the analysis of mercury(I) salts is based on direct weighing of mercury formed by complete disproportionation of Hg_2^{2+}, accomplished by complexing the mercury(II) with bromide or iodide. The free mercury is obtained in the form of a bright metallic globule, which is easily washed and dried for weighing. The method has been applied to the analysis of mercury(I) chloride and mercury(I) nitrate, and has been compared with titrimetric methods involving oxidation of mercury(I) with iodate and with iron(III).

RÉSUMÉ

Une méthode rapide et sûre est proposée pour l'analyse des sels de mercure(I): elle est basée sur la pesée directe du mercure formé par complète dismutation de Hg_2^{2+} obtenue en complexant le mercure(II) avec bromure ou iodure. Le mercure libre se présente sous forme d'un globule métallique brillant, se lavant, et séchant facilement afin d'être pesé. Ce procédé a été appliqué à l'analyse du chlorure de mercure(I) et du nitrate de mercure(I). Les résultats obtenus ont été comparés à ceux des méthodes titrimétriques par oxydation du mercure(I) au moyen d'iodate et de fer(III).

ZUSAMMENFASSUNG

Es wird eine schnelle, zuverlässige Methode für die Analyse von Quecksilber(I)-Salzen vorgeschlagen. Sie beruht auf der direkten Wägung des Quecksilbers, das durch vollständige Disproportionierung, unterstützt durch Komplexbildung des Quecksilber

(II) mit Bromid oder Jodid, gebildet wird. Das freie Quecksilber wird als metallische Kugel erhalten, welche leicht für die Wägung gewaschen und getrocknet werden kann. Die Methode wurde bei der Analyse von Quecksilber(I)-Chlorid und -Nitrat angewandt und titrimetrisch mit Jodat und Eisen(III) zum Vergleich bestimmt.

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HOMOGENEOUS PRECIPITATION OF BERYLLIUM BY MEANS OF TRICHLOROACETIC ACID HYDROLYSIS AND DETERMINATION AS PHOSPHATE

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Several analytical procedures for the determination of beryllium are based on the precipitation of beryllium ammonium phosphate of various degrees of hydration[1-6]. The compound is either weighed, after ignition, as $Be_2P_2O_7$ [6] or the phosphate equivalent is determined titrimetrically[7] or colorimetrically[8]. The advantages of urea hydrolysis for the homogeneous precipitation of beryllium as phosphate have been reported earlier by PATKAR AND VARDE[9].

In the course of a detailed investigation of the composition and properties of the phosphates of beryllium[10], it was observed that the hydrolysis of trichloroacetate ion could be utilized for the homogeneous precipitation of compounds of the type $BeMPO_4 \cdot xH_2O$, where M is either NH_4 or H. According to VERHOEK[11], "Trichloroacetate ion, under the influence of heat, yields carbon dioxide and strongly basic trichloromethyl ion, which in turn reacts with water to form chloroform". The reactions are represented as:

$$\begin{array}{ll} CCl_3COOH & \rightarrow CCl_3COO^- + H^+ \\ CCl_3COO^- & \rightarrow CCl_3^- + CO_2 \\ CCl_3^- + H_2O & \rightarrow CHCl_3 + OH^- \\ \hline CCl_3COOH & \rightarrow CHCl_3\uparrow + CO_2\uparrow \end{array}$$

The net effect being equivalent to the neutralisation of trichloroacetic acid, the pH attained at the end of the hydrolysis will be the same as that before the addition of trichloroacetic acid provided that no other reactions take place. Hence, trichloroacetic acid hydrolysis permits a close pH control in the homogeneous precipitation.

EXPERIMENTAL

Reagents

All reagents were of recognised analytical purity.

Standard beryllium solution. A 0.10 *M* solution was prepared by dissolving beryllium sulphate tetrahydrate in water, and standardising the solution by precipitation of the hydroxide followed by ignition to oxide[12].

^{42}K tracer was prepared by irradiating 50 mg of potassium nitrate in the Apsara reactor at a flux of 10^{11} n cm^{-2} sec^{-1}, for 6 h. After irradiation, the salt was dissolved in water and made up to volume. The purity of the tracer was checked by following the decay under the 1.53-MeV photopeak and comparing the observed half-life with that reported in the literature[13].

Control of pH

The control of pH achieved in the hydrolysis of TCA was studied as follows. Solutions containing sodium acetate–acetic acid mixtures or diammonium hydrogen phosphate were adjusted to pH values between 4.0 and 5.7. To 100 ml of each of these solutions, 10 ml of 10% (w/v) trichloroacetic acid was added. The solutions were kept boiling for 1 h, cooled and the pH measured using a Cambridge model GS pH meter. The results are given in Table I.

TABLE I

FINAL pH ATTAINED IN TCA HYDROLYSIS

Solution (volume 100 ml)	*pH*	
	Initially set[a]	*Finally attained*
Sodium acetate + acetic acid	4.2	4.1
Sodium acetate + acetic acid	4.8	4.8
Sodium acetate + acetic acid	5.0	4.9
Sodium acetate + acetic acid	5.5	5.6
0.1 *M* Ammonium phosphate	5.4	5.0
0.1 *M* Ammonium phosphate	5.0	4.9
0.1 *M* Ammonium phosphate + 1% EDTA	5.7	5.2
0.1 *M* Ammonium phosphate + 1% EDTA	5.1	4.9

[a] After addition of 10 ml of 10% TCA, the initial pH values changed in the range 2.5–2.9.

Recovery of beryllium from pure solutions

Transfer a suitable aliquot of standard beryllium solution to a 400-ml beaker, add 10 ml of 10% (w/v) EDTA solution (disodium salt) and 10 ml of 1 *M* diammonium hydrogen phosphate solution and dilute to 200 ml. Adjust the pH between 5.5 and 6.0 (indicator paper). Add sufficient 10% (w/v) trichloroacetic acid solution to dissolve the amorphous precipitate formed, and maintain the solution at boiling point. After about 15 min, the granular precipitate of beryllium phosphate appears. Add a few drops of bromocresol green indicator (0.05% in 1:1 ethanol) and continue boiling till the colour turns from yellow to blue (pH *ca.* 5.4), indicating the completion of the hydrolysis of TCA. Digest the precipitate for 2 h on a steambath, and collect on a Whatman No. 42 filter paper. Recover any precipitate from the walls of the beaker as follows: add a little dilute hydrochloric acid to the beaker along the walls, and reflux the solution in the covered beaker on a wire gauze for 5 min; to the clear solution add a few drops of ammonium phosphate and just enough ammonia to change the colour of the indicator to blue and filter through the same paper. Wash the precipitate free of phosphate ions with 2% ammonium nitrate solution, buffered to pH 5.5 with ammonium acetate. Complete the determination either gravimetrically[6] or titrimetrically with bismuthyl perchlorate solution[7]. Table II shows the results obtained for different aliquots of standard beryllium solution. In the titrimetric method, the refluxing step was not necessary since the precipitate on the

TABLE II

TITRIMETRIC AND GRAVIMETRIC DETERMINATION OF BERYLLIUM

Be taken (mM)	*$Be_2P_2O_7$ expected (mg)*	*Titrimetric*		*Gravimetric*	
		Found (mg)	*Error (%)*	*Found (mg)*	*Error (%)*
0.6	57.6	58.3	+1.2	57.8	+0.3
0.7	67.2	—	—	(66.4)[a] 67.0	(−1.2) −0.3
0.8	76.8	75.8	−1.3	(75.2)	(−2.1)
0.9	86.4	—	—	86.5	+0.1
1.0	96.0	97.0	+1.0	96.7 (92.7)	+0.7 (−3.4)
1.1	105.6	—	—	104.5	−1.1

[a] Figures in brackets refer to recoveries in the absence of the refluxing procedure.

TABLE III

ANALYSIS OF BERYLS

Sample no.	*% BeO by other methods*[a]	*% BeO by TCA hydrolysis*[b]	*Difference*
1.	9.23	9.22	0.01
2.	10.92	11.06	0.14
3.	12.10	12.13	0.03
4.	8.57	8.55	0.02
5.	11.05	10.89	0.26
6.	12.36	12.24	0.12
7.	13.44	13.50	0.06
8.	10.14	10.08	0.06
9.	8.82	8.88	0.06

[a] Samples 1–5 were analysed by the method of HURE *et al.*[6] and the rest by the method of SANKAR DAS AND ATHAVALE[7].

[b] Beryllium was determined gravimetrically for samples 1–5 and titrimetrically for the rest.

filter, after being washed, was transferred to the original beaker by dissolution in dilute perchloric acid.

Application to beryls

Fuse 0.500 g of the beryl sample for 5 min with 2 g of sodium fluoride in a platinum crucible. Cool, add 6 ml of concentrated sulphuric acid, and expel silica and hydrofluoric acid carefully on a sandbath. Then heat for a few minutes to thick fumes of sulphur trioxide over a free flame. Dissolve the cooled mass in 100 ml of water and dilute the solution to 250 ml. Pipette a 100-ml aliquot into a beaker and complete the determination as described above.

For comparison, precipitation was carried out by alternative methods[6,7] in a second 100-ml aliquot. The results are given in Table III.

Choice of flux

Sodium fluoride and potassium bifluoride were tested for opening the beryl sample. The use of sodium fluoride gave satisfactory results as shown in Table III. But the precipitate obtained after potassium bifluoride fusion, on ignition, turned into a hard mass, quite different from the residue obtained normally and gave positive errors. In a typical case, the ignited residue weighed 94.0 mg, whereas the expected weight of $Be_2P_2O_7$ was only 70.5 mg. Hence, the effect of potassium ions was studied by carrying out the precipitation in the presence of excess of potassium ions. Potassium was estimated by a tracer technique. An aliquot of the ^{42}K tracer was added to the clear solution, before TCA hydrolysis. The total potassium ion content of the solution was known from the amount of potassium salts used in the precipitation. The precipitate, after being washed free of phosphate, was dissolved in the minimum volume of 6% perchloric acid and transferred to a counting vial. The γ-activity of ^{42}K under the 1.53-MeV photopeak was measured and compared with that of a standard. The solution was transferred to a flask and the determination of beryllium was completed titrimetrically[7]. The results are recorded in Table IV.

TABLE IV

INFLUENCE OF POTASSIUM IONS

Sample no.	*Precipitant*	*K/NH₄*	*Analysis of ppt.*[a]		*K/Be in ppt.*
			Be (mM)	*K (mM)*	
1.	1 *M* Diammonium hydrogen phosphate	1 : 1	0.523	0.288	0.55
2.	1 *M* Diammonium hydrogen phosphate	1 : 1	0.677	0.545	0.80
3.	1 *M* Dipotassium hydrogen phosphate	1 : 0	0.778	0.617	0.79

[a] The precipitate corresponding to Sample 1 was analysed immediately on formation and that corresponding to Sample 2, after prolonged digestion on a steambath.

DISCUSSION

The results given in Table I show that, in the trichloroacetic acid (TCA) hydrolysis method, the final pH could be controlled around the desired value, thus providing a means of studying the effect of pH on the composition of beryllium alkali phosphates, precipitated homogeneously. When urea is used in homogeneous precipitations[9] ammonium ions are liberated, so that the effect of other alkali ions in the absence of ammonium ions, cannot be studied.

The data in Table II show that milligram amounts of the precipitate stick to the walls of the beakers, causing negative errors in the gravimetric determination of beryllium. This could be overcome by the refluxing procedure recommended by GORDON *et al.*[14]. This adsorption of a film of the precipitate was of no consequence in the titrimetric procedure because the precipitate was dissolved back in acid in the original beaker before titration.

The accuracy of the method is satisfactory, as can be seen from the results of Table III, wherein comparative data for the analysis of samples are given.

A noteworthy observation is the influence of different alkali ions on the composition of beryllium alkali phosphates. SMITH[15] has observed that in the presence of large amounts of alkali ions, the precipitate of beryllium ammonium phosphate gave a fused mass on ignition. In the present work, when precipitation by TCA hydrolysis was carried out in the presence of sodium ions (derived mostly from the sodium fluoride used in the fusion), the expected value for the weight of the ignited product was obtained, indicating the absence of contamination by sodium ions. However, in the presence of large amounts of potassium ions, a hard fused mass was obtained and the gravimetric results showed a positive error. The results of the tracer experiments with ^{42}K given in Table IV, confirm that potassium ions are incorporated in the precipitate. Further studies have shown that an ion-exchange mechanism of the type,

$$NH_4^+BePO_4^- + K^+ \rightleftarrows K^+BePO_4^- + NH_4^+$$

operates and that the selectivity of the exchange is poor for sodium compared to potassium. Detailed studies on this feature of beryllium ammonium phosphate are in progress and will be reported elsewhere.

The authors wish to thank Dr. M. SANKAR DAS and Dr. V. T. ATHAVALE for their keen interest and helpful discussions during the progress of this work.

SUMMARY

A solution of trichloroacetic acid, on heating, undergoes gradual decomposition to chloroform and carbon dioxide, accompanied by a rise in pH. This principle has been applied for the homogeneous precipitation of beryllium in presence of phosphate ions. The effect of alkali ions (Na and K) on the composition of the precipitate has been investigated. The method has been successfully applied for the determination of beryllium in beryls.

RÉSUMÉ

Une solution d'acide trichloracétique à chaud se décompose graduellement en chloroforme et anhydride carbonique avec élévation du pH. Cette réaction permet une précipitation homogène de béryllium en présence de phosphates. On examine l'influence des ions alcalins (Na et K) sur la composition du précipité. Cette méthode a pu être appliquée avec succès au dosage du béryllium dans des béryls.

ZUSAMMENFASSUNG

Eine Lösung von Trichloressigsäure zersetzt sich beim Erhitzen allmählich unter Bildung von Chloroform und Kohlendioxid unter gleichzeitiger Erhöhung des pH-Wertes. Dies Verhalten wurde für die homogene Fällung von Beryllium in Gegenwart von Phosphationen angewandt. Der Einfluss von Alkaliionen auf die Zusammensetzung des Niederschlages wurde untersucht. Die Methode wurde erfolgreich zur Bestimmung von Beryllium in Beryl angewandt.

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AN ANALYTICAL STUDY OF A NEW TYPE OF HALIDE-SENSITIVE ELECTRODE PREPARED FROM SILVER HALIDES AND THERMOPLASTIC POLYMERS

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Several investigations have been made to obtain membrane ion-selective electrodes of various types[1]. For cation-selective electrodes, PARSONS[2] moulded commercial ion-exchange resin with a plastic binder, whereas SHATKAY[3] prepared polyvinyl chloride membranes incorporating tributylphosphate and thenoyltrifluoroacetone. The behaviour of these electrodes is, however, affected by ions of the same charge present in a solution. Selective ion electrodes which do not have this limitation have been obtained by using inorganic salts in various forms. At present, the halide-sensitive electrodes commercially available are the Orion solid-state electrodes[4], which are made of cast pellets of silver halides as the active membrane materials, and the PUNGOR electrodes[4,5] which are prepared by incorporating a silver halide precipitate in a polymerized silicone rubber matrix. These electrodes are reported to display favorable mechanical properties and good chemical durability.

In the present paper, the preparation of a different type of heterogeneous membrane and its use in the preparation of electrodes sensitive to iodide, bromide or chloride are described.

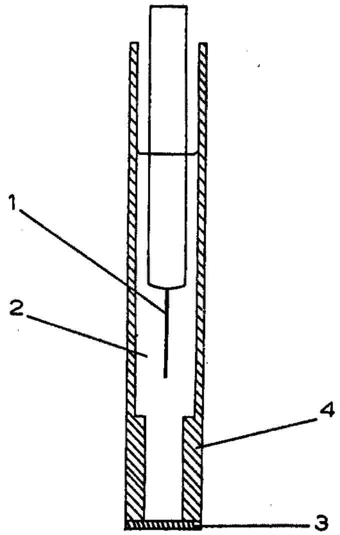
EXPERIMENTAL

Membrane electrode preparation

An insoluble precipitate is thoroughly mixed with a thermoplastic polymer and the mixture is moulded to obtain a rigid and uniform membrane. Any thermoplastic polymer could probably be used, but the present work has been limited to metacrylic esters and polythene.

As an example, the preparation of an iodide-selective electrode is described[6]: silver iodide was prepared by adding sufficient 0.5 *M* silver nitrate to 0.1 *M* potassium iodide to give a slight excess of silver. After thorough washing the precipitate was filtered and dried at 80°. The precipitate was sieved and the powder passing a 230 mesh was mixed in a mortar with a finely powdered thermoplastic polymer such as Lucite 45 (E. I. Du Pont de Nemours, Wilmington, U.S.A.).

The mixture was then set in a moulding press (Buehler AB 20—1312 Standard, Evanston, U.S.A.) between two stainless steel polished rams. The mixture was electrically heated in the press to 130–150° under a pressure of 300–400 atm and then left to cool. The mass ratio between the precipitate and the polymer was not critical, though more satisfactory results were obtained by using rather high percentages of the halide precipitate (50–70%). The thickness of the membrane used in electrode construction was *ca.* 1 mm. The membrane was soldered onto perspex tubing by means of dichloroethane and the electrode was set as indicated in Fig. 1. The internal reference electrode was a silver halide electrode and was dipped into a 10^{-3} *M* halide solution inside the electrode case in the usual way. The internal resistance of the membrane electrode was about 0.2 MΩ measured by means of a circuit similar to that described by ECKFELDT AND PERLEY[7].



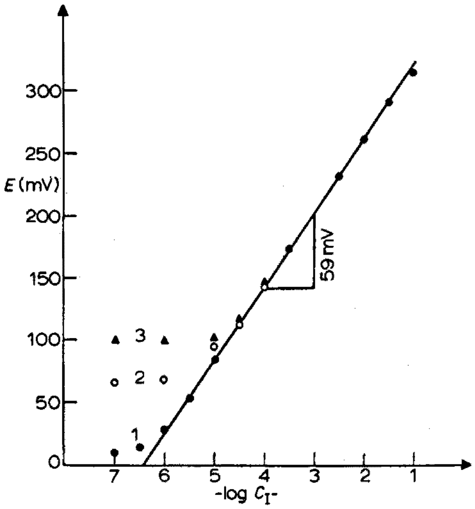


Fig. 1. Halide indicator membrane electrode: (1) reference electrode, Ag/Ag halide; (2) filling solution, 10^{-3} *M* halide; (3) membrane sensitive to halide ion; (4) electrode plastic body.

Fig. 2. Calibration curves for an iodide membrane electrode. (●) Pure iodide solution. (○) Iodide solutions containing 10^{-1} *M* chloride. (▲) Iodide solutions containing 10^{-1} *M* bromide.

The electrodes were stored at room temperature in an air-dry state. They were prepared for measurements by soaking them for 1–2 h in water or in a 10^{-3}–10^{-4} *M* solution of the corresponding halide. If the electrodes were left for a considerable length of time (*i.e.* overnight) in concentrated halide solutions, they could yield erratic results; in this case, the electrodes were thoroughly washed and soaked in water for a few hours.

Procedure

Potentiometric measurements were made in the conventional manner by using the halide-sensitive membrane electrode as the indicator electrode and a saturated calomel electrode (fiber type; Beckman 39170) as the reference electrode. A Beckman Research pH meter 1019 was used. When the chloride electrode was used, the connection to the reference electrode was made through a saturated potassium nitrate agar bridge. In every case, the response electrode was fast and equilibrium was achieved in a few minutes, except for very dilute solutions. Repeated measurements, if carried out on the same day, were reproducible to better than 1 mV.

RESULTS

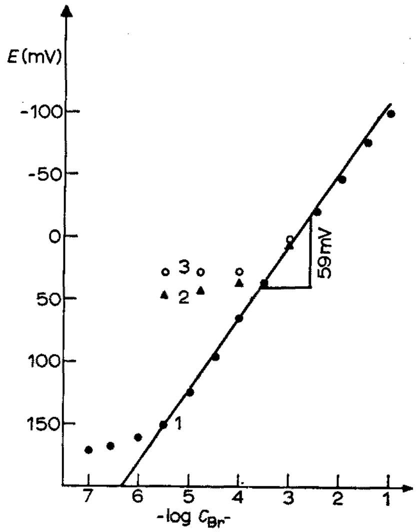
About 20 electrodes selective for each of the three halide ions were tested to evaluate their sensitivity, their response to concentration and their behaviour in the presence of other ions; data for calibration curves for single iodide, bromide or chloride membrane electrodes are reported in Table I. The actual values of e.m.f. differ from one electrode to another but the plots of e.m.f. *vs.* log C, where C is the halide concentration, yield straight lines over well-defined ranges (as shown in Figs. 2–4). The working ranges are about 10^{-6}–10^{-1} *M* for the iodide, 10^{-5}–10^{-1} *M*

TABLE I

CALIBRATION DATA AT 25° FOR AN IODIDE, A BROMIDE AND A CHLORIDE ELECTRODE

(e.m.f. *vs.* S.C.E.)

Concentration of solution (I^-, Br^- or Cl^-) (M)	*AgI electrode* E (mV)	*AgBr electrode* E (mV)	*AgCl electrode* E (mV)
H_2O	−10	170	280
10^{-7}	−10	170	—
10^{-6}	−29.5	160	—
10^{-5}	−84.4	123.3	270
10^{-4}	−144.2	64.5	237.5
10^{-3}	−202.3	7.8	184.0
10^{-2}	−261.1	−48.8	126.5
10^{-1}	−314.5	−101.6	74.0



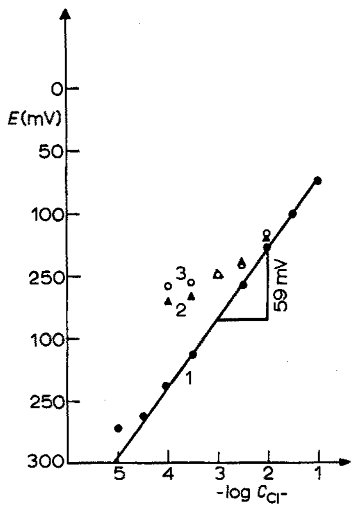


Fig. 3. Calibration curves for a bromide membrane electrode. (●) Pure bromide solution. (▲) Bromide solutions containing 10^{-1} *M* chloride. (○) Bromide solutions containing 10^{-4} *M* iodide.

Fig. 4. Calibration curves for a chloride membrane electrode. (●) Pure chloride solution. (▲) Chloride solutions containing 10^{-4} *M* bromide. (○) Chloride solutions containing 10^{-4} *M* iodide.

for the bromide and 10^{-4}–10^{-1} *M* for the chloride electrode. The slopes were found to range from a low of about 53 mV per decade concentration to a high of 59.8 mV. The results indicate that the electrodes follow the Nerst equation in a similar way to other silver halide electrodes.

The effect of possible interferences on these membrane electrodes may be evaluated with the aid of the Nernst equation as modified by GARRELS *et al.*[8].

$$E = E_0 - \frac{RT}{F} \ln \left(a_{\mathrm{Hl}} + K_{\mathrm{Hl\text{-}X}}\, a_{\mathrm{X}}^{1/n}\right)$$

where E, E_0 and R, T, F have the usual meaning, n is the valence of the interfering ion, X^{n-}, a_X its activity, a_{Hl} the activity of the halide ion and $K_{\mathrm{Hl\text{-}X}}$ is the selectivity constant of a halide electrode in the presence of the ion X^{n-}. The selectivity constant is calculated by means of the following expression:

$$\frac{E_2 - E_1}{RT/F} = \ln K_{\mathrm{Hl\text{-}X}}$$

where E_2 is the e.m.f. value of the cell when the halide electrode is placed in a 0.1 *M* solution of the tested anion, and E_1 is the e.m.f. of the same cell where the halide concentration is $[\mathrm{Hl}] = (0.1)^n$. The selectivity constants for the bromide and chloride electrodes have about the same order of magnitude, and the results are similar to those found for the silicone rubber membrane electrodes[5,9]. The performance of the proposed electrodes in the presence of other halides is shown in Figs. 2–4. The selectivity constants for various other ion pairs are shown in Table II.

TABLE II

SELECTIVITY CONSTANTS FOR THE IODIDE ELECTRODE

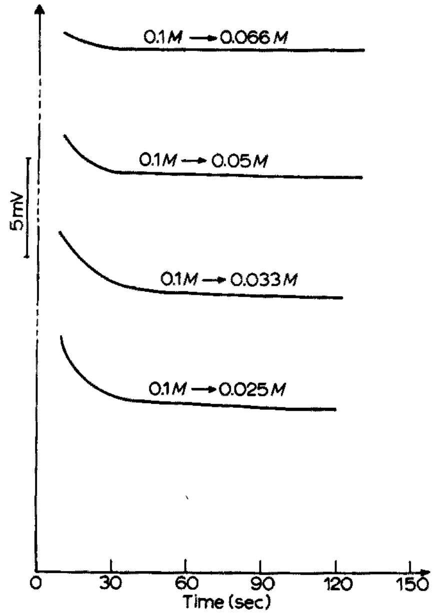
Ions	$E_2 - E_1$ *(mV)*	*Selectivity constant* K_{HlX}
I^-/NO_3^-	310	$5 \cdot 10^{-6}$
I^-/NO_2^-	310	$5 \cdot 10^{-6}$
I^-/SO_4^{2-}	300	10^{-5}
I^-/SO_3^{2-}	200	$3.5 \cdot 10^{-4}$
I^-/PO_4^{3-}	200	$3.5 \cdot 10^{-4}$
I^-/ClO_4^-	315	$4 \cdot 10^{-6}$
I^-/F^-	325	$2.5 \cdot 10^{-6}$
I^-/Cl^-	300	10^{-5}
I^-/Br^-	235	10^{-4}

Dynamic response

The dynamic response of the electrodes was evaluated by submitting the electrodes to rapid changes in the halide concentration, and recording the relative e.m.f. *vs.* time. The concentrations were changed either by dilution with distilled water or by addition of a more concentrated stock solution. In both cases, the e.m.f. values expected from the calibration curves were achieved. As an example, the dynamic response of a bromide electrode to dilution is shown in Fig. 5. In order to compare the behaviour of these electrodes and the PUNGOR electrodes, the time of equilibration for the cell e.m.f. was measured after a 2-fold dilution or concentration, as suggested by RECHNITZ *et al.*[9]. In all cases the time $(E_{\text{fin}} - E_{\text{init}})/2$ was less than 5 sec, which is shorter than the equivalent time for the PUNGOR electrodes[9].

Behaviour in mixed solvents

The behaviour of the electrodes was checked in mixed solvents consisting of water–ethanol and water–acetone containing up to 80% of the organic solvent. The slope of the *E vs.* halide concentration plot was lower than in water and the deviation tended to increase as the concentration of the organic solvents increased. In 80% ethanol, the slope was 53 mV/decade concentration, and in 80% acetone about 35–40 mV/decade.



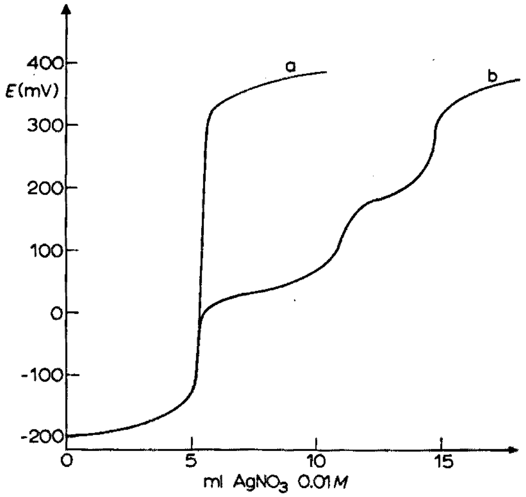


Fig. 5. Dynamic response of bromide electrode to changes in bromide concentration.

Fig. 6. Potentiometric titrations with 10^{-2} *M* silver nitrate and the membrane electrode. (a) Iodide. (b) A mixture of iodide, bromide and chloride.

Analytical application

The electrodes were examined as indicator electrodes in potentiometric titrations. Examples of potentiometric titrations of iodide and of a mixture of iodide, bromide and chloride with an iodide indicator electrode are given in Fig. 6; the well-defined S-shape of the titration curve and the large e.m.f. change at the end-point permits accurate results to be obtained. As can be seen from Fig. 6, the silver iodide electrode can also serve as an indicator for other halides in a mixture of halides; the Nerstian coefficient was found to be slightly lower in the electrometric determination of chloride and bromide ion.

Potentiometric titrations can be carried out in mixed solvents (aqueous ethanol or acetone) and the halide content can be determined with the same accuracy as that obtained in aqueous solutions.

DISCUSSION

The operation of membrane electrodes is by no means fully understood; their performance is similar to that of glass electrodes and a mechanism involving adsorption and ion exchange at the interface is usually invoked.

The electrodes described in this paper are similar in nature to the PUNGOR silicone rubber electrodes, being heterogeneous membrane electrodes. They have a number of interesting features; they are rugged, yield highly reproducible results and can be prepared quite simply. The ratio between the weight of the organic matrix and the silver halide is not critical.

The preparation of the halide precipitates and their particle size is not a determining factor with these electrodes: various batches of silver halides prepared under different conditions always yielded similar results. The preparation of a membrane with a smooth surface without imperfections seems to be the most important factor in the final performance of these electrodes; the procedure described, which involves heat treatment combined with pressure, appears to fulfil this requirement. Variations of the membrane thickness (about 0.3–1.5 mm) do not affect the behaviour of the electrode.

The procedure described in this paper should also be useful for the preparation of other membrane electrodes by incorporating other insoluble precipitates in a thermoplastic polymer.

SUMMARY

A new type of halide-selective membrane electrode is described. Membranes selective for iodide, bromide and chloride can be prepared by thorough mixing of a silver halide precipitate with a thermoplastic polymer followed by heat treatment under pressure. The ranges of linear response to changes in halide concentration are similar to those for other types of silver halide membrane electrode. The selectivity of the electrodes and their behaviour in aqueous–organic solvents is described.

RÉSUMÉ

On décrit un nouveau type d'électrode à membrane sélective-halogénure. Des membranes sélectives pour iodure, bromure et chlorure peuvent être préparées, par traitement thermique sous pression, en mélangeant un précipité d'halogénure d'argent avec un polymère thermoplastique. L'échelle de réponse linéaire aux variations de concentration en halogénure est pareille à celle d'autres types d'électrode à membrane d'halogénure d'argent. On examine également la sélectivité de ces électrodes et leur comportement en milieux solvants organiques aqueux.

ZUSAMMENFASSUNG

Es wird ein neuer Typ halogenidempfindlicher Membranelektroden beschrieben. Membranen, die selektiv für Jodid, Bromid und Chlorid sind, können durch Mischen von gefälltem Silberhalogenid mit thermoplastischen Polymeren und anschliessender Behandlung unter Druck hergestellt werden. Der Linearitätsbereich ist dem anderer

Typen von Silberhalogenidelektroden ähnlich. Die Selektivität der Elektroden und ihr Verhalten in wässrig-organischen Lösungsmitteln wird beschrieben.

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N-ACETYLSALICYLOYL-N-PHENYLHYDROXYLAMINE AS AN ANALYTICAL REAGENT FOR TITANIUM(IV)

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Although many methods have been proposed for the detection and determination of titanium, few methods are available for microdeterminations and the analysis of most of these[1] are prone to interference from commonly associated cations. Recently, hydroxamic acid derivatives have been found to possess superior qualities as analytical reagents for titanium. Thus, salicylhydroxamic acid[2], N-benzoyl-N-phenylhydroxylamine[3], and N-phenylsalicylhydroxamic acid[4] have been used for gravimetric or spectrophotometric determinations or for both. All of these reagents form yellow complexes with titanium(IV) in neutral or acidic solutions, the complexes being soluble in organic solvents, but none is as selective as the one described here.

During work on the preparation of new organic reagents and their analytical applications, it was found that N-acetylsalicyloyl-N-phenylhydroxylamine formed coloured complexes with a few cations in strong acidic media. The reagent forms a yellow, chloroform-soluble complex with titanium in strong hydrochloric acid solutions. The selectivity and sensitivity of the colour reaction can be increased considerably if the reaction is carried out in presence of a large excess of thiocyanate. Based on this colour reaction a virtually specific spot test and spectrophotometric method were developed for titanium.

The reagent forms with titanium in 1–2 *M* hydrochloric acid solutions a yellow granular precipitate which can be dried to constant weight. This gravimetric method is again superior in selectivity to earlier methods.

EXPERIMENTAL

Preparation of the reagent

N-Acetylsalicyloyl-N-phenylhydroxylamine was prepared by condensing acetylsalicyloyl chloride and phenylhydroxylamine in presence of sodium hydrogen carbonate; the method of BAMBERGER[5] as modified by LUTWICK AND RYAN[6] was followed. Acetylsalicyloyl chloride was prepared as described by RIEGEL AND WITTCOFF[7]. The reagent was soluble to the extent of 0.25% in water at 30°. The compound was recrystallised from ethanol–water mixture (m.p. 128°. Found C, 66.9; H, 4.8; N, 5.1%. Calculated for $C_{15}H_{13}O_4N$: C, 66.42; H, 4.79; N, 5.16%).

Apparatus, reagents and solutions

A Bausch and Lomb Spectronic-20 spectrophotometer with matched tubes was used for absorbance measurements.

A standard solution of titanium was prepared by dissolving AnalaR potassium titanyl oxalate in a predetermined volume of distilled water, and standardized gravimetrically with cupferron[8].

Chloroform for extraction was purified from alcohol and other impurities by washing successively with dilute ammonia, dilute sulphuric acid and water and finally by distillation.

A 0.5% (w/v) solution of the reagent in chloroform was prepared for spectrophotometric work and spot tests. For gravimetric work, a 4% (w/v) solution of the reagent in ethanol was used.

Freshly prepared 4 *M* ammonium thiocyanate solution was used.

Solutions of diverse ions were prepared from AnalaR chemicals.

Spot test for titanium

Procedure. In a micro test tube, place 0.05 ml of titanium solution and 0.05 ml of 4 *M* ammonium thiocyanate solution followed by 0.1 ml of 10 *M* hydrochloric acid. Shake for 1 min with 0.2 ml of the reagent solution. A stable deep yellow chloroform layer indicates the presence of titanium.

The limit of identification was found to be 0.1 μg Ti with a dilution limit of 1:2,000,000.

Effect of variables. Maximum colour intensity was found in 4.5–8 *M* hydrochloric acid solutions. In sulphuric acid media of the same strength, the sensitivity was considerably less. The complex was stable for 24 h at room temperature and variation in temperature from 15 to 55° had no effect. For stability and maximum coloration, an excess of thiocyanate was required; under the experimental conditions, 0.05 ml of 4 *M* solution sufficed.

Interference of various ions. The spot test described above was highly selective. No interference was found with Tl(I), Cd(II), Hg(II), Zn(II), Mg(II), Be(II), Fe(II), Pb(II), Mn(II), Ca(II), Sr(II), Ba(II), Al(III), Bi(III), Cr(III), Sb(III), As(III), Fe(III), La(III), Th(IV), Sn(IV), Zr(IV), Ce(IV), V(V), Ta(V), Mo(VI), W(VI), U(VI), Te(VI), and Os(VIII) even in 1000-fold amounts. Copper(II) was tolerated in 1000-fold amounts in the presence of EDTA. Niobium(V) gave a similar colour under the experimental conditions, but could be masked in 1000-fold amounts by complexing with oxalate. Of the various anions, only fluoride interfered, but the interference could easily be avoided by the use of boric acid. Tartrate, citrate, oxalate, borate, persulphate, phosphate and EDTA were tolerated in greater than 1000-fold amounts.

Spectrophotometric determination of titanium

Procedure. Place an aliquot of titanium(IV) solution containing 12.5–88 μg of the metal in a separatory funnel and add 2–4 ml of 4 *M* ammonium thiocyanate solution followed by enough 10 *M* hydrochloric acid to make the solution 4.5–8 *M* with respect to the acid. Then add 3–4 ml of a 0.5% (w/v) solution of the reagent in chloroform. Shake the mixture gently for about 2 min. with 5 ml of purified chloroform. Transfer the deep yellow chloroform layer to a small beaker containing a few g of anhydrous sodium sulphate. Extract again with 5 ml of chloroform and collect in the same vessel. Transfer the combined extract to a 25-ml volumetric flask and dilute to the mark with chloroform. Measure the absorbance at 390 nm against a reagent blank.

Absorbance spectra. The reagent in chloroform absorbs below 410 nm, whereas the absorption of the complex increases continuously from 480 nm towards the ultraviolet region, no definite absorption maximum being obtained (Fig. 1). The most suitable wavelength for spectrophotometric work seemed to be 390 nm, since at this wavelength the absorbance due to the reagent was negligible in comparison with that of the complex (Fig. 1).

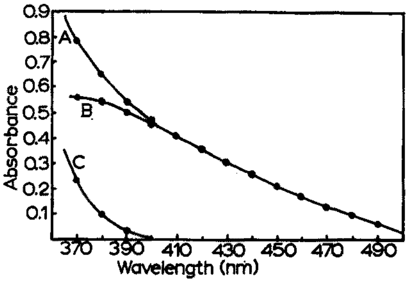


Fig. 1. Absorbance spectra. (A) 2 p.p.m. titanium against chloroform blank; (B) 2 p.p.m. titanium against reagent blank; (C) 3 ml of 0.5% (w/v) solution of reagent in 25 ml against chloroform blank.

Effect of acid strength. Only in 4.5–8 *M* hydrochloric acid media was the maximum colour intensity obtained. Sulphuric acid was not suitable owing to decreased sensitivity.

Effect of reagent and thiocyanate. For maximum colour development, 3 ml of 4 *M* thiocyanate sufficed. Larger concentrations of thiocyanate had no effect, but lower amounts decreased the stability and sensitivity of the colour system. The optimum concentration of the reagent was found to be 3 ml of a 0.5% solution in chloroform. Increasing concentrations of the reagent had no effect provided that absorbances were measured against blanks containing the same amount of reagent.

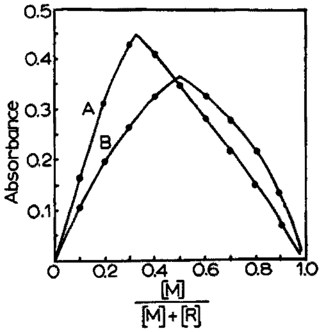
Stability of the colour. The complex was stable at room temperature for 24 h and afterwards the absorbance increased with the eventual formation of a turbidity. Changes in temperature from 15 to 55° had no marked effect, after allowance for changes in volume with temperature.

Optimum range, sensitivity and photometric error. The colour system obeyed Beer's law from 0.25 to 4 p.p.m. of titanium at 390 nm and the optimum concentration range determined by the method of RINGBOM[9] was 0.5–3.5 p.p.m. In this range the percentage relative analytical error per 1% absolute photometric error[10] was 1.85. The photometric sensitivity[1] of the method was 0.004 μg Ti/cm^2 at 390 nm and the molar absorptivity was 10900.

Composition of the complex. The stoichiometric composition of the complex formed between titanium, N-acetylsalicyloyl-N-phenylhydroxylamine and thiocyanate was established by the continuous variation[11] as well as the molar ratio[12] methods.

For Job's method, two series of solutions were prepared. In one series the mole fraction of titanium and the reagent were varied, with a large excess of thiocyanate. From the curve thus obtained (curve A, Fig. 2), the molar ratio of titanium to reagent was found to be 1:2. Equimolar solutions of both the metal and thiocyanate were then used with a constant excess of the reagent. From the maximum in the curve (curve B, Fig. 2), a ratio of titanium to thiocyanate of 1:1 was obtained.

The composition of the complex was also established by the application of molar ratio method; again two series of solutions were used. In one series, equimolar solutions of titanium and the reagent were used, and in the other equimolar solutions of the metal and thiocyanate were used, the third component being kept in large excess in both cases. The curves thus obtained (Fig. 3) supported the previous conclusions regarding the composition of the complex.



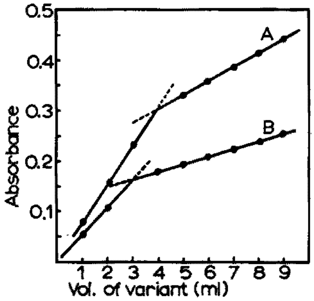


Fig. 2. Job's method. (A) titanium = reagent = $1 \cdot 10^{-3}$ *M*; (B) titanium = thiocyanate = $2 \cdot 10^{-3}$ *M*.

Fig. 3. Molar ratio method. (A) titanium = reagent = $1 \cdot 10^{-3}$ *M*, 2 ml of titanium solution taken; (B) titanium = thiocyanate = $2 \cdot 10^{-3}$ *M*, 3 ml of titanium solution taken.

Interferences. The effect of various foreign ions was the same for this spectrophotometric method as for the spot test described above. All the commonly associated ions were tolerated in amounts greater than 1000-times excess.

Gravimetric determination of titanium

Procedure. Dilute the solution containing 10–25 mg of titanium(IV) to 150 ml and add 15–20 ml of 10 *M* hydrochloric acid. Heat to 70–80° and then add 2–3 times the theoretical quantity of the reagent in ethanol with stirring. Immediately a lemon yellow precipitate is formed. Heat to boiling and allow to stand at room temperature for about 2 h. Filter through a No. 4 sintered glass crucible, wash several times with cold water containing 0.05% of the reagent and dry to constant weight at 105–115°. Calculate the titanium content from the stoichiometric factor 0.07931.

Composition of the complex. The weight of precipitate obtained from a known amount of titanium agreed with the formula $TiO(C_{15}H_{12}O_4N)_2$, which was proved by analysis. (Found: Ti, 7.92; N, 4.62%. Calculated: Ti, 7.93; N, 4.64%.)

Thermogravimetric study. The thermogram of the complex, obtained with a Stanton Thermobalance showed no change in weight up to 185°. Afterwards the substance lost weight gradually up to 560°, above which titanium dioxide remained. The complex could thus be safely dried below 185° for weighing.

Effect of variables. The optimum acid strength for quantitative precipitation was found to be 1–2 *M* in hydrochloric acid. Sulphuric acid caused high recoveries. Quantitative precipitation was obtained with 2–3 times the theoretical quantity of reagent. A greater concentration of the reagent should be avoided because the solubility of the reagent in water at 30° is only 0.25%. Typical results obtained by the method are shown in Table I.

Interferences. Titanium (10–15 mg) was determined by the above method in mixtures containing potassium titanyl oxalate and varying amounts of cations and anions. Table II lists the cations, with concentrations in parentheses, which did not interfere; in addition to these cations Tl(I) (250 mg), Th(IV), U(VI) and V(IV) (100 mg each) were also found not to interfere. The interference of vanadium(V) was eliminated by reduction with hydroxylamine hydrochloride. Niobium was masked with oxalate. Serious interferences are W(VI), Mo(VI) and Ta(V). Of the anions tested, phosphate (200 mg), oxalate, borate, acetate, citrate, tartrate and EDTA (500 mg each) showed no evidence of interference, but thiocyanate (100 mg) and fluoride (5 mg) interfered. Fluoride interferences were easily avoided by the use of boric acid.

TABLE I

GRAVIMETRIC DETERMINATION OF TITANIUM

Ti taken (mg)	*Weight of precipitate (mg)*	*Ti found (mg)*	*± Error (mg)*
5	62.8	4.982	−0.018
10	126.0	9.992	−0.008
15	189.0	14.970	−0.030
20	252.6	20.040	+0.040

TABLE II

EFFECT OF FOREIGN IONS

Group I	Cu^{2+} (150 mg)
Group II	Be^{2+}, Mg^{2+}, Zn^{2+} (200 mg each), Cd^{2+}, Hg^{2+} (100 mg each)
Group III	Al^{3+} (200 mg), Ce^{4+} (100 mg)
Group IV	Zr^{4+} (100 mg)
Group V	As^{3+}, Sb^{3+}, Bi^{3+} (100 mg each)
Group VI	Cr^{3+} (100 mg)
Group VII	Mn^{2+} (200 mg)
Group VIII	Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} (100 mg each)

TABLE III

DETERMINATION OF TITANIUM IN ILMENITE

Reagent	*Method*	*% TiO_2*[a]
N-Acetylsalicyloyl-N-phenylhydroxylamine	Spectrophotometric	58.13
Hydrogen peroxide	Spectrophotometric	58.01
N-Acetylsalicyloyl-N-phenylhydroxylamine	Gravimetric	58.24
Cupferron	Gravimetric	58.30

[a] Average of two experiments.

Applications

The spectrophotometric and gravimetric methods were applied to the determination of titanium in ilmenite (Table III). Finely powdered ilmenite (1 g) was fused with 10 g of sodium bisulphate in a silica crucible and extracted with 500 ml of saturated ammonium oxalate solution. For the spectrophotometric determination this solution was further diluted; the results thus obtained were compared with those of the hydrogen peroxide method[13]. Aliquots of the extracted solution were taken for the gravimetric determination of titanium by means of N-acetylsalicyloyl-N-phenylhydroxylamine and also by cupferron[13].

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SUMMARY

N-Acetylsalicyloyl-N-phenylhydroxylamine is readily prepared and can be used for the detection and the spectrophotometric or gravimetric determination of titanium(IV). The reagent forms a deep yellow chloroform-soluble complex with titanium(IV) and thiocyanate in 4.5–8 *M* hydrochloric acid media. The limit of identification of the spot test based on this reaction is 0.1 μg of titanium (dilution limit is $1:2 \cdot 10^6$). The spectrophotometric method is also highly selective, the sensitivity being 0.004 μg Ti/cm^2 at 390 nm. The optimum concentration range is 0.5–3.5 μg Ti/ml, the relative photometric error is being 1.85. The complex is stable at room temperature for 24 h, and contains the metal, reagent and thiocyanate in the ratio 1:2:1. Commonly associated ions can be tolerated in amounts greater than 1000-fold. Gravimetric determination of titanium(IV) is also very selective; the yellow precipitate formed in 1–2 *M* hydrochloric acid media can be weighed directly after drying at 105–115°. Both methods can be applied to the determination of titanium in ilmenite.

RÉSUMÉ

La N-acétylsalicyloyl-N-phénylhydroxylamine peut se préparer facilement et peut être utilisée pour l'identification et le dosage spectrophotométrique ou gravimétrique du titane(IV). Ce réactif forme avec le titane(IV) et le thiocyanate un complexe jaune foncé soluble dans le chloroforme, en milieu acide chlorhydrique 4.5–8 *M*. La limite d'identification du test qualitatif, basé sur cette réaction est 0.1 μg de titane (limite de dilution $1:2 \cdot 10^6$). La méthode spectrophotométrique est également très sélective; sensibilité 0.004 μg Ti/ml à 390 nm. Le complexe est stable à la température ordinaire pendant 24 h et renferme métal, réactif et thiocyanate dans le rapport 1:2:1. Les ions accompagnant généralement le titane peuvent être présents en quantités 1000 fois supérieures, le dosage gravimétrique est également très sélectif. Le précipité jaune formé en milieu acide chlorhydrique 1–2 *M* peut être pesé directement après séchage à 105–115°. Ces deux méthodes peuvent être appliquées au dosage du titane dans l'ilménite.

ZUSAMMENFASSUNG

N-Acetylsalicyloyl-N-phenylhydroxylamin wurde auf einfachem Wege synthetisiert und zum Nachweis und für die spektralphotometrische oder gravimetrische Bestimmung von Titan(IV) verwendet. Das Reagenz bildet einen tiefgelben chloroformlöslichen Komplex mit Titan(IV) und Thiocyanat in 4.5–8 M salzsaurer Lösung. Die Nachweisgrenze beim Tüpfeltest beträgt 0.1 μg Titan (Grenzkonzentration: $1:2\cdot10^6$). Die spektralphotometrische Methode ist mit einer Empfindlichkeit von 0.004 μg Ti/cm^2 bei 390 nm ebenfalls hochselektiv. Der optimale Konzentrationsbereich liegt bei 0.5–3.5 μg Ti/ml mit einem relativen photometrischen Fehler von 1.85. Der Komplex ist bei Raumtemperatur 24 Std. lang stabil und enthält Metall, Reagenz und Thiocyanat im Verhältnis 1:2:1. Übliche Begleitelemente können in mehr als 1000-fachem Überschuss vorhanden sein. Die gravimetrische Bestimmung des Titan(IV) ist ebenfalls sehr selektiv. Der in 1–2 M Salszäure gebildete gelbe Niederschlag kann nach Trocknen bei 105–115° direkt gewogen werden. Beide Methoden können bei der Bestimmung von Titan in Ilmenit angewandt werden.

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SHORT COMMUNICATIONS

Mass spectral studies of some substituted phosphines

Recent mass spectral investigations[1] have been carried out on the fluoroalkyl and fluoroaryl derivatives of phosphorus in order to gain more information about molecular rearrangements and mechanisms for the transfer of fluorine from carbon to phosphorus. MILLER[1] has examined the mass spectra of a series of pentafluorophenyl derivatives of phosphorus. Bond-forming rearrangements were observed such as the elimination of PF_2 from the $(C_6F_5)_2P^+$ species giving $(C_6F_4)_2^+$. CAVELL AND DOBBIE[2] have observed extensive rearrangement and transfer of fluorine during the fragmentation of the trifluoromethylphosphines. WILLIAMS *et al.*[3] have used deuterium labelling to study reactions induced by electron-impact in triphenylphosphine, triphenylphosphine oxide and methylenetriphenylphosphorane. The mass spectra of the dimethylaminohalophosphines are of particular interest because recent investigations have demonstrated the ability of the phosphorus atom to act as a Lewis base in the presence of various electron acceptors, and which suggest that the P–N bond is easily cleaved[4-8].

Results and discussion

Examination of the mass spectrum of tris(dimethylamino)phosphine (Table I) shows a high abundance of two types of positive ions: (i) the group of immonium ions with the positive charge stabilized by nitrogen, which are analogous to those obtained from dimethylamine[9]; and (ii) the group of disubstituted phosphorus ions of

TABLE I

PERCENT TOTAL IONIZATION[a] OF PRINCIPAL IONS[b]

(Complete listing of all ions is presented in EXPERIMENTAL section; A = $[(CH_3)_2N]$)

Ion	A_3P	A_2PF	A_2PCl	A_2PBr	APF_2	$APCl_2$	$APBr_2$
$[(CH_3)_2N]_3P^+$	6.3						
$[(CH_3)_2N]_2P^+$	*23.1*		9.0	*26.4*			
$(CH_3)_2NHP^+$	22.5	1.0	11.7	22.1			
CH_3NP^+	9.6	2.0	9.4	11.7		2.7	6.7
$(CH_3)_2N^+$	19.7	12.6	10.4	5.6	1.7	3.8	7.3
$(CH_2)_2N^+$	7.8	17.0	11.9	11.0	*41.6*	17.4	16.7
CH_3	10.9	13.7	10.8	10.2	13.5	12.2	9.9
$[(CH_3)_2N]_2PX^+$		7.9	9.7	1.6			
$(CH_3)_2NPX^+$		*39.8*	*26.3*	7.1	5.1	*22.3*	*38.6*
$(CH_3)_2NPX_2^+$		2.6			22.5	8.4	3.0
P^+			0.7	1.5	0.8	4.3	3.4
PX^+		1.4		2.6	2.7	4.4	5.6
PX_2^+		1.9			12.1	15.1	4.0
PX_3^+						4.9	1.3
X^+						4.5	3.6

[a] Defined as $\Sigma(\text{Int})_n$ where n includes only those ions appearing in the Table.
[b] Base peak is italicized.

TABLE II

MASS SPECTRUM OF COMPOUNDS EXAMINED

(With mass/charge ratio, relative intensity and tentative assignments respectively)

Tris(dimethylamino)phosphine

15, 47.4, CH_3^+; 17, 3.3, ?; 18, 21.2, NH_4^+, H_2O^+; 27, 7.2, ?; 28, 54.3, N_2^+; 29, 3.6, ?; 30, 15.0, $CH_2NH_2^+$, CH_2NPH^{2+}; 32, 3.3, ?; 33, 3.9, ?; 39, 2.2, ?; 40, 5.0,?; 41, 5.8, ?; 42, 33.7, $C_2H_4N^+$; 43, 13.6, $C_2H_5N^+$; 44, 85.5, $C_2H_6N^+$; 45, 37.9, $C_2H_7N^+$; 46, 3.6, ?; 47, 4.7, ?; 59, 3.8, ?; 60, 41.8, CH_2NPH^+; 61, 2.4, ?; 74, 2.2, $C_2H_5NP^+$; 75, 11.1, $(CH_3)_2NP^+$; 76, 97.7, $(CH_3)_2NPH^+$; 77, 2.9, $(CH_3)_2NPH_2^+$; 81.5, 3.6, $[(CH_3)_2N]_3P^{2+}$; 94, 3.7, ?; 110, 4.4, ?; 119, 100.0, $[(CH_3)_2N]_2P^+$; 120, 5.5, $[(CH_3)_2N]_2PH^+$; 163, 27.5, $[(CH_3)_2N]_3P^+$; 164, 2.2, $[(CH_3)_2N]_2PH^+$.

Bis(dimethylamino)fluorophosphine

15, 34.3, CH_3^+; 16, 2.1, ?; 17, 19.5, ?; 18, 77.8, NH_4^+, H_2O^+; 27, 2.6, ?; 28, 13.4, N_2^+; 29, 2.0, ?; 30, 16.2, $CH_2NH_2^+$, CH_2NPH^{2+}; 40, 2.6, ?; 41, 4.0, ?; 42, 42.7, $C_2H_4N^+$; 43, 5.9, $C_2H_5N^+$; 44, 31.7, $C_2H_6N^+$; 45, 2.6, $C_2H_7N^+$; 50, 3.5, PF^+; 51, 6.1, PHF^+; 60, 5.1, CH_2NPH^+; 65, 5.2, $(CH_3)_2NH\cdot HF^+$?; 69, 4.7, PF_2^+; 76, 2.6, $(CH_3)_2NPH^+$; 78, 7.6, CH_2NPF^+; 80, 1.7, ?; 93, 7.0, $C_2H_5NPF^+$; 94, 100.0, $(CH_3)_2NPF^+$; 95, 5.2, $(CH_3)_2NPHF^+$; 112, 6.3, $C_2H_5NPF_2^+$; 113, 6.5, $(CH_3)_2NPF_2^+$; 138, 19.7, $[(CH_3)_2N]_2PF^+$.

Bis(dimethylamino)chlorophosphine

15, 54.2, CH_3^+; 18, 6.6, NH_4^+, H_2O^+; 27, 3.5, ?; 28, 25.8, N_2^+; 30, 12.6, $CH_2NH_2^+$, CH_2NPH^{2+}; 31, 3.5, P^+; 32, 5.4, ?; 33, 6.6, ?; 36, 2.8, ?; 40, 3.5, ?; 41, 6.0, ?; 42, 59.8, $C_2H_4N^+$; 43, 9.4, $C_2H_5N^+$; 44, 52.0, $C_2H_6N^+$; 45, 8.2, $C_2H_7N^+$; 46, 4.4, ?; 47, 6.3, ?; 58, 2.3, ?; 59, 7.8, CH_2NP^+; 60, 47.3, CH_2NPH^+; 67, 4.1, ?; 69, 2.2, ?; 74, 2.6, $C_2H_5NP^+$; 75, 13.5, $(CH_3)_2NP^+$; 76, 58.8, ?; 77, 2.6, $(CH_3)_2NPH_2^+$; 81, 3.1, $(CH_3)_2NH\cdot H^{35}Cl^+$?; 94, 6.1, $CH_2NP^{35}Cl^+$; 96, 2.4, $CH_2NP^{37}Cl^+$; 109, 5.4, $C_2H_5NP^{35}Cl^+$; 110, 100.0, $(CH_3)_2NP^{35}Cl^+$; 111, 2.4, $C_2H_5NP^{37}Cl^+$; 112, 31.4, $(CH_3)_2NP^{37}Cl^+$; 119, 45.5, $[(CH_3)_2N]_2P^+$; 120, 2.6, $[(CH_3)_2N]_2PH^+$; 154, 36.5, $[(CH_3)_2N]_2P^{35}Cl^+$; 156, 12.0, $[(CH_3)_2N]_2P^{37}Cl^+$.

Bis(dimethylamino)bromophosphine

15, 38.8, CH_3^+; 18, 4.5, NH_4^+, H_2O^+; 27, 2.9, ?; 28, 17.5, ?; 30, 8.0, $CH_2NH_2^+$, CH_2NPH^{2+}; 31, 5.6, P^+; 32, 4.3, ?; 33, 5.9, ?; 40, 2.7, ?; 41, 5.1, ?; 42, 41.6, $C_2H_4N^+$; 43, 6.2, $C_2H_5N^+$; 44, 21.3, $C_2H_6N^+$; 45, 5.9, $C_2H_7N^+$; 46, 3.8, ?; 47, 6.2, ?; 59, 7.3, CH_2NP^+; 60, 44.2, CH_2NPH^+; 74, 2.9, $C_2H_5NP^+$; 75, 15.9, $(CH_3)_2NP^+$; 76, 84.3, $(CH_3)_2NPH^+$; 77, 2.4, $(CH_3)_2NPH_2^+$; 85, 2.9, ?; 94, 2.9, ?; 110, 7.2, $P^{79}Br^+$; 112, 2.7, $P^{81}Br^+$; 119, 100.0, $[(CH_3)_2N]_2P^+$; 120, 5.3, $[(CH_3)_2N]_2PH^+$; 124, 7.7, ?; 154, 13.4, $(CH_3)_2NP^{79}Br^+$; 156, 13.4, $(CH_3)NP^{81}Br^+$; 198, 3.0, $[(CH_3)_2N]_2P^{79}Br^+$; 200, 3.0, $[(CH_3)_2N]_2P^{81}Br^+$.

Dimethylaminodifluorophosphine

15, 32.4, CH_3^+; 18, 4.4, NH_4^+, H_2O^+; 27, 2.5, ?; 28, 31.1, N_2^+; 30, 3.8, $CH_2NH_2^+$; 31, 2.0, P^+; 32, 7.1, ?; 40, 4.5, ?; 41, 5.6, ?; 42, 100.0, $C_2H_4N^+$; 43, 10.2, $C_2H_5N^+$; 44, 4.0, $C_2H_6N^+$; 50, 6.4, PF^+; 51, 3.5, $CH_3NH_2\cdot HF^+$?; 65, 2.0, $(CH_3)_2NH\cdot HF^+$?; 69, 29.1, PF_2^+; 78, 3.2, CH_2NPF^+; 94, 12.2, $(CH_3)_2NPF^+$; 112, 54.1, $C_2H_5NPF_2^+$; 113, 54.1, $(CH_3)_2NPF_2^+$.

Dimethylaminodichlorophosphine

15, 70.2, CH_3^+; 18, 9.1, NH_4^+, H_2O^+; 26, 2.5, ?; 27, 6.3, ?; 28, 25.6, N_2^+; 29, 3.2, ?; 30, 17.2, $CH_2NH_2^+$, CH_2NPH^{2+}; 31, 24.6, P^+; 32, 7.7, ?; 33, 6.0, ?; 35, 19.3, $^{35}Cl^+$; 36, 15.1, $H^{35}Cl^+$; 37, 6.3, $^{37}Cl^+$; 38, 5.3, $H^{37}Cl^+$; 39, 3.2, ?; 40, 6.0, ?; 41, 9.1, ?; 42, 100.0, $C_2H_4N^+$; 43, 29.1, $C_2H_5N^+$; 44, 21.8, $C_2H_6N^+$; 45, 8.1, $C_2H_7N^+$; 46, 3.2, $C_2H_8N^+$; 47, 4.6, ?; 50, 2.5, ?; 58, 3.8, $CHNP^+$; 59, 4.5, CH_2NP^+; 60, 15.3, CH_2NPH^+; 61, 2.0, CH_3NPH^+; 66, 18.5, $P^{35}Cl^+$; 67, 5.9, $HP^{35}Cl^+$; 68, 6.5, $P^{37}Cl^+$; 69, 3.1, $HP^{37}Cl^+$; 81, 4.8, ?; 85, 5.2, ?; 94, 10.5, ?; 101, 49.0, $P^{35}Cl_2^+$; 103, 32.2, $P^{35}Cl^{37}Cl^+$; 105, 5.4, $P^{37}Cl_2^+$; 109, 2.5, ?; 110, 96.9, $(CH_3)_2NP^{35}Cl^+$; 111, 3.4, $(CH_3)_2NPH^{35}Cl^+$; 112, 31.2, $(CH_3)_2NP^{37}Cl^+$; 113, 0.9, $(CH_3)_2NPH^{37}Cl^+$; 129, 3.2, ?; 136, 12.4, $P^{35}Cl_3^+$; 138, 11.7, $P^{35}Cl_2{}^{37}Cl^+$; 140, 3.8, $P^{35}Cl^{37}Cl_2^+$; 142, 0.4, $P^{37}Cl_3^+$; 144, 3.3, $C_2H_5NP^{35}Cl_2^+$; 145, 27.7, $(CH_3)_2NP^{35}Cl_2^+$; 146, 2.9, $C_2H_5NP^{35}Cl^{37}Cl^+$; 147, 17.8, $(CH_3)_2NP^{35}Cl^{37}Cl^+$; 148, 0.9, $C_2H_5NP^{37}Cl_2^+$; 149, 3.1, $(CH_3)_2NP^{37}Cl_2^+$.

Dimethylaminodibromophosphine

15, 50.2, CH_3^+; 18, 4.7, NH_4^+, H_2O^+; 27, 3.8, ?; 28, 21.3, N_2^+; 29, 2.2, ?; 30, 9.7, $CH_2NH_2^+$, CH_2NPH^{2+}; 31, 17.2, P^+; 32, 7.8, ?; 33, 6.0, ?; 36, 2.5, ?; 40, 4.7, ?; 41, 8.2, ?; 42, 84.6, $C_2H_4N^+$; 43, 10.3, $C_2H_5N^+$; 44, 36.7, $C_2H_6N^+$; 45, 8.2, $C_2H_7N^+$; 46, 3.4, ?; 47, 5.0, ?; 58, 3.1, $CHNP^+$; 59, 7.9, CH_2NP^+; 60, 33.8, CH_2NPH^+; 74, 2.6, $C_2H_5NP^+$; 75, 11.0, $(CH_3)_2NP^+$; 79, 9.1, $^{79}Br^+$; 81, 9.3, $^{81}Br^+$; 110, 17.7, $P^{79}Br^+$; 111, 3.3, $HP^{79}Br^+$; 112, 10.6, $P^{81}Br^+$; 113, 3.2, $HP^{81}Br^+$; 125, 2.5, ?; 127, 2.5, ?; 154, 100.0, $(CH_3)_2NP^{79}Br^+$; 155, 3.3, $(CH_3)_2NPH^{79}Br^+$; 156, 95.1, $(CH_3)_2NP^{81}Br^+$; 157, 2.8, $(CH_3)_2NPH^{81}Br^+$; 189, 5.3, $P^{79}Br_2^+$; 191, 9.9, $P^{79}Br^{81}Br^+$; 193, 4.8, $P^{81}Br_2^+$; 233, 4.0, $(CH_3)_2NP^{79}Br_2^+$; 235, 7.5, $(CH_3)_2NP^{79}Br^{81}Br^+$; 237, 3.7, $(CH_3)_2NP^{81}Br_2^+$; 268, 0.9, $P^{79}Br_3^+$; 270, 2.5, $P^{79}Br_2{}^{81}Br^+$; 272, 2.3, $P^{79}Br^{81}Br_2^+$; 274, 0.7, $P^{81}Br_3^+$.

the general formula PXY^+ where X may or may not be identical to Y. The predominance of these two types of ions supports the hypothesis[10] that the stabilization of the electron deficiency by phosphorus is through participation of the d-shell rather than the formation of a phosphonium ion.

Two metastable transitions in the mass spectrum of tris(dimethylamino)-phosphine were observed. The first of these transitions (eqn. 1) results in the formation of the ion at *m/e* 119. The metastable peak occurs at *m/e* 87.0 and was calculated to be at *m/e* 86.9. The process which results in the formation of the ion at *m/e* 76 (eqn. 2) probably involves a 1–3 hydrogen shift to phosphorus. The metastable peak observed at *m/e* 48.6 was calculated to be at *m/e* 48.5

$$m^*86.9\ [(CH_3)_2N]_3P^+ \rightarrow [(CH_3)_2N]_2P^+ + (CH_3)_2N \quad (1)$$

$$m^*48.5\ [(CH_3)_2N]P^+ \rightarrow (CH_3)_2NPH^+ + CH_2{=}NCH_3 \quad (2)$$

This datum is in agreement with the observations of BRATERMAN[11], who has observed in a study of transition metal carbonyl derivatives of tris(dimethylamino)phosphine a similar rearrangement with a 1–4 hydrogen transfer to the metal (eqn. 3).

$$FeP[N(CH_3)_2]_3^+ \rightarrow HFeP[N(CH_3)_2]_2^+ + CH_2{=}NCH_3 \quad (3)$$

The peak at *m/e* 60 in the spectrum of $[(CH_3)_2N]_3P$ is of interest because of its relatively high intensity. This ion may best be represented as $CH_2{=}NPH^+$ or a CH_3NP fragment. The process which gives rise to the postulated $CH_2{=}NPH^+$ fragment may be the elimination of a neutral CH_4 group from the ion at *m/e* 76, but no metastable evidence was observed for such a transition.

It is difficult to pinpoint the center of positive charge in the phosphorus-containing ion; there may be a sharing of the electron deficiency between the phosphorus and nitrogen atoms. The relatively high abundance of the immonium ion species suggests that during fragmentation, the amine nitrogen can accommodate the electron deficiency nearly as well as phosphorus.

Bis(dimethylamino)halophosphines. The mass spectral data for the bis-(dimethylamino)halophosphines has been summarized in Table I. Comparison of the data shows trends which indicate the relative stabilities of each of the molecules to electron-impact.

The mass spectrum of $[(CH_3)_2N]_2PF$ exhibits features which make it unique among the spectra of the bis(dimethylamino)halophosphines. The number of different ion fragments is small compared to the number in the spectra of $[(CH_3)_2N]_2PCl$ and $[(CH_3)_2N]_2PBr$. In the spectrum of the fluorophosphine are two fragments of the type $(CH_3)_2NPX_2^+$ and PX_2^+, which could not have arisen from simple fragmentation of the parent molecule. These ions, which do not occur in the spectra of the other two compounds (Table II), could have been formed by an ion–radical reaction involving atomic fluorine or they could have occurred by disproportionation of the original compound in the heated ion source. The PF_2^+ ion has been shown to be an extremely stable species formed by rearrangement in the spectra of the fluoroalkyl[2] and fluorophenylphosphines[1]. A metastable transition corresponding to that shown in eqn. (2) was observed in the mass spectra of both $(CH_3)_2NPCl_2$ and $(CH_3)_2NPBr_2$.

The most abundant ion in the spectrum of each of the bis(dimethylamino)-halophosphines is a disubstituted phosphorus fragment of the type PXY^+, where $X = Y = (CH_3)_2N$ for the bromo compound. There is a higher abundance of immonium type ions in the spectra of the fluoro and chloro compounds than in the spectrum of the bromo compound (see Table I). Conversely, there is a higher percentage of phosphorus-containing ions in the spectrum of the bromophosphine.

The ion represented by the general formula $(CH_3)_2NPX^+$ is of interest because it occurs in the spectrum of the fluorophosphine in a high abundance. The percentage of this ion decreases sharply in the chloro compound and reaches a minimum in the bromo compound. This evidence suggests that there is a decrease in stability to electron-impact of the bis(dimethylamino)halophosphines as the atomic weight of the substituted halogen increases. This probability is a reflection of the relative strengths of the phosphorus–halogen bond.

Dimethylaminodihalophosphines. As would be expected, the dimethylaminodifluorophosphines show a higher abundance of fragments which contain phosphorus and halogen only (see Table I). In contrast to the bis(dimethylamino)halophosphines, there are few fragments without a halogen which contain an amino group attached to phosphorus. Again the fluorine-containing compound shows a considerably lower number of different positive ion fragments than the analogous dichloro- and dibromophosphines. In contrast to the series of bis(dimethylamino)halophosphines, $(CH_3)_2NPF_2$ is the only member of the dihalophosphine series which shows a metastable transition (eqn. 3).

$$m^{*}111.0\ (CH_3)_2NPF_2 \xrightarrow{-H} C_2H_5NPF_2 \qquad (4)$$

The metastable peak was observed at *m/e* 111.0 and was calculated to be at *m/e* 111.0. It should be noted that the peak at *m/e* 112 arising from the metastable transition (eqn. 3) is as intense as the molecular ion, M, at *m/e* 113. Processes which give rise to the molecular ion, M, and the M – 1 ion are much more important in $(CH_3)_2NPF_2$ than in the corresponding molecules, $(CH_3)_2NPCl_2$ and $(CH_3)_2NPBr_2$. This suggests that when the molecule is subjected to electron-impact, the preferred method of accommodating the electron deficiency involves the elimination of a hydrogen radical with charge stabilization by an immonium nitrogen, which results in considerably less fragmentation of the M and M – 1 ions. This may reflect the increased stability of the phosphorus–nitrogen bond due to participation of the lone pair of electrons on nitrogen into the empty d-orbitals of phosphorus in $(CH_3)_2NPF_2$. This appears to occur to a greater extent, as expected, in the difluoro compound than in the other dihalo compounds.

There are other trends in the series of dimethylaminodihalophosphines which are important. The PX_3^+ type fragment is absent in the spectrum of the difluorophosphine, but this ion is present in low abundance in the spectra of the other two compounds. This suggests that the possibility of recombination or disproportionation is greater for the dichloro- and dibromophosphines than for the difluoro compound. It is possible that the heated ion source may be responsible for this. The abundance of the ion with the general formula $(CH_3)_2NPX^+$ increases with increasing atomic weight of the halogen substituent (Table I). This is in direct contrast to the behavior of the bis(dimethylamino)halophosphines. The decreasing abundance of the molecular ion with increasing molecular weight further suggests that the dichloro and dibromo compounds are considerably less stable to electron-impact than is the difluoro compound. This conclusion is in agreement with the data calculated by FARRAN[12] for the phosphorus–halogen force constants in compounds of the general formula $(CH_3)_2NPX_2$.

Experimental

All mass spectra were determined with a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer using the gas inlet system and a nominal source pressure of $4 \cdot 10^{-5}$ torr. The ion-source temperature was 250°. The ionizing voltage used was 70 eV.

The purity of all compounds with boiling points above 25° was determined to be greater than 99% by vapor-phase chromatography. The instrument used was an Aerograph Model A90-P3 with Sargent Recorder SR. The column was $5' \times \frac{1}{4}''$ packed with 20% SE-30 on Chromosorb W.

The purity of all compounds with boiling points below 25° was determined to be greater than 99% on the basis of vapor pressure data.

Preparation of compounds. The compounds discussed were prepared, purified, and characterized by the most convenient literature methods, some with slight modifications which are noted herein. The tris(dimethylamino)phosphine was prepared by the method of BURG AND SLOTA[13]. A minor modification of the method involved the addition of the dimethylamine through a dry ice condenser into the reaction flask containing phosphorus trichloride dissolved in ether.

The bis(dimethylamino)chlorophosphine was prepared by the method of NOTH AND VETTER[14]. The bis(dimethylamino)fluorophosphine was prepared by fluorinating $[(CH_3)_2N]PCl$ with zinc difluoride. The method was adapted from a description of the preparation of $(CH_3)NPF_2$ by NOTH AND VETTER[15]. The bis(dimethylamino)bromophosphine and dimethylaminodibromophosphine were prepared as described by NOTH AND VETTER[14].

Dimethylaminodichlorophosphine and dimethylaminodifluorophosphine were prepared by the methods of MORSE *et al.*[16].

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Separation of osmium and ruthenium by solvent extraction

In earlier work, BERG AND SANDERS[1] studied the behavior of the bromo complexes of iridium, palladium, platinum and rhodium as they were partitioned between hydrobromic acid solutions and various organic solvents. The present study is an outgrowth of that work and pertains to the extractive separation of the bromo complexes of osmium and ruthenium. The complexes are partitioned between hydrobromic acid solution and methyl isobutyl ketone, and the separations are followed with radioactive isotopes of osmium and ruthenium.

Apparatus

Tagged samples were counted with a Technical Measurement Corporation Pulse-Height Analyzer, 400 channels, Model 401, in conjunction with a Technical Measurement Corporation Resolver Integrater, Model 522. Detection was by means of a 2-in well-type NaI scintillation detector.

Extractions were carried out in 4-oz narrow-mouth screw-cap polyethylene bottles which were shaken with a Burrell mechanical shaker, Model BB. Samples taken for counting were placed in 17 mm (i.d.) × 55 mm snap-top polyethylene vials.

Reagents

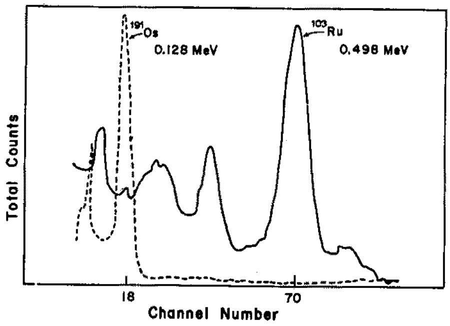
Osmium tetroxide (A. D. Mackay, Inc.) was dissolved in 100 ml of 0.2 *M* sodium hydroxide in a 250-ml Erlenmeyer flask. The solution was filtered into a 1-l volumetric flask and diluted to the mark with water. The solution was standardized by means of the 1,2,3-benzotriazole procedure[2]. The final osmium concentration was 780 p.p.m.

Ruthenium trichloride trihydrate (A. D. Mackay, Inc.) was dissolved and diluted to 1 l with 6 *M* hydrochloric acid. The solution was standardized by taking aliquots to dryness in Rose crucibles and igniting the residue under hydrogen to reduce the ruthenium to the elemental state. The final ruthenium concentration was 820 p.p.m.

Bromo complexes of osmium and ruthenium were formed by taking aliquots of the stock solutions, adding an equal amount of concentrated hydrobromic acid and evaporating to dryness. This procedure was repeated with additional concentrated hydrobromic acid. The residue was then dissolved in 6 *M* hydrobromic acid and brought back to its original volume. When necessary, further dilutions were made by taking aliquots of the concentrated bromide solution and diluting with 6 *M* hydrobromic acid.

Osmium-191 (Oak Ridge National Laboratory) was obtained as a solution of sodium osmate. The γ-spectrum of osmium-191 is shown in Fig. 1. The isotope has a half-life of 15 days and emits a 0.128-MeV γ-ray.

Ruthenium-103 was prepared by neutron irradiation of ruthenium tribromide in the reactor at Georgia Institute of Technology. The γ-spectrum of ruthenium-103 is shown in Fig. 1. The isotope has a half-life of 40 days and emits a 0.498-MeV γ-ray. The ruthenium sample was not pure; it contained an unknown amount of iridium-192 plus some unidentified impurities.



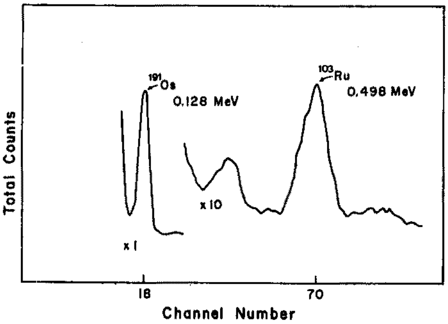


Fig. 1. γ-Ray spectrum of Os-191 and Ru-103.

Fig. 2. γ-Ray spectrum of osmium–ruthenium mixture before extraction.

Measurement of distribution coefficients

Bromo complexes of osmium and ruthenium containing tagged isotopes were equilibrated with methyl isobutyl ketone. The volume ratio of extractant to raffinate was 2:1. Samples of extractant and raffinate (2 ml each) were taken for counting. The distribution coefficient, K, was defined as

$$K = \frac{\text{counts per minute of extractant} - \text{background}}{\text{counts per minute of raffinate} - \text{background}}$$

Separation technique

The osmium and ruthenium bromides, formed by taking a sample solution almost to dryness with concentrated hydrobromic acid, were taken up in 10 ml of 6 M hydrobromic acid previously saturated with methyl isobutyl ketone. The sample size was such that in the final volume there was not more than 300 p.p.m. of each metal. The hydrobromic acid solution was placed in the polyethylene bottle. Sufficient radioactive isotopes were added to give an initial activity of about 2000 counts/min for both osmium and ruthenium. A 2-ml sample was taken for determining the initial activity. Methyl isobutyl ketone (16 ml) previously saturated with 6 M hydrobromic acid was added and the mixture was shaken for 2-min on the Burrell shaker. The phases were allowed to separate, and 2-ml samples of each phase were taken for counting.

Results and discussion

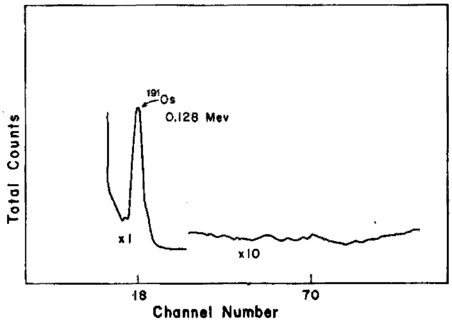
The effect of acidity on the extraction of osmium and ruthenium with methyl isobutyl ketone is shown in Table I. These data show that with equal volumes of extractant and raffinate, about 78% of the osmium was extracted in a single equilibration at an acid concentration of 6 M hydrobromic acid. However, when both extractant and raffinate were pre-saturated with each other, a much better separation was obtained. Essentially, a quantitative extraction of osmium occurred in a single 2-min equilibration when pre-saturated solvents were employed. The distribution coefficient calculated for ruthenium would indicate about 2% extraction; however, it is believed that the measured activity in the extractant after a single equilibration is due to the presence of one of the impurities in the ruthenium sample.

TABLE I

DISTRIBUTION COEFFICIENTS OF BROMO COMPLEXES OF OSMIUM AND RUTHENIUM AS A FUNCTION OF ACIDITY WITH PHASES THAT WERE NOT PRE-SATURATED

HBr concentration (M)	K_{Ru}	K_{Os}
1	0.01	2.93
2	0.02	2.91
3	0.02	2.80
4	0.02	3.20
5	0.03	3.25
6	0.07	3.51
6	0.05[a]	206.5[a]

[a] Extractant and raffinate phases pre-saturated with each other before extraction of osmium and ruthenium.



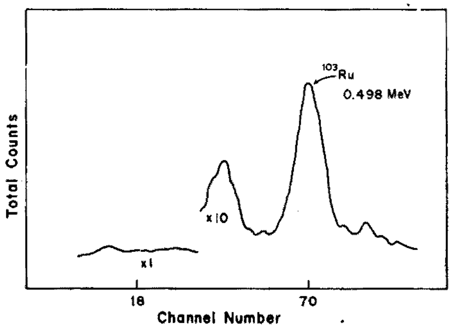


Fig. 3. γ-Ray spectrum of extractant after phase equilibration.

Fig. 4. γ-Ray spectrum of raffinate after phase equilibration.

Figure 2 shows the γ-spectrum of a sample of mixed osmium and ruthenium bromides before extraction, and Figs. 3 and 4 show the γ-spectra of the extractant and raffinate, respectively, after phase equilibration. The osmium-191 peak in the extractant is not as intense as that in the initial sample because the extractant was twice the volume of the raffinate. Notice that no osmium activity can be seen in the raffinate and no ruthenium activity is seen in the extractant. Six replicate determinations gave the same result, namely, a quantitative extraction of bromo-osmate after a single 2-min equilibration.

The results of increasing the concentration of osmium and ruthenium upon

TABLE II

EFFECT OF INCREASING CONCENTRATION OF METAL ON THE EXTRACTION OF BROMO COMPLEXES OF OSMIUM AND RUTHENIUM INTO 4-METHYL-2-PENTANONE AT AN ACID CONCENTRATION OF 6 *M* HBr

Osmium		*Ruthenium*	
p.p.m.	K_{Os}	*p.p.m.*	K_{Ru}
75	243	82	0.05
150	178	246	0.08
225	147	410	0.15
300	74		
450	81		

the efficiency of extraction are shown in Table II. It can be seen that there is an appreciable increase in the distribution coefficient of ruthenium and a decrease in the distribution coefficient of osmium as the concentration of osmium and ruthenium increases. For quantitative separations the concentration of osmium and ruthenium in the sample should not exceed 300 p.p.m.

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An acid–base–isocyanate method for the analysis of admixtures of hydrazine with 1,1-dimethylhydrazine, and monomethylhydrazine with 1,1-dimethylhydrazine

Hydrazine and its derivatives are now used extensively as rocket fuels, in fuel cells, and in a wide variety of industrial processes. A gas-evolution method for the determination of milligram amounts of hydrazines has recently been described[1], together with a brief review of the other methods of analysis available.

Mixtures of hydrazine with its methyl derivatives are, however, now commonly used; chemical and instrumental methods of analysis for such mixtures have been described[2–7], including a differential reaction-rate acetylation method[8] and, most recently, a proton magnetic resonance method[9]. Rapid, chemical methods offer many advantages, however, *e.g.* for field investigations, and this communication describes a useful differential reaction-rate method in which either phenylisocyanate or naphthylisocyanate can be used.

In alcoholic solution, with ethanolic hydrochloric acid as titrant, hydrazine (N_2H_4), monomethylhydrazine (MMH), and 1,1-dimethylhydrazine (UDMH) all react with isocyanates at about the same rate to form semicarbazides. In anhydrous acetic acid, however, N_2H_4 and MMH react rapidly (MMH slightly slower than N_2H_4) with isocyanates, but UDMH does not react appreciably in less than 2 h at room temperature.

Reactions

The experimental procedure is based on the reaction of N_2H_4, MMH, and UDMH with *either* phenylisocyanate *or* naphthylisocyanate (R.NCO) to give the semicarbazides $NH_2 \cdot NH \cdot CO \cdot NH \cdot R$, $CH_3 \cdot NH \cdot NH \cdot CO \cdot NH \cdot R$, and $(CH_3)_2 \cdot N \cdot NH \cdot CO \cdot NH \cdot R$ respectively. In acetic acid, the rate of formation of the latter is very slow.

Preparation of sample

By pipette, add the mixture of hydrazines (0.4 ml) to a tared volumetric flask (50 ml) containing about 30 ml of anhydrous acetic acid; obtain the sample weight by difference. Make up to the mark with the acetic acid and mix carefully.

Determination of total hydrazines

Add an aliquot (5.00 ml) of the mixture of hydrazines to a 50-ml beaker containing 20 ml of a mixture of acetic acid and dioxan (1:1). Add 4 drops of quinaldine red indicator, 0.2% in acetonitrile. Titrate to a colourless end-point with 0.1 *N* perchloric acid in dioxan to obtain titre "A". Titrate a blank for the reagents and indicator to obtain titre "a".

Determination of 1,1-dimethylhydrazine

Add an aliquot (5.00 ml) of the mixture of hydrazines to a 50-ml beaker containing 20 ml of the acetic acid–dioxan mixture and 1 ml of either naphthylisocyanate or phenylisocyanate. (Use 2 ml for MMH/UDMH mixtures.) Set aside for 30 min (a white precipitate forms). Add 4 drops of the quinaldine red indicator, and titrate to a colourless end-point to obtain titre "B". By titrating a blank similarly, obtain titre "b".

Calculations

$$\%N_2H_4 \text{ (or MMH)} = \frac{(A-a)-(B-b)\cdot N\ HClO_4 \cdot 3.20 \text{ (or 4.60)}}{10 \text{ (sample weight)}},$$

$$\%UDMH = \frac{(B-b)\cdot N\ HClO_4 \cdot 6.01}{10 \text{ (sample weight)}}$$

Results and discussion

The effect of time and of the isocyanate concentration on the reactions is

TABLE I

EFFECT OF TIME ON THE REACTION OF VARIOUS HYDRAZINES WITH PHENYLISOCYANATE (1.0 ml) AT 19°

Time (min)	*ml $HClO_4$ (0.1 N) used*		
	For N_2H_4	*For MMH*	*For UDMH*
	7.90[a]	5.00[a]	7.10[a]
5	0.26	1.90	7.10
15	0.19	1.19	7.08
30	0.15	1.05	7.09
45	0.16	0.77	7.10
60	0.18	0.70	7.08
75	0.17	0.30	7.05

[a] Without phenylisocyanate.

shown in Tables I and II. At least 0.4 ml of phenylisocyanate and a reaction time of 15 min must be used for the effective 0.04 ml of hydrazine used here. For MMH, however, 2 ml of the isocyanate and 30 min reaction time is required; UDMH gives no significant reaction under these conditions. After 3 h at 19°, however, white crystals of 1,1-dimethylphenylsemicarbazide begin to form, but the reaction solutions are still basic after 18 h.

TABLE II

EFFECT OF VARIOUS CONCENTRATIONS OF PHENYLISOCYANATE[a]

Phenylisocyanate (ml)	*ml $HClO_4$ (0.1 N) used*		
	For N_2H_4	*For MMH*	*For UDMH*
0.0	8.20	5.06	7.05
0.2	3.00	2.05	7.05
0.4	0.17	1.25	7.05
0.6	0.18	0.75	7.05
0.8	0.14	0.80	7.03
1.0	0.21	0.55	7.00
2.0	—	0.10	7.00
3.0	—	0.06	—

[a] 20–40 min allowed for the reactions at 19°.

Water affects the analysis of hydrazines with isocyanates by causing the end-point of quinaldine red (red to colourless) to revert to red. The reason for this is shown in the equations below; hydrolysis of the isocyanate gives the amine which eventually reacts with sufficient isocyanate to give a substituted urea derivative.

$$R{\cdot}NCO + H_2O \rightarrow R{\cdot}NH\,CO_2\,H \rightarrow R{\cdot}NH_2 + CO_2 \qquad (1)$$

$$R{\cdot}NH_2 + R{\cdot}NCO \rightarrow R{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}R \qquad (2)$$

The water content of the acetic acid can be reduced satisfactorily by the molecular-sieve technique[3]. Acetic anhydride cannot be used since it reacts[9] with N_2H_4 and MMH; it can, however, be added as required during the titration of UDMH. Potassium cyanate, potassium cyanide, lead thiocyanate, phenyl and methyl isothiocyanates give no reaction with N_2H_4, MMH, or UDMH in acetic acid media.

TABLE III

ANALYSIS OF N_2H_4/UDMH ADMIXTURES

Experimental (%)		*Theoretical (%)*		*Variation (%)*	
N_2H_4	*UDMH*	*N_2H_4*	*UDMH*	*N_2H_4*	*UDMH*
82.4	13.9	82.6	14.0	+0.2	+0.1
74.0	23.6	73.4	23.5	−0.6	−0.1
64.7	32.6	65.1	32.2	+0.4	+0.4
60.1	37.6	59.6	37.9	−0.5	+0.3
54.1	44.0	53.6	44.3	−0.5	+0.3
48.9	49.4	48.4	49.6	−0.5	+0.2
42.5	55.8	42.2	56.0	−0.3	+0.2
32.7	66.0	32.0	66.7	−0.7	+0.7
20.2	78.5	19.5	79.0	−0.7	+0.5

TABLE IV

ANALYSIS OF MMH/UDMH ADMIXTURES

Experimental (%)		*Theoretical (%)*		*Variation (%)*	
MMH	*UDMH*	*MMH*	*UDMH*	*MMH*	*UDMH*
76.1	23.7	76.8	23.2	+0.7	−0.5
85.6	13.6	85.8	14.2	+0.2	+0.6
11.2	88.7	10.8	89.2	−0.4	+0.5
25.5	74.0	25.8	74.2	+0.3	+0.2
47.0	52.4	47.5	52.4	+0.5	0.0
51.4	47.5	51.8	47.1	+0.4	−0.4

A series of mixtures of N_2H_4/UDMH and MMH/UDMH were prepared for test analyses; the results are shown in Tables III and IV.

For industrial-grade hydrazines, greater accuracy can be obtained if the "contaminant titration values" for each of the hydrazines is known. MALONE AND BIGGERS[9] reported contaminant titration values of 0.20, 0.12, and 0.04 ml for N_2H_4, MMH, and UDMH respectively; these are corrections for any impurities in N_2H_4 and MMH which behave similarly to another hydrazine (UDMH) and *vice-versa*.

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The colorimetric determination of rhenium with 1-phenyl-2-thiourea

In order to extend the usefulness of the 1-phenyl-2-thiourea[1,2] reagent to the determination of rhenium in molybdenite and other complex materials, a prior separation of the rhenium is necessary. Both the potassium ethyl xanthate[3-5] separation and the tetraphenylarsonium chloride[6-9] separation were investigated. Since the 1-phenyl-2-thiourea procedure only has a molar absorptivity of about 9500, the recovery from the prior separation had to be almost complete. Minor changes in the potassium ethyl xanthate procedure failed to yield such recovery, but minor variations to the tetraphenylarsonium chloride procedure yielded rhenium recoveries of 99%. The rhenium recovery solution lends itself directly to the color development phase of the 1-phenyl-2-thiourea procedure.

Reagents

Potassium ethyl xanthate solution. Dissolve 54 g of potassium ethyl xanthate in 70 ml of water. Filter and dilute to 100 ml with water. Prepare fresh daily.

Rhenium standard solutions (40 µg/ml, 20 µg/ml and 5 µg/ml). Dissolve suitable amounts of ammonium perrhenate (Cleveland Refractory Metals, a Division of Chase Brass and Copper Co.) in distilled water.

Equipment

Gilford Spectrophotometer Model 240.

The potassium ethyl xanthate–furildioxime method

A standard curve can be prepared by developing the rhenium–furildioxime complex without going through the potassium ethyl xanthate separation step. The use of this curve as reference will indicate the efficiency of the total procedure including the prior separation which is necessary in the case of molybdenite samples. The procedure is as follows: transfer the sample or standard solution at a pH 8–9 to a separatory funnel. Adjust the volume to 25 ml with water. Add 5 ml of potassium ethyl xanthate solution, mix, add 6 ml of concentrated hydrochloric acid and mix. Then add 50 ml of chloroform and shake for 0.5 min. Allow the layers to separate and drain the chloroform layer and discard it. Repeat this extraction with two 25-ml portions of chloroform. Transfer the aqueous layer to a 100-ml volumetric flask. Add 0.1 *M* potassium permanganate solution dropwise until a pink color persists. Then, destroy the excess of permanganate by dropwise addition of 10% tin(II) chloride solution in 10% hydrochloric acid. Then add 26 ml of 0.35% (w/v) furildioxime solution in acetone and mix. Add 10 ml of the above tin(II) solution and make to volume with water. Mix and let stand for at least 2 h before determining absorbance in 1-cm cells at 532 nm. When by-passing the potassium ethyl xanthate separation step, add the sample or standard at a pH of 8–9 to a 100-ml volumetric flask. Adjust the volume to 25 ml with water, then oxidize with potassium permanganate and complete the procedure as described.

The tetraphenylarsonium chloride–1-phenyl-2-thiourea method

Transfer a standard or sample solution to a 100-ml beaker. Adjust the volume to at least 25 ml with water. Add 2.0 g of sodium citrate and mix until dissolved.

Adjust the pH to 8–10 with 1 *M* hydrochloric acid or sodium hydroxide as needed. Then transfer to a separatory funnel but reserve the beaker. Add 2 ml of aqueous 2% (w/v) tetraphenylarsonium chloride solution, mix and let stand for 5 min. Then add 10 ml of chloroform and shake for 1 min. Reserve the chloroform layer in a second separatory funnel. Repeat the 10-ml chloroform extraction of the aqueous solution. Combine this chloroform layer with the first in the second separatory funnel and discard the aqueous layer. Add 15 ml of concentrated hydrochloric acid to the second separatory funnel and shake for 1 min. Discard the chloroform layer and decant the hydrochloric acid layer into the original beaker. Then add 10 ml of water to the separatory funnel and decant into the original beaker. Repeat with a second 10-ml portion of water. To the beaker add 5 ml of 10% tin(II) chloride solution in 20% hydrochloric acid and 10 ml of 2.5% (w/v) 1-phenyl-2-thiourea in ethanol. Mix and let stand for 1.5 to 3.5 h. Then transfer the solution to a separatory funnel and add 10 ml of chloroform. Shake for 0.5 min and reserve the chloroform layer in a dry 25-ml volumetric flask. Repeat the extraction with a second 10-ml portion of chloroform. Combine in the volumetric flask and make to volume with absolute ethanol. Determine the absorbance in 1-cm cells at 410 nm. When by-passing the tetraphenylarsonium chloride separation step, add the sample or standard solution to a beaker. Add 15 ml of hydrochloric acid and adjust the volume to 35 ml with water. Add 5 ml. of the above tin(II) chloride solution and 10 ml of the 1-phenyl-2-thiourea solution and continue as described.

Sample preparation

Samples may be dissolved in hydrochloric, hydrofluoric or sulfuric acid, but the rhenium must be oxidized with hydrogen peroxide in neutral or alkaline solution. Mineral samples are best dissolved by an oxidizing fusion. Add a 1–2 g sample to a zirconium crucible and mix with 8 g of sodium peroxide. Then cover with 2 g of sodium peroxide. Cover with a lid and cautiously increase temperature of burner until crucible is dull red. Cool and place the crucible and melt in a 250-ml beaker. Add 40 ml of water and 10 ml of concentrated hydrochloric acid. Allow the melt to dissolve, heating when necessary to complete the dissolution. Remove the crucible and lid and filter into a volumetric flask such that an appropriate aliquot in 25 ml or less will contain 25–400 µg of rhenium.

Results and conclusions

Potassium ethyl xanthate–furildioxime method. A comparison of two standard curves, one with and one without the prior ethyl xanthate separation is shown in Table I. The separation curve indicates a loss of 12% in sensitivity. This must be due to either loss of rhenium or interference of the excess of potassium ethyl xanthate. A dummy extraction with chloroform on a pair of 400 µg of rhenium standards gave corrected absorbances of 0.854 and 0.850 which is 99% of the nonextracted curve. There was additional trouble with the procedure when there was a large excess of the potassium ethyl xanthate reagent uncomplexed by such elements as molybdenum.

The separation from molybdenum has to be reasonably complete. Table II shows the effect of molybdenum when no prior separation is employed, the readings being readily reproducible. There is loss of sensitivity even with less than 0.1 mg of molybdenum, hence significant errors are caused by major amounts of molybdenum.

TABLE I

COMPARISON OF FURILDIOXIME METHODS

µg Re	*Without prior separation*			*With prior separation*		
	Abs. 532 nm	*Corr. abs.*	*Abs./1 ng Re*	*Abs. 532 nm*	*Corr. abs.*	*Abs./1 ng Re*
0	0.003			0.002		
80	0.180	0.177	2.213	0.156	0.154	1.925
	0.179	0.176	2.200	0.153	0.151	1.888
200	0.444	0.441	2.205	0.393	0.391	1.955
	0.442	0.439	2.195	0.392	0.390	1.950
400	0.862	0.859	2.148	0.777	0.775	1.938
	0.864	0.861	2.152	0.777	0.775	1.938

TABLE II

EFFECT OF MOLYBDENUM ON 400 µg OF RHENIUM BY THE FURILDIOXIME METHOD

mg Mo	0.00	0.10	0.20	0.40	0.60	0.80
Abs. 532 nm	0.850	0.824	0.802	0.778	0.747	0.665

Tetraphenylarsonium chloride and 1-phenyl-2-thiourea method. Table III shows a comparison of two standard curves, one with and one without the prior tetraphenylarsonium chloride separation. Clearly, there is no loss in sensitivity from the prior separation by this method. Table IV indicates that there is no significant effect on the sensitivity of the 1-phenyl-2-thiourea procedure in the presence of small amounts of molybdenum. A standard curve for 0–400 µg of rhenium in the presence of 100 mg of molybdenum by the entire tetraphenylarsonium chloride and 1-phenyl-2-thiourea

TABLE III

COMPARISON OF 1-PHENYL-2-THIOUREA METHODS

µg Re	*Without prior separation*		*With prior separation*	
	Abs. 410 nm	*Abs./1 ng Re*	*Abs. 410 nm*	*Abs./1 ng Re*
0	0.000		0.000	
100	0.204	2.040	0.199	1.990
	0.199	1.990	0.201	2.010
200	0.410	2.050	0.405	2.025
	0.408	2.040	0.403	2.015
300	0.609	2.030	0.609	2.030
	0.612	2.040	0.611	2.037
400	0.821	2.052	0.820	2.050
	0.818	2.045	0.818	2.045

TABLE IV

EFFECT OF MOLYBDENUM ON 400 µg OF RHENIUM BY THE 1-PHENYL-2-THIOUREA PROCEDURE

mg Mo	0	0.40	0.80	1.20	1.60
Abs. 410 nm[a]	0.816	0.815	0.816	0.816	0.815

[a] Average of 2 results.

method as outlined above showed excellent agreement with the data given in Table III.

The use of tetraphenylarsonium chloride has been modified in two ways from the previous literature. An increased amount of tetraphenylarsonium chloride has been added in order to obtain quantitative extraction of 400 μg of rhenium, and concentrated hydrochloric acid has been used in order to obtain quantitative back-extraction. Back-extraction with 1:1 hydrochloric acid showed only 50 to 60% recovery of rhenium.

The tetraphenylarsonium chloride–1-phenyl-2-thiourea method appears to be satisfactory for the determination of rhenium in any type of material. The precision is excellent, although there is a slight positive deviation from Beer's law.

The procedure was tested for smaller amounts of rhenium by preparing a standard curve with 5-cm cells. The absorbance per ng of rhenium varied from 0.994 for 25 μg Re to 1.013 for 75 μg Re. Thus trace amounts of rhenium could be determined but comparison would have to be made to slightly non-linear curve.

To verify the procedure based on tetraphenylarsonium chloride and 1-phenyl-2-thiourea, two samples of a ReS_2–MoS_2 mixture were oxidized in air at 500° for 2 h in a tube furnace. The gases leaving the furnace passed through a glass-frit bubbler which contained a dilute solution of hydrogen peroxide. An analysis was made on the initial ReS_2–MoS_2 material, on the residue left after the oxidation, and on the gas-absorber solution. The total rhenium balance (Table V) demonstrates the accuracy of the experimental oxidation procedure and the analytical procedure for rhenium.

TABLE V

MATERIAL BALANCE ON ReS_2–MoS_2 OXIDATION

Expt.	*Starting material*		*Products*				*Difference (%)*
	Re (%)	*Re (mg)*	*Re (%)*	*Re (mg)*	*Absorber solution Re (mg)*	*Total Re (mg)*	
A	1.86	18.6	0.046	0.38	17.6	17.98	3.3
B	2.64	26.4	0.054	0.45	25.9	26.35	0.2

The special samples from the oxidation of ReS_2–MoS_2 were supplied by PAUL R. AMMANN of the Kennecott Copper Corporation.

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Hydrofluoric acid decomposition–atomic absorption analysis of nine silicate mineral and rock reference samples

To supplement the reference samples G-1 and W-1 issued by the U.S. Geological Survey (USGS), various institutions have processed new series of samples. The present paper reports on the analysis of several of these samples: GSP-1 (a granodiorite), AGV-1 (an andesite), DTS-1 (a dunite) and BCR-1 (a basalt) prepared by USGS*; GA and GH (2 granites) and BR (a basalt) prepared by Centre de Recherches Pétrographiques et Géochimiques (CRPG), France; and the Nordic reference samples ASK-Larkivit (Tvedalen, Langangen) and ASK-skifer (ordovician schist, Oslo).

The samples were decomposed by hydrofluoric acid by the technique described elsewhere[1]; the sample solutions, or aliquot parts of these solutions were used for the determination of silicon, aluminium, the total content of iron, magnesium, calcium, sodium, potassium, titanium and manganese by atomic absorption spectrophotometry.

Experimental

The instruments, apparatus, reagents and solutions were the same as used previously[1]. The samples AGV-1, GA and GH, were decomposed in 125-ml Erlenmeyer flasks made from polycarbonate, the stoppered flasks being heated on a boiling water bath. The other samples were attacked at 110° in a polytetrafluoroethylene-lined bomb; before this attack the sample of schist was heated for 1 h at 1000 ± 25°.

Five 0.2000-g portions of the air-dried sample were decomposed, the content of water being determined on a separate sample.

The sample of schist was opened up with a mixture of 5.00 ml of hydrofluoric acid, 0.75 ml of hydrochloric acid and 0.25 ml of nitric acid. Sample CRPG-BR was attacked with a mixture of 5.00 ml of hydrofluoric acid and 0.5 ml of nitric acid. Other samples were decomposed in the ordinary way with 5.00 ml of hydrofluoric acid.

Silicon, aluminium, magnesium, calcium and titanium were determined with acetylene–nitrous oxide flames and the other elements with acetylene–air flames.

The high content of magnesium in the sample of dunite presented a special problem. In order to avoid a large dilution, the determination was made with the burner turned 90° from its standard position. In the sample of dunite aluminium was not detected, though amounts ranging from 0.04 to 0.23% Al_2O_3 have been found by other methods.

Results

The analytical results are given in Table I, which also contains some statistical data and preferred values from other analyses.

A comparison of the present data with the preferred values should not be made without taking into consideration the content of water. The laboratories participating in these analyses are geographically separated, hence the differing results for hygroscopic water may originate from varying humidity conditions during storage.

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* Analytical data for the new reference rock USGS G-2 (a granite) obtained by the present technique are given in a previous paper[1].

TABLE I

ANALYTICAL DATA FOR NINE SILICATE MINERAL AND ROCK REFERENCE SAMPLES

Sample	[a]	*Si* *as* SiO_2 (%)	*Al* *as* Al_2O_3 (%)	*Total Fe* *as* Fe_2O_3 (%)	*Mg* *as MgO* (%)	*Ca* *as CaO* (%)	*Na* *as* Na_2O (%)	*K* *as* K_2O (%)	*Ti* *as* TiO_2 (%)	*Mn* *as MnO* (%)	H_2O (110°) (%)
USGS	$\bar{x}$	67.07	15.49	4.29	0.97	1.94	2.86	5.56	0.64	0.040	0.04
GSP-1	S	0.74	0.14	0.01	0.01	0.03	0.12	0.06	0.005	0.001	
Split/Pos.	C	1.1	0.90	0.23	1.0	1.5	4.2	1.0	0.8	2.5	
15/22	A	67.39	15.00	4.27	0.98	2.12	2.78	5.50	0.64	0.04	0.03
USGS	$\bar{x}$	59.65	17.50	6.73	1.50	4.94	4.25	2.72	1.01	0.096	0.05
AGV-1	S	0.83	0.28	0.08	0.04	0.11	0.05	0.08	0.01	0.002	
Split/Pos.	C	1.4	1.6	1.2	2.7	2.2	1.2	2.9	0.99	2.1	
47/20	A	59.09	16.90	6.75	1.46	4.92	4.21	2.89	1.04	0.10	1.20
USGS	$\bar{x}$	40.47	not	8.43	49.82	0.053	0.068	not	not	0.110	0.03
DTS-1	S	0.24	de-	0.03	0.76	0.002	0.015	de-	de-	0.002	
Split/Pos.	C	0.59	tected	0.36	1.5	3.7	22	tected	tected	1.8	
30/19	A	40.61	0.16	8.63	49.67	0.18	0.00	0.00	0.002	0.12	0.00
USGS	$\bar{x}$	54.36	13.66	13.58	3.57	6.73	3.12	1.72	2.19	0.181	0.04
BCR-1	S	0.33	0.31	0.19	0.07	0.07	0.04	0.07	0.01	0.003	
Split/Pos.	C	0.61	2.3	1.4	1.9	1.0	1.3	4.0	0.46	1.7	
77/4	A	54.50	13.41	13.46	3.41	6.98	3.23	1.68	2.22	0.19	0.71
CRPG	$\bar{x}$	69.70	14.65	2.71	0.90	2.31	3.63	4.26	0.36	0.082	0.04
	S	0.39	0.15	0.04	0.01	0.08	0.08	0.14	0.01	0.003	
GA	C	0.56	1.0	1.5	1.1	3.4	2.2	3.2	2.8	3.7	
	A	69.71	14.61	2.83	0.97	2.48	3.57	4.03	0.37	0.09	0.10
CRPG	$\bar{x}$	75.15	12.75	1.39	0.028	0.63	3.79	5.01	0.077	0.046	0.05
	S	0.37	0.33	0.05	0.001	0.08	0.06	0.33	0.002	0.001	
GH	C	0.49	2.5	3.5	3.6	13	1.6	6.6	2.6	2.2	
	A	75.58	12.63	1.41	0.07	0.68	3.83	4.78	0.08	0.05	0.06
CRPG	$\bar{x}$	38.85	10.28	12.78	13.43	13.42	3.08	1.50	2.69	0.192	0.07
	S	0.68	0.17	0.07	0.14	0.18	0.02	0.09	0.02	0.004	
BR	C	1.7	1.7	0.55	1.0	1.3	0.65	6.0	0.74	2.1	
	A	38.49	10.31	12.87	13.21	13.89	3.07	1.38	2.61	0.20	0.50
ASK	$\bar{x}$	58.79	19.22	4.46	1.16	3.45	6.24	4.29	0.98	0.129	0.02
Larkivit	S	0.56	0.09	0.05	0.04	0.10	0.18	0.19	0.01	0.003	
Series I											
Bottle no. 2	C	0.95	0.47	1.1	3.4	2.9	2.9	4.4	1.0	2.3	
ASK[b]	$\bar{x}$	54.82	18.56	7.39	2.04	0.75	0.79	5.21	0.90	0.034	0.07
Schist	S	0.30	0.05	0.06	0.05	0.04	0.11	0.12	0.01	0.002	
Series I											
Bottle no. 37	C	0.55	0.27	0.81	2.5	5.3	14	2.3	1.1	5.9	

[a] $\bar{X}$ = average of 5 analyses; S = standard deviation; C = relative standard deviation; A = preferred values[2,3].
[b] Loss of ignition 9.3%

A direct comparison of results from various laboratories could be facilitated by reporting all data on a moisture-free basis.

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Determination of nitrogen in uranium nitride by the Dumas technique

For the analysis of nitrogen in uranium nitride* following the conventional Dumas method[1], copper oxide is generally used as the oxidising agent to assist in the thermal decomposition of the sample. About 100 mg of sample is mixed with *ca.* 3 g of copper oxide and decomposed at 900–1000° [2–5]. However, when this method was used, erroneous results were obtained on account of the nearly explosive reaction of the sample material with copper oxide.

If the carbon dioxide gas could take over the oxidising task of the copper oxide, the rate of the sample decomposition would be regulated smoothly by variation of the carbon dioxide flow. The carbon monoxide formed during the reaction would then be oxidised in the main furnace and eliminated by the potassium hydroxide solution in the nitrometer. An extra advantage would be the elimination of mixing and grinding of the sample. This modification was introduced by KIRSTEN[6] for the determination of nitrogen in organic materials; he worked with a temperature of 1050–1100° and used nickel oxide to ensure complete decomposition of volatilized products. TAKAHASHI[5] used this principle for the analysis of uranium nitride but, working with decomposition temperatures up to 900°, he obtained low results. NAOUMIDIS *et al.*[7,8] claimed 1000° to be the optimal temperature for decomposition of uranium nitride by the carbon dioxide. The decomposition rate was sufficient and sintering of the sample was still negligible.

However, in the present work, in agreement with KIRSTEN's results for organic compounds, a temperature of 1100° was found to be necessary to obtain complete recovery of the nitrogen from uranium nitride. The results obtained at this temperature were so good that the generally used Pregl-type nitrometer became the limiting factor for the precision of the analysis. For this reason the absorption chamber of the Pregl nitrometer was replaced by a separate vessel wherein the potassium hydroxide solution could be stirred[1]. The measuring tube of the nitrometer was

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* On account of its good thermal conductivity and high uranium density, UN is a possible fuel material for nuclear reactors.

replaced by a piston burette. A significant increase in precision was obtained by thermostatting the absorption vessel and burette with water mantles, so that errors caused by ambient temperature fluctuations and by heat generated during the absorption were eliminated.

Copper oxide was used for oxidation of the carbon monoxide formed during sample decomposition. The reaction tube was constructed so as to allow the analysis of six samples in sequence without opening the instrument. With this method, nitrogen determinations could be made with a precision of 0.02% absolute on samples weighing 75–125 mg.

Chemicals

Carbon dioxide, copper oxide granules (30–60 mesh), copper granules (30–60 mesh obtained from copper oxide by reduction with hydrogen), aqueous potassium hydroxide solution (50% w/w), and stopcock lubricant: see ref. 1, p. 422. Asbestos wool, refluxed with concentrated hydrochloric acid, rinsed with water and ignited in air at 800°, was also used.

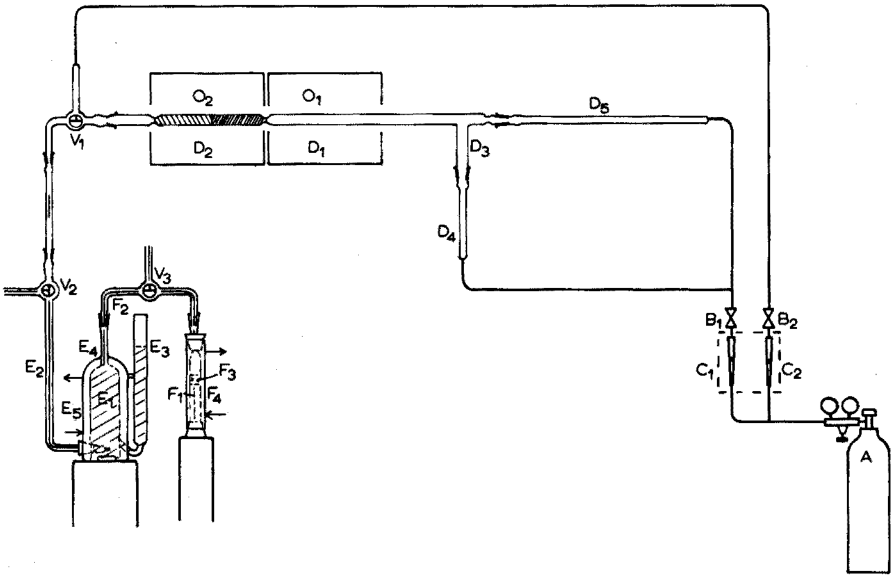

Fig. 1. General layout of the instrument. (A) Cylinder with CO_2 containing max. 0.025% total impurities. (B) Needle valves. (C) Flowmeters. (D) Reaction system composed of quartz reaction tube proper D_{1-3} and pyrex tubes $D_{4,5}$ for sample introduction; D_1 decomposition chamber, D_2 purification chamber filled with CuO and Cu granules 30–60 mesh, D_3 space for sample storage; $D_{4,5}$ equipped with alundum push rods with iron ends for the transport of samples from D_3 into D_1 by means of a ring magnet. (E) Absorbing system composed of absorption chamber E_1 filled with KOH solution, capillary tube E_2 with slitted rubber outlet, open side vessel E_3 and capillary tube E_4 with marks for adjustment of the meniscus of the liquid; E_5 circulating water mantle at 23.0°. (F) Measuring system: Metrohm burette cylinder of 10 ml F_1, capillary connecting tube F_2, teflon piston F_3 with mercury between the piston rings to avoidance of gas leaks; F_4 circulating water mantle at 23.0°. ($O_{1,2}$) Ovens. (V_{1-3}) Three-way stopcocks.

Apparatus

The general layout of the apparatus is shown in Fig. 1. The important parts are the reaction tube D and absorption chamber E with measuring system F; E_1 and F_1 are equipped with water mantles at 23.0°. The quartz sampling vessels, S, used were nearly rectangular, 15 mm long, 12 mm wide and 6 mm high. All connections were made of stainless steel, connected to the glass parts via pyrex/steel joints.

Procedure

To bring the instrument into operation, pass carbon dioxide at 30 ml/min from cylinder A continuously through reaction tube D via valve B_1 and flow meter C_1. Bring the furnaces O_1 and O_2 to temperatures of respectively 1100° and 600°. Fill absorption chamber E_1 with fresh hydroxide solution and start the stirring motor.

Sample introduction. Remove tube D_4 and force carbon dioxide at *ca.* 60 ml/min into the reaction tube by opening valve B_2 and turning three-way cock V_1. Introduce a maximum of 6 samples (75–125 mg) in vessels S into side tube D_3. Replace tube D_4, close valve B_2 and turn tap V_1 to its original position.

Determination of the blank. Turn tap V_3 "open", and move piston F_3 of the burette to about 1 ml from its highest position. Reduce the gas flow to nearly zero and stop the stirrer. Adjust the liquid surfaces in capillary E_4 and side vessel E_3 to the marks by removal (or addition) of some hydroxide solution from (or to) vessel E_3. Then close V_3 and read the burette. Start the stirrer again and reset the carbon dioxide flow to 30 ml/min by valve B_1. Set piston F_3 in its highest position; in this way a gas volume of about 1 ml is formed below the mark on E_4 and the rise of hydroxide solution into the capillary is avoided. After 30 min, reduce the gas flow again to nearly zero and stop the stirrer. Lower piston F_3 in the burette until the liquid surface in the capillary E_4 just reaches the mark. If necessary, remove some hydroxide solution from side vessel E_3; reset the burette piston if necessary and measure the collected volume of nitrogen. Repeat this whole procedure until a constant blank value of 0.050–0.060 ml/30 min is obtained. Usually two determinations are sufficient.

Analysis of the sample. After adjustment of the burette as mentioned above, read its value. Then start the stirrer and reset the gas flow to 30 ml/min. After this move the train of sampling vessels S in D_3 with the alundum rod in D_4 until the first vessel enters tube section D_1. Push this vessel into the middle of the decomposition chamber with the alundum rod in D_5. After 30 min, reset the burette and measure. In this way six sample aliquots can be analysed in one sequence without opening the instrument. Collect the exhausted samples in the left part of tube section D_1 and later remove them by withdrawal via side tube D_3.

Calculation of nitrogen concentration. The nitrogen concentration in the sample in % w/w was calculated with the equation[1]:

$$\text{Concn.} = \frac{(V-V_0)\cdot(P-6.8)}{W}\cdot 0.15167\ \%$$

where $(V-V_0)$ is the volume of the nitrogen measured, after correction for the blank, in ml with a precision of 0.01 ml at barometric pressure P, in mm; W is the sample weight in mg with a precision of 0.05 mg.

Discussion

The results obtained for six unsintered samples of uranium nitride (A–F) and one sintered sample (P) of different origin are shown in Table I. Sample F was also analysed by the Kjeldahl method with hydrochloric–hydrofluoric acid as the dissolving liquid[9]. The results obtained by different methods of analysis correspond quite well.

The determination of nitrogen in uranium nitride by the Dumas technique can thus be done with a precision of 0.02% absolute.

TABLE I

DETERMINATION OF NITROGEN IN URANIUM NITRIDE

Sample	*Method*	*N% (w/w) found*
A	Dumas	5.37, 5.37, 5.36, 5.35
B	Dumas	5.39, 5.38, 5.41, 5.37
C	Dumas	5.38, 5.38, 5.36, 5.36
D	Dumas	5.37, 5.36, 5.39, 5.38
E	Dumas	5.28, 5.28, 5.29, 5.28, 5.29
F	Dumas	5.33, 5.32, 5.32, 5.35, 5.34
F	Kjeldahl	5.38, 5.32, 5.31
P	Dumas	5.31, 5.32, 5.32, 5.33, 5.33

When a decomposition temperature of 1100° was used, 99% of the nitrogen present in samples A–F was collected in the burette after 7 min. After 15 min all the nitrogen had been gathered, so that the extra 15 min were added for the sake of security only. When a decomposition temperature of 1000° was used, *ca.* 99% of the nitrogen was collected after 30 min. At a temperature of 900°, only *ca.* 96% was collected after 30 min.

In sintered sample P the release of nitrogen was slower: after 30 min at 1100°, 99% of the nitrogen had been collected and the decomposition time had to be lengthened to 60 min for complete recovery.

Obviously the method described is not restricted to the analysis of uranium nitride but can be used in all cases where carbon dioxide is able to liberate nitrogen quantitatively from the sample. The method can also be used for trace analysis, and has been applied, for instance, to the determination of nitrogen in U_3O_8 in the concentration range of 0.01–0.1%.

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Determination of sodium acetate in alkali and clay mixtures

Analytical control of sodium acetate additive was essential to some studies regarding the properties of clay batches. This paper deals with an analytical development program which permitted a precise determination of 1% sodium acetate in the presence of clay and 10% sodium hydroxide. The determination of acetate in this mixture proved a rather difficult task which involved the exploration of several methods of separation and determination. Some of the separation techniques attempted included direct distillation, ion exchange, and steam distillation. Methods of determination studied include spectrophotometry (visible and UV), and acidimetry involving colorimetric and potentiometric end-point detection.

A thorough literature search showed that essentially only three methods are available for determining acetate in rather complicated matrices. The first method involved a straight distillation of acetic acid from a mineral acid medium followed by titration of the distillate with standard base[1]. The second method consisted of a distillation followed by a spectrophotometric finish[2]. The third method employed distillation followed by a chromatographic finish[3]. In each of these analytical procedures, the precision was not adequate for the present requirements. Methods based upon elemental carbon determinations were not considered inasmuch as low concentration levels of both carbonaceous materials and carbonates were present in the clay batches.

Two known clay batch samples were specially prepared for purposes of method development. These batches were identical in composition except that batch I contained sodium acetate while batch II did not; both contained a nominal 10% sodium hydroxide. Thus, during developmental studies, batch II served as a blank while the various separations and determinations were evaluated. Also, recovery studies were completed by spiking batch II with known weights of sodium acetate to determine the degree of separation attainable by the various techniques. The following is a summary of the results of this investigation that led to the recommendation of steam distillation as the distinctly superior method.

Apparatus

Micro-Distillation Apparatus (Sargent Catalogue No. S-63636).

Direct distillation

The usual recommended approach for the separation of acetate is a distillation of acetic acid from dilute phosphoric or sulfuric acid at a temperature of 120° (b. p. of acetic acid is 118°); 3 h is required to collect the 200 ml of distillate specified by this procedure. When separation of acetate from clay batches was attempted, unsatisfactory results were obtained. Not only was the shape of the potentiometric titration curves inconsistent, but, more important, analysis of spiked samples indicated that recovery was erratic and not quantitative. Spectrophotometric analysis with the molybdovanadophosphoric acid method showed that the inconsistent results and high blanks were due to the carryover of significant amounts of phosphoric acid. As much as 10–15 mg of phosphorus pentoxide was present in the distillate. When distillation from dilute sulfuric acid was attempted, the results were likewise inconsistent, indicating that small amounts of sulfuric acid were similarly being swept over with the distillate. The blank values obtained at 127° were very erratic as were those obtained at 120° and 100° .The most complete recoveries with standard sodium acetate were made at 127°, but, since the scatter was so great, the results had little significance.

An attempt was made to minimize the carryover of mineral acid into the distillate by incorporating a Kjeldahl vapor trap and a reflux column into the distillation apparatus. Even with this more elaborate apparatus, the blank remained erratic with appreciable carryover of mineral acid. Rather than continuing with the direct distillation technique, the application of cation-exchange resins was investigated.

Ion exchange

If a solution of sodium acetate is passed through a cation-exchange resin, acetic acid is formed by the exchange of sodium ions for an equivalent amount of hydrogen ions. Both strong (Dowex 50-X8, 100–200 mesh) and weak (Rexyn 102H, 100–200 mesh) cation-exchange resins were evaluated. Before use, the Dowex 50–X8 resin was conditioned by washing the resin with 1:5 hydrochloric acid solution and distilled water. The Rexyn 102H resin was conditioned by washing with 1:50 hydrochloric acid solution and distilled water. The resin was then poured into columns and rinsed with distilled water until neutral.

The clay samples were prepared by adding 2 g of clay batch to a test tube and leaching overnight with distilled water on a steam bath. The solution was then centrifuged and the extract siphoned with capillary tubing. An additional 5 ml of distilled water was added to the tube, mixed, centrifuged and siphoned again. The combined extract was then passed through the cation-exchange resin and eluted with distilled water. In general, the potentiometric titration curves for acetic acid in the effluent as well as titrations with visual indicators yielded inconsistent results. No significant difference was noted in the titration curves developed from strong cation-exchange and weak cation-exchange resins. Standard sodium acetate solutions were passed through Dowex 50 resin and then titrated potentiometrically with standard sodium hydroxide solution. The recoveries were very close to 100%. The addition of sodium hydroxide to sodium acetate in the ratio of 10:1 before passage of the solution through the column did not affect the results.

Spectrophotometry (visible and ultraviolet)

The spectrophotometric method described by WHITEHEAD AND WRIGHT[2] is based on the formation of a blue acetate complex of undetermined structure through the addition of specific amounts of ammonium hydroxide, iodine, and lanthanum. The method worked moderately well with standard solutions but behaved very erratically when applied to the aqueous leach of the clay. Compared to most spectrophotometric procedures, this one was definitely inadequate, particularly in regard to freedom from interferences and stability.

Ultraviolet spectrophotometry of standard solutions of acetic acid, lead acetate, and sodium acetate was also evaluated for determining acetate in the distillate or ion-exchange effluent. The sensitivity, as indicated by Beer's law plot, proved to be in the descending order of lead acetate > sodium acetate > acetic acid, the acetic acid plot being non-linear. Since lead acetate had a higher absorptivity, addition of lead to the distillate or ion-exchange effluent was evaluated to see if a more sensitive method for determining acetate could be developed. To this end, the absorbance spectra of lead acetate, lead nitrate, and lead perchlorate solutions were measured; each spectrum showed a peak at about 210 nm, but the absorptivity of lead perchlorate was not sufficiently different from that of lead acetate, hence this approach was abandoned. Owing to its much higher absorptivity, use of lead nitrate was out of the question.

Steam distillation

The simplest, yet most effective, approach for the determination of acetate in clays consisted of steam distilling the acetate as acetic acid from a sulfuric acid medium in a micro steam distillation apparatus. The distillate was titrated with standard sodium hydroxide solution.

Determination of the blank. Distilled water (10 ml) and 5 ml of concentrated sulfuric acid were added to the sample chamber and steam-distilled until *ca.* 500 ml of distillate were collected. The unit was turned off and the water allowed to back-up into the outer chamber and then drained. The distillate was titrated with standard sodium hydroxide solution (0.100 *N*), in presence of phenolphthalein indicator or potentiometrically.

Analysis of clay batch sample. A clay batch (2 g) was weighed to the nearest milligram, and transferred to the sample chamber with a minimum volume of distilled water. Concentrated sulfuric acid (5 ml) was added and distilled in the same manner as the blank. The sample chamber was cleaned by adding distilled water, allowing it to back-up into the outer chamber and then draining. This step was repeated at least once. The distillate was titrated either visually or potentiometrically as above.

Assay of sodium acetate

The salt was assayed by nonaqueous titration[4,5] where standard 0.1 *N* perchloric acid was used as a titrant for sodium acetate in an acetic acid medium. The results by this technique indicated that the assay was 99.3%. The manufacturer's certified value was 99.4% minimum.

Discussion

When the steam-distillation technique was used, the blank values (batch II) were consistently low. Such results can be attributed to less carryover of acid vapor at the reduced temperature (100°) of the steam distillation in comparison to the direct distillation. This was established by adding phosphoric acid to the sample chamber, completing the distillation, and testing spectrophotometrically for phosphate in the distillate. The results indicated that only 1–2 mg of phosphorus pentoxide was present compared to 10–15 mg carried over in direct distillation technique. The total analytical time expended per sample was about 1 h. Repeated (10) analysis of 20.5 mg of sodium acetate by the steam-distillation method gave an average recovery of 99.85% with a variance[6] of 0.21 and a standard deviation of 0.458 with 95% confidence limits[6] of ±0.328.

The effect of carbonates was investigated by transferring up to 200 mg of sodium carbonate to the distillation chamber with distilled water, adding 5 ml of sulfuric acid, and completing the distillation. Titration of the distillate with standard alkali indicated that this amount of sodium carbonate did not interfere in the procedure.

Since clays, under certain conditions, have a strong affinity for ions, tests ascertained the effectiveness with which acetate was recoverable from clay batches. When the blank (batch II) was spiked with *ca.* 40 mg of sodium acetate, 98.6% was recoverable. At the 1% sodium acetate level, this recovery was considered essentially quantitative. Table I indicates the results obtained for the analysis of several clay batch samples.

TABLE I

DETERMINATION OF ACETATE IN CLAYS BY STEAM DISTILLATION

Sample	*Acetate (%)*	*Mean (%)*
Clay batch no. I	0.80, 0.80	0.80
Clay batch no. II	0.069, 0.074, 0.082	0.075
A	0.24, 0.25	0.24
B	1.18, 1.19	1.18
C	1.30, 1.28	1.29
D	0.88, 0.87, 0.88	0.88
E	0.88, 0.91	0.89

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The composition of complexes of type A_mB_n: a modification of the straight-line methods of Holme and Langmyhr

When the straight-line methods of HOLME AND LANGMYHR[1] were employed to determine the composition of complexes formed in the iron(III)–quinizarin-2-sulphonic acid (QSA or Q, 1,4-dihydroxy-9,10-anthraquinone-2-sulphonic acid) system, certain difficulties arose. Reevaluation of the HOLME–LANGMYHR methods suggested that confusion with regard to one term in particular yielded spurious results. These difficulties are outlined and explained, an equation of HOLME AND LANGMYHR is further modified and an example given of the use of this modified function.

Theory

Pertinent parts of the HOLME–LANGMYHR methods will be reviewed, basically using their notation.

Method II. As explained by HOLME AND LANGMYHR, "for the complex A_mB_n, the value of m/n is determined by varying the excess of the reactant A, the concentration of B being maintained constant" in a series of solutions whose extinctions are then measured. The following equation is basic to this method:

$$\frac{1}{[A]^{m/n}} = \frac{1}{\left(a - \frac{mE}{nE_0}b\right)^{m/n}} = \left(\frac{1}{K}mb^{m-1}\right)^{1/m}\left(1 - \frac{E}{E_0}\right)\left(\frac{E_0}{E}\right)^{1/m} \qquad (1)$$

where a and b are analytical concentrations of A and B respectively, $E \equiv$ extinction and $E_0 \equiv$ an upper extinction limit.

Making the approximation (which is fulfilled in a practical sense) that $E = E_0$, a plot of $1/\left[\left(a - \frac{m}{n}b\right)^{m/n}\right]$ *vs.* $1/E$ will for the correct value of m/n produce a straight line, with intercept $1/E_0$. For incorrect values, curved lines of varying degrees will be obtained.

Method I. "By preparing and measuring a second series of solutions in which the concentration A is kept constant and in excess, while the concentration of B is varied, the value of n is determined." The theoretical equation for this method is:

$$\frac{1}{[B]^n} = \frac{1}{\left(b - \frac{nE}{mE_0}a\right)^n} = \frac{1}{K}ma^{m-1}\left(1 - \frac{E}{E_0}\right)^m \frac{E_0}{E} \qquad (2)$$

The plot of $1/[B]^n$ *vs.* $1/E$ will for the correct value of n yield a straight line. "Both series contain an excess of the reactant A and consequently the values of the coefficients m and n can be assumed to belong to the same complex. The curves above relating to Method I are strictly theoretical and are not based on any approximations. In order to apply Method I to actual systems, it is necessary to know the value of E_0. The value of E_0 is preferably established graphically from a diagram resulting from the use of Method II, the curves in this diagram cutting the abscissa at $1/E_0$."

Analysis of E_0

It is in the determination of the value of E_0 to use in Method I that confusion may occur, resulting in negative values for the concentration of uncomplexed reagent B. If the value of E_0 obtained from the extrapolation of Method II were used as implied in the second expression of eqn. (2) to calculate $1/[B]_n$, a negative value of [B] would generally be calculated. This can easily be seen, once a value of m/n is determined. For example, if $m/n = 1$ and the experiment has been carried out as suggested, then, in broad terms,

$$\frac{1}{E} > \frac{2}{E_0} \text{ or } \frac{E}{E_0} < 0.5$$

Reagent A could be present in no greater than 100% excess, or

$$\left(b - \frac{nE}{mE_0} a\right) < 0.$$

Experimental conditions in the literature[1-3], as well as the experience of this laboratory, indicate that greater excesses of one reagent are commonly used, and may be indeed necessary[4]. The definition of E_0 must be examined.

In Method II the concentration of B was held constant and the concentration of reagent A was varied while in excess. The concentration of the complex approaches an upper limit as the excess is increased:

$$\lim_{a \to \infty} [A_mB_n] = \frac{b}{n}$$

with a corresponding upper extinction limit of E_0. Note that the specific value of E_0 is dependent on a particular concentration of complex A_mB_n, which is established by the chosen concentration of the reagent which is held constant. To emphasize this point, the notation $E_0{}^b$ is introduced to represent the limiting extinction for a specific value of b.

Similarly, if the concentration of reagent A were held constant and the concentration of reagent B varied, then

$$\lim_{b \to \infty} [A_mB_n] = a/m$$

with a corresponding upper extinction limit of $E_0{}^a$. Either $E_0{}^a$ or $E_0{}^b$ may be determined by extrapolation of the straight-line graphs of Method II with data from the appropriate experiment. It is obvious that the values of $E_0{}^a$ or $E_0{}^b$ are generally not equal and not interchangeable. Only if the analytical concentration of A were "m"-molar or that of B were "n"-molar would that equality exist ($E_0{}^a = E_0{}^b = \varepsilon d$, where $\varepsilon \equiv$ the molar extinction coefficient of the complex and $d \equiv$ path length in cm). Consequently, to apply eqn. (2) in Method I, the value of $E_0{}^a$ for the selected analytical concentration of A is required and use of Method II as described has provided only $E_0{}^b$.

Two considerations may prevent the determination of $E_0{}^a$ by an application of eqn. (1) for a given ${}^{\mathrm{I}}a$ (the superscript designates that the value was chosen for or refers to Method I). It may be experimentally impossible or impractical to record the extinctions of the solutions of such an experiment. More importantly, however, this procedure assumes that as an excess of A (Method I) is replaced by an excess of B (Method II to obtain $E_0{}^a$) the same complex predominates. A principal advantage of the HOLME AND LANGMYHR method has been lost and one might have employed the method of KLAUSEN AND LANGMYHR[5].

Since $E_0{}^b$ and $E_0{}^a$ are characteristic of the concentration of the complex A_mB_n, they can be related to each other by the Beer–Lambert law. At the limit

$$\varepsilon d = \frac{m^{\mathrm{I}}E_0{}^a}{{}^{\mathrm{I}}a} = \frac{n^{\mathrm{II}}E_0{}^b}{{}^{\mathrm{II}}b} \tag{3}$$

or

$${}^{\mathrm{I}}E_0{}^a = \frac{n^{\mathrm{I}}a}{m^{\mathrm{II}}b}\,{}^{\mathrm{II}}E_0{}^b$$

Substituting eqn. (4) into eqn. (2):

$$\frac{1}{[\mathrm{B}]^n} = \frac{1}{\left({}^{\mathrm{I}}b - \dfrac{{}^{\mathrm{I}}E}{{}^{\mathrm{II}}E_0{}^{b}}\,{}^{\mathrm{II}}b\right)^n} = \frac{1}{K}\, ma^{m-1}\left(1 - \frac{{}^{\mathrm{I}}E}{{}^{\mathrm{I}}E_0{}^{a}}\right)^m \frac{{}^{\mathrm{I}}E_0{}^{a}}{{}^{\mathrm{I}}E} \tag{5}$$

Therefore, the value of the coefficient n in the complex $\mathrm{A}_m\mathrm{B}_n$ may be determined from the straightest line in a plot of

$$1/\left[\left({}^{\mathrm{I}}b - \frac{{}^{\mathrm{I}}E}{{}^{\mathrm{II}}E_0{}^{b}}\,{}^{\mathrm{II}}b\right)^n\right] \ vs.\ 1/{}^{\mathrm{I}}E,\ n=1,\ 2,\ \ldots$$

based on eqn. (5), after the ratio m/n and ${}^{\mathrm{II}}E_0{}^{b}$ have been determined as described in Method II. An excess of one reagent has been maintained throughout the two experiments.

Experimental

Apparatus. All volumetric glassware was Class A and transfer pipettes were calibrated. Spectrophotometric measurements were made with a Beckman DU instrument at 590 nm, in cells with a 0.3-cm path length. All measurements were made at a room temperature of 25°.

Reagents. A stock solution ($9.998 \cdot 10^{-4}\,M$) of quinizarin-2-sulphonic acid (Allied Chemical Corporation, Harmon Colours, Industrial Chemicals Division) was prepared from the sodium salt which had been once recrystallized. The solvent was 0.100 M perchloric acid and the solution was standardized spectrophotometrically. It was stored in the dark.

The stock iron(III) perchlorate (G. F. Smith Chemical Co.) solution ($8.927 \cdot 10^{-3}\,M$) was prepared by dilution of a more concentrated solution that had been standardized against potassium dichromate. The solvent in each case was 0.100 M perchloric acid. All water used was demineralized.

TABLE I

METHOD II APPLIED TO AN $\mathrm{Fe}_m\mathrm{Q}_n$ COMPLEX

Solution	*Volume of Fe soln. (ml)*[a]	*C_{Fe} (10^3 M)*	*Extinction 590 nm (0.3 cm)*	*$Q^{\mathrm{Q}}_{\mathrm{FeQ}}$* [b] *($10^{-2}$) M^{-1}*
1	10.00	3.571	0.341	4.51
2	8.00	2.857	0.292	3.99
3	6.00	2.142	0.247	3.91
4	4.00	1.428	0.178	3.50
5	3.50	1.250	0.162	3.51
			Average:	3.88

[a] The $8.927 \cdot 10^{-3}\,M$ Fe(III) solution was added from a 10-ml burette. To each 25-ml flask, 9.98 ml of $9.998 \cdot 10^{-4}\,M$ QSA solution were added. Solutions were diluted to volume with 0.100 M $\mathrm{HClO_4}$: final concentration of QSA $= 3.991 \cdot 10^{-4}\,M$. pH of all solutions: 1.06 ± 0.01 units at 25°.

[b] Stability quotient $Q^{\mathrm{Q}}_{\mathrm{FeQ}} = [\mathrm{FeQ}]/[\mathrm{Fe}][\mathrm{Q}]$.

TABLE II

MODIFIED METHOD I APPLIED TO AN Fe_mQ_n COMPLEX

Solution	*Volume of QSA soln. (ml)*[a]	C_Q *(10^4 M)*	*Extinction*[b] *590 nm (0.3 cm)*	Q_{FeQ}^{Q}[c] *(10^{-2}) M^{-1}*
1	12.00	4.799	0.387	3.97
2	9.00	3.599	0.299	4.18
3	8.00	3.199	0.268	4.24
4	7.00	2.799	0.233	4.14
5	6.00	3.399	0.206	4.45
6	4.00	1.600	0.137	4.36
			Average:	4.22

[a] To each 25-ml flask, 9.98 ml of $8.927 \cdot 10^{-3}$ M Fe(III) solution were added: final concentration of Fe(III) = $3.564 \cdot 10^{-3}$ M. The $9.998 \cdot 10^{-4}$ M QSA solution was added from a 50-ml burette. pH of all solutions: 1.07 ± 0.01 units at 25°.
[b] ${}^{II}E_0{}^Q = 0.568$.
[c] $[FeQ] = \dfrac{{}^{I}E\ {}^{II}C_Q}{n\ {}^{II}E_0^Q}$

Procedure. The solutions for Method II and modified Method I were prepared as indicated in Tables I and II, respectively. After the solutions had stood in the dark for several hours, their extinctions were measured.

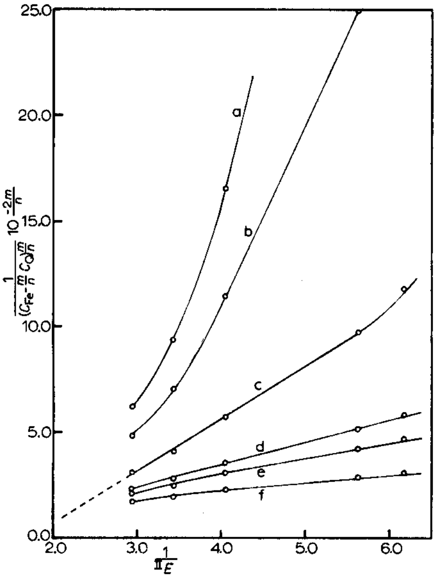
Results and discussion

Assuming values of m/n of 2, $\frac{3}{2}$, $\frac{4}{3}$, 1, $\frac{3}{4}$, $\frac{2}{3}$, $\frac{1}{2}$, in turn, values of $1/[Fe]^{m/n}$ were calculated from data in Table I and plotted in Fig. 1 (with the exception of the curve, $m/n=2$). Curves d–f, although appearing straight on the scale of the diagram, are in fact slightly curved below $1/E \sim 4.0$. The straightest line is given for $m/n=1$ and a value of ${}^{II}E_0^Q = 0.568$ was extrapolated. Noticeable curvature in curve c begins at $1/E \sim 6.0$ as would be expected since the region of applicability (below $2/E_0{}^Q$) has been exceeded. While the curves given here have the same general shape as the experimental curves of HOLME AND LANGMYHR[1], they approach $1/E_0$ asymptotically to the straight line rather than exhibiting a "crossover region" as in the boric acid–quinizarin system.

In Fig. 2, curves are plotted by applying the modified Method I to the data of Table II. Curve d, where $n=1$, yields the straightest line of those obtained when values of $n=1$, 2, 3 and 4 were assumed. A pronounced crossover region is noted. These results provide strong evidence that the composition of an iron(III)–QSA complex, formed at very low pH ($\sim$1.0) with maximum extinction at 590 nm is represented by the formula FeQ; this complex is then mononuclear, not polynuclear as previously suggested[6].

Temporary or initial estimates of an overall stability quotient, Q_{FeQ}^{Q}, have been tabulated in Tables I and II, the average value from both series being $4.07 \cdot 10^2$ M^{-1}. This value is a factor of ten different from the value, $4.87 \cdot 10^3$ M^{-1}, reported previously for a medium of 0.1 ionic strength (in which chloride ion was used) at 29° [6].

In the course of this investigation, evidence of another complex forming in the system was noted; the composition of this complex is still under investigation.



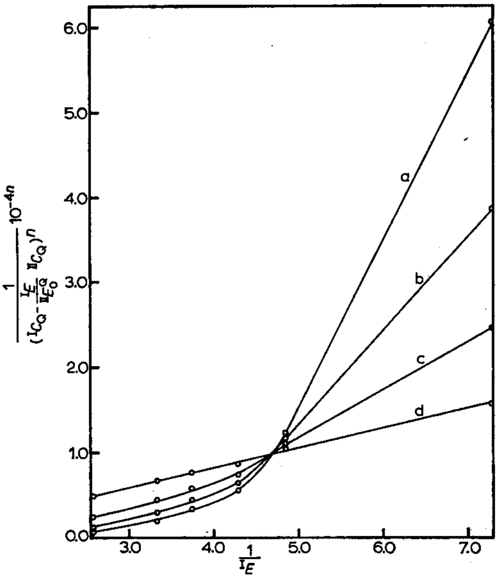


Fig. 1. The determination of the ratio, m/n, for an Fe_mQ_n complex (Method II). (a) $m = 3$, $n = 2$; (b) $m = 4, n = 3$; (c) $m = n = 1$; (d) $m = 3, n = 4$; (e) $m = 3, n = 2$; (f) $m = 1, n = 2$.

Fig. 2. The determination of the coefficient, n, in an Fe_mQ_n complex (modified Method I). (a) $n = 4$; (b) $n = 3$; (c) $n = 2$; (d) $n = 1$.

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An improved potentiostat attachment for a conventional polarograph

Among recent electrochemical instruments based on operational amplifiers, two simple circuit designs by ANNINO AND HAGLER[1] utilizing vacuum-tube operational amplifiers, which convert a conventional polarograph to a three-electrode instrument, retain their attractive features of simplicity and low cost. According to the classification by SCHWARZ AND SHAIN[2], the configurations of these circuits, when combined with a polarograph, are equivalent to types i and c, respectively, of the single-amplifier potentiostat designs. Though these types control the electrode potential regardless of the *iR* drop across the cell, type i is affected by the *iR* drop across the signal generator (polarographic scanning potentiometer etc.) and that across the current-measuring resistor. The effect of the latter *iR* drop is eliminated in type c.

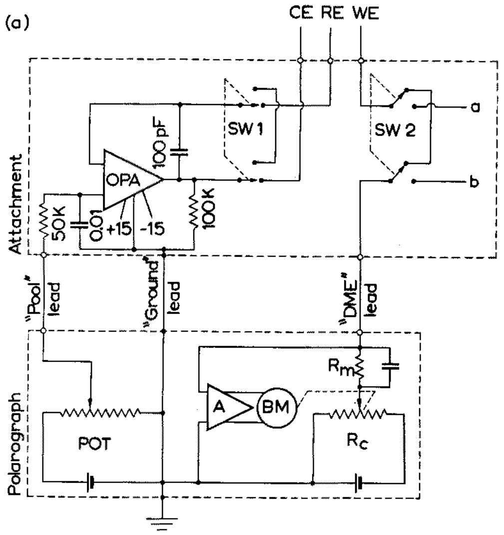
While the effect of the resistances of the scanning potentiometer and other signal-generating potentiometers in conventional polarographs is insignificant when the current drawn from the polarograph is small, it can be appreciable when the current drawn is larger, *e.g.* of the order of 10^{-4} A. Besides, this kind of *iR* drop error is difficult to correct for, because it changes its value even during the recording of a single polarogram. Such large currents are not infrequently encountered in studies of catalytic currents[3] or current maxima. It was necessary to construct a polarographic attachment which would be free from the effect of the *iR* drop either across the cell or the signal generator, for the polarograph currently used in this laboratory (Yanagimoto PA-102).

Modified circuits

The configuration of the complete basic circuit (Fig. 1a) is equivalent to type h of the single-amplifier potentiostats, according to the classification by SCHWARZ AND SHAIN[2], and is capable of controlling the electrode potential regardless of the cell resistance and the signal generator resistance, though it is affected by the *iR* drop across the current-measuring resistor. Fortunately, the recorder in the above-mentioned polarograph works as a low-impedance current recorder, when the sensitivity settings are higher than 40 μA/full scale, and the polarograph output lead to the working electrode is always bound at ground potential as long as the recorder is in balance, so that its effect on the electrode potential may be disregarded (see Fig. 1). An additional advantage of this type of potentiostat design is that an RC filter of small values may be inserted between the scanning potentiometer and the amplifier circuit; this is effective in removing the noise and the stray pickup in the applied voltage, which was appreciable (up to 10–20 mV) and quite disturbing, with the original polarograph.

The above circuit performed excellently with the above-mentioned polarograph, with higher sensitivity settings than 40 μA/full scale. With lower sensitivity settings, however, a serious loss of accuracy was experienced, because the polarograph recorder was designed to work in this range as a voltage recorder of low sensitivity (100 mV/full scale), which measures the *iR* drop across a resistor. This *iR* drop is not compensated. It was therefore necessary to add a 100:1 current attenuator based on the current–voltage transducer[4], following the working electrode, to avoid the use of lower sensitivity settings (Fig. 1b). This attenuator had the effect of reversing the direction of the current through the recorder, but this drawback was not serious.

The attenuation was finely adjusted by means of a 200-ohm trimmer potentiometer in the feedback circuit of the attenuator.



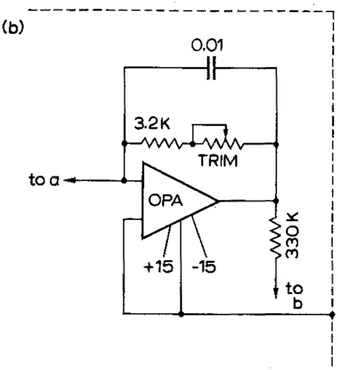


Fig. 1a. Polarograph with potentiostat attachment. POT: scanning potentiometer, 150 Ω; A: detector amplifier; BM: balancing motor; R_c: recorder slide wire, 5 Ω; R_m: current-measuring resistor; OPA: solid-state differential operational amplifiers. See text for specifications. "Common" leads are not necessary for some types of amplifiers; SW 1: DPDT switch for cell disconnection; "in" or "out"; SW 2: DPDT switch for range selection; ×1 or ×100; CE: lead to counter electrode; RE: lead to reference electrode; WE: lead to working electrode; a and b: connections to current attenuator.

Fig. 1b. Current attenuator. TRIM: ten-turn trimmer potentiometer (Sakaye Tsushinki, Tokyo, Japan).

The two solid-state differential operational amplifiers were either Ampet 9814 (Aiko Denki, Tokyo, Japan), QFT-2 or 1009 (Philibrick/Nexus Research, Dedham, Mass., U.S.A.), which were at hand. Many other similar solid-state amplifiers with high input impedances, common-mode rejection ratio and adequate current capacities should work equally well in this circuit. For most amplifiers of this type, the maximum output voltage is about 10 V, and the current available is several mA; these figures are satisfactory for the present purpose. If necessary, voltage and current boosters are commercially available.

Before construction of this attachment, it is important to check the polarograph circuit, especially for its grounding principle, which may vary from one instrument to another. Minor modification of the attachment circuit and/or the polarograph may be necessary if it is not the same as the above-mentioned Yanagimoto polarograph (see Fig. 1a); in most cases, it would be possible to find a simple way of adapting the attachment for different types of polarograph.

Experimental tests

The above arrangement was used for taking polarograms of the catalytic wave due to 0.118 m*M* pyridine in aqueous buffer containing 0.05 *M* sodium acetate and

0.05 *M* acetic acid. The cell had three compartments; the center one contained the polarographic solution, and another contained saturated calomel electrode. The counter electrode, a spirally wound 0.4-mm platinum wire, was placed in a saturated potassium chloride solution contained in the last compartment. The connections between the compartments were made by the usual agar plugs supported by sintered glass disks. A limiting current of 200 μA was obtained, and the half-wave potential was located at -1.677 V *vs.* S.C.E. Then, the counter electrode was disconnected, and the lead wire to it was connected to the reference electrode. The polarogram thus obtained was not compensated for the iR drop across the cell, and was more drawn-out than the first one. The half-wave potential was 21 mV more negative than was obtained before. The last polarogram was recorded with the original polarograph without the attachment; the half-wave potential was 76 mV more negative than in the first polarogram. The last figure apparently represents the error introduced by the iR drop within the polarograph itself (scanning potentiometer and the current-measuring resistor) in addition to that across the cell. It is to be noted that a small error of potential caused by the iR drop at the mercury thread of the polarographic capillary is not compensated by this attachment. A low-resistance capillary has been proposed[5].

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Amperometric titration of α-tocopherol and mixed tocopherol concentrates with cerium(IV) sulfate

Cerium(IV) salts, especially the sulfate, are widely used for the titration of oxidizable organic molecules[1]. The titration of tocopherols (vitamin E) with cerium sulfate[2] has been accepted by "The National Formulary"[3]; α-tocopherol is determined in 80% ethanolic 0.5 *N* sulfuric acid solution with visual detection of the end-point by means of diphenylamine indicator. However, accurate interpretation of the end-points requires experience, because observation is complicated by solubility problems; tocopherol and its oxidation product, tocopherylquinone, are soluble in ethanol but insoluble in water, whereas cerium(IV) and cerium(III) salts are soluble in water but not in ethanol. Furthermore, the titration can be performed only with samples containing high tocopherol concentration and fails for mixed tocopherol concentrates where the presence of oil worsens the solubility problem considerably[4].

In the present communication, an amperometric method is proposed for the end-point detection in the above titration; the platinum indicator electrode with bubbling described in a previous paper[5] is used. This method is advantageous because low tocopherol concentrations can be determined, and because the applicability of the method is independent of the limited solubility of the cerium salts. The optimal conditions for the amperometric determination of tocopherols have been studied, together with the possible interferences caused by the presence of other vitamins.

Instrumentals and reagents

The voltammograms and the amperometric titrations were measured with an Atlas, Selector D type polarograph and a normal thermostatted (25±0.2°) polarographic cell. A platinum indicator electrode with bubbling[5] (surface 0.08 cm^2) was employed, with periodic renewal of the solution at the electrode surface by removing the solution by 6 mm in each 3 sec. A standard calomel reference electrode was connected to the solution in the cell by a sintered glass bridge filled with saturated potassium chloride solution. Oxygen was removed by bubbling nitrogen through the solution; this gas was first passed through a gas bottle containing the same solvent as that in the cell.

Stock solutions of tocopherols were prepared from Fluka and Merck products, the purity of which was controlled by measuring the corresponding $E_{1\,\mathrm{cm}}^{1\%}$ values[6]. Cerium(IV) sulfate solutions were standardized against arsenic(III) oxide with ferroin indicator.

Preliminary tests

In a previous paper[7] it was shown that tocopherols in 75% ethanolic sulfuric acid solution give well-defined anodic waves at a bright platinum electrode with periodical renewal of the diffusion layer[8], of which the electrode with bubbling employed here represents a simplified and more readily applicable version. These waves are due to electrooxidation of the tocopherols to an instable intermediate which is transformed to the corresponding tocopherylquinone in a very fast purely chemical reaction, in accordance with the mechanism suggested for oxidation of α-tocopherol at the D.M.E.[9]. While the electrode process is polarographically reversible on a platinized platinum electrode, it shows a slight overpotential on bright platinum. However, since the voltammetric response at a platinized platinum electrode in a 75% ethanolic solution is worsened by the irreproducible surface conditions on the electrode, it is preferable to use a bright platinum electrode. The waves obtained with this electrode in 75% ethanolic $1N$ H_2SO_4 solutions show the following half-wave potential values: α-tocopherol +0.515V, β- and γ-tocopherol +0.600V, δ-tocopherol +0.685V. During a gradual oxidation of tocopherols by chemical or electrochemical methods, no cathodic–anodic waves appear, since the oxidation product is transformed rapidly to tocopherylquinone which is electroreducible only at potentials much less positive than those of the waves of tocopherols. The cathodic wave of tocopherylquinone cannot be observed in 75% ethanolic $1N$ sulfuric acid solution with the platinum electrode since it is covered by the hydrogen discharge.

The oxidation of tocopherols at the electrode is controlled by diffusion; the limiting current is rigorously proportional to the concentration and decreases linearly when cerium(IV) solution is added at room temperature.

Cerium(IV) salts are only slightly soluble in 70–75% ethanolic medium and show only ill-defined waves in the potential range +0.5–+0.8V; these show a certain proportionality to concentration within the restricted limits of the solubility. Cerium (III) salts are also only slightly soluble and show no wave in the potential range considered.

The reaction between cerium(IV) and α-tocopherol is sufficiently fast at room temperature and equilibrium is achieved 1–2 min after addition of the reagent. The reaction between cerium(IV) and mixed tocopherol concentrates requires a longer time to reach equilibrium. On the basis of the results obtained, the following procedures are suggested.

Amperometric titration of α-tocopherol

Place 50 ml of 1*N* sulfuric acid in 75% ethanolic solution containing 4–40 mg of α-tocopherol in the polarographic cell which is thermostatted at 25°. Remove oxygen by bubbling pure nitrogen, which has been previously saturated with the vapours of the solvent present in the cell. Titrate with 0.04*N* cerium(IV) sulfate solution at +0.6V (S.C.E.), bubbling nitrogen through the solution after each addition of the reagent. If the concentration of α-tocopherol is so high that more than 1 ml of the 0.04*N* solution is required, the solution in the cell becomes turbid because of the formation of a cerium(III) precipitate, but this does not interfere with the determination. After correction for dilution, plot the values of the limiting current observed, after stabilization, against the volume of the reagent added. Determine the equivalen-

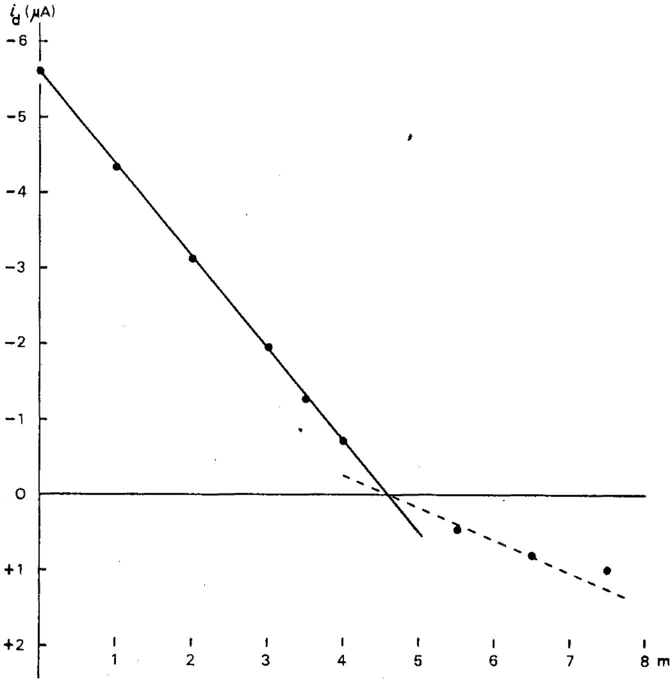

Fig. 1. Amperometric titration of α-tocopherol in 75% ethanolic 1 *N* sulfuric acid with 0.0420 *N* cerium(IV) solution. Applied voltage: +0.60V (S.C.E.).

ce-point from the intersection of this plot with the zero line which corresponds to the residual current of the supporting electrolyte at +0.60V (Fig. 1). The positive current in Fig. 1 corresponds to the electroreduction of the excess of titrant. The quantity of α-tocopherol can be calculated from the following equation:

$$x = \frac{1}{2}\,(v \times N \times 430.72)$$

where x = quantity of α-tocopherol (mg), v = volume of titrant added (ml), and N = normality.

The results of some titrations by the above procedure with various quantities of α-tocopherol are shown in Table I.

Amperometric titration of mixed tocopherol concentrates

Place 50 ml of 85% ethanolic 1N sulfuric acid solution containing 10–80 mg of mixed oily tocopherol preparation in the polarographic cell and deaerate as described above. Titrate with 0.04N cerium(IV) sulfate solution at +0.8V (S.C.E.).

TABLE I

AMPEROMETRIC TITRATION OF α-TOCOPHEROL WITH 0.0420N CERIUM(IV) SOLUTION

(Applied voltage: +0.60V (S.C.E.))

α-Tocopherol added (mg)	*Other vitamin present (mg)*	*α-Tocopherol found (mg)*	*Error (%)*
41.4		41.1	−0.7
41.4		41.8	+1.0
41.4		41.2	−0.5
41.4		41.5	+0.3
31.0		30.8	−0.7
31.0		30.3	−2.3
20.6		20.5	−0.5
20.6		20.6	0
20.6	200 D_2	21.0	+1.9
20.6	200 K_1	20.9	+1.5
20.6	200 K_3	20.9	+1.5
8.3		8.4	+1.2
8.3		8.4	+1.2
4.14		4.35	+5.0

After each titrant addition bubble nitrogen through the solution for 6–7 min with simultaneous magnetic stirring. The solution becomes turbid after the first addition of titrant because the oil diminishes the solubility of the cerium salts. Read the limiting current when it has stabilized and, after correction for dilution, plot its value *vs.* the volume of titrant added, taking the value of the residual current at 0.40V (S.C.E.) as the zero line. This latter approximation is possible, since in the potential range between +0.70 and +0.85V, the height of the limiting current of the waves corresponding to tocopherol oxidation, remains constant and parallel to the instrumental zero line.

The results of some titrations of various mixed tocopherol concentrations are summarized in Table II.

TABLE II

AMPEROMETRIC TITRATION OF MIXED TOCOPHEROL CONCENTRATES WITH 0.0420N CERIUM(IV) SOLUTION

(Applied voltage: +0.80V (S.C.E.))

Mixed tocopherols added (mmol)	*Mixed tocopherols found (total) (mmol)*	*Error (%)*
0.0877	0.0855	—2.5
0.0877	0.0870	—0.8
0.0585	0.0600	+2.6
0.0585	0.0588	+0.5
0.0234	0.0239	+2.1

Amperometric titration in the presence of other fat-soluble vitamins

In amperometric titration of vitamin E, no interference is caused by vitamins K_1, K_3 and D_2 even if these are present in 10-fold amounts (Table I). Vitamin A interferes because it is electroactive at a potential near to that of the oxidation wave of tocopherols.

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BOOK REVIEWS

H. DETERMANN, *Gel Chromatography: A Laboratory Handbook*, Springer-Verlag, Berlin, xii+195 pp., Clothbound, DM 32,– ($8.00).

This is the English translation of DETERMANN's *Gel-chromatographie*, published in German in 1967. Herein lie the major sources for criticism. Although the text is written authoritatively, it has suffered in places at the hand of the translator who has frequently given too rigid a translation from the German; it is not difficult to find whimsicalities and minor errors. More serious, however, is the fact that the text, which gives very few references indeed to work published later than 1966, is based mainly on work of the 1960–1966 period. This effectively limits the value of a volume dealing with such a rapidly developing chromatographic technique as this.

After the Introduction, chapters are devoted to Materials and Methods; Theory; Principles of Application. The final chapter, entitled "Results", ranges broadly over the fields of enzymology, endocrinology, clinical chemistry, proteins, nucleic acids, and carbohydrates.

There is undoubtedly a lot of information, nicely summarised, in this book, but it is likely to be of historical interest only to specialists who have watched the technique expand over the past 12 years. It is the reviewer's belief, however, that this chromatographic technique is still not used to full advantage in many fields of study: for students, and for more mature scientists who have yet to use the technique, this book will provide a useful introductory summary of its pattern of growth.

Analytical Gel Permeation Chromatography, Edited by J. F. JOHNSON AND R. S. PORTER, J. Polymer Science, Part C, Polymer Symposia, vi+344 pp., 135 s.

This addition (Part 21) to Series C of the *Journal of Polymer Chemistry* maintains the high standard set by the earlier Parts and gives the 27 papers read at the Analytical Gel Permeation Chromatography Symposium held in Chicago in September 1967.

Several contributions deal with the mechanism and interpretation of the separation processes; others describe applications to specific problems. Features are the attention given to the newer column-packing materials which are not gels, *e.g.* porous silica or glass, to the extension of the technique to aqueous systems, and to the conjoint use of infrared absorbance so that different functional groups in an eluate can be monitored on a continuous basis.

This is a very useful volume, but its cost is likely to restrict its purchase to library subscriptions only.

D. M. W. ANDERSON (Edinburgh)

Annual Review of N.M.R. Spectroscopy, Vol. 1, Edited by E. F. MOONEY, Academic Press Inc., London, 1968, x + 353 pp., price 95 s.

This volume consists of seven reviews by contributory authors covering the literature up to the end of 1966. The first, *a General Review of Proton Magnetic Resonance* by R. A. Y. JONES, is an extremely useful survey of the literature of 1966 and early 1967 written in the style of Annual Reports of the Chemical Society (referred to as Reviews in the Editorial Preface). *N.M.R. Spectroscopy in Conformational Analysis* is covered by W. A. THOMAS in a chapter in which some unfortunate but possibly unavoidable overlap with Chapter 1 occurs (*cf.* p. 12 and 58,59). The third review is an excellent account of *The Interpretation of High Resolution N.M.R. Spectra* by E. O. BISHOP. A useful review of ^{19}F spectra by E. F. MOONEY AND P. H. WINSON, and reviews on *Heteronuclear Magnetic Double Resonance, N.M.R. of Polymers,* and *Methods of Signal to Noise Enhancements* are included.

This volume must be compared with *Advances in Magnetic Resonance* and *Progress in N.M.R. Spectroscopy* with which considerable overlap must (and already does) occur. However, this volume presents reviews suitable for those more interested in the application of N.M.R. rather than a full rigorous treatment of the fundamentals. Editorial co-operation would minimise future overlap.

The volume contains a very comprehensive index and is suitably free from trivial errors although the rate of nitrogen inversion in pyridine (indexed on p. 351) makes an amusing exception.

W. R. JACKSON (Belfast)

Die analytische Chemie in der erzeugenden und verarbeitenden Hüttenindustrie, Verlag Stahleisen M.B.H., Düsseldorf, 1968, 391 pp., price DM 59,—.

The coverage of this book, whilst primarily of interest to the analyst, extends over wider scientific fields within the ferrous and non-ferrous metallurgical industries. For example, the identification of phase compositions is usually considered within the province of the metallurgist rather than that of the analyst. The 19 sections, comprising on average 20 pages each, have all been contributed by well-known specialists.

Dissertations on problems of general interest predominate, and include such topics as statistics, sampling of molten metal, the determination of gases and trace constituents, polarography, mass spectroscopy, electron microscopy, and X-ray analysis.

W. T. ELWELL (Birmingham)

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ANNOUNCEMENTS

SECOND INTERNATIONAL AIR POLLUTION CONFERENCE OF THE INTERNATIONAL UNION OF AIR POLLUTION PREVENTION ASSOCIATIONS

December 6–11, 1970
Washington, D.C. (U.S.A.)

The International Union of Air Pollution Prevention Associations is a union of the following associations:

Asociación Argentina Contra la Contaminación del Aire.
Association pour la Prévention de la Pollution Atmosphérique, France.
Kommission Reinhaltung der Luft, Germany.
National Society for Clean Air, Great Britain.
Kanto-Shin-Etsu Heat Control Society, Japan.
Air Pollution Control Association, U.S.A.–Canada.
Clean Air Society of Australia & New Zealand.

Its President is Dr. CHRISTOPHER E. BARTHEL, JR. and its Executive Secretary is Mr. ARNOLD ARCH. The Air Pollution Control Association (U.S.A.–Canada) is the host association for the 1970 conference.

The Second International Air Pollution Conference will include the conference, an exposition and a number of social events. The General Conference Chairman is Mr. JOSEPH W. MULLAN. The First International Conference of the Union was held in London in 1966. The co-chairmen of the Program Committee are Mr. JOHN S. LAGARIAS and Prof. ARTHUR C. STERN.

The Conference will consist of plenary sessions at which only specifically solicited papers, reports and speeches will be presented in either English, French, German, Japanese or Spanish, and at which there will be simultaneous translation into these five languages; and concurrent sessions for papers chosen from among those submitted in response to this invitation. The concurrent sessions will be limited to presentations and simultaneous translation in English and French, the two official languages of the International Union. Preprints will be in both languages.

It is presently planned to have concurrent sessions in the following 6 subject areas:

1. Air Pollution Chemistry and Physics—Papers on sampling, analysis, instrumentation, aerosols, and on effects on non-biological systems.
2. Air Pollution Meteorology—Papers on transport, diffusion, modeling, forecasting, and stacks.
3. Air Pollution Medicine and Biology—Papers on effects on people, animals, and vegetation.
4. Air Pollution Engineering—Papers on sources, their engineering control and control equipment.
5. Air Pollution Control Administration—Papers on legislation, regulations, inspection, and control program operation.
6. Air Pollution Surveys—Papers reporting community and area studies.

Papers on air quality criteria will be assigned to "Air Pollution Medicine and Biology". Papers on air pollution standards will be assigned to "Air Pollution Control Administration". If enough papers on the social science aspects of air pollution are offered, we will consider creating a concurrent session series in this area.

The decision as to whether papers will be presented in their entirety, by abstract, or by title only will depend upon the number of sessions decided upon for each subject, and upon the number of papers accepted for each session.

Proposals to present papers, which must be received before January 31st, 1970, should include a provisional title, an outline limited to 200 words and the names, titles, affiliations of the proposed authors and address of the principal author. Proposals may be submitted in the language of the author, but accepted papers must be written in English or French, and may not be offered for publication elsewhere in these languages.

Although proposals will be accepted in letter form, they preferably should be submitted on forms obtainable from the appropriate national association or from:

Professor ARTHUR C. STERN, Program Co-Chairman, Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, P. O. Box 630, Chapel Hill, N.C. 27514, U.S.A.

NATIONAL CONFERENCE OF ANALYTICAL CHEMISTRY

Constantza, Romania
24–28 September, 1969

A conference on analytical chemistry will be organized by the Romanian National Council of Engineers and Technicians at Constantza-Mamaia, Romania during the period 24–28th September, 1969.

The sections of the conference will cover: chemical methods of analysis, physical methods of analysis, construction of equipment, and automation techniques.

Further information can be obtained from Dr. GHEORGHE BAIULESCU, Organizing Committee, National Council of Engineers and Technicians, Calea Victoriei 118, Bucuresti, Romania.

VI INTERNATIONAL SYMPOSIUM ON CHROMATOGRAPHY AND ELECTROPHORESIS

Brussels
September 14 to 16, 1970

The Belgian Society of Pharmaceutical Sciences has the honour to announce that they will organize the VI Symposium on the theoretical aspects and the various practical applications of Chromatography and Electrophoresis, from September 14 to 16, 1970.

All persons interested in chromatography are cordially invited to attend this symposium. Registration will be accepted until August 1st, 1970. Participants who wish to present a paper should register before July 1st, 1970.

The official languages of the Symposium are French, Dutch, German and English. During the symposium, a scientific exhibition will be organized.

Full information concerning this symposium can be obtained from the Secretariat of the Belgian Society of Pharmaceutical Sciences, 11, rue Archimède, Brussels 4.

The proceedings of the V symposium will be submitted to the participants during May 1969. All other persons interested in these proceedings may obtain them from the editor of "Presses Académiques Européennes", 98, chaussée de Charleroi, Brussels 6.

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Short Communications

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